CONTROL OF CORROSION AND SCALING IN GEOTHERMAL SYSTEMS

Project coordinated by BRGM (I. Ignatiadis)
B.P. 6009, 45060 Orléans Cedex 2, France

Contract No JOU2-CT-92-0108

7th Periodic Report,
Covering the period from
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Date: June 10th, 1996
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PRESENTATION FOR THE 7th PERIODIC REPORT OF THE CONTRACTORS

by I. Ignatiadis, coordonator (BRGM DR/GGP, Orléans, France)

JOULE II Project, Contract No JOU2-CT92-0108
Title: Control of corrosion and scaling in geothermal systems
PRESENTATION OF THE 7th PERIODIC REPORT
OF THE CONTRACTORS

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1. FOREWARD

This periodic report, which presents the scientific contributions of all the partners in the Joule 2 programme, contract Nos. JOU2-CT92-0108 and CIPD-CT93-0314 (entitled Control of corrosion and scaling in geothermal systems), is the seventh for BRGM, CEBELCOR, CPERI, CPR, and ICEHT, the research groups that have been involved in the project from the beginning of the programme (December 1, 1992), and the fourth for the groups from Central and Eastern European countries (BBPDICM, CAEL, CRIC, ICPE C-60 and ICVL) who joined the project in 1994.

In this report, all of the research groups present at least one paper (except CEBELCOR, sub-contractor of the BRGM). Although some of these have already been presented in previous reports, the versions herein have been improved, taking into account the progression of the project. Some papers, as in previous periodic reports, are final reports of completed work.

This report will be presented at the 7th biannual meeting that will take place in Paris (head office of the BRGM), France, on July 18, 1996. The official end of the programme is July 31, 1996. The final meeting and report presentation of all the contributions will be held on July 19th, 1996, in the same venue as the 7th meeting.

The outline adopted for this report is as follows:

An introduction, presenting the aims of the research, and, for each group, the particular objectives, deliverables and work performed to date. To facilitate reading, part of each of the two work programmes of the contract are given in two appendixes to this introduction.

The present report is made up of the scientific contributions of each group in the form of 19 articles. However, these articles have not been grouped according to the 6 main themes of the project as defined at the 3rd biannual meeting in Udine (1: corrosion prevention, 2: scale prevention, 3: corrosion studies, 4: scale formation and modelling, 5: corrosion and scaling monitoring, and 6: corrosion and scaling in diphasic flow conditions). Although this classification according to these 6 themes was proposed in order to facilitate the presentation of this (and the final) report, it has not been applied because numerous articles deal with two or more themes and furthermore, marked particularities are observed between the methodologies used (both experimental and theoretical). The various contributions of each group along with the various themes covered are shown in Table 1 below.
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Main themes approached in the various scientific contributions.
2. GENERAL OBJECTIVES AND CONTENT OF THE PROJECT

The aim of the programme is to resolve the problems caused by corrosion and scaling in the exploitation of low and high enthalpy geothermal systems. The increased costs resulting from these problems decrease the profitability of the projects and, in certain cases, can be inimical to the development of the uses of geothermal energy. The geothermal plants most concerned are those currently operating in the Paris Basin in France, at Larderello in Italy, in Greece, and those in the planning stage in these and other countries.

The mechanisms of corrosion and the formation of scale encountered are similar, even when the geothermal fluids have different physico-chemical characteristics. Very few European research centres are currently working on these highly specific and complex aspects of corrosion in deoxygenated media in France, Italy and Greece. Since the energetic (or economic) value of the resource is low, it is necessary to develop processes that are both very efficient and inexpensive.

The immediate objectives of the programme are to determine the conditions under which corrosion takes place and which lead to the formation and growth of scale (iron sulphide, calcium carbonate, silica, lead sulphide), and to develop predictive models.

This will lead to the design of processes for industrial application to control corrosion and scaling, using corrosion and crystal growth inhibitors, vapour-cleaning systems and treatment of condensates before injection.

The work programme is carried out by the following groups:

- Bureau de Recherches Géologiques et Minières, Direction de la Recherche, Research Division, Département Géomatériaux et Géoprocédés, Department of Geotechnical Engineering and Mineral Technology, (BRGM, Dr. I. Ignatiadis, Coordinator) Orleans, France;
- Centre Belge de l'Etude de la Corrosion (CEBELCOR, Dr. Pourbaix) Brussels, Belgium;
- Chemical Process Engineering Research Institute (CPERI, Prof. A. Karabelas) Thessaloniki, Greece;
- Institute of Chemical Engineering and High Temperature Chemical Processes (ICE/HT, Prof. P. Koutsoukos) Patras, Greece, and
- Consorzio Pisa Ricerche, Centro TEA (CPR, Prof. P. Andreussi) Pisa, Italy.

The possibilities for developing the use of geothermal energy in other European countries (Hungary, Romania, Lithuania, etc.) led us to propose an extension of the programme to allow the association of new research partners. This extension was prompted by the European Union programme for "Cooperation in Science and Technology with Central and Eastern European Countries, 1993". The additional work programme is carried out by the following groups:

- Central Research Institute for Chemistry (CRIC, Prof. E. Kalman), Budapest, Hungary,
- Electrochemical Technologies and Active Anticorrosive Protection Laboratory of the Research and Design Institute for Electrical Engineering (ICPE C-60, Dr. I. Lingvay), Bucharest, Romania,
- Computer Aided Electrochemistry Laboratory (CAEL, Dr. V. Cotarta) of the "Politehnica" University of Bucharest, Romania,
- Bioactive and Biocompatible Polymers Department of the Petru-Poni Institute of Macromolecular Chemistry (BBPDICM, Prof. A. Carpov), Iasi, Romania,
- Institute of Chemistry (ICVL, Dr. E. Juzeliunas), Vilnius, Lithuania.

Parts of the initial work programme and the programme including Central and Eastern European partners are given in two appendixes to this introduction.
3. WORK PERFORMED TO DATE BY THE TEN SCIENTIFIC GROUPS

The aims and deliverables for the laboratories of the European Union are defined in the initial work programme given in Appendix 1. The general objectives, particular objectives and deliverables for laboratories in Central and Eastern European countries are defined in the additional and specific work programme given in Appendix 2.

3.1. BRGM, ORLEANS, FRANCE

The first six-monthly report (meeting in Patras, Greece, September 30 - October 1, 1993) related work undertaken over the period from 01/12/92 to 31/05/93 regarding:
- determination of the extent of corrosion as a function of exploitation conditions. This part of study had not been entirely completed and exploited (aim n° 4, deliverable 4.1.4.2);
- evaluation of the precipitation kinetics of iron sulphides in the presence and absence of inhibitor substances (aim n° 1, deliverable 4.1.1.1);
- estimation of the solubility product of the iron sulphides based on the results of analyses of geothermal fluids currently exploited in the Paris region in view of its utilisation in the calculation code (aim n° 1, deliverable 4.1.1.5);
- evaluation of the effect of degassing of the geothermal fluid on corrosion and deposition interpreting the results obtained in situ at the Chelles geothermal operation (aim n° 5, deliverable 4.1.5.1).

The second six-monthly report (meeting in Paris, France, February 7, 1994) related work undertaken over the period from 01/6/93 to 30/11/93 regarding:
- determination of the extent of corrosion as a function of exploitation conditions (aim n° 4 deliverable 4.1.4.2 and aim n° 2 deliverables 4.1.2.1 and 4.1.2.2). This part of study was the continuation of the previous study (first six-monthly report). Here new developments were presented but this study has not been entirely completed nor exploited;
- methods for monitoring corrosion and the efficiency of treatment by corrosion inhibitor on the geothermal projects of the Paris basin (aim n° 4, deliverable 4.1.4.2);
- influence of some physico-chemical parameters and exploitation conditions on corrosion and scaling in geothermal wells in the Paris basin (aim n° 4 deliverable 4.1.4.2 and aim n° 2 deliverables 4.1.2.1 and 4.1.2.2);
- study of the deposition phenomena in geothermal wells in the Paris Basin (aim n° 1, deliverables 4.1.1.4 and 4.1.1.6);
- methods for detecting perforations in casings of wells exploiting geothermal fluids (aim n° 4, deliverable 4.1.4.1).

The third six-monthly report (meeting in Udine, July 8, 1994) related work undertaken over the period from 01/12/93 to 31/05/94 regarding:
- behaviour of a carbon steel in a real and treated geothermal environment in order to optimize the use of corrosion inhibitors in low enthalpy geothermal systems (aim n° 4 deliverable 4.1.4.2 and aim n° 2 deliverables 4.1.2.1 and 4.1.2.2);
- modelling of deposition phenomena in low enthalpy geothermal wells (aim n° 1, deliverable 4.1.1.7).

The fourth six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:
- behaviour of a carbon steel in an actual or modified and treated geothermal environment (aim n° 4 deliverable 4.1.4.2 and aim n° 2 deliverables 4.1.2.1 and 4.1.2.2);
- modelling of deposition phenomena in low enthalpy geothermal wells (aim n° 1, deliverable 4.1.1.7);
- behaviour of some non metallic materials in actual and treated geothermal environment (aim n° 2, deliverable 4.1.2.3).
The fifth six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:
- comparative study of the effectiveness of various organic surfactants in inhibiting carbon steel corrosion in a natural geothermal environment by using rapid electrochemical tests (aim no 4 deliverable 4.1.4.2 and aim no 2 deliverables 4.1.2.1 and 4.1.2.2);
- influence of iron sulfide scale on the corrosion of carbon steel in geothermal installations (aim no 1, deliverables 4.1.1.4 and 4.1.4.6, aim no 4 deliverable 4.1.4.2 and aim no 2 deliverables 4.1.2.1 and 4.1.2.2).

The sixth semester report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:
- comparative study of the effectiveness of various organic surfactants in inhibiting carbon steel corrosion in a partial reconstituted geothermal environment (aim no 2 deliverables 4.1.2.1 and 4.1.2.2);
- comparative study (long-term) of the carbon steel corrosion rate in untreated and treated geothermal fluids using coupons (aim no 4 deliverables 4.1.4.2);
- a module (CALDEP 1 and 2) that enables the simulation of corrosion and scaling phenomena on steel casings of geothermal wells (aim no 1, deliverable 4.1.1.7). This model takes into account the application of the Volmer-Heyrovsky reactive mechanism, Fick's diffusion laws, the variation of the thickness of the diffusion layer due to scale growth and the porosity of the scale;
- presentation of the transfer of MODEP code from VAX-microsystem to Personal Computer (FORTRAN-Lahey under Windows) (aim no 1, deliverable 4.1.1.7).

The present seventh semester report (meeting in Paris, France, July 18, 1996) relates work undertaken over the period from 01/12/95 to 31/05/96 regarding:
- comparative study of the effectiveness of various organic additives (including those from Professor Carpov) in inhibiting carbon steel corrosion in a natural geothermal environment by using rapid electrochemical tests (aim no 2 deliverables 4.1.2.1 and 4.1.2.2);
- comparative study of the effectiveness of various organic surfactants (including those from Professor Carpov) in inhibiting iron sulfide precipitation in a natural geothermal environment using electrochemical methods both in the laboratory and in situ (aim no 2 deliverables 4.1.2.1 and 4.1.2.2);
- improvement of the PRINPIMO down-hole fluid sampler (aim no 4 deliverable 4.1.4.3);
- modelling of corrosion and scaling phenomena in low enthalpy geothermal wells (aim no 1, deliverable 4.1.1.7).

3.2. CPR, PISA, ITALY

The first six-monthly report (meeting in Patras, Greece, September 30 - October 1, 1993) related work undertaken over the period from 01/12/92 to 31/05/93 regarding:
- abatement of hydrochloric acid in geothermal steam (aim no 3, deliverable 4.1.3.1).

The second six-monthly report (meeting in Paris, France, February 7, 1994) related work undertaken over the period from 01/6/93 to 30/11/93 regarding:
- design of a structured packing column for steam washing (aim no 3, deliverable 4.1.3.1);
- thermodynamic analysis in processes of dry removal of HCl from a geothermal steam (aim no 3, deliverable 4.1.3.1).

The third six-monthly report (meeting in Udine, July 8, 1994) related work undertaken over the period from 01/12/93 to 31/05/94 regarding:
- steam washing in the well. A preliminary study (aim no 3, deliverable 4.1.3.1).

The fourth six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:
- the influence of coalescence on droplet transfer in vertical annular flow (aim no 5, deliverable 4.1.5.1);
- dry removal of hydrochloric acid from geothermal steam (aim no 3, deliverable 4.1.3.1).
The fifth six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:
- analysis and modelling in wet processes of HCl removal from geothermal steam (aim n° 3, deliverable 4.1.3.1).

The sixth semester report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:
- dry removal of hydrochloric acid from geothermal steam (aim n° 3, deliverable 4.1.3.1, 4.1.3.2, 4.1.3.3).

The present seventh semester report (meeting in Paris, France, July 18, 1996) related work undertaken over the period from 01/12/95 to 31/05/96 regarding:
- steam washing in the well (aim n° 3, deliverable 4.1.3.1);
- stimulation of chemical equilibria in the equipment of a geothermal power plant: the GEA (Geothermal Equilibria Assessment) Code (aim n° 3, deliverables 4.1.3.1., 4.1.3.2, 4.1.3.3.).

3.3. ICE/HT, PATRAS, GREECE.

The first six-monthly report (meeting in Patras, Greece, September 30 - October 1, 1993) related work undertaken over the period from 01/12/92 to 31/05/93 regarding:
- control of corrosion and scaling in geothermal systems (aim n° 1, deliverables 4.1.1.1 and 4.1.1.9).

The second six-monthly report (meeting in Paris, France, February 7, 1994) related work undertaken over the period from 01/06/93 to 30/11/93 regarding:
- control of corrosion and scaling in geothermal systems (aim n° 1, deliverables 4.1.1.1 and 4.1.1.9).

The third six-monthly report (meeting in Udine, July 8, 1994) related work undertaken over the period from 01/12/93 to 31/05/94 regarding:
- control of corrosion and scaling in geothermal systems (aim n° 1, deliverables 4.1.1.1 and 4.1.1.9).

The fourth six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:
- FeS scale formation and implications on corrosion of steel. This work concerns;
- spontaneous precipitation of iron sulfides at various supersaturations at 25 °C and 80 °C (aim n° 1, deliverables 4.1.1.1 and 4.1.1.9);
- preparation of pyrite seed crystals to be used for seeded growth studies (aim n° 1, deliverables 4.1.1.1 and 4.1.1.9);
- electrochemical investigations of the corrosion of steel in sulfide and NaCl containing media (aim n° 4, deliverable 4.1.4.2).

The fifth six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:
- iron sulfide scale formation and implications on corrosion of steel alloys in geothermal systems (aim n°1, deliverables 4.1.1.1 and 4.1.1.9).

The sixth semester report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:
- iron sulfide scale formation and implications on corrosion of steel alloys in geothermal systems (aim n° 1, deliverables 4.1.1.1 and 4.1.1.9).

The present seventh semester report (meeting in Paris, France, July 18, 1996) relates work undertaken over the period from 01/12/95 to 31/05/96 regarding:
- a comparative study of the effectiveness of various organic additives (including those from Professor Carpov) in inhibiting carbon steel corrosion in a natural geothermal environment by using rapid electrochemical tests (aim n° 2 deliverables 4.1.2.1 and 4.1.2.2);
a comparative study of the effectiveness of various organic surfactants (including those from Professor Carpov) in inhibiting iron sulfide precipitation in a natural geothermal environment; (those from Professor Carpov) using electrochemical methods both in the laboratory and in situ (aim n°2 deliverables 4.1.2.1 and 4.1.2.2);

• iron sulfide scale formation and implications on corrosion of steel alloys in geothermal systems;

• (aim n 1, deliverables 4.1.1.1 and 4.1.1.9).

3.4. CPERI, THESSALONIKI, GREECE.

The first six-monthly report (meeting in Patras, Greece, September 30 - October 1, 1993) related work undertaken over the period from 01/12/92 to 31/05/93 regarding:

• sulphide scaling: a) remodelling of the experimental set-up, b) on modelling of sulphide scale formation (aim n° 1, deliverables 4.1.1.1 and 4.1.1.7);

• colloidal particle coagulation: selection of numerical methods for simulating coagulation (aim n° 1, deliverable 4.1.1.7);

• two-phase flow: liquid layer characteristics in stratified/atomization flow (aim n° 5, deliverable 4.1.5.1).

The second six-monthly report (meeting in Paris, France, February 7, 1994) related work undertaken over the period from 01/6/93 to 30/11/93 regarding:

• iron sulphide scale formation (aim n° 1, deliverables 4.1.1.1 and 4.1.1.7);

• simulation of particle evolution and scale formation along the flow path (aim n° 1, deliverable 4.1.1.7).

The third six-monthly report (meeting in Udine, July 8, 1994) related work undertaken over the period from 01/12/93 to 31/05/94 regarding:

• iron sulphide scale formation (aim n° 1, deliverables 4.1.1.1);

• colloidal particle coagulation: The effect of roughness on energy of repulsion between colloidal particles (aim n° 1, deliverables 4.1.1.7);

• a study of stratified/atomization flow: A new flow loop for detailed measurements (aim n° 5, deliverable 4.1.5.1).

The fourth six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:

• iron sulphide scale formation: effect of liquid velocity (aim no. 1, deliverables 4.1.1.1.);

• colloidal particle coagulation: improvement of algorithm for predicting precipitation/scaling in pipe flow (aim no. 2, deliverables 4.1.2.4.);

• a study of stratified/atomization flow: flow loop, experimental techniques and description of experiments (aim no. 5, deliverables 4.1.5.1.).

The fifth six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:

• iron sulphide scale formation (aim no. 1, deliverables 4.1.1.1.);

• colloidal particle coagulation: the influence of surface dynamics on electric double-layer forces between particles (aim no. 2, deliverable 4.1.2.4.);

• a study of stratified/atomization flow (aim no. 5, deliverable 4.1.5.1.).

The sixth semester report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:

• scale formation inhibition. Tests to examine inhibitors of caused by iron sulphide and calcium carbonate scale (aim No 1 deliverable 4.1.1.1.);

• measurements of the axial component of the velocity of gas phase in stratified flow (aim No 5 deliverables 4.1.5.1.).
Control of corrosion and scaling in geothermal systems

The present seventh semester report (meeting in Paris, France, July 18, 1996) relates work undertaken over the period from 01/12/95 to 31/05/96 regarding:

- experimental study of flow characteristics in stratified / atomization gas/liquid flow (aim N°5, deliverable 4.1.5.1).

3.5. CEBELCOR, BRUSSELS, BELGIUM.

CEBELCOR did not present a report at the first (Patras, September 30 - October 1, 1993) and the second (Paris, February 7, 1994) bi-annual meetings.

Its first six-monthly report (presented at the third bi-annual meeting in Udine, July 8, 1994) related work undertaken over the period from 01/12/93 to 31/05/94 regarding:

- localised corrosion of carbon steel in geothermal systems (aim n° 1, deliverables 4.1.1.2 and 4.1.1.3).

The fourth six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:

- localised corrosion of carbon steel in geothermal systems (aim n°1, deliverables 4.1.1.2 and 4.1.1.3).

The fifth six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:

- localised corrosion of carbon steel in geothermal systems (aim n°1, deliverables 4.1.1.2 and 4.1.1.3).

In the sixth semester report (period from 01/06/95 to 30/11/95, meeting in Thessaloniki, Greece, December 15, 1995) CEBELCOR did not present a report.

In the present seventh semester report (period from 01/12/95 to 31/05/96, meeting in Paris, France, July 18, 1996) CEBELCOR will not present a report.

3.6. CAEL, BUCHAREST, ROMANIA.

The CAEL contribution to the additional research program is included in general objectives 2, 4 and 5. CAEL did not present a report at the first (Patras, September 30 - October 1, 1993), second (Paris, February 7, 1994) or third (Udine, July 8, 1994) bi-annual meetings since CAEL joined the project in 1994.

The first six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:

- anode dissolution of iron in geothermal water with Cl⁻ and HS⁻ contents (particular objective 2, deliverable 2).

The second six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:

- oscillating phenomena during anodic polarization of Fe electrodes in geothermal waters: modelling the periodic oscillations (particular objectives 2 and 3, deliverables 2 and 3);
- multiplicity and stability analysis for systems of equations associated to anodic Fe dissolution in geothermal water with high Cl⁻ content (particular objective 2, deliverable 2).

The third six-monthly report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:

- integral method for the determination of iron corrosion kinetic parameters in geothermal water;
- (particular objective 2, deliverable 3);
- corrosion of carbon steel in CO₂ saturated brine with a small amount of H₂S;
- (particular objective 2, deliverable 3).
The present fourth semester report (meeting in Paris, France, July 18, 1996) relates work undertaken over the period from 01/12/95 to 31/05/96 regarding:
- design of a computer assisted system for corrosion tests (particular objective 3, deliverable 1);
- cylindrical tanks inner cathodically protected with external current source (particular objective 1, deliverable 1);
- cathodic protection of steel pipes without external source (particular objective 2, deliverable 1).

3.7. BBPDICM, IASI, ROMANIA.

The BBPDICM contribution to the additional research program is included in general objective 1. BBPDICM did not present a report at the first (Patras, September 30 - October 1, 1993), second (Paris, February 7, 1994) and third (Udine, July 8, 1994) bi-annual meetings since BBPDICM joined the project in 1994.

The first six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:
- synthesis and physico-chemical and structural characterization of various polyelectrolytes (particular objective 1, deliverable 1).

The second six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:
- control of corrosion and scaling in geothermal systems: synthesis of new water-soluble salts of maleic copolymers and terpolymers (particular objective 1 and 2, deliverable 1 and 2).

The third six-monthly report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:
- experiments concerning the synthesis of new maleic copolymers such as maleic anhydride - N - vinyl-pyrrolidone binary or ternary copolymers, monoamides of maleic anhydride copolymers with different aliphatic amines, new monoesters of maleic anhydride copolymers with ethylene glycol monoethers and some organic salts of maleic acid copolymers;
- synthesis of 6 samples to be tested at ICEM/HT Patras, in addition to other 7 samples sent before;
- synthesis of a new small pilot scale sample of Na\(^+\)/Zn\(^2+\) salt of a maleic acid - vinyl acetate copolymer (40 liters);
- synthesis of very pure samples of maleic copolymers (acids, monoesters, monoamides) to develop a specific methodology to study polyelectrolytes by potentiometric titration with a new automatic titrator.

The present fourth semester report (meeting in Paris, France, July 18, 1996) relates work undertaken over the period from 01/12/95 to 31/05/96 regarding:
- synthesis of maleic copolymers containing a) piperazine or its derivatives b) aromatic amines (particular objective 1 and 2, deliverables 1.2, 1.3. and 2);
- testing of our maleic polyelectrolytes as scale/corrosion inhibitors by BRGM (particular objective 1 and 2, deliverable 2, see report of the BRGM);
- testing of maleic polyelectrolytes in collaboration with ICEM/HT and ICPE C-60 (particular objective 1 and or 2, deliverables 1 and 2, see report of the ICEM/HT and ICPE C-60).

3.8. ICVL, VILNIUS, LITHUANIA

The ICVL contribution to the additional research program is included in general objectives 2 and 3. ICVL did not present a report at the first (Patras, September 30 - October 1, 1993), second (Paris, February 7, 1994) and third (Udine, July 8, 1994) bi-annual meetings since ICVL joined the project in 1994.
Control of corrosion and scaling in geothermal systems

The first six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:
• laboratory studies of iron corrosion in geothermal fluid from west-Lithuanian aquifers (particular objective 2, deliverables 2 and 3).

The second six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:
• laboratory studies of iron corrosion and oxide-layer formation in geothermal fluid from west-Lithuanian aquifers (particular objective 2, deliverables 2 and 3).

The third six-monthly report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:
• EQCM preparations for the study of iron corrosion in geothermal fluid from west-Lithuanian aquifers (particular objective 1, deliverables 1 and 2).

The present fourth semester report (meeting in Paris, France, July 18, 1996) relates work undertaken over the period from 01/12/95 to 31/05/96 regarding:
• EQCM study of iron corrosion in geothermal fluid from west-Lithuanian aquifers (particular objective 1, deliverables 1 and 2).

3.9. CRIC, BUDAPEST, HUNGARY

The CRIC contribution to the additional research program is included in general objective 1. CRIC did not present a report at the first (Patras, September 30 - October 1, 1993), second (Paris, February 7, 1994) and third (Udine, July 8, 1994) bi-annual meetings since CRIC joined the project in 1994.

The first six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/6/94 to 30/11/94 regarding:
• modelling of scale formation of calcium carbonate (particular objectives 2 and 3, deliverables 3 and 4).

The second six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:
• modelling of equilibrium scale formation from thermal water (particular objectives 2 and 3, deliverables 3 and 4).

The third six-monthly report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:
• modelling of scale formation from thermal water (particular objectives 2 and 3, deliverables 3 and 4);
• systematic study of the structure and the corrosion and scale inhibitor ability of newly synthetised molecules (particular objectives 1 and 3, deliverables 1 and 2);
• monitoring the laboratory experiments (particular objectives 2 and 3, deliverables 2 and 4).

The present fourth semester report (meeting in Paris, France, July 18, 1996) relates work undertaken over the period from 01/12/95 to 31/05/96 regarding:
• quantitative relationships between the structure and activity of corrosion inhibitors (particular objectives 1 and 3, deliverables 1 and 2);
• mechanism of inhibition in neutral solutions (particular objective 2, deliverable, 3);
• modelling of scale formation from thermal water. 4. modelling of equilibrium profiles of the gas pressures and the equilibrium solubility along the well particular objectives 2 and 3, deliverables 3 and 4).
3.10. ICPE C-60 BUCHAREST, ROMANIA

The ICPE C-60 contribution to the additional research program is included in general objectives 1, 3, 4 and 5. ICPE C-60 did not present a report at the first (Patras, September 30 - October 1, 1993), second (Paris, February 7, 1994) or third (Udine, July 8, 1994) bi-annual meetings.

The first six-monthly report (meeting in Budapest, Hungary, December 9, 1994) related work undertaken over the period from 01/06/94 to 30/11/94 regarding:
- the study of the possibility to apply the active anticorrosive protection for the outside metallic surfaces from geothermal systems (particular objective 5, deliverable 1);
- the conception of the system and the design elements; installation of the electronics equipment - experimental model for active anticorrosive protection (particular objective 4 and 5, deliverable 1);
- the kinetic parameters determination of the electrochemical corrosion reactions at the metal/geothermal waters interface from systems in operation - Romania - the BIHOR basin - the ORADEA area (particular objective 3, deliverable 2);
- the corrosion inhibition effect determination for 13 various polyelectrolytes - with antiscaling effect (particular objective 1, deliverable 3).

The second six-monthly report (meeting in Pisa, Italy, May 20, 1995) related work undertaken over the period from 01/12/94 to 31/05/95 regarding:
- active anticorrosive protection of the outside metallic surfaces from geothermal systems: prototype installation (particular objective 4 and 5, deliverable 1);
- the kinetic parameters determination of the electrochemical corrosion reactions at the metal/geothermal waters interface: samples investigations with $S^{2-}$ and/or $SO_{4}^{2-}$ from the Bihor basin, Romania (particular objective 3, deliverable 2);
- the study of the geothermal waters corrosiveness with polyelectrolyte addition: polyelectrolyte salts with triethanolamine (particular objective 1, deliverable 3).

The third six-monthly report (meeting in Thessaloniki, Greece, December 15, 1995) related work undertaken over the period from 01/06/95 to 30/11/95 regarding:
- active anticorrosive protection of the outside metallic surfaces from geothermal systems: prototype installation and its resting (particular objective 4 and 5, deliverable 3);
- design and building of a multifunctional transducer device for continuous measurement of corrosion and scaling in relation with temperature (general objective 4, particular objective 4 and 5, deliverable 1);
- study and design of an injection apparatus (injection pump and special engine unite) with controled flowrate of inhibitors (general objective 2 and 4, particular objective 4, deliverable 1).

The present fourth semester report (meeting in Paris, France, July 18, 1996) relates work undertaken over the period from 01/12/95 to 31/05/96 regarding:
- the study of the geothermal water corrosiveness with polyelectrolyte addition: copolymers of maleic acid and n-vinilpirolidine with piperazine and its derivatives (particular objective 1, deliverable 3);
- the study of the geothermal water corrosiveness with polyelectrolyte addition: copolymers of maleic acid with aromatical amines (particular objective 1, deliverable 3);
- study of monitoring possibility of scaling rate in geothermal systems (particular objective 1, deliverable 3).
APPENDIXES TO THE INTRODUCTION
APPENDIX 1. PART OF THE INITIAL WORK PROGRAMME

JOULE 2, Contract N° JOU2-CT92-0108

May, 1993

1. TITLE: CONTROL OF CORROSION AND SCALING IN GEOTHERMAL SYSTEMS

2. OBJECTIVES

The proposed research programme aims to eliminate the problems due to corrosion and scaling in the exploitation of low and high enthalpy geothermal systems. It focuses on solving real problems encountered during exploitation of geothermal resources.

In this perspective the fields studied are the low enthalpy Dogger of the Paris basin (41 doublets in operation representing a thermal power of more than 400 MW), and the high enthalpy projects at Larderello (ENEL-VDAG) and Milos (electrical power of more than 500 MW). The approach taken is both progressive and global.

Geothermal energy systems consist of wells and surface installations. The relative complexity, and thus the economic impact, of these two parts is very different for high and for low enthalpy projects.

To take this difference into account, the study of low enthalpy projects focuses on phenomena in the well, whereas for high enthalpy projects it focuses on the problems in the surface installations.

The research programme aims on the one hand, on the theoretical level, to develop understanding of the reaction mechanisms which control corrosion and scaling, and on the other hand, on the technological level, it aims to improve the solutions currently employed and to develop new, less costly and/or more reliable solutions.

The proposed programme, which is a continuation of the previous programme co-financed by the European Community (contract JOUG-0005-C), is expected to produce the following results:

Aim n°1. Establishment of the kinetics of the formation and growth of the scale most frequently encountered, with the development of appropriate numerical simulation codes.
Aim n°2. Selection of the most efficient products for inhibiting corrosion or crystal growth.
Aim n°3. Development of a process for eliminating chlorides by washing the vapour.
Aim n°4. Development of the metrology associated with the monitoring of corrosion and scaling.
Aim n°5. Identification of diphasic flow conditions which aggravate corrosion and scaling.

To achieve those goals, the partners will realize theoretical studies (thermodynamic aspects) and will use experimental loops on laboratories or on geothermal plants.

The range of skills of the partners makes possible a global approach to the field of research, and their combined facilities enable a wide range of laboratory experiments to be undertaken:
- high enthalpy flow test loops: CPERI, CPR Pisa and ENEL-VDAG;
- sampling tools: BRGM;
- simulation of scaling: CEPRl, ICE/HTCP, BRGM and CEBELCOR;
- treatment pilots: CPR Pisa and ENEL-VDAG, CPERI, BRGM.

The means used will serve for both low and high enthalpy projects, and access is possible to the installations of the Dogger of Paris basin (FR), Larderello (IT), Milos or Nisyros (GR).
Control of corrosion and scaling in geothermal systems

2.1. Improvement of the tools for sampling in geothermal loops, and of sampling methods

Sampling for the analysis of reactive species has required the development of a special sampler, as concerns both its mechanical design (mobile piston with counter pressure for avoiding degassing) and its constituent materials (hastelloy, titanium, teflon).

Modifications of the sampler will be studied and implemented to adapt it to the conditions of high enthalpy geothermal projects (temperature up to 350°C) in order to increase its range of application.

2.2. Modeling of corrosion and scaling (BRGM, CPERI, ICE/HTCP, CEBELCOR)

The mechanism of the formation of scale in the casing will be studied by laboratory and in situ experiments. These will measure the influence of the type of flow and certain physical, chemical and bacteriological parameters (pH, concentrations of reactive species, temperature, presence of SRB) on:

- the mechanisms and rates of corrosion;
- the mechanisms and the kinetics of the formation of scale (notably iron sulphides and silica), their adhesion and detachment to the metal walls;
- corrosion beneath the scale;
- coagulation of sulfides and silica in the brine.

This work will be taken into account notably in a numerical model for calculating scaling in geothermal installations (BRGM, CPERI).

2.3. New methods of protection of the metal surfaces (BRGM, Consorzio Pisa Ricerche, ENEL-VDAG and CPERI).

In the framework of high enthalpy geothermal energy, the programme will concentrate on flows and certain specific processes for tackling scaling and corrosion. In this perspective we intend to study certain diphasic flows and the effect of local characteristics on the increase of corrosion, the effectiveness of the treatments by inhibitor and the formation of scale (Consorzio Pisa Ricerche and CPERI).

The CPERI will also carry out exploratory work to control the thickness and strength of metal sulfide scale.

The Consorzio Pisa Ricerche and ENEL-VDAG will study the elimination, at high temperatures, of chlorides present in the water vapour, upstream of the turbines, by wet (washing with an alkaline solution) or dry (adsorption) methods.

With respect to low enthalpy energy, we will endeavour to improve the efficiency of current treatments using organic inhibitors, while continuing to develop the protection of casing by silica.

The use of organic inhibitors will be validated by:

- assessing the risks of the occurrence of corrosion by pitting;
- studying the effectiveness of the inhibiting agents on metallic surfaces coated by corrosion products;
- research into possible harmful effects on the non-metallic materials of the geothermal loop (notably electrical insulators).

2.4. Detection of perforations of the casing (BRGM).

Perforations of the casing due to corrosion can cause pollution by the geothermal water (treated by inhibitor or otherwise), of the shallow groundwater used for potable water supplies. We shall endeavour to develop a general methodology for the detection and assessment of perforations.
3. ROLE OF PARTICIPANTS

BRGM's Joint Geothermal Institute (IMRG) is the coordinator of the proposed programme.

CEC

BRGM Coordinator

BRGM

CPERI

Consorzio

ICE/HTCP

Pisa Ricerche

of Patras

CEBELCOR

(associated contractor)

ENEL - VDAG

(sub-contractor without CEC support)

Cooperation between the partners is organized by a consortium agreement which will be renewed for the period 1993-95, for which four main themes have been defined. Each will have a coordinator/reporter who will be responsible for transferring information between the teams:

1. The study of scaling processes (ICE/HTCP Patras);
2. The measurement of corrosion (BRGM);
3. The study of the flow of fluids (CPERI);
4. Recommendations for design and exploitation (CPR Pisa).

Also, the partners will organize exchanges of researchers for short study missions (about 15 days) to facilitate and reinforce their mutual cooperation.

The group also possesses many well-equipped analytical laboratories (notably in the departments of geochemistry and analysis of BRGM). On the theoretical level the group is well-equipped with computer facilities for the use or development of computation codes.

Each six months, a meeting will be organized between the partners and the CCE Experts for the reporting of the results of research.

4. DELIVERABLES

Aim n°1. Establishment of the kinetics of the formation and growth of the scale most frequently encountered, with the development of appropriate numerical simulation codes.

4.1.1.1 BRGM, CPERI and ICE/HTCP will determine the kinetics of precipitation of iron sulphides, on a reconstituted (Fe2O3 - H2S - NaCl - H2O system) and an actual geothermal fluid, at atmospheric pressure, and temperatures 60-75°C and ambient.

4.1.1.2 CEBELCOR will study the effects of trace amounts of oxidant on corrosion in H2S environment: small amounts of oxygen will be added to well defined H2S solutions, and pH, redox potential, electrode potential and corrosion rates will be measured. The nature of the oxidized forms of sulphur and of iron sulphides will be analyzed. CEBELCOR will identify the corrosion process (corrosion mode, corrosion rate) when both sulphides and chlorides are present together: well defined solutions of H2S with given amounts of chloride will be exposed to controlled oxidation. The type of corrosion, the corrosion rate, pH, redox potential, electrode potential, thiosulphate and tetrathionate concentration will be observed and measured.

4.1.1.3 CEBELCOR will construct the stability E-pH diagrams for the Fe-S-H2S system.

4.1.1.4 BRGM will study the feasibility of using the isotopic tracer H2S (or radioactive one) for the determination of the mechanisms of growth of scale produced by corrosion (migration of iron to the surface or of HS- towards the metal).
4.1.1.5 BRGM will use the results of chemical analyses, carried out on samples of fluids taken at the surface, and of the conclusions of the work carried out by the CEA in the framework of JOULE1, with the appropriate computer processing (TPDEGAZ, EQ 3/6, SOLMINEQ) to calibrate the solubility of iron sulphides at the temperature and pressure at which these samples were taken.

4.1.1.6 BRGM will study the nature and the stratification of the various phases (by examining the redox potentials of the various layers) with a view to determining the risks of corrosion continuing beneath the scale - deposits.

4.1.1.7 BRGM will realize a modelling of scale of iron sulfides, in order to obtain the variation with time and along the well wall of the scale and to study the effects of the main parameters (flow, pH, H2S, Cl, ...) on scaling, taking into account the kinetic parameters evaluated by the above experiments (4.1.1.1).

4.1.1.8 ICE/HTCP will determine the stability of the supersaturated solutions and the adhesion properties of iron sulfide particles formed after the desuperaturation process.

4.1.1.9 ICE/HTCP will determine the significance of various factors favoring deposition (scaling rates and scale characteristics, measurement of nucleation and growth characteristics). For the experiments, ICE/HTCP will use both batch and continuous flow systems (in cooperation with CPERI). The effect of the presence of organophosphorous compounds and of inorganic orthophosphate in the precipitation of iron sulfides, shall be investigated.

4.1.1.10 CPERI will study the effect of particle/crystal detachment, which may have a great influence on overall scaling rates.

4.1.1.11 CPERI will study silica particle polymerization and deposition, in continuation of the previous programme (JOUG 0005-C).

4.1.1.12 CPERI will realize a computer code for the prediction of the evolution with time or along the pipe line, of the colloidal particle size distribution, the active species concentration and the deposit formation.

Aim n°2. Selection of the most efficient products for inhibiting corrosion or crystal growth.

4.1.2.1 BRGM will evaluate the capacities of various inhibitors to cover new steel casing and/or already coated by scale (iron sulfides). BRGM will determine in each case their kinetics of adsorption- desorption according to the exploitation parameters and the composition of the fluids.

4.1.2.2 BRGM will study the risks of corrosion by pitting due to the presence of the inhibitor by using electrochemical impedance measurement systems.

4.1.2.3 BRGM will examine the behaviour of non-metallic materials used on the low enthalpy geothermal sites, on contact with the geothermal fluid treated by the inhibitor (electrical insulators, seals, etc.).

4.1.2.4 CPERI will study the main parameters which promote coagulation of colloidal particles (sulfides, silica) and allow their separation from the brine prior to reinjection.

Aim n°3. Development of a process for eliminating chlorides by washing the vapour.

4.1.3.1 CPR will study the behaviour of cyclone scrubbers for steam washing with a basic solution (wet washing) and the behaviour of solid sorbents for the same operation (dry washing).

4.1.3.2 ENEL-VDAG will collect the field data on steam, on the efficiency on chloride abatement in existing facilities and on the corrosion in the ENEL's geothermal plants.

4.1.3.3 ENEL-VDAG will give its contribution to the analysis of the results obtained by all partners in order to establish design and management rules or recommendations for geothermal plants.
Aim n°4. Development of the metrology associated with the monitoring of corrosion and scaling.

4.1.4.1 BRGM will determine the limitations and the precision of the various methods of detection (physical measurements, chemical analysis, spot tests) of the appearance of perforations due to the corrosion of the wall wells.

4.1.4.2 BRGM, ICE/HTCP, CEBELCOR and CPR will develop the use of electrochemical measurement systems for the determination of the corrosion modes and the rates of corrosion.

4.1.4.3 BRGM will modify his down hole sampler (developed during the previous programme) in order to be able to be used in high enthalpy geothermal plants (up to 350°C).

Aim n°5. Identification of diphasic flow conditions which aggravate corrosion and scaling.

4.1.5.1 CPERI, BRGM and CPR will study the effect of multi phase flow structure on corrosion rates in pipelines:
- CPERI will study characteristics of the liquid layer at the pipe wall (local velocity, shear stress) affecting corrosion and scaling.
- CPERI will study liquid droplet properties (size, concentration, velocity), essential for two-phase flow computer codes required for the corrosion and fouling predictions and for design recommendations.
- CPR will determine the interactions between the flow structure (steam-brine flow) and corrosion by using a specially designed rig operating with hot water-N₂-CO₂ mixtures.
- BRGM will study the corrosion rate (by using coupons) in monophasic and diphasic zones in an artesian production well.
APPENDIX 2. PART OF THE ADDITIONAL WORK PROGRAMME (PECO)

Cooperation in Science and Technology with Central and Eastern European Countries, 1993

Additional work programme to the non nuclear energy programme JOULE 2,
Contract Nos JOU2-CT92-0108 and CIPD-CT93-0314
"Control of corrosion and scaling in geothermal systems"

Coordinated by the Institut Mixte de Recherches Géothermiques
(Bureau de Recherches Géologiques et Minières, BRGM), Orleans, France.
November 1993

1. PROGRAMME

The comprehension of corrosion and scaling mechanisms and the improvement of means for combatting these phenomena are the main objectives of the Joule 2 programme "Control of corrosion and scaling in geothermal systems". The application of the results concern primarily existing and/or planned French and Greek low enthalpy geothermal plants and Italian and Greek high enthalpy plants. This research programme (which five scientific groups from Central and Eastern European countries are applying to join) is expected to produce the following results:

1. Determination of the kinetics of formation and growth of the scale most frequently encountered, and development of appropriate numerical simulation codes.
2. Selection of the most efficient products for inhibiting corrosion and crystal growth.
3. Development of processes for eliminating chloride ions by washing the vapour.
5. Identification of diphasic flow conditions which aggravate corrosion and scaling.

To achieve these goals, the partners of the programme: BRGM - lMRG (Dr. Ignatiadis, Coordinator) Orleans, France; CEBELCOR (Dr. Pourbaix) Brussels, Belgium; CPERI (Prof. Karabelas) Thessaloniki, Greece; ICE/HT (Prof. Koutsoukos) Patras, Greece, and CPR (Prof. Andreussi) Pisa, Italy, carry out theoretical studies and use experimental loops in laboratories or in geothermal plants.

The possibilities for developing the use of geothermal energy in Hungary, Romania and Lithuania have led us to propose an extension of the programme which would allow the association of new research partners.

This proposal was jointly worked out with:
- the Central Research Institute for Chemistry (CRIC), in Budapest (Hungary),
- the Electrochemical Technologies and Active Anticorrosive Protection laboratory of the Research and Design Institute for Electrical Engineering (ICPE C-60), in Bucharest (Romania),
- the Computer Aided Electrochemistry Laboratory (CAEL) of the University "Politehnica" of Bucharest (Romania) and
- the Bioactive and Biocompatible Polymers Department of the Petru-Poni Institute of Macromolecular Chemistry (BBPDICM), in Iasi (Romania).
- the Institute of Chemistry (ICVL), in Vilnius (Lithuania).

The general objectives of the proposed programme relative to the problems encountered when exploiting geothermal resources (corrosion, scale,...) are the following:

1. Creation and testing of corrosion and/or scaling inhibitors, well adapted to corrosion and scaling problems (CRIC, BBPDICM and ICPE C-60);
2. Determination of the influence of ions (Cl, HS), pH and inhibitors on the corrosion process (CAEL and ICVL);
3. Determination of the corrosion parameters and collection of existing data in currently operational geothermal plants, especially in Romania (ICPE C-60) and Lithuania (ICVL);
4. Design and testing of a prototype for the measurement of corrosion (ICPE C-60 and CAEL);
5. Solving the problems of external corrosion of tubings and reservoirs by means of an automatically monitored cathodic protection system (CAEL, for modelling phenomena and ICPE C-60 for the design and experimentation of the electrical and electronic systems);
6. Definition, harmonization and synthesis of the work to be carried out in the project (IMRG/BRGM coordinator or the other contractants, if necessary).

The programmes of the five laboratories are described in detail below.

Taking into account the JOULE 2 programme presently in progress at the CPERI in Thessaloniki (Greece), the ICE/HT in Patras (Greece), the CPR in Pisa (Italy), the CEBELCOR in Brussels (Belgium) and the IMRG/BRGM in Orleans (France), the optimisation of means will be sought for attaining these objectives, particularly with regard to modelling of corrosion and scale formation in tubing, the design of the system for corrosion measurement and the testing of corrosion and scaling inhibitors.

2. OBJECTIVES AND DELIVERABLES OF THE FIVE SCIENTIFIC GROUPS

2.1. Objectives and deliverables of the CRIC (Central Research Institute for Chemistry Hungarian Academy of Sciences, BUDAPEST)

The general objectives of our research programme are:
• to create and test corrosion and/or scaling inhibitors, well adapted to corrosion and scaling problems (objective n°1).

Objectives:
The particular objectives of our research programme are:
1. to make a systematic study of the structure and the reactivity of newly synthetized molecules in order to develop new type of anti-scale agents and anti-corrosion agents for use in geothermal systems;
2. to develop a mathematical model for inhibition of mineral scaling and metal corrosion in geothermal wells exploited in Hungary, for computer simulation of these processes (including equilibrium thermodynamic relationships, temperature, pressure and water chemistry dependence, adsorption and desorption kinetics of inhibitor compounds);
3. to carry out laboratory experiments in a flow model of wells;
4. to accumulate experimental data in cooperation with partners;

Deliverables:
1. Synthesis of new inhibitor molecules (with different steric and polar characteristics) containing N and/or P with inhibiting effect on scale formation;
2. Laboratory experiments to verify inhibitor efficiency of these compounds;
3. Development of a model for metal corrosion including dissolution, adsorption and desorption of inhibitor molecules;
4. Verification of the model and computer simulation predictions based on existing data in currently operational geothermal plants, especially in Hungary.

2.2. Objectives and deliverables of the ICPE C-60 (Electrochemical Technologies and Active Anticorrosive Protection laboratory of the Research and Design Institute for Electrical Engineering (BUCHAREST).

The general objectives of our research programme are:
• to create and test corrosion and/or scaling inhibitors, well adapted to corrosion and scaling problems (objective n°1);
• to determine the corrosion parameters and to collect the existing data in currently operational geothermal plants, especially in Romania (objective n°3);
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• to design and test a prototype for the measurement of corrosion (objective n°4);
• to solve problems of external corrosion of tubings and reservoirs by means of an automatically monitored cathodic protection system (objective n°5);

Objectives:
The particular objectives of our research programme are:
1. to design, build and test a prototype for active cathodic protection with potentiostatic control for exterior corrosion (metal/ground) of collecting-transport pipes;
2. to determine the kinetic parameters of corrosion in geothermal systems exploited in Romania, and elsewhere if requested;
3. to develop corrosion inhibitor (possibly including crystal growth properties - accordingly to the proposal of Prof. Adrian Carpov); the effectiveness of the inhibitor will be determined by us or by other collaborators;

Deliverables:
1. Design, build and test a prototype for active cathodic protection with potentiostatic control for exterior corrosion (metal/ground) of collecting-transport pipes; this equipment is composed of electronic equipment and adequate sensor; determination of reliability.
2. Determination of the kinetic parameters of corrosion in geothermal systems exploited in Romania, and elsewhere if requested;
3. Attempts to develop corrosion inhibitor (possibly including crystal growth properties - accordingly to the proposal of Prof. Adrian Carpov); the effectiveness of the inhibitor will be determined by us or by other collaborators.

2.3. Objectives and deliverables of the CAEL (Computer Aided Electrochemistry Laboratory University Politechnica), BUCHAREST

The general objectives of our research programme are:
• to determine the influence of ions (Cl-, H^+), pH and inhibitors on the corrosion process (objective n°2);
• to design and test a prototype for the measurement of corrosion (objective n°4);
• to solve problems of external corrosion of tubings and reservoirs by means of an automatically monitored cathodic protection system (objective n°5).

Objectives:
The particular objectives of our research programme are:
1. to model the corrosion processes in large volumes (reservoirs, ducts), using multigrid and finite element methods, in order to simulate the distribution of current and potential field, for an optimum position of anodes in cathodic protection. Primary results will be supplied by ICPE-Romania, where a pilot plant for the study of cathodic protection will be built;
2. to study the corrosion processes due to the presence of HS^- and Cl^- anions. Pitting corrosion as an instability phenomenon will be investigated. Corrosion processes, with oscillating current, the role of pH in damped oscillations, as the additives influence (inhibitors) will be investigated;
3. to develop a programme for monitoring and control of corrosion processes (software for data acquisition using A/D and D/A converter cards).

Deliverables:
1. Determination of the potential distribution and current densities in large volume (reservoirs) systems by using experimental data with a theoretical approach, and corrosion control by cathodic or anodic protection.
2. Determination of the behaviour of iron and iron alloys in the presence of HS^- anion such as instability phenomena. Analysis of the current oscillatory range such as type and oscillation forms.
3. Determination of the kinetic parameters of corrosion in the range of oscillating current.
2.4. Objectives and deliverables of the BBDICM (Academia Romana PETRU-PONI Institute of Macromolecular Chemistry, Bioactive and Biocompatible Polymers Department), IASI

The general objective of our research programme is:
• to create and test corrosion and/or scaling inhibitors, well adapted to corrosion and scaling problems (objective n°1).

Objectives:

The particular objectives of our research programme are:
1. to develop new types of anti-scale agents for geothermal waters, eventually anti-corrosion agents;
2. to study the correlation between the structural composition and physico-chemical properties of polyelectrolytes in the physico-chemical process of the inhibition of crystallisation of carbonates or other components of brine in wells or in installations (heat exchangers, etc.).

This objective will be reached only in close collaboration with other research units of CEC and PECO.

Deliverables:
1. Synthesis and physico-chemical and structural characterization of various polyelectrolytes:
   - Synthesis by radical polymerization of different copolymers of maleic anhydride with hydrophilic or hydrophobic acryl, methacrylic and vinyl monomers.
   - Synthesis of terpolymers of maleic anhydride with two other different comonomers (hydrophilic or hydrophobic).
   - Hydrolysis or chemical modification of the copolymers or terpolymers synthesized
   - Preparation of half salts or salts of the polyelectrolytes obtained
   - Preliminary physico-chemical characterization of the polyelectrolytes obtained

2. Testing of samples of zinc salts of polyelectrolytes as anti-corrosion agents by Mr. Iosif Lingvay from the research and design Institute for Electrical Engineering Bucharest.

2.5. Objectives and deliverables of the ICVL (Institute of Chemistry), VILNIUS

The general objectives of our research programme are:
• to determine the influence of ions ($\text{Cl}^-$, $\text{HS}^-$), pH and inhibitors on the corrosion process (objective n°2);
• to determine the corrosion parameters and to collect the existing data in currently operational geothermal plants, especially in Lithuania (objective n°3).

Objectives:

The particular objectives of our research programme are:
1. to better understand the properties of the interphase layer and the kinetics of its formation in geothermal systems and the influence of this layer on corrosion kinetics;
2. to make it possible to determine the measures necessary to avoid harmful corrosion effects.

Deliverables:

1. Measurement of mass changes and corrosion rate of by EQCM and Rp methods in the system of Fe-$\text{H}_2\text{S}$ geothermal fluid. Determination of the thickness and the composition of the interphase layer by X-Ray photoelectron spectroscopy and Auger electron spectroscopy using the surface etching with an ionized argon.
2. Measurement of mass changes and corrosion rate by EQCM and Rp methods in the system of Fe-geothermal fluid in nitrogen, carbon dioxide, and in air.
3. Study of the influence of exposure time, temperature and chloride ion content on the results mentioned above.
SCIENTIFIC CONTRIBUTIONS
OF THE CONTRACTORS

JOULE II Project, Contract No JOU2-CT92-0108

Title: Control of corrosion and scaling in geothermal systems
COMPARATIVE STUDY OF THE EFFECTIVENESS OF VARIOUS ORGANIC ADDITIVES IN INHIBITING CARBON STEEL CORROSION IN A NATURAL GEOTHERMAL ENVIRONMENT BY USING RAPID ELECTROCHEMICAL TESTS

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SUMMARY

In a continuation of studies reported in the 4th and 5th annual reports, we present here a series of electrochemical tests, "rapid tests", carried out to measure the effectiveness of corrosion inhibitors. This series of tests, complementary to the previous series, provides more precise information on how inhibitors work and their adsorption rate, and enables us to assess the risk of pitting in the presence of each inhibitor. By combining results of the different electrochemical techniques used in the two series of electrochemical tests proposed in the last two 6-monthly reports, called "long term tests" and "rapid tests" we can determine which inhibitor is best adapted to a given metallic material in a given environment. In this study, we evaluated the effectiveness of eight inhibitors by comparing the response of the carbon steel to the various electrochemical techniques of the rapid test. Of these eight inhibitors, Solamine 129 was the most effective.

1. GENERAL CONTEXT

The waters of the Dogger aquifer of the Paris Basin have a pH which is close to neutral and "low" hydrogen sulfide concentrations (Ignatiadis et al., 1991; Ignatiadis and Teton, 1992). The scale formed under these conditions is not protective and causes serious corrosion problems and loss of head. Geothermal installations have been treated for corrosion and scale during the last 8 years with various organic corrosion inhibitors (fatty amines and quaternary ammonium salts) which have already proved their effectiveness in the petroleum field. The inhibitors are injected with a Well Bottom treatment tube. Using a surface pump, sufficient quantities of inhibitors are injected at the bottom of the production well to reach a concentration of around 2.5 mg/l.

The organic corrosion inhibitors on the market are made up of various molecules. Their exact formulae are commercial secrets. It is often difficult to distinguish between products of various origins since they contain the same basic anti-corrosion agent. The formulae on the market generally consist of one or more inhibitor compounds to which other additives such as tensioactive agents, scale boosters, demulsifiers, oxygen eliminators, etc. have been added. The
solvent of the inhibitor can also determine the characteristics of solubility and dispersability and therefore the application of products and the results obtained.

The three corrosion inhibitors which are at the present time the most commonly used for the treatment of wells are Solamine 129® (SEPPIC, Paris, France), Norust 491® (CECA, La Défense, France) and Aquaprox MDC1300® (PROTEX, Levallois, France). All of these products are known to be anticorrosive at the recommended doses (2.5 mg/l) and bactericide at large doses.

Treatment with the inhibitors has decreased the corrosion rates in most cases. Although some of the problems encountered when using these products have been resolved, their use is far from being risk-free. Other difficulties must be overcome, such as scaling which reduces the internal diameter of well casings, under-deposit corrosion which, in most cases, takes the form of pitting (Amalhay and Ignatiadis, 1992; Amalhay et al., 1994a, 1994b, 1995a, 1995b), and a change in the physical and chemical nature of the scale (Amalhay and Ignatiadis, 1995c). These problems are often related to the lack of data concerning the inhibitors used and possibly to a poor adaptation to the specific problems of Dogger geothermal conditions.

The objective of this study is to try to better understand the mechanisms controlling the action of these inhibitors and compare their effectiveness to those of other molecules or formulae which have not been marketed and provided from Prof. A. Carpov (BBPDCM, Iasi, Romania).

To compare the effectiveness of these 8 inhibitors (4 commercial and 4 prepared in the laboratory of Prof. A. Carpov) in reducing the corrosion rate in the presence and absence of scale, we tested them with "rapid tests" (Amalhay and Ignatiadis, 1995d) where electrochemical techniques used to monitor the response of carbon steel electrodes treated from the start with 10 mg/l of each inhibitor, for short periods of about three and a half hours.

2. GENERAL PRINCIPLE AND OPERATING CONDITIONS

The geothermal fluid was collected at the production wellhead and sent through insulated pipes to measurement cells upstream from which a flowrate regulator enabled us to maintain constant flowrates. The inhibitor was injected into the two electrochemical cells (one containing a stationary sample, the other a rotating sample) by means of two HPLC pumps type. The Melun l'Almont site was chosen because it is one of the few Dogger sites that have not yet been treated, and because the fluid there is generally representative of the sites to the south of Paris (total dissolved salts = 12.7 g/l; surface pH = 6.4; production temperature = 72°C; concentrations (mg/l): [Na+] = 4250, [Ca^{2+}] = 580, [Cl⁻] = 7200, [SO₄²⁻] = 680, alkalinity [HCO₃⁻] = 317.0, [SiO₂] = 42.5; dissolved gas (GLR=14.9%), mainly CO₂ = 17.6%, CH₄ = 53.3%, N₂ = 19.7%. The production flow rate varies over the year between 25 m³/h (in a thermosiphon) and 150 m³/h. The bubble point pressure is around 7 bars. Dissolved sulfur content does not vary with flow rate and is 14 mg/l in S²⁻ equivalent.

The working electrodes are made from an API K55 type carbon steel supplied by Valourec Industries (Montbard, France). The average composition by weight per cent of the steel samples is: C: 0.42% (±0.04), Mn: 1.08% (±0.001), Mo: 0.014% (±0.01), Si: 0.34% (±0.04), Ni: 0.092% (±0.005), Cr: 0.100% (±0.005), S: 0.004% (± 0.005).
The commercial tested inhibitors were Solamine 129, Mexel 432, Busperse 59LO (Buckman, Ghent, Belgium) and Aquaprox MMC 7300. The last inhibitor is used in the reijection well of Melun l’Almont. The additives which provided from Prof. A. Carpov and tested in this geothermal site were AV 142.7.1, AV 142.5.2, AP 28.5.2 and ATP 6.2. These additives were choosen for test in Melun geothermal site after electrochemical examination in the ICE/HT as described in the 6th report (Harmadas et al., 1995a and 1995b).

In order to rapidly determine the mode of action and the effectiveness of the 8 inhibitors studied in reducing corrosion, we carried out a series of rapid and successive tests using stationary and transitory electrochemical techniques which consisted in electrochemical monitoring, for short periods of around three and a half hours, of the response of carbon steel electrodes.

Before immersing the electrodes, the inhibitor was injected into the geothermal fluid flowing at a rate of 15 l/h to reach a steady concentration of 10 mg/l, which was maintained throughout each experiment. For a perfect comparison of the performance of the inhibitors, the tests were synchronized (Fig. 1). Stationary and rotating electrodes were also electrochemically monitored in the absence of inhibitor.

The stationary and rotating (1000 rpm) electrodes were left in the solution until they reached a steady state. Preliminary tests showed that 20 minutes was sufficient for electrodes to reach equilibrium and for their open circuit potential to stabilize. This phase, when compared to open circuit corrosion potential values for electrodes in non treated fluid, enabled us to measure variations in open circuit corrosion potential caused by the adding of inhibitors.

After 20 minutes of $E_{\text{corr}}$ monitoring, we switched to the potentiostatic regime and for 10 minutes measured the open circuit corrosion current $I_1$ at $E_{\text{corr}}$.

After measuring the open circuit corrosion potential, we switched to the potentiodynamic regime (0.1 mV/s) to measure the steel's polarization resistance in the various media.

After one hour of immersion, we measure electrochemical impedance in the range of $10^5$ to $10^{-2}$ Hz at the open circuit potential. The amplitude of the superimposed ac signal in the range between $10^5$ and 5 Hz was 5 mV and 10 mV at low frequencies (5 to $10^{-2}$ Hz). These measurements were used not only to determine the resistance of the electrolyte, the polarization resistance or charge transfer resistance and the double layer capacitance, but also to identify the corrosion kinetics and determine the effectiveness of inhibitors.

After 1.5 hours of immersion, we switched to the potentiodynamic regime by scanning the corrosion potential of each sample from an initial potential $E$ ($E_{\text{corr}}$ - 150 mV) to a final potential $E_{f1}$ ($I = 0.5$ mA/cm$^2$). In order to have quasi-stationary conditions, we chose a scanning rate of 0.15 mV/s. When the desired anodic current value was reached, we switched to the potentiostatic regime and for 10 minutes kept the electrode at the limit anodic potential $E_{f2}$ and measured the variations in the currents ($I_2$). At this anodic potential, $I_2$ usually increases with time, certainly indicating the development of localized corrosion (Podobaev et al., 1985) or an increase in anodic activity due to the desorption of the inhibitor which is caused by the imposed polarization (Podobaev et al., 1988).
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The $I_3$ current was then measured for 10 minutes in potentiostatic regime at $E = E_{corr}$ ($E_{corr}$ is here the open circuit corrosion potential of the sample before the second polarization).

All polarization was then stopped for 10 minutes and in a final step, we passed again to the potentiodynamic regime (0.15 mV/s) by polarizing the sample from its new open circuit corrosion potential up to an anodic potential ($E_{f2}$) where the current is again equal to 0.5 mA/cm².

Also, we tested some of the previous additives in the overnight A.C.-Impedance experiments for evaluation of their effectiveness for larger time periods. These experiments were done only with static electrode and constant injection of additive at 10 mg/l of geothermal fluid. The additives tested at these experiments are Solamine 129, Aquaprox MMC 7300, Mexel 432, AP 28.52.1 and AV 142.7.1.

Finally, experiments for the evaluation of behaviour of NORUST 491 were done at the geothermal site of Coulommiers. This additive is used at the production well of Coulommiers at concentration of 5 mg/l. Stationary and rotating electrodes were used at these experiments. Experiments without NORUST 491 or in the presence of previous additives were not done because Norust 491 continuously injected at the bottom of the production well. Thus, the only useful measured parameter for the evaluation of the effectiveness of Norust 491 was the polarization resistance. The monitoring of polarization resistance was done with successive D.C and A.C. measurements.

3. RESULTS AND DISCUSSION

3.1. Monitoring of the open circuit corrosion potential

Monitoring of open circuit corrosion potential of carbon steel just after its immersion in Melun geothermal fluid, treated or untreated prior to immersion with various inhibitors, clearly shows an increase in the potential with the addition of Solamine 129, Mexel 432 and Aquaprox MMC 7300. The potential of the metal increased from 20 to 60 mV during the first 20 minutes of immersion (Figs. 2 et 3). On the other hand, no significant increase of open circuit corrosion potential was observed in the addition of Busperse 59LO, AP 28.52.1, AV 142.52.1, AV 142.7.1 and ATP 6.2. This increase in the open circuit potential is due to the adsorption of inhibitor (for the first three additives) on the surface of the steel and a reduction in the rate of dissolution of the metal in contact with the fluid. The variations in open circuit corrosion potential of the samples in the presence of each inhibitor might therefore indicate its adsorption rate on the surface of the metal. The inhibitors seem to have different adsorption rates depending on whether the electrode is stationary or rotating. Solamine 129 caused the greatest increase in carbon steel corrosion potential under these conditions. On the other hand, Aquaprox MMC 7300 and Mexel 432 seem to increase the potential of the metal ($\Delta E_1$ and $\Delta E_2$) during the period of immersion (Table 1). In the case of rotating electrodes, the effect of the rotation and the hydrodynamic regime created give a difference in the adsorption rate of inhibitors than in the case of stationary electrodes. Solamine 129 caused again the greatest increase in corrosion potential of carbon steel in comparison with AV 142.52.1 and AV 142.7.1 as shown in the figure 4. On the contrary, in the presence of AV 142.52.1 and AV 142.7.1 is observed a increase in the potential of the specimen ($\Delta E_1$ and $\Delta E_2$) during the immersion (Table 1).
3.2. Analysis of electrochemical impedance diagrams

Electrochemical impedance diagrams clearly show a significant change in the behaviour of the steel-geothermal fluid interface when corrosion inhibitor is added. In the absence of corrosion inhibitor, the impedance diagram of stationary electrode forms a semi-circle, slightly off-centre from the axis of real impedance values on the Nyquist plane (Fig. 5). At low frequencies, this diagram shows the tendency to approach the axis of real impedances, the polarization resistance thus derived are weak compared to those obtained when a effective additive added. In the presence of Solamine 129, Aquaprox MMC 7300 and Mexel 432 the diagrams form only the half of a circle as shown in the figure 6. On the contrary in the presence of Busperse 59LO, ATP 6.2, AV 142.52.1, AV 142.7.1 and AP 28.52.1 the diagramms were found similar as in the absence of the additives (Fig. 5). From the impedance diagramms (Fig. 5 and 6), in the presence of Solamine 129, Aquaprox MMC 7300 and Mexel 432 at low frequencies the curves show the tendency to form a second larger semicircle. This tendency indicates a mixed regime of charge transfer and diffusion-convection. On the contrary, from the curves shape in the presence of the other tested additives and in the absence of additives a charge-transfer mechanism seems to be predominant.

Polarization resistance values obtained by linear polarization ($R_p$) and by analysis of impedance diagrams ($R_{pw}$) for similar immersion times are comparable (Table 2). The double layer capacities decreased significantly with the addition of Solamine 129 and Aquaprox MMC 7300.

3.3. Polarization tests

Using the polarization range chosen for the first potentiodynamic test ($E_{corr}$ - 150 mV; $E_{f1}$ ($I = 0.5$ mA/cm$^2$)), we studied the effect of inhibitors on the anodic and cathodic processes of the corrosion reaction. The effect of each inhibitor was compared to the response to the system at the same polarizations without treatment. We known that in the presence of $H_2S$, iron sulfides formed when iron dissolves participate and form a more or less protective layer (Podobaev et al., 1988 and 1989). According to these authors, the increase in the anodic potential:

1) favours the formation of iron sulfide and therefore the formation of a protective layer

2) contributes to the rupture of this layer and therefore to localized dissolution of iron.

This localized corrosion can be seen on the polarization curve ($E$, $Log(I)$) by a sharp increase in the anodic activity. Under our physico-chemical and experimental conditions, the corrosion seems to remain uniform.

3.3.1. Cathodic behaviour

The adding of corrosion inhibitor sharply decreased the cathodic current, especially in the case of stationary electrodes where the current was reduced by a factor of 10 for an overvoltage of 100 mV. For rotating electrodes it was reduced only by a factor of 4.
For a better graphic comparison of cathodic and anodic components, we superimposed the Tafel polarization curves (E, LogI) with a translation, on the axis of the potentials, of the curves relative to the treated electrodes. The values of the translation potentials for each type of inhibitor are given in millivolts in the legend after the name of the inhibitor (Figs. 6 and 7).

The most effective on the average, for stationary electrodes, were Solamine 129® and Aquaprox MMC 7300 and for rotating electrodes was Solamine 129. The results of analyses of polarization curves of stationary and rotating electrodes are given in Table 3.

In the absence of inhibitor treatment, the reduction reaction is controlled by transfer of charge, as shown by the impedance diagrams. The Tafel cathodic constant, Bc, is about 245 mV/decade for stationary electrodes and 850 mV/decade for rotating electrodes.

With treatment, and especially with stationary electrodes, some inhibitors reduced the diffusion from the solution towards the interface of the metal of species participating in the cathodic reaction to such an extent that the corrosion rate became partially controlled by diffusion. The shape of the impedance diagrams (figures 5 and 6) shows this change in kinetic behaviour. In this case, Bc values no longer represent true Tafel constants but are simply a means of comparison of the tendency towards depolarization of the steel in the presence of each inhibitor.

3.3.2. Anodic behaviour

As described in the experimental section, we recorded two anodic polarization values for each electrode during a 30 minute time interval between the end of the first and the start of the second polarization. The final anodic current is 0.5 mA/cm². In comparison with untreated electrodes, Solamine 129 and Aquaprox MMC 7300 produce the large reduction in the anodic current of iron dissolution. As in the case of cathodic processes, Solamine 129 was more effective with stationary electrodes than with rotating electrodes (Table 3).

The anodic curves show no passivation zone (Figs. 7 and 8). The dissolution rate of iron to the anode seems to be controlled by charge transfer. The Tafel anodic constants (second polarization: Bₐ₁, and third polarization: Bₐ₂) increased with treatment, for Solamine 129 and Aquaprox MMC 7300, indicating a slowing down or a blocking of the iron ionization process. Solamine 129® was the inhibitor which reduced the anodic current of the stationary and rotating electrodes the most.

For the ATP 6.2, AV 142.7.1, AV 142.52.1 and AP 28.52.1 the polarization curves and measured currents are similar with those in the absence of additives. The measured current for the commercial additives decreases with the following order:

Blank > Busperse 59LO ≡ Mexel 432 > Aquaprox MMC 7300 > Solamine 129

as shown in the Figure 8. The measured corrosion rates from the polarization curves shown in the Table 3. The lower corrosion rate determined for Solamine 129 and Aquaprox MMC 7300. The corrosion rate in the presence of Mexel 432 was found twice in comparison with corrosion rate for the Solamine 129 and in the presence of Busperse 59LO was found three times larger than in the presence of Solamine 129. For the all the other additives the corrosion rate was found similar to the corrosion rate determined in the absence of additives.
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By monitoring $I_3$ and using the second anodic polarization, we were able to test the ability of inhibitors to stabilize the surface of the metal after the metal had been subjected to "strong polarizations" during the second polarization and the monitoring of $I_2$ at $E_{f1}$ for 10 minutes. The higher the overvoltage ($\Delta E_{p2} = E_{p2} - E_2$) and the lower the $I_3$ current (even to negative values), the more effective is the inhibitor.

Indeed, since we polarize all of the samples from the open circuit corrosion potential up to $E_f$ ($I = 0.5$ mA/cm²), the most effective inhibitor is that which most increases the anodic overvoltage ($\eta = E_f - E$ (0.5 mA/cm²)). We can therefore define a "resistance to depolarization" (RD) that steel acquires in the presence of each inhibitor:

$$RD = \frac{\eta}{I} \text{ (ohm.cm²)}$$

knowing that :

$$\Delta E_{p1} = E_{f1} (I = 0.5 \text{ mA/cm²}) - E_1$$
$$\Delta E_{p2} = E_{f2} (I = 0.5 \text{ mA/cm²}) - E_{cor2}$$

with:

- $E_1$ being the corrosion potential of the sample at the second polarization
- $E_{cor2}$ being the open circuit corrosion potential of the sample before the third polarization

In our tests where $I = 0.5$ mA/cm²:

$$RD_1 = 2 \Delta E_{p1} \text{ and } RD_2 = 2 \Delta E_{p2}.$$ 

The difference between these two RD is also a good indicator of the effectiveness of inhibitors. The effectiveness of the inhibitor is measured by its adsorption rate and its ability to provide a good protection of the metal when there are strong localized currents, for example in the case of localized corrosion, or uniform corrosion as in the case of the first polarization. In our case, the most effective inhibitor is therefore the one with the largest ($\Delta E_{p2} - \Delta E_{p1}$).

Solamine 129 gave the larger increase in the anodic overpotential in comparison with the other commercial additives. The increase of anodic overpotential for the commercial additives follows the below serie with decreasing order:

$$\text{Solamine 129} > \text{Aquaprox MMC 7300} > \text{Mexel 432} > \text{Busperse 59LO} > \text{Blank}$$

The results given in table 3 show that with stationary electrodes, Solamine and Aquaprox MMC 7300 seem to be the most effective, while Solamine 129 seem to be the most effective for rotating electrodes.

3.4. Potentiostatic behaviour

Potentiostatic monitoring of the corrosion current is another method for evaluating the effectiveness of inhibitors and qualifying the interfacial stability of the electrode. As described in the experimental section, we measured the current for periods of 10 minutes for different immersion times and under different conditions ($I_1$, $I_2$, $I_3$) (Table 4). $I_1$ currents are for the most part anodic, except when Busperse 59LO and AP 28.52.1 were used with stationary electrodes. This might be due to their low adsorption rate (Fig. 2). The corrosion potential continued to increase after the first 20 minutes of immersion ($E > E_{corr}$), resulting in the cathodic currents measured during potentiostatic monitoring at $E_{corr}$. 

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With rotating electrodes, Solamine has cathodic \( I_1 \) current. This shows a decrease in the adsorption rate of this additive which might be due to the hydrodynamic movement of the water at the surface of the electrode. Open circuit potential values for rotating electrodes showed that the potential continues to increase during the first two hours of immersion (Table 1).

Without inhibitor, \( I_1 \) is always stable and anodic for all electrodes.

During the 10 minutes of monitoring of \( I_2 \) at Efl, there was a drop in anodic current from 0.5 to 0.35 mA/cm\(^2\) for stationary and rotating electrodes in untreated fluid. The same behaviour was observed for the most of the tested inhibitors. The drop in the steel dissolution current during the potentiostatic monitoring at Efl, is certainly due to a passivation of the electrode surface by iron sulfide scale. Solamine 129 and Aquaprox MMC 7300 gave a small \( I_2 \) decrease for stationary electrodes and Solamine 129 gave a increased \( I_2 \) for the rotating electrodes.

In the presence of inhibitors, the increase in the \( I_2 \) current might be due to several factors:

- a progressive desorption of inhibitors at high anodic corrosion potentials, resulting in the decrease in the potential of the steel and therefore in a shift of the potential intensity curve towards cathodic potentials (to the left), accompanied by a logical increase in the anodic current;
- the appearance of localized corrosion which might be the result of an insufficient amount of inhibitor at these anodic potentials;
- a blocking of inhibitors in the interphase due to the large flux of ferrous ions created by this dissolution.

Monitoring the \( I_3 \) current after the first anodic polarization and potentiostatic monitoring at Efl enable us to evaluate the ability of inhibitors to restore the stability of the sample and counteract high anodic activity in the case, for example, of pitting. The most effective inhibitors are those which are able to decrease the current, or induce a cathodic control of the reaction. Solamine 129, Aquaprox MMC 7300 and Busperse 59LO were able to do this (Table 3). The obtention of a \( I_3 \) current lower than the \( I_1 \) current is also a criteria for effectiveness of inhibitor.

### 3.5. Complementary experiments

In figure 10 we present the variation of open circuit potential of stationary carbon steel electrodes with time in the presence and in the absence of additives. The additive AP 28.52.1 gave the larger shift in the open circuit potential. This probably is due in the presence of zinc ions in this additive. From the commercial additives Solamine 129 and Aquaprox MMC 7300 gave the higher shifts in open circuit potential. Also, in figure 11 the variation of polarization resistance of stationary carbon steel electrodes with the time is presented. Only for Solamine 129 and Aquaprox MMC 7300 the polarization resistance was found significantly higher in comparison with the other additives.
3.6. Study of the effect of NORUST 491 in the corrosion of carbon steel at Coulommiers geothermal site

The production well at the Coulommiers geothermal site is treated with corrosion inhibitor NORUST 491 (CECA, La Defense, France) at concentration 5 mg/l. Thus, we not executed any rapid test for the selected additives as at Melun l’Almont. We measured only the polarization resistance of stationary and rotating carbon steel electrodes using A.C. and D.C. - electrochemical techniques. The variation of polarization resistance for both electrodes with time is presented in figure 12. The polarization resistance of stationary carbon steel electrode shows a small increase with time in comparison with the increase of polarization resistance of rotating carbon steel electrode. The NORUST 491 seems to be more effective for rotating electrodes than stationary electrodes. This is verified from the previous "rapid tests" for NORUST 491 at Melun l’Almont (Amalhay and Ignatiadis, 1995d in the 5th periodic report,).

Also, as shown in figure 13 the open circuit potential of rotating electrode is more anodic than open circuit potential of static electrode under the same experimental conditions and the same time. This is caused by the stronger adsorption of Norust 491 to rotating electrode. The calculated capacitance of double layer from impedance diagrams for rotating electrode decreases with time from 4 mF to 1.7 mF (for time period 6h). On the contrary, the capacitance of double layer for static electrode increases from 8.5 mF to 11.3 mF for the same time period. The decrease of double layer capacitance shows strong adsorption of Norust 491 on the surface of carbon steel electrode. The same effect is observed for the double layer capacitance and effectiveness in the impedance diagrams from "rapid tests" for Solamine 129 and Aquaprox MMC 7300 at Melun l’Almont as shown in Table 2.

4. CONCLUSIONS

After 2 hours of immersion, polarization resistance values of stationary and rotating electrodes were measured in the presence and absence of corrosion inhibitors. The anodic and cathodic constants measured on polarization curves under the same conditions enabled us to calculate the corrosion currents.

We have evaluated the effectiveness of inhibitors on stationary and rotating electrodes by comparing corrosion currents measured in the case of electrodes without treatment. These measurements showed that the inhibitors are more effective on stationary electrodes than on rotating electrodes except NORUST 491.

Solamine 129®, the most effective inhibitor in this test, protects both stationary and rotating electrodes.

Polarization curves and impedance diagrams show a decrease in anodic and cathodic activity of steel in the geothermal fluid.

Solamine 129® and Aquaprox MMC 7300 have the same effectiveness on stationary electrodes.

NORUST 491 shows better behaviour in rotating electrodes than static electrodes at the tests in Coulommiers geothermal site.
5. REFERENCES


6. TABLES AND FIGURES

Fig. 1 - Sketch showing the electrochemical monitoring for the comparative study of the effectiveness of inhibitors
Control of corrosion and scaling in geothermal systems

### Table 1 - Evolution of the carbon steel corrosion potential of the stationary (0 rpm) and rotating (1000 rpm) electrodes as a function of the inhibitor injected ([inhib.]= 10 mg/l), DE1 = E_{cor1} - E_{corr} (0.3 h); DE2 = E_{cor2} - E_{corr} (0.3 h).

<table>
<thead>
<tr>
<th></th>
<th>without inhibitor</th>
<th>Solamine 129</th>
<th>Mexel 432</th>
<th>Busperse 59LO</th>
<th>Aquaprox MMC730</th>
<th>ATP 6.2</th>
<th>AV 142.52.1</th>
<th>AV 142.7.1</th>
<th>AP 28.52.1</th>
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<tbody>
<tr>
<td><strong>Ecorr/nV</strong></td>
<td>1.78</td>
<td>-719</td>
<td>-757</td>
<td>-776</td>
<td>-737</td>
<td>-779</td>
<td>-778</td>
<td>-774</td>
<td>-769</td>
</tr>
<tr>
<td><strong>DE1 (mV)</strong></td>
<td>-5</td>
<td>10</td>
<td>11</td>
<td>6</td>
<td>19</td>
<td>-4</td>
<td>20</td>
<td>1</td>
<td>3</td>
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<tr>
<td><strong>DE2 (mV)</strong></td>
<td>2</td>
<td>37</td>
<td>31</td>
<td>9</td>
<td>38</td>
<td>12</td>
<td>29</td>
<td>14</td>
<td>20</td>
</tr>
<tr>
<td><strong>Ecorr/nV</strong></td>
<td>-733</td>
<td>-662</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-746</td>
<td>-737</td>
<td>-</td>
</tr>
<tr>
<td><strong>DE1 (mV)</strong></td>
<td>-1</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>33</td>
<td>23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>DE2 (mV)</strong></td>
<td>2</td>
<td>38</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>49</td>
<td>46</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 2 - Results of analyses of impedance diagrammes relative to stationary (0 rpm) and rotating (1000 rpm) electrodes of carbon steel in Melun geothermal fluid in the presence of various additives after 1 h 12 min of immersion.

<table>
<thead>
<tr>
<th></th>
<th>without inhibitor</th>
<th>Solamine 129</th>
<th>Mexel 432</th>
<th>Busperse 59LO</th>
<th>Aquaprox MMC730</th>
<th>ATP 6.2</th>
<th>AV 142.52.1</th>
<th>AV 142.7.1</th>
<th>AP 28.52.1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R_p (ohm.cm²)</strong>*</td>
<td>160</td>
<td>1070</td>
<td>235</td>
<td>189</td>
<td>348</td>
<td>212</td>
<td>178</td>
<td>171</td>
<td>142</td>
</tr>
<tr>
<td><strong>R_{nw} (ohm.cm²)</strong></td>
<td>150</td>
<td>1549</td>
<td>297</td>
<td>246</td>
<td>355</td>
<td>260</td>
<td>126</td>
<td>195</td>
<td>181</td>
</tr>
<tr>
<td><strong>f_{Z_{max} (mHz)}</strong></td>
<td>470</td>
<td>210</td>
<td>290</td>
<td>350</td>
<td>470</td>
<td>470</td>
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<tr>
<td><strong>C (mF)</strong></td>
<td>20.4</td>
<td>8.95</td>
<td>13.7</td>
<td>19.4</td>
<td>6.4</td>
<td>13.2</td>
<td>18.3</td>
<td>13</td>
<td>16.3</td>
</tr>
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**EEC** - **DG XII** - Joule Programme - contract No JOU2-CT92-0108 - 7th periodic report
Control of corrosion and scaling in geothermal systems

<table>
<thead>
<tr>
<th>without inhibitor</th>
<th>Solamine 129</th>
<th>Meezel 432</th>
<th>Busperse 59LO</th>
<th>Aquaprox MMC 7300</th>
<th>ATP 6.2</th>
<th>AV 142.52.1</th>
<th>AV 142.7.1</th>
<th>AP 28.52.1</th>
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<tbody>
<tr>
<td>DEp1 (mV)</td>
<td>50</td>
<td>126</td>
<td>62</td>
<td>56</td>
<td>74</td>
<td>55</td>
<td>48</td>
<td>47</td>
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<tr>
<td>DEp2 (mV)</td>
<td>46</td>
<td>124</td>
<td>150</td>
<td>47</td>
<td>149</td>
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<td>43</td>
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<tr>
<td>(DEp1-DEp2) (mV)</td>
<td>-4</td>
<td>-2</td>
<td>88</td>
<td>-9</td>
<td>75</td>
<td>-5</td>
<td>-9</td>
<td>-4</td>
</tr>
<tr>
<td>Ba1 (mV)</td>
<td>72</td>
<td>87</td>
<td>62</td>
<td>52</td>
<td>49</td>
<td>67</td>
<td>66</td>
<td>60</td>
</tr>
<tr>
<td>Ba2 (mV)</td>
<td>53</td>
<td>103</td>
<td>60</td>
<td>54</td>
<td>156</td>
<td>55</td>
<td>46</td>
<td>48</td>
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<tr>
<td>Bc (mV)</td>
<td>245</td>
<td>365</td>
<td>288</td>
<td>227</td>
<td>106</td>
<td>257</td>
<td>368</td>
<td>307</td>
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<tr>
<td>$R_p$ (ohm.cm$^2$)</td>
<td>202</td>
<td>1218</td>
<td>349</td>
<td>220</td>
<td>604</td>
<td>229</td>
<td>178</td>
<td>189</td>
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<tr>
<td>C.R. (mmppy)</td>
<td>1.196</td>
<td>0.209</td>
<td>0.416</td>
<td>0.627</td>
<td>0.236</td>
<td>1.022</td>
<td>1.361</td>
<td>1.222</td>
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Table 3 - Parameters relative to the behaviour of stationary (0 rpm) and rotating (1000 rpm) electrodes of carbon steel in the presence of various additives.

<table>
<thead>
<tr>
<th>without inhibitor</th>
<th>Solamine 129</th>
<th>Meezel 432</th>
<th>Busperse 59LO</th>
<th>Aquaprox MMC 7300</th>
<th>ATP 6.2</th>
<th>AV 142.52.1</th>
<th>AV 142.7.1</th>
<th>AP 28.52.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>II (mA/cm$^2$)</td>
<td>16.6</td>
<td>2.9</td>
<td>25</td>
<td>-5.4</td>
<td>1.3</td>
<td>36.3</td>
<td>4.6</td>
<td>29</td>
</tr>
<tr>
<td>I2 (mA/cm$^2$)</td>
<td>0.4</td>
<td>0.46</td>
<td>0.34</td>
<td>0.46</td>
<td>0.42</td>
<td>0.3</td>
<td>0.47</td>
<td>0.37</td>
</tr>
<tr>
<td>I3 (mA/cm$^2$)</td>
<td>10</td>
<td>18</td>
<td>34</td>
<td>-20</td>
<td>10.6</td>
<td>40</td>
<td>30</td>
<td>39</td>
</tr>
<tr>
<td>Icorr (mA/cm$^2$)</td>
<td>102</td>
<td>17.8</td>
<td>62</td>
<td>53.5</td>
<td>35.9</td>
<td>87.1</td>
<td>116</td>
<td>104</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4 - Comparison of the response of stationary (0 rpm) and rotating (1000 rpm) electrodes to the three potentiostatic tests ($I_1$, $I_2$, $I_3$) as a function of the inhibitor injected and the effectiveness of the inhibitor after 2 h of immersion ($I_{corr}$).
Control of corrosion and scaling in geothermal systems

Fig. 2 - Variations in the open circuit potential of API K55 steel in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l as a function of immersion time at 0 rpm.

Fig. 3 - Variations in the open circuit potential of API K55 steel in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l as a function of immersion time at 0 rpm.
Fig. 4 - Variations in the open circuit potential of API K55 steel in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l as a function of immersion time at 1000 rpm.

Fig. 5 - Impedance diagrams for API K55 after 1 h of immersion in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l at 0 rpm.
Control of corrosion and scaling in geothermal systems

Fig. 6 - Impedance diagrams for API K55 after 1 h of immersion in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l at 0 rpm.

Fig. 7 - Polarization curves for API K55 (0 rpm) after 2 h of immersion in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l (shifted to the same $E_{\text{corr}}$).
Control of corrosion and scaling in geothermal systems

Fig. 8 - Polarization curves for API K55 steel (0 rpm) after 2 h of immersion in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l (shifted to the same E_{corr}).

Fig. 9 - Polarization curves for API K55 after 2 h of immersion in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l at 1000 rpm (shifted to the same E_{corr} potential).
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Fig. 10 - Variation in the open circuit potential of API K55 steel in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l as a function of immersion time at 0 rpm.

Fig. 11 - Variation in the polarization resistance of API K55 in Melun geothermal fluid in the presence of additives at concentration of 10 mg/l as a function of immersion time at 0 rpm.
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Fig. 12 - Variations of polarization resistance of API K55 steel in Coulommiers geothermal fluid in the presence of 5 mg/l of NORUST 491 at 0 rpm and 1000 rpm.

Fig. 13 - Variation of open circuit potential of API K55 steel in Coulommiers geothermal fluid in the presence of 5 mg/l of NORUST 491 at 0 rpm and 1000 rpm.
Control of corrosion and scaling in geothermal systems

COMPARATIVE STUDY OF THE EFFECTIVENESS OF VARIOUS ORGANIC SURFACANTS IN INHIBITING IRON SULFIDE PRECIPITATION IN A NATURAL GEOTHERMAL ENVIRONMENT

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1. Institute of Chemical Engineering and High Temperature Chemical Processes and the Department of Chemical Engineering, University of Patras, P.O.Box 1414, GR-26500 Rio-Patras, Greece.
2. BRGM, Research Division, Department of Geotechnical Engineering and Mineral Technology, 3, Avenue C. Guillemin, BP 6009, 45060 Orleans, France.

SUMMARY

Continuing the FeS precipitation laboratory experiments carried out in the ICE/HT as presented in the previous semi-annual reports, a series of on-site experiments were done. The objective of these experiments was to obtain experimental data concerning the nature of the solid forming by direct precipitation of iron sulfide in supersaturated natural geothermal fluid and the kinetics of formation of the precipitate. The effectiveness of various organic additives in inhibiting the formation of iron sulfide precipitates under the same conditions, was also tested. Seven organic additives were tested, being the same as those tested for their corrosion inhibition properties.

The phase which was found to form in all experiments (blank and treated with additives) was mackinawite. The kinetics of mackinawite formation indicated a surface controlled mechanism for the process. Of the seven additives tested as iron sulfide scale formation inhibitors, none was found to be adequately effective. The only substance found to exhibit significant inhibition effectiveness in solutions of low supersaturation, was ATP 6.2.

1. GENERAL CONTEXT

The waters of the Dogger aquifer of the Paris Basin have a pH which is close to neutral and "low" hydrogen sulfide concentrations (Ignatiadis and Teton, 1992). The scale formed under these conditions is not protective and causes serious corrosion problems and loss of head. Geothermal installations have been treated for corrosion and scale during the last 8 years with various organic corrosion inhibitors (fatty amines and quaternary ammonium salts) which have already proved their effectiveness in the petroleum field. The inhibitors are injected with a Well Bottom treatment tube. Using a surface pump, sufficient quantities of inhibitors are injected at the bottom of the production well to reach a concentration of around 2.5 mg/l.

The organic corrosion inhibitors on the market are made up of various molecules. The exact formulae of the commercial corrosion inhibitors are commercial secrets. It is often difficult to distinguish between products of various origins since they contain the same basic anti-
corrosion agent. The formulae on the market generally consist of one or more inhibitor compounds to which other additives such as tensioactive agents, scale boosters, demulsifiers, oxygen eliminators, etc. have been added. The solvent of the inhibitor can also determine the characteristics of solubility and dispersability and therefore the application of products and the results obtained.

The three corrosion inhibitors which are at the present time the most commonly used for the treatment of wells are Solamine 129® (SEPPIC, Paris, France), Norust 491® (CECA, La Défense, France) and Aquaprox MDC1300® (PROTEX, Levallois, France). All of these products are known to be anticorrosive at the recommended doses (2.5 mg/l) and bactericide at large doses.

Treatment with the inhibitors has decreased the corrosion rates in most cases. Although some of the problems encountered when using these products have been resolved, their use is far from being risk-free. Other difficulties must be overcome, such as scaling which reduces the internal diameter of well casings, under-deposit corrosion which, in most cases, takes the form of pitting (Amalhay and Ignatiadis 1992; Amalhay et al., 1994a, 1994b, 1995a, 1995b), and a change in the physical and chemical nature of the scale (Amalhay and Ignatiadis, 1995). These problems are often related to the lack of data concerning the inhibitors used and possibly to a poor adaptation to the specific problems of Dogger geothermal conditions.

The objective of this study is to try to understand better the mechanisms controlling the action of these inhibitors and compare their effectiveness to those of other molecules or formulae which have not been marketed and are synthesized and provided by the group of Prof. A. Carpov (BPDICM, Iasi, Romania).

To evaluate the effectiveness of the 7 additives used, (4 commercially available and 3 prepared in the laboratory of Professor A. Carpov) in reducing the rate of FeS precipitation, we carried a series of free-drift precipitation experiments, including experiments without the addition of any compound (blank), and with addition of the additives tested at a concentration level of 5 mg/l. The experiments were carried out at various supersaturations created by enriching the geothermal fluid with Fe²⁺ ions.

2. GENERAL PRINCIPLE AND OPERATING CONDITIONS

The Melun l’Almont geothermal site has two production wells, PM2 a 26 years-old well and PM4 a one year-old (production started in July 1995). This site was chosen because it is one of the few Dogger sites that have not yet been treated, and because the fluid there is generally representative of the sites to the south of Paris. During this study only the geothermal fluid of PM-4 well was collected at the production wellhead. The main physico-chemical characteristics of this fluid are: (total dissolved salts = 13.6 g/l; surface pH = 6.4; production temperature = 72°C; concentrations (mg/l): [Na⁺] = 4440, [Ca²⁺] =595, [Cl⁻] = 7400, [SO₄²⁻] = 600, alkalinity [HCO₃⁻] = 331.0, dissolved gas (GLR=13%), mainly CO₂ = 12 %, CH₄ = 52%, N₂ = 25%. The production flow rate varies over the year between 25 m³/h (in a thermosiphon) and 220 m³/h. The bubble point pressure is around 7 bars. Dissolved sulfur content is 10.5 mg/l in S²⁻ equivalent.
The geothermal fluid was collected at the production wellhead of PM-4 well and sent through insulated pipes to a reaction cell upstream from which a flowrate regulator enabled us to maintain constant flowrates. The reaction cell was the same double walled vessel used in the laboratory experiments as it has been described in previous (5th) six-monthly report (Harmandas et al., 1995a). The hot fluid circulated through the water-jacketed part of the cell, in order to maintain constant temperature conditions for the reactor, same as those in the production wellhead. A three-way valve was fitted on the outflow tube immediately after the reactor cell and was used in order to collect the appropriate volume of geothermal fluid to be used as the working solution. The experimental setup is illustrated in figure 1.

The fluid to be used was collected a few moments before starting the experiment. Next it was immediately filtered through 0.22 μm cellulose membranes to remove any suspended particles, and transferred in the thermostated reactor which was instantly sealed with a lid. The time needed for the entire procedure never exceeded 2 minutes, so that changes in temperature and loss of gases was minimized. Magnetic stirring was then switched on and the appropriate volume of concentrated compound to be tested was added in the reactor. The solution was allowed for another two minutes to reequilibrate at the original temperature, and then a small amount of Fe²⁺ solution was added to create the desired supersaturation in the working solution with respect to iron monosulfides. Immediately, the precipitation of black iron sulfide was apparent in the working solution. The progress of the reaction was followed by retrieving small aliquots of the working solution in regular small time intervals to be analysed for total iron with Atomic Absorption Spectroscopy. The evolution of the working solution's pH value was recorded by the computer controlled system which has been described in the previous reports (Harmandas et al., 1995a). The precipitation reaction was allowed to proceed for 10 minutes. Next the working solution was filtered and the solid collected was kept in a desiccator at an inert atmosphere for further characterization. Various levels of supersaturation were used for each set of experiments, for a more thorough evaluation of the inhibiting efficiency of the various compounds.
The commercially available inhibitors tested were Norust 450, Solamine 129, Busperse and Aquaprox MMC 7300. The latter compound is used in the reinjection wellhead of Melun l'Almont. The additives which were provided by Prof. A. CARPOV and tested in this geothermal site were AV 142.52.1, AP 28.52.1 and ATP 6.2. These additives were chosen to be tested, after preliminary examination at ICE/HT (Harmandas et al., 1995b).

3. RESULTS AND DISCUSSION

The Melun l'Almont (PM-4 well) geothermal water is not supersaturated with respect to iron monosulfides as it has been calculated using the HYDRAQL computer code, and verified by the stability of several samples of the fluid for adequately long periods of time. This is due to the low iron concentration on one hand, and to the high ionic strength on the other. The S²⁻ concentration was rather high and ranged between 10 mg/l (in winter period) and 17 (in summer period) mg/l. In order to perform iron sulfide precipitation experiments, therefore the Fe²⁺ concentration in the working solution should be enriched so as to attain spontaneous precipitation of FeS.

Due to the high gas content of the geothermal fluid mainly CO₂ and H₂S, the computer controlled automatic system was restricted in just recording the pH value of the working solution throughout each experiment. Loss of CO₂ and/or H₂S to the air space over the working solution, led to a shift of the pH to higher values, screening out the pH decrease caused by the proton-releasing FeS precipitation process (Fig. 2). Taking into account the fact that the change in the redox potential of the working solution cannot be related to the progress of FeS precipitation (as found in earlier laboratory experiments), no measurable physicochemical property was available so as to apply the constant supersaturation experimental techniques used in our laboratory. As a consequence we have followed the free-drift experimental approach.

![Fig. 2 - Typical pH versus time curve for the free-drift experiments.](image-url)
Control of corrosion and scaling in geothermal systems

The solid phase found was identified to be mackinawite. Following the analysis of the samples withdrawn from all working solutions, plots of the iron concentration versus the time lapsed during precipitation were derived. The initial supersaturations of the working solutions with respect to mackinawite were also calculated using the HYDRAQL computer program. The data used concerning the concentrations of the various ions contained in the geothermal fluid are taken from the analyses carried out in Melun l'Almont by BRGM during the performance our experiments. Data for the initial Fe$^{2+}$ concentration are taken from analysis of the first sample for each experiment (withdrawn just before the addition of Fe$^{2+}$ solution) in combination with the known amount of Fe$^{2+}$ ions added.

A typical [Fe$^{2+}$] versus time plot is shown in figure 3. It is obvious that the 10 minutes time that each experiment lasted, was enough for the precipitation process to complete. From the [Fe$^{2+}$] versus time profiles, the rates for iron sulfide precipitation were calculated for each experiment. The removal of one mole of Fe$^{2+}$ from the working solution, corresponds to the precipitation of one mole of FeS according to the reaction (1):

$$\text{Fe}^{2+} + \text{HS}^{-} \leftrightarrow \text{FeS} + \text{H}^{+} \quad (1)$$

Taking the first derivative of the equation fitted to the [Fe] versus time experimental points, at the point t=0 we can calculate the rate of FeS precipitation at the initial supersaturation conditions.

![Figure 3](attachment:image.png)

Fig. 3 - Typical evolution of iron concentration vs. time curve for the free-drift experiments.

The supersaturations calculated were not identical for replicate experiments, performed to assess the reproducibility and the precision of the rates measured. This was attributed to the slight changes in flow of geothermal fluid in the wellhead and the fluctuation of Fe$^{2+}$ concentrations from day to day. In order to compare the results obtained at various conditions, a dimensionless treatment of the kinetics data was applied.
An unambiguous way to describe the rate of a precipitation reaction is the linear rate of growth along a direction perpendicular to a particular crystal face. Such a treatment however leads to very complex representation of the growth rate. For polycrystalline solids as FeS, it is more useful to express the extent of crystallization as an average linear growth rate, converting the mass deposition data $dW/dt$, to average linear growth rates $dr/dt$ using the relation (2):

$$\frac{dr}{dt} = \frac{dW}{dt} \frac{1}{\rho A}$$  \hspace{1cm} (2)$$

where $\rho$ is the density of the precipitating solid and $A$ its surface area at the beginning of the precipitation process.

Van Leeuwen and Blomen (19XX), proposed a uniform representation of growth data, expressing the growth rate as a dimensionless quantity. The dimensionless growth rate is given by:

$$S_d = \frac{dr/dt}{V_mC_{eq}e^\beta} \sqrt{\frac{2\pi M}{RTNA^2}}$$  \hspace{1cm} (3)$$

where $V_M$ is the molecular volume of the crystal, $M$ the molecular weight of the species growing, $N_A$ Avogadro's number, $\beta$ is defined as

$$\beta = \frac{\Delta\mu}{RT} = \frac{1}{2RT} \ln \Omega$$  \hspace{1cm} (4)$$

and $C_{eq}$ is the equilibrium concentration of the solute in solution taken as

$$C_{eq} \equiv \sqrt{K_{sp}}$$  \hspace{1cm} (5)$$

where $K_{sp}$ is the thermodynamic solubility product of the precipitating salt.

An effective order of growth is defined as

$$\frac{S_d}{e^\beta} = k_T \beta^n$$  \hspace{1cm} (6)$$

where $k_T$ is a constant.

This treatment of crystal growth data is attractive since it suggests that a dimensionless driving force $\beta$ and also a dimensionless growth rate $S_d$ should be used when comparing experimental results so as to eliminate any possibility for misinterpretation. Using this expression, one can bring together growth rate curves for compounds crystallizing under different conditions and even for different compounds.

Equation 6 can be written as

$$\ln S_d - \beta = \ln k_T + n \ln \beta$$  \hspace{1cm} (7)$$

allowing the calculation of the actual order of growth, $n$, from the slope of the linear plot of the quantity $\ln(S_d) - \beta$ versus $\ln(\beta)$.

The conditions for the experiments carried out in Melun l'Almont geothermal site are summarized in table 1. All experiments were done at the pH range 6.4-6.6 and temperature 67°C.
A direct comparison of the experimental results concerning the effectiveness of the various additives tested, can be applied by plotting the dimensionless rate $S_d$ versus the dimensionless driving force $\beta$ for all experiments together. This plot is presented in figure 4. It can be easily seen that for all experiments, the rates calculated fall in the same region of values for each region of $\beta$ values. For the experimental set using ATP 6.2 compound, we get a decrease in the rate but only for the low $\beta$ values. For high $\beta$ values the rate calculated lays in the vicinity of the rates calculated for the other experimental sets.

The same picture is derived when plotting the quantity $\ln(S_d) - \beta$ versus $\ln(\beta)$ as shown in figure 5. The linear fits shown on the plots show a tendency for convergence at higher supersaturations a fact that calls for more careful consideration concerning the effectiveness of the ATP 6.2 additive. The apparent decrease of the precipitation rates at lower supersaturations when using this compound, may indicate a sequestration of the $\text{Fe}^{2+}$ ions in the solution and not an actual inhibition of crystal growth. This aspect is reinforced by the disappearance of the compound’s apparent effectiveness at higher supersaturations.

4. CONCLUSION

In general, all the additives tested in this experimental investigation did not prove to have any scaling inhibition effectiveness. Yet, if we take a closer look at figures 4 and 5 we can see that in some cases, some of the compounds accelerated the formation of iron sulfide precipitate. Considering that the concentration used (5 mg/l) was in the same order of magnitude as $\text{Fe}^{2+}$ concentration, these compounds cannot be recommended for use as scale formation inhibitors.
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Table 1 - Experimental conditions and calculated dimensionless quantities for the experiments at Melun l’Almont (PM-4) geothermal site.

<table>
<thead>
<tr>
<th>EXP #</th>
<th>$\Omega_{\text{mack}}$</th>
<th>Additive (5mg/l)</th>
<th>$S_d$</th>
<th>$\beta \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEL2</td>
<td>1.98</td>
<td>-</td>
<td>51.48</td>
<td>1.3778</td>
</tr>
<tr>
<td>MEL4</td>
<td>6.57</td>
<td>-</td>
<td>40.34</td>
<td>3.7970</td>
</tr>
<tr>
<td>MEL5</td>
<td>19.20</td>
<td>-</td>
<td>56.88</td>
<td>5.9600</td>
</tr>
<tr>
<td>BL2</td>
<td>2.37</td>
<td>-</td>
<td>38.46</td>
<td>1.7400</td>
</tr>
<tr>
<td>BL3</td>
<td>7.22</td>
<td>-</td>
<td>60.71</td>
<td>3.9870</td>
</tr>
<tr>
<td>BL4</td>
<td>17.50</td>
<td>-</td>
<td>44.54</td>
<td>5.7700</td>
</tr>
<tr>
<td>MEL7</td>
<td>2.07</td>
<td>Norust</td>
<td>44.99</td>
<td>1.4670</td>
</tr>
<tr>
<td>MEL8</td>
<td>6.68</td>
<td>Norust</td>
<td>62.52</td>
<td>3.8300</td>
</tr>
<tr>
<td>MEL9</td>
<td>17.80</td>
<td>Norust</td>
<td>69.23</td>
<td>5.8100</td>
</tr>
<tr>
<td>MEL12</td>
<td>1.88</td>
<td>Busperse</td>
<td>55.99</td>
<td>1.2730</td>
</tr>
<tr>
<td>MEL11</td>
<td>6.45</td>
<td>Busperse</td>
<td>60.41</td>
<td>3.7600</td>
</tr>
<tr>
<td>MEL10</td>
<td>18.50</td>
<td>Busperse</td>
<td>70.06</td>
<td>5.8800</td>
</tr>
<tr>
<td>MEL15</td>
<td>1.79</td>
<td>Solamine</td>
<td>53.37</td>
<td>1.1700</td>
</tr>
<tr>
<td>MEL16</td>
<td>5.85</td>
<td>Solamine</td>
<td>50.30</td>
<td>3.5600</td>
</tr>
<tr>
<td>MEL17</td>
<td>14.90</td>
<td>Solamine</td>
<td>61.16</td>
<td>5.4500</td>
</tr>
<tr>
<td>MEL20</td>
<td>2.10</td>
<td>AP 28.52.1</td>
<td>43.15</td>
<td>1.4960</td>
</tr>
<tr>
<td>MEL19</td>
<td>5.82</td>
<td>AP 28.52.1</td>
<td>43.26</td>
<td>3.5500</td>
</tr>
<tr>
<td>MEL18</td>
<td>15.60</td>
<td>AP 28.52.1</td>
<td>58.55</td>
<td>5.5400</td>
</tr>
<tr>
<td>MEL23</td>
<td>2.10</td>
<td>AV 142.52.1</td>
<td>47.28</td>
<td>1.4960</td>
</tr>
<tr>
<td>MEL24</td>
<td>7.40</td>
<td>AV 142.52.1</td>
<td>40.93</td>
<td>4.0370</td>
</tr>
<tr>
<td>MEL25</td>
<td>16.60</td>
<td>AV 142.52.1</td>
<td>42.10</td>
<td>5.6600</td>
</tr>
<tr>
<td>MEL28</td>
<td>2.43</td>
<td>ATP 6.2</td>
<td>13.59</td>
<td>1.7900</td>
</tr>
<tr>
<td>MEL27</td>
<td>6.86</td>
<td>ATP 6.2</td>
<td>9.10</td>
<td>3.8800</td>
</tr>
<tr>
<td>MEL26</td>
<td>20.20</td>
<td>ATP 6.2</td>
<td>44.53</td>
<td>6.0000</td>
</tr>
<tr>
<td>MEL31</td>
<td>1.75</td>
<td>Aquaprox</td>
<td>43.90</td>
<td>1.1280</td>
</tr>
<tr>
<td>MEL32</td>
<td>5.90</td>
<td>Aquaprox</td>
<td>61.50</td>
<td>3.5800</td>
</tr>
<tr>
<td>MEL33</td>
<td>18.10</td>
<td>Aquaprox</td>
<td>61.10</td>
<td>5.8400</td>
</tr>
</tbody>
</table>
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Fig. 4 - Plot of the dimensionless rate of precipitation $S_d$ versus the dimensionless driving force $\beta$.

Fig. 5 - Plot of $\ln(S_d)$-$\beta$ versus $\ln(\beta)$ for the free-drift experiments.
5. REFERENCES


IMPROVEMENT OF THE PRINPIMO)
DOWN-HOLE FLUID SAMPLER

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SUMMARY

To be able to bring its research programmes on geothermal wells to successful completion, the BRGM needed to develop a down-hole sampler that was capable of taking fluid samples whilst preserving the physico-chemical characteristics of the sample point.

During the initial phase (project JOULE 1, Final Report, contract No JOUG-0005-C, Boisdet et al., 1992), the tool (PRINPIMO down-hole sampler) was validated for low-enthalpy environments. As part of this second phase (JOULE 2), the sampler has been modified so that it can also be applied to high-enthalpy and HDR domains. As a result, sampling was carried out under satisfactory conditions and the chemical analysis results proved extremely useful, particularly for corrosion and scaling problems.

However, due to technological limitations, it does not seem feasible to be able to extend the field of application of the sampler to conditions of higher pressure and temperature.

1. INTRODUCTION: THE IMPORTANCE OF DOWN-HOLE SAMPLES

In practice, there are two major technological options for taking fluid samples at a precise point in a well:
- Specific tubes adjusted to the required depth.
- Tool lowered down into the well that takes samples at the required depth.

Although the first technique is specifically adapted to monitoring over long periods fluids from a precise zone of the casing, the second offers the advantage of being able to preserve, at least in part, the fluid's physico-chemical characteristics during its ascent to the surface.

The physico-chemical characteristics of a fluid at its sampling point are difficult to obtain by calculation using data that can be measured at the surface. This is even more the case when the fluid consists of a mixture from several producing levels, and only in-situ sampling at a given depth can overcome the problems induced by the following levels.

It is well established that modification of the physico-chemical characteristics during fluid rise in the well can influence data interpretation and/or analysis. This is particularly so with large
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Pressure variations that induce degassing phenomena and, to a lesser extent, with temperature variations. Consequently, sampling using submerged tubes sometimes provide uncertain results if are not preceded by fluid analysis using a down-hole sampler that preserves the fluid pressure during its ascent.

In low-enthalpy geothermal exploitation, these two options were tested by BRGM as part of the 1992 Final Report contract N'JOUG-0005-C (Boisdet et al., 1992) with the aim of obtaining data useful for modelling corrosion and scaling phenomena using the computation code MODEP (Boisdet et al., 1992, Abou Akar and Ignatiadis, 1992, 1994, Ignatiadis et al., 1992; 1994a and 1994b). For both cases, the values measured with the sampling device were slightly different from those measured at the well head (Table 1) and it was possible to draw conclusions with respect to the physico-chemical phenomena.

<table>
<thead>
<tr>
<th>Production well water samples</th>
<th>[Fe^{2+}] (mg/l)</th>
<th>[S^{2-}] (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ris Orangis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>by the PRINPIMO</td>
<td>0.60</td>
<td>0.57</td>
</tr>
<tr>
<td>by the head of the production well</td>
<td>1.55</td>
<td>0.57</td>
</tr>
<tr>
<td>Orly 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>by the well-bottom treatment tube</td>
<td>0.73</td>
<td>2.84</td>
</tr>
<tr>
<td>by the head of the production well</td>
<td>3.20</td>
<td>2.13</td>
</tr>
</tbody>
</table>

Table 1 - Sampling in Ris Orangis and Orly 1 geothermal production wells. In Ris Orangis, the iron contents differ. There is no precipitation of iron sulfide. In Orly 1, both the iron and sulfide contents differ. Corrosion and deposition occurs.

The above samples were taken from the Paris Basin where temperature and pressure conditions are relatively moderate. Temperature does not exceed 85°C and down-hole pressure is about 200 bars. As the temperature is much higher for medium-enthalpy geothermics it becomes difficult to use synthetic materials such as those classically used for casing in the well bottom. Only a sampler such as PRINPIMO can be used in these conditions, provided that it is adapted to high temperatures. This was the aim of this programme because none of the devices available on the market were suitable for fluid sampling, for example, the case with the Hot Dry Rock (HDR) operation in Soultz sous Forêts, France.

2. USE OF DOWN-HOLE FLUID SAMPLERS

2.1. General nature and state-of-the-art (patents)

The classical means for obtaining deep water samples is the "Nansen bottle" which is essentially a tube open at both ends equipped with remote-controlled closures. The bottles are generally lowered to the desired depth and a command signal actuates these closures. This method is obviously unsuitable if an uncontaminated fluid sample is required.

Several patents reflect the progress made for technologies able to bring good quality samples to the surface; all related to this context were invented before the eighties, e.g. the patents of Urbanosky (1973) and Archibald (1966).
In practice, the problem becomes increasingly complicated when samples are required of fluids at high temperatures and pressures, sometimes polyphase (oil, water and gas) or charged. Furthermore, devices were designed to compensate for temperature and pressure variations during ascent of the sampler. In the 1978 French patent No. 78 00122, Bimond et al., (1978) touch upon temperatures of 160°C, but without guaranteeing the smooth running of their device in such conditions.

It very quickly became clear that the sampler also needed to incorporate the capacity for fluid transfer towards the analytical tools. These characteristics are, for example, useful for measuring the gas to liquid ratio (GLR). Some good examples are illustrated by the 1988 English patent No. 8902377.4 where Toon et al., (1988) describe fluid-transfer sequences, and by the 1991 World patent No. WO 91/12411 where Oilphase Sampling Services Limited describe the performances of its device applied to petroleum fluids.

2.2. The inert sampler with mobile piston (in french "PRéleveur INerte à Piston MOible" - PRINPIMO)

Generally, all down-hole fluid samplers referred to above are restricted by temperature conditions that can be encountered during geothermal exploitation. BRGM has developed a tool that, without it being entirely innovative, nevertheless offers unique characteristics.

2.2.1. Reminder of the initial and/or basic specifications (specification sheet and/or needs)

The aim was to develop a "down-hole fluid sampler" that would make it possible to bring a sample of monophase fluid to the surface whilst preserving its original physical and chemical characteristics and without inducing any chemical pollution. The sampler was also required to measure bubble point and gas to liquid ratios and, of course, to allow transfer of the sampled fluid under controlled conditions. As detailed in the Final Report JOUG-0005-C (Boisdet et al., 1992), the sampler can be summed up as below.

The main characteristics of the fluids to be sampled were:
- Maximum temperature: 200°C.
- Pressure at the moment of sampling: 250 bar.
- Highly saline (up to 35 g/l), containing H2S (up to 150 mg/l).
- Dissolved gases with high bubble point (max. 20 bar).
- GLR 20% or less.

Additional technical limitations were defined:
- Sample volume: about one litre.
- External diameter: had to allow the implement to pass through a 2"1/2 pipe.
- Length: less than 3 metres.
- Mechanically and electrically connected by 4- or 7-strand Gerhart Owen cable head.
- Use of materials that would not pollute the fluid to be sampled.
- Strainer: had to allow the passage of particles of at least 25 microns.
The basic technical solutions chosen were:

- A variable-volume sampling chamber (zero volume at start of sampling), with a "free" piston to vary volume.
- Use of a double non-return valve at the inlet to isolate the fluid sample from the external medium.
- Control of piston velocity from start to end of filling by a controlled pressure drop in the transit gas (calibrated constriction).
- A solenoid valve, isolated from the fluid to be sampled, operating in the transit gas (nitrogen).
- Use of inert materials such as titanium and Hastelloy C-22 (Haynes International Inc.) for those parts in contact with the fluid sample.
- Joints sealed with inert material for those parts in contact with the fluid to be sampled.

The only limitation of the above apparatus is the electro-valve where the temperature may "burn" the insulation. The operating limit is about 200/220°C whereas the inside temperature of the electro-valve is about 250°C. These characteristic are in accordance with present BRGM applications, i.e. temperature generally lower than 180°C and pressure lower than 250 bar.

2.2.2. Operating Principle

Preparation

Before the sampler is lowered down the well, the mobile piston is positioned at the bottom of the sampling chamber, which reduces the volume of the chamber to virtually nil. The piston is held in place by pressure exerted by the transit inert gas (nitrogen) into the space between the piston and solenoid valve, which we will refer to as the "compensation chamber". The pressure must be adjusted to remain higher than that of the fluid to be sampled under the in-situ conditions. The evacuation chamber, above the solenoid valve, is at a lower pressure (generally atmospheric pressure), regulated according to the amount of fluid required. The solenoid valve is closed.

Sampling

Once the sampler is in position in the well, sampling is triggered by activating the electro-valve. Thus the transit gas passes into the evacuation chamber through the calibrated constriction that restricts the gas flowrate. The pressure this gas exerts on the piston is then reduced, allowing the piston to rise and the fluid to fill the space thus created in the sampling chamber. The pressure in the evacuation chamber, and hence the filling of the sampling chamber, are monitored by a pressure transducer remotely controlled by surface instrumentation. Depending to initial adjustments, sampling ends either when the piston meets the top of the evacuation chamber or when there is equal pressure in the sampling chamber, evacuation chamber and compensation chamber. This state is monitored at ground level and identified by a plateau in the pressure curve. The sampler is then raised to the surface while a non-return valve closes the bottom intake of the sampling chamber. The electro-valve is kept open while the sampler is brought up to maintain the fluid sampled under pressure, otherwise the pressure would tend to fall rapidly with the drop in temperature on the way up.
Recovery

The sample is recovered at surface by opening the non-return valve with a special tool. If required, and depending on the adjustment of initial conditions, the gas and liquid phases can be separated in the sampling chamber by controlling the pressure drop in the compensation chamber until atmospheric pressure is reached. Both gaseous and liquid phases can be successively recovered by re-expanding the evacuation chamber.

3. EXPLOITATION OF THE SAMPLER

3.1. Recall: first development stage
(Final JOULE 1 Report N° JOUG-0005-C)

Preliminary tests to validate the use of the sampler (IMRG Annual Report, 1991)

- In the GPF (Géologie Profonde de la France - Deep Geology of France) well near Couy, Cher, France, during February and March 1991. The sampler was lowered several times between 400 and 1620 m.

- In the SOGECLER well near Clermont-Ferrand, La Croix de Nérat, France, in December 1991. Fluid temperature was about 90°C.

- In the EPS-1 well near Soultz-sous-Forêts, Alsace, France. Average temperature of the fluid was about 145°C.

During this preliminary phase, problems of joint resistance were detected and resolved.

Operational uses (IMRG Annual Report, 1992)

The prototype of PRINPIMO (only one of which has been made) was first used in an operating production well in June 1992 to bring up a fluid sample from the bottom of the well casing (GRO-2) of Ris Orangis (Essonne, France) (Ignatiadis et al., 1992a). The bottom and head of the well were simultaneously sampled with the artesian flowrate at about 74 m³/h. The results are shown in Table 1.

It is interesting to note that sulphide contents in the well bottom were identical to those at the well head, whereas dissolved iron contents increased. The results helped estimate the supply of iron by corrosion of the casing, the average corrosion rate was calculated to be 58 μm per year.

3.2. Second development stage - Testing under nominal pressure and temperature conditions

During the second phase, which corresponds to the present JOULE project, the programme was particularly dedicated to improving the performance of the sampler, with the main aim of sampling the well at Soultz-sous-Forêts, France (HDR project). Improvements were first of all made to the electro-valve, the sampling chamber and the joints. Then the sampler was tested in a simulator and on an experimental well before sampling at Soultz.
Testing at LATERA

On January 13 1993, the sampler was lowered down the LATERA-5 well in the Bolsena Caldera, Italy, to a depth of 2000 m with a pressure of 172 bar and temperature of 197°C. Sampling lasted five minutes following a three-hour descent. After bringing back up the sampler and retrieving 800 cc of water, inspection revealed the deterioration of the PTFE/Ekonol joints that were guaranteed up to a temperature of 320°C. Tolerance of machining the grooves was then reduced to avoid joint creep. The O-Ring joints were replaced by a lip seal.

Autoclave tests at MESY (Bochum, Germany)

This test, carried out in April 1993, was requested by the Socomine company before intervention on the well GPK-1 at Soultz. Compared to sampling in GPK-1, this test was not entirely representative because a relatively pure and totally degassed water was used. The procedure followed was:
- Sequence of temperature rise (8 hours)
- Sequence of pressure rise (a few minutes)
- Bearing at 350 bar and 180°C
- Electro-valve triggering test (30 min)
- Controlled depressuring of the autoclave (1 hour)
- Temperature drop to ambient temperature
- Transfer of liquid (unfortunately degassed)
- Disassembly and checking of sampling parts

Sampling at Soultz-sous-Forêts (IMRG Annual Report, 1993)

During a venting test from May to June 1993, one of the objectives was to produce unpolluted formation fluid. It was the first production test since the well had been drilled. After a volume of about 525 m³ of water had been produced, down-hole sampling was carried out at a depth of 3470 m at a temperature of about 160°C. Surface and down-hole samples were analysed on site for the liquid phase, and isotopic and gas analyses were carried out at BRGM (Aquilina et al., 1995).

As with samples from low-enthalpy geothermal wells, significant differences are observed for certain contents between the well bottom and the surface (Table 2). This confirms the importance for sampling in the well bottom to be carried out under controlled sampling and transfer conditions.

<table>
<thead>
<tr>
<th>GPK-1 water samples</th>
<th>F⁻ (mg/l)</th>
<th>Fe²⁺ (mg/l)</th>
<th>HCO₃⁻ (mg/l)</th>
<th>SiO₂ (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>by the head of the production well</td>
<td>5.0</td>
<td>135.2</td>
<td>347.0</td>
<td>273.0</td>
</tr>
<tr>
<td>by the PRINPIMO</td>
<td>7.1</td>
<td>45.1</td>
<td>165.0</td>
<td>230.0</td>
</tr>
</tbody>
</table>

Table 2 - Differences between well head and well bottom chemical analyses.
4. TECHNOLOGY ANALYSIS

Although the sampling planned was successfully carried out, certain technological restrictions were brought to light, mainly concerning the control electro-valve and the mobile piston (used in almost all down-hole samplers).

The electro-valve uses insulating material, as do many electric actuators, that has a temperature limit controlled by the synthetic resin. The limit is of the order of 250°C for continuous use. Considering the temperature rise due to current circulation in the solenoid, the temperature of the electro-valve is always 20-50°C greater than the temperature of the environment. Consequently, the temperature of the fluid to be sampled within which the sampler is immersed cannot exceed 200-220°C. Other possible command modes exist, but the link cable and the various joints, which also contain synthetic material, nevertheless impose a temperature limit of around 250°C.

The concept of the mobile piston requires joints that resist large temperature differences. High friction is induced, not very compatible with the slow and controlled movement of the piston during the sampling phase. Malfunctioning was observed during sampling, but resolved by adapting the machining tolerance. However, the sampler then becomes less versatile because a set of joints is required for each range of sampling conditions. Furthermore, it becomes particularly difficult to not score or deteriorate the joints.

BRGM has carried out a pre-study of the replacement solutions; these solutions were added during 1993 to the application for the French patent N°92.03308. However, in view of the lack of a market for down-hole samplers under high temperatures and pressures, BRGM has abandoned the procedure of taking out a patent.

5. CONCLUSION

On the whole, the objectives set were met with successful completion of the planned sampling (work programme, aim N°4, objective 4.1.4.3), especially that carried out as part of CEC contracts. However, limitations of the concept were discovered with respect to the mobile piston and also the electro-valve, which was active during the entire sampling period. Solutions adapted to such high-temperature and pressure conditions do exist and have been considered by BRGM, but in the light of the lack of a market and internal needs, their development is not anticipated.

6. REFERENCES


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IGNATIADIS I., ABOU AKAR A. (1992) - Prélèvement d'échantillons de fluide géothermal en fond de puits de production au moyen du préleveur de fond PRINPMO sur le site de Ris Orangis (GRO-2). Rapport BRGM n° R 36055 IRG SGN 92, 68 p.


IGNATIADIS I., ABOU AKAR A., LAFFORGUE M., BRAY Ph. (1992) - Prélèvement d'échantillons de fluide géothermal par le tube d'injection d'additifs en fond de puits de production sur le site d'ORLY 1 (GOR-2). Rapport BRGM n° R 34513 IRG SGN 92, 76p.

7. PATENTS


MODELLING OF CORROSION AND SCALING PHENOMENA IN LOW ENTHALPY GEOTHERMAL WELLS

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ABSTRACT

In the sixth half-yearly report, a digital model that enables the simulation of corrosion and scaling phenomena on steel casing walls of geothermal wells was presented. The simulation of casing corrosion is based on application of the Volmer-Heyrovski reactive mechanism. The calculations take into account Fick's diffusion laws, the variation of the thickness of the diffusion layer due to scale growth, and the porosity of the scale (assumed to be made up of mackinawite Fe$_{1+x}$S, the main scale constituent). The rate of mackinawite precipitation is calculated using the solubility product, $K_s$. The equation system posed by application of mass action and mass balance laws was solved by a dichotomy of the pH and flux of the iron precipitated. This module, which is made up of CALDEP1 program and its subroutines VAREP1, 2 and 3, and Resoil 1 and 2, has been tested individually. The present report begins with a review of the characteristics of the CALDEP1 program and its routines, then tackles the coupling of this program and the MODEP computation code, and describes the recent improvements made to this code (calculation algorithm or consequences of transferring the code from the VAX system to the FORTRAN Lahey under PC). The last part of the report is dedicated to the simulation of the behaviour of a representative geothermal well in the Paris Basin, with presentation and discussion of the evolution of the major parameters, such as corrosion rate, scale thickness, contents of dissolved species and casing diameter, all as a function of exploitation duration and depth. Considering the complexity of the real phenomena, certain simplifying hypotheses are included into the program. However, the MODEP code is currently operational and calculates trends resulting from variations in the major parameters in the aquifer and/or the casing.

1. INTRODUCTION

The CALDEP1 module, which enables simulation of corrosion and scaling phenomena on steel casing walls, was written on the basis of a certain number of hypotheses and considerations that were discussed in depth in the previous six-monthly reports (Abou Akar, 1994a and 1994b; Abou Akar and Boens, 1995). This module has undergone autonomous testing and initial results were presented in the previous six-monthly report. The objectives of the present report are:
2. PRESENTATION OF THE CALDEP1 PROGRAM AND ITS SUBROUTINES

2.1. Description of the program

The module Caldepl can run as a self-contained program that uses the routines Varep and Resol. These routines were designed to solve the non-linear equation system with five unknowns generated by the mathematical model presented in the sixth half-yearly report (Abou Akar and Boens, 1995). Caldepl is designed to calculate scale thickness, the time necessary for this scale to form and finally, the mass transfer between the fluid vein and the diffusion layer. This consists of optimizing the simulation length (and thus the scale thickness) with a constraint of a variation of the mass transfer less than the fixed threshold limit. Fixed values are used for temperature, concentrations, equilibrium constants and activity coefficients in the fluid vein, whereas an introduced value is used for the thickness of the hydrodynamic diffusion layer. When CALDEPl is coupled with MODEP, these calculations can be carried out at each stage in the rise of geothermal water in the well. The MODEP code is used to calculate the distribution of species whether dissolved, gaseous or solid after each disturbance to the system (pressure and temperature variations, mass transfer with the wall during the previous stage). This new distribution will be the starting point for calculating the new mass transfer between the fluid vein and the wall. MODEP also ensures all logistics necessary for this coupling, such as data transmission from the well-bottom file and command file (Abou Akar et al., 1995) and memorization of the events and certain calculated values. Finally, MODEP calculates the thickness of the hydrodynamic diffusion layer, head losses in the well, casing diameter as a function of time and depth, and the new flowrate before each new water rise in the well (cf. § 4).

The five unknowns mentioned above are: [H\(^+\)], [Fe\(^{2+}\)], [HS\(^-\)], [CO\(_{32-}\)] and J\(_{Fe}\) precipit. They represent the concentrations of chemical species on the metal wall and the iron flux that precipitates as mackinawite on this same wall. The system of the five equations is given below:

\[
\begin{align*}
\left[\text{Fe}_{\text{tot}}\right]_{\text{fluid vein}} = \frac{8}{D} \times (-i_{\text{corr}} / (2 \times F) + J_{\text{Fe precipit}}) = \left[\text{Fe}_{\text{tot}}\right]_{X=0} \\
= [\text{Fe}^{2+}] + (K_{\gamma 56/K_{56}})[\text{Fe}^{2+}][\text{H}^+] + (K_{\gamma 55/K_{55}})[\text{Fe}^{2+}][\text{CO}_3^{2-}] \\
+ (K_{\gamma 51/K_{51}})[\text{Fe}^{2+}][\text{Cl}^-] + (K_{\gamma 61/K_{61}})[\text{Fe}^{2+}][\text{HS}^-]^3 + (K_{\gamma 60/K_{60}})[\text{Fe}^{2+}][\text{HS}^-]^2 \quad (1)
\end{align*}
\]

\[
\begin{align*}
\left[\text{CO}_3^{2-}\right]_{\text{fluid vein}} = \left[\text{CO}_3^{2-}\right]_{X=0} \\
= [\text{CO}_3^{2-}] + (K_{\gamma 25/K_{25}})[\text{H}^+]^2[\text{CO}_3^{2-}] + (K_{\gamma 24/K_{24}})[\text{H}^+] + [\text{CO}_3^{2-}] \\
+ (K_{\gamma 56/K_{56}})[\text{Fe}^{2+}][\text{H}^+][\text{CO}_3^{2-}] + (K_{\gamma 55/K_{55}})[\text{Fe}^{2+}][\text{CO}_3^{2-}] \\
+ (K_{\gamma 29/K_{29}})[\text{H}^+][\text{Na}^+][\text{CO}_3^{2-}] + (K_{\gamma 30/K_{30}})[\text{Na}^+][\text{CO}_3^{2-}] \quad (2)
\end{align*}
\]
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\[ [HS_{\text{tot}}]_{\text{fluid vein}} - J_{Fe \text{ precipit}} \times \delta/D = [HS_{\text{tot}}]_{x=0}. \]
\[ = [HS^-] + (K_{\gamma28}/K_{28}) [H^+] [HS^-] \]
\[ + 2 (K_{\gamma60}/K_{60}) [Fe^{2+}] [HS^-]^2 \]
\[ + 3 (K_{\gamma61}/K_{61}) [Fe^{2+}] [HS^-]^3 \]

\[ (J_{H^+})_{\text{fluid vein}} + (-i_{\text{corr}}/F + J_{Fe \text{ precipit}}) \times \delta = J_{H^+} = 0 \]
\[ = D_{H^+} [H^+] - D_{OH^-} (K_{20}/K_{\gamma20}) [H^+]^2 \]
\[ + D ((K_{\gamma56}/K_{56}) [Fe^{2+}][H^+] [CO_3^{2-}] + (K_{\gamma29}/K_{29}) [H^+] [Na^+][CO_3^{2-}] \]
\[ + 2. (K_{\gamma25}/K_{25}) [H^+] [CO_3^{2-}] + (K_{\gamma24}/K_{24}) [H^+] [CO_3^{2-}] + (K_{\gamma28}/K_{28}) [H^+] [HS^-] \]

If \( J_{Fe \text{ precipit}} = 0 \rightarrow [Fe^{2+}] [HS^-]/[H^+] < K_s \)
If \( J_{Fe \text{ precipit}} \neq 0 \rightarrow [Fe^{2+}] [HS^-]/[H^+] = K_s \)

The unknown variables \((H^+)_{x=0}\) and \(J_{Fe \text{ precipit}}\) are determined by dichotomy (Subroutine VAREP1). However, simplifications are involved in the diffusion regime for corrosion or precipitation.

a) When the diffusion length becomes great enough, a purely diffusional regime takes over for precipitation and the \([HS_{\text{tot}}]\) content on the metal wall sharply diminishes. This decrease in \((HS^-)_{\text{total}}\) enables easier calculation of \(J_{Fe \text{ precipit}}\) because the following equation is satisfied:

\[ J_{Fe \text{ precipit}} = [HS_{\text{tot}}]_{\text{fluid vein}} \times D/\delta. \]

Varep2 takes over from Varep1 when the criterion \(((HS_{\text{tot}})_{x=0} / [HS_{\text{tot}}]_{\text{fluid vein}} < 10^{-3})\) is verified. Henceforth, this algorithm only performs dichotomy on the pH value.

b) When the diffusion length increases further, a purely diffusional regime takes over for corrosion. The pH at the metal surface is a simple function of the diffusion length. Varep3 takes over from Varep2 when the criterion \((J_{H^+} = 0 / (J_{H^+})_{\text{fluid vein}} < 10^{-3})\) is satisfied. This algorithm mainly amounts to the RESOL subroutine, which calculates the values of \((Fe^{2+})_{x=0}\), \((HS^-)_{x=0}\) and \((CO_3^{2-})_{x=0}\).
2.2. Summary charts

2.2.1. Summary chart of the CALDEP1 program

- Input data for CALPED:
  - concentration of chemical species in the feed water
  - values of chemical equilibrium constants
  - values of activity coefficients
  - diffusion layer thickness

- Thickening of mass transfer scale corresponding to a time increment \( \Delta t \) : the diffusion path length increases
- Initial increment: \( \Delta i = 24h \)

- 1st passage:
  - Calculation of initial mass fluxes

- Calculation of mass fluxes for this new diffusion path length

- Variation of fluxes test comparison with initial fluxes
  - Variation is less than the limit
  - Variation is greater than the limit

- Modelling of the data:
  - Decrease of \( \Delta t \)

- Decision for optimal simulation length when the time is greater than 24 hours

- VAREP1, 2 or 3:
  - Thickening of mass transfer scale corresponding to a time increment of 24 hours

- Calculation of mass fluxes for this new diffusion path length

- Variation of fluxes test comparison with initial fluxes
  - Variation is less than the limit
  - Variation is greater than the limit

- Exit from the CALDEP subroutine

We have developed:
- the new thickness of the scale
- the new thickness of transported iron
- the fluxes of iron, soluble and precipitated iron
- the optimal simulation length for this depth
2.2.2. Summary chart of the VAREP1 subroutine

Input data for VAREP 1:
- concentration of chemical species in the fluid vein
- values of chemical equilibrium constants and activity coefficients
- diffusion path length

Initial pH on the wall = pH in the fluid vein

Calculation of the corrosion current:

\[ \text{J Fe precip} = p \times \text{LIB} \]

Modification of pH according to the test results

\[ p = 0 \]

Determination of the concentration in carbonate, formate and sulfide ions on the metal wall by REXOL

Calculation of the fluid saturation index with respect to mackinawite (\( \Omega_{\text{mack}} \))

\[ \Omega_{\text{mack}} \text{ value is not close enough to 1} \]

Modification of \( p \) according to the mackinawite solubility coefficient

\[ \text{value is close enough to 1} \]

The results are:
- the precipitation flux
- the corrosion current value

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2.2.3. **Summary chart of the VAREP2 subroutine**

The diffusion regime for precipitation is reached.

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Input data for VAREP2:
- concentration of chemical species in the fluid vein
- values of chemical equilibrium constants and activity coefficients
- diffusion path length

Calculation of the precipitation flux: $\text{Precip.} = \text{[HfSO4]} \times \text{[H]}$

Initial pH on the wall = pH in the fluid vein

Calculation of the corrosion current:

Determination of the concentration in carbonates, ferric and sulphide ions on the metal wall by RESOL

Test the pH value

Positive test: the pH is determined on the wall

We obtain:
- the precipitation flux
- the corrosion current values

Negavie test

Modification of pH according to the test results
2.2.4. Summary chart of the VAREP3 subroutine

The diffusion regimes for precipitation and corrosion are reached.

Input data for VAREP3:
- concentration of chemical species in the fluid vein
- values of chemical equilibrium constants and activity coefficients
- diffusion path length

Calculation of the precipitating flux:
\[ J_{\text{Fe precip}} = [\text{HS}_{\text{tot}}] \times \frac{D}{d} \]

Calculation of the corrosion current:
\[ i_{\text{corr}} = \frac{J_{\text{Fe precip}}}{d + J_{\text{Fe precip}}} \times F \]

We obtain:
- the precipitation flux
- the corrosion current value
3. MODELLING OF WATER RISING IN THE WELL: INSERTION OF CORROSION PHENOMENA IN MODEP

The modelling of casing corrosion and scaling phenomena described above is based on the knowledge of the chemistry of the fluid vein. The MODEP program is used to model the nature of this fluid vein. Our computation subroutines will thus be associated with MODEP.

3.1. Changes in the medium during a water rise in the well

Such changes affect:
- the values of equilibrium constants and activity coefficients (as a result of variations in temperature and pressure moving up through the well). These physical variations are considered to be constant in time at a given depth;
- the \( (\text{Fe}_{\text{tot}}), (\text{H}_{\text{tot}}) \) and \( (\text{HS}_{\text{tot}}) \) contents (as a result of corrosion and scaling phenomena). One of the difficulties of modelling is due to the temporal dependence of these phenomena.

The variation of equilibrium constants and activity coefficients during a water rise in the well is processed by MODEP.

Corrosion of the steel casing and mackinawite scale change the composition of the fluid vein due to iron, proton and sulphide fluxes. During a rise in the well, the enrichment or impoverishment of these chemical species must thus be calculated.

3.2. Management of rising in the well

The main aim here was to reduce calculation time, which meant reducing the number of rises in the well in order to model the events that occurred over a given period of time.

During modelling at a given depth, a stage is reached where the thickness variation of mackinawite scale will cause a non-negligible disturbance of mass fluxes between the wall and the fluid vein. It is then necessary to move onto the depth above (i.e. go to the next \( Z \) which corresponds to a new variation in pressure and temperature \( (\Delta \text{P}, \Delta \text{T}) \)). This change in flux results in the variation of the function "chemical composition of the fluid vein as a function of the depth in the well". For a given depth, tests will be carried out to calculate the length of time during which scaling can take place without the relative variation of these fluxes exceeding the tolerance threshold. Furthermore, the time increment must be identical at all depths in the well. The procedure is as follows:

During a first rise, the "optimal" simulation length, i.e. the maximum length of time during which the variation of fluxes remains within the tolerance range, is calculated for each depth by the CALDEP1 subroutine. If the "optimal" duration varies from one depth to another, it is necessary to carry out a second rise, and attribute the shortest of these "optimal" simulation lengths to all the depths of the well. This is done by the CALDEP2 subroutine.
NB: The joint operation of the MODEP code with the CALDEP1 and CALDEP2 routines required a great deal of work, including:

- adaptation of the MODEP code to the calling of these new routines without condemning the old menus that use different approaches to the corrosion and scaling problem;

- using the MODEP code to process the supply of iron towards the fluid vein from the diffusion layer, and the loss of sulphides and protons from this vein towards the diffusion layer. The code will recalculate the new distribution of chemical species and will correct the total concentrations of species that will be sent to the CALDEP1 routine at the following depth;

- using the MODEP code to manage the duration of each iteration and to choose the minimum duration that will be imposed at all levels during the following simulation (CALDEP2);

- using the MODEP code to manage the evolution of the diameter of the casing as a function of time and depth of the well;

- carrying out numerous tests and checks.
3.3. Summary charts

3.3.1. Summary chart of the coupled system MODEP-CALDEP

Start at the well location:

P = initial P
T = initial T

Arrival at the top of the well:

1st rise: test the optimal simulation length. If the test is negative (the optimal simulation length is different from the others), a 2nd rise is carried out by CALDEP2. The simulation length is set at the shortest of the optimal simulation lengths identified by CALDEP1 for each depth. If the test is positive, the time is incremented.

Possible 2nd rise: the time is incremented.

Calculation of the new concentrations in chemical species in the fluid vein due to exchange with the diffusion layer.

Input data for CALDEP1:
- concentration of chemical species in the fluid vein
- values of chemical equilibrium constants
- values of activity coefficients
- diffusion layer thickness

Input data for CALDEP2:
- concentration of chemical species in the fluid vein
- values of chemical equilibrium constants
- values of activity coefficients
- diffusion layer thickness
- optimal simulation length at the given depth calculated by CALDEP1.

Possible 2nd rise

Rise in the well:

\[ T = \text{round} \quad 2 \times \Delta T \]

We obtain:
- the new thickness of the scale
- the new thickness of corroded iron
- the new thickness of corroded iron
- the optimal simulation length for this depth

We obtain:
- the new thickness of the scale
- the new thickness of corroded iron
- the new thickness of corroded iron
- the optimal simulation length for this depth

Possible 2nd rise
3.3.2. Summary chart of the CALDEP2 subroutine

The CALDEP2 subroutine is used when the optimal simulation lengths calculated during the first rise in the well (by CALDEPI) are not the same for all levels. A second rise is carried out using a set simulation length of the lowest of the simulation lengths calculated during the first rise.

Input data for CALDEP2:
- concentration of chemical species in the fluid state
- values of chemical equilibrium constants
- values of solubility coefficients
- diffusion layer thicknesses
- optimal simulation length

Optimal simulation length is less than 24 hours

VAREP1, 2 or 3

Thickening of naceouswise scale corresponding to the optimal length

If the simulation length equal to the optimal simulation length?

Yes

No

VAREP1, 2 or 3

Thickening of naceouswise scale corresponding to a 24 hour period

Exit from the CALDEP2 subroutine
We have determined:
- new thickness of the scale
- the new thickness of corroded layer
- the flux of ions, sulphate and grease introduced into the fluid state
4. NEW MODIFICATIONS TO THE MODEP COMPUTATION CODE

This part deals with the latest improvements made to the MODEP calculation code. Certain were carried out to provide greater flexibility and security, whereas others were needed because of incompatibility problems between the two compilers during transfer of the code from VAX to the Fortran Lahey under PC. Some new calculation sequences necessary for the development of the code have also been added.

4.1. Modifications to format

Wherever possible, "IF" tests have been replaced by "select case", which makes programming easier and quicker. In addition, the "case default" now offers the advantage of security that was not possible with the former "IF". The possible error has been dealt with wherever this change has been carried out.

The many "GOTO" instructions have also been eliminated wherever possible, as their use is dangerous and commonly leads to problems of code readability. Nevertheless, many of these instructions still remain because complete elimination would require total destruction of the structure of the existing code and thus, its rewriting. A good policy to adopt henceforth would be to avoid this type of jump whenever possible and to use "DO WHILE" instructions.

4.2. Modifications to file opening

The major difference is the elimination of default options commonly used previously in the version that ran on VAX. All options are explicit during opening and closing of files, which commonly avoids reading or writing problems. Furthermore, the "Status" option of the Open command, which indicates if the file to be opened exists or not, has been changed to "unknown" in all files. This is to avoid the Input/Output (I/O) error generated by the Lahey system upon running when the status of the file opened is incorrect.

4.3. Modifications to reader format

The formats used for reading data files did not operate in the same way under PC and VAX, probably due to interpretation differences between the two compilers. This problem was solved by systematic use of the "*" format for reading, which provides the same results and considerably simplifies the code.

4.4. Modifications to variable names

The role of implicit declaration was minimized wherever possible. If all variables are not declared, possible typing errors in these variable names will not be reported during compilation, and the debugger has to search for them in the warnings, which is not the simplest of solutions. Furthermore, the new variable thus created takes a value of zero which is propagated into the calculation. This is one of the most difficult errors to detect in Fortran, and
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it invalidates all the digital results. Therefore, all new variables used have been explicitly declared, as well as certain existing variables, to avoid errors.

Transfer from VAX to PC revealed a further incompatibility between these two compilers caused by the parameters and variables pooled from the main program and the routines. A discrepancy between attributions occurred in certain cases, and although this problem was not reported by the compiler, it was easily detected by the lack of logic in certain results and by the systematic printing of values transferred from main program to routines. The problem was solved by dividing up the "COMMON"s concerned into real and integer variables. It is possible to represent these two types of variables in the same COMMON provided that real variables are entered first.

4.5. Modifications to Input/Output

These modifications are only located in the main program, known as "MAIN.FOR". They enable control of the executable program "MDP.EXE" by a command file which, for simplicity, is always called "MODEP.CMD".

The protected zone. The zone of the code where the command file is read is referenced as the "protected zone", which simply means that reading order takes priority here, and that modifications between opening and closing of the command file could provoke an I/O error or even confusion between two orders, which is difficult to identify.

The configuration zone. "Select Case" in the protected zone enables the entry of supplementary parameters required by a later developer. This is where the notions of supplementary parameter numbers and the number of digital inputs introduced in the interface MODEP1 (that generates the command file "MODEP.CMD" developed in Visual Basic) come into play. The configuration zone is the only place where the developer can input supplementary parameters, and thus the only place where reading of the command file can be modified. Any other modification will be transferred into the program.

4.6. Modifications to the algorithm

These modifications directly concern the running of calculations, some of which enable extension of the application field of algorithms and render them more secure.

4.6.1. Automatic correction of the degassing step

One of the current problems with the MODEP code, which can lead to the end of the calculation or infinite loops, is the choice of the parameter DX, i.e. the initial incremental step imposed for the variable of the advancement of degassing reactions. By definition, an increment of DX corresponds to the vaporization of DX water mole. As with TPDEGAZ (Czernichowski-Lauriol, 1988), the value of this parameter is left to the user's judgement. This problem, which is minor in TPDEGAZ because it only simulates one water rise in the well, is considerably more serious in MODEP that simulates from several tens of rises up to a few hundred. A degassing step that runs well up until rise "i" can sometimes not function for rise "i+1".
Two modifications were made concerning DX in the DEGAZ routine to solve two different problems:

- For a wide range of DX values, the calculation can lead to a logarithm of a negative value during degassing because the DX chosen is no longer adapted to the approximation of values that are too low. The modification consists of testing during degassing to see if the current DX value leads to an error, and if so, DX is automatically divided by 5 and then re-tested, rather than stopping the code as with TPDEGAZ. The final value after correction is thus adapted to the new conditions, and the error is removed.

- The other problem encountered with the degassing variable is the risk of an infinite loop forming due to a test with a convergence output condition. This convergence is reached or is impossible depending on the value at a given moment of the DX parameter which influences all the others. The difficulty lies in identifying the criteria of non-convergence. In this procedure, one can express:

\[ DX_{n+1} = f(DX_n) \]

where the function \( f \) is unknown and depends on the calculation conditions in this context. This repetition relationship sometimes leads to a fixed point, which generates the infinite loop, because the output criteria are dependent on DX.

Analytical determination of this fixed point is a complex digital-analysis problem. Furthermore, even when the loop criterion is known, it is difficult to do other than modify the initial DX step. This modification will henceforth be carried out automatically by the code as soon as the infinite loop appears.

The solution applied, which worked on the examples tested, consists of inserting a counter that checks that the number of consecutive passages in the loop does not go beyond 50, the value retained after testing. In this case, the code has three other DX values that it tests, and for each one, the calculations in the degassing routine are taken from the beginning. After three unsuccessful corrections, the code displays this on the screen signifying the end of the program. When this occurs, examination of one of the results files (.OUT) provides detail of the running of the calculations and can help define the problem and to start again with new incremental steps.

### 4.6.2. Automatic correction of DT at the pump

If the well is equipped with a submerged pump, which is commonly the case in the Paris Basin, an error occurs when the temperature of the geothermal water at the well bottom is not the same as that at the well head. Pressure and temperature evolution as a function of depth is linear since DP and DT incremental steps are taken away from P and T at each stage of the rise (DP being set by the user and DT calculated using DP and bottom-hole and surface conditions).

In the TPDEGAZ code, the presence of a pump introduces a discontinuity in the pressure which is not compensated for by a temperature discontinuity because by definition, the fluid passes through the pump in an adiabatic manner. This causes the final temperature to be reached prematurely and a division by zero (value reached by the DT incremental step) in the algorithm. Once this error had been identified, it was possible to correct it by recalculating DT at the pump output.
4.6.3. DZ memorization

Whatever simulation method is chosen by the user, the MODEP calculation code always starts by launching a first rise of the standard type, as described in the Joule I Final Report (i.e. like TPDEGAZ with or without corrosion, but without a diffusion layer). In addition to the possibility of using the code as TPDEGAZ, this first rise has other important roles that enable:

- Memorization of the DZ paths, and thus the respective depths, corresponding to the pressure increments DP. The pressure increment is constant at first as this is set by the user, but is automatically modified by the code when the casing straightens after a deviated section, or when it has a different diameter. This automatic correction of DP was programmed in order to maintain a mass of water constant regardless of the casing diameter corresponding to this DP. During the rise of the following water segments, the code reproduces the memorized DZ for each level, then calculates the corresponding DP depending on the parameters involved, including flowrate and casing diameter. The evolution of these two parameters will be discussed further below.

- Calculation and memorization of certain parameters that are temperature and pressure dependent, such as the viscosity and specific volume of the solution. These parameters are vital for calculating the new flowrate before launching a new water segment (cf. § XX).

4.6.4. Kinetics of mackinawite precipitation

The user who selects the new approach in Windows interface (Abou Akar et al., 1995) then chooses between a thermodynamic and kinetic mode for mackinawite precipitation. The kinetic parameters tested are the same as those established during former work (Ignatiadis, 1993; Peyrot et al., 1995). However, the test regarding the precipitated iron sulphide flux is only carried out for the Varepl routine, which only simulates the first few days of exploitation of a given well. With this routine the code chooses between kinetic and thermodynamic precipitation mode. After switching to Varep2, precipitation of chemical species only depends on the total sulphide content in the fluid vein, although precipitation also depends on the diffusion coefficient, D, and the virtual thickness of the diffusion layer or diffusion path (Abou Akar and Boens, 1995).

4.6.5. Precipitation of other minerals

In addition to mackinawite precipitation, the new approach enables the precipitation and deposition of up to five mineral species on the walls of the well casing. The mineral species were chosen due to their presence in the scale examined (Fouillac et al., 1986; Honegger et al., 1986a, 1986b, 1988a, 1988b; Abou Akar and Lafforgue, 1994; Amalhay et al., 1994, 1995): pyrrhotite (Fe$_1$-$x$S), goethite ($\alpha$-FeOOH), siderite (FeCO$_3$), amorphous silica (SiO$_2$) and calcite (CaCO$_3$). The principle of precipitation and deposition of each of the five mineral species is identical to that proposed for mackinawite in the standard approach (Boisdet et al., 1992): Testing the saturation index of geothermal water in the fluid vein with respect to each species, precipitation of the excess and finally, calculation of the new redistribution of simple or complex chemical species in the solution. The volume precipitated is then converted into scale on the casing wall. The casing diameter is recalculated according to the thickness of iron dissolved by corrosion and that of mackinawite and the other five mineral species deposited on the wall.
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*NB. Certain mineral species can be supersaturated in the aquifer (their Ionic Activity Product (IAP) being greater than their solubility product (Ks)). Precipitation of these species in the well according to equilibrium adjustment (IAP=Ks), causes intensive deposition in the well bottom that can lead to clogging. To avoid this problem, not observed in reality, the equilibrium state retained at each step was that of the aquifer. When the IAP\textsubscript{aq} (in the aquifer) of a given mineral species is greater than its Ks, it is the water saturation index in the aquifer (IAP/Ks) with respect to this species that is retained as the reference value (equilibrium) instead of 1.*

### 4.6.6. Calculating flowrate

The calculation code TPDEGAZ uses three inter-related parameters, flowrate, bottom-hole pressure and well-head pressure, which are entered into the well-bottom file by the user. This workplan often leads to a calculated pressure for the well head that is different to the recorded value in the data file, leading to a premature end to the calculations or continuation of the simulation above the surface.

In order to avoid this problem, which is common to both TPDEGAZ and MODEP, two new routines have been added that enable calculation of the flowrate called Caldébit and Caldébit2. The first routine is called before the first rise and the second before each following rise. The operating principle of these two routines is similar as they both:

- use the same calculation method: a Gringarten-type formula which already figures in the code for calculating head loss in the well;
  \[
  \Delta D = 1.023 \times 10^4 \cdot \frac{\eta \cdot Q^{2-\alpha} \cdot \Delta L}{D^{4-\alpha}}
  \]  
  (where coefficient $\alpha = 0.21$)
  
  - $D$ : internal casing diameter in mm
  - $\Delta P$ : head loss in bars
  - $\Delta L$ : well segment covered in m
  - $\eta$ : dynamic viscosity of geothermal water in cP (centipoise)
  - $Q$ : flowrate in m$^3$/h.

- regard bottom-hole and surface pressure as extreme pressures. Where the well is equipped with a pump, the pressure at the pump input is used instead of well-head pressure;

- allow a unique change of the casing diameter by entering the value of the new diameter and its depth point in the command file (Abou Akar et al., 1995);

- take into account the possibility of having a well bottom treatment tube (WBTT) in the well bottom and the associated new head loss that this will generate.

The differences between the two routines are:

- the first uses a nominal well diameter (or two, if there is a change), and average viscosity and specific volume values calculated for the entire length of the casing;

- the second uses average values for diameter, viscosity and specific volume calculated for each incremental step during the previous rise.

After variation of the casing diameter as a result of corrosion-scaling phenomena, the second routine calculates the new flowrate before each new rise in the well, which is then used for other calculations relative to this rise. This correction has the advantage of maintaining a
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constant pressure profile and of monitoring flowrate evolution of geothermal water depending on the evolution of casing diameter.

If the user wishes, the calling up of these two routines can be made inoperative in which case, the code uses the flowrate in the data file. This will create an evolution of the pressure profile along the length of the casing.

4.6.7. Integration of a well bottom treatment tube (WBTT)

Most wells exploiting the Dogger aquifer in the Paris Basin are equipped with a bottom-hole additive injection tube to help prevent corrosion-scaling phenomena. This equipment induces a supplementary head loss in the well which we feel should be taken into account and included in the MODEP calculation code routines. This work is now completed and WBTT (diameter and depth) can be managed using the user interface that generates the command file MODEP.CMD.

4.7. Modifications to the graphic interface

The graphic interface that generates the command file (MODEP.CMD) was modified by integrating new parameters necessary for the improved MODEP code (kinetics, presence of a Well-Bottom Treatment Tube (WBTT), etc.). Mgraph, the software for the graphic display of results that was also presented in the sixth half-yearly report (Abou Akar et al., 1995), has been modified to make it more flexible and quicker. The version Mgraph3 is operational and offers better definition of scales and the possibility of transferring graphics in the form of a "Bitmap" image. Furthermore, the data presented on the graphs are automatically saved and formatted so that they can be transferred directly to any spreadsheet software, e.g. Excel, Grapher, etc.

5. DIGITAL RESULTS OBTAINED USING THE COMPUTER MODEL

5.1. Introduction

The MODEP calculation code is based on certain hypotheses that were put forward as the code's writing progressed, hypotheses that have been referred to and discussed in previous work (Boisdet et al., 1992; Abou Akar and Ignatiadis 1994, 1995; Abou Akar and Boens, 1995). The calculations carried out by the code are thus based on these hypotheses, and their validity is interdependent.

The results obtained by the calculations do not, therefore, represent "absolute reality", but rather trends that enable the monitoring of the evolution of various parameters, such as corrosion rate, thickness of dissolved iron, scale thickness, casing diameter, contents of certain species, and geothermal fluid flowrate as a function of a given variable (temperature, pressure, concentration of dissolved species).

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The main results are grouped into the `<output>.CSV` file, the name of which is chosen by the user in the graphic interface (Abou Akar *et al.*, 1995). This file is in the form of a table that includes, in the following order:

- **IW**: number of the rise (related to exploitation duration),
- **JW**: number of the step or stage (related to depth),
- **temps**: exploitation duration (in days),
- **Z**: total depth of the stage (in metres),
- **P**: well pressure (in abs. bar),
- **pH**: pH of the fluid vein,
- **Diam**: present casing diameter (in cm),
- **Logt2mack**: saturation index of the fluid vein with respect to mackinawite,
- **Fetot**: content of total dissolved iron in the fluid vein (in mg/kg water),
- **HStot**: content of total dissolved sulphide in the fluid vein (in mg/kg water),
- **Edep**: thickness of deposit (in cm),
- **EpFe**: thickness of corroded iron (in cm),
- **Fe pa**: content of free iron on casing wall (in mg/kg water),
- **CO$_3$ pa**: content of free carbonate on casing wall (in mg/kg water),
- **pH pa**: pH on the casing wall,
- **HS pa**: content of free sulphide on casing wall (in mg/kg water),
- **Débit**: flowrate of geothermal fluid (in m$^3$/h),
- **Vcor**: corrosion rate of casing (in mm/yr).

The first four values are x-coordinates, and the others y-coordinates.

For each rise and depth, MODEP prints values of the various parameters above in the `<output>.csv` file. Because certain rises are double (Caldep1 and Caldep2, (Abou Akar and Boens, 1995)), the program Convert was written to eliminate values calculated by Caldep1 from the `<output>.csv` file when they are invalidated. This final file will be processed by the Mgraph software dedicated to the `.csv` file, or by other software such as Excel and Grapher. However, handling of `.csv` by software other than Mgraph is not very easy and it is preferable to trace graphics using Mgraph and then recover them on Excel for better processing and display.

Results obtained during processing an example of a geothermal plant in the Paris basin are presented below. MODEP was run two times on the same `.dat` file, where the fluid has a high sulphide content, 36 ppm, and the following parameters:

- **Well-head temperature**: 58.4°C
- **Well-bottom temperature**: 58.4°C
- **Well-head pressure**: 7.5 bar
- **Well-bottom pressure**: 160.8 bar
- **Total measured depth**: 1980 m
- **Casing diameter**: 15.94 cm
- **Depth of deviation**: 843.40 m
- **Angle of deviation**: 45° 45'
- **Depth of pump**: 160 m
- **Pressure at the pump level**: 9 bar
- **Increase in pressure at pump level**: 14.80 bar
- **pH of fluid in reservoir**: 6.19
The difference lies in the command file ".cmd" where two conditions have been imposed:

1. no corrosion or scaling in the rising pipe and only mackinawite deposition on the remainder of the casing (DEP2805C.CSV),

2. no corrosion or mackinawite deposition in the rising pipe, precipitation without deposition of the five other mineral species in the rising pipe, and deposition of both mackinawite and the five other mineral species the length of the rest of the casing (DEP2805D.CSV).

5.2. First case: DEP2805C.CSV

This example relates to the first case above. Figure 1 shows the evolution of the corrosion rate of the casing relative to depth and the exploitation duration of the well. The corrosion rate is very high at first (10-11 mm/yr) because of the bare metal, but drops dramatically after the first day to below 3 mm/yr, continues to fall as a function of time to below 0.3 mm/yr at the end of the first year, and to 0.12 mm/yr after 10 years of exploitation. Figure 2 shows the corrosion rate as a function of time and for different depths. It is observed that, regardless of depth, the corrosion rate remains relatively constant for the given duration. However, a small increase with depth is observed.

Figures 3 and 4 show the evolution of the thicknesses of iron dissolved from the casing and mackinawite deposited, also as a function of depth and exploitation duration of the well. As for the corrosion rate, the thickness of dissolved iron increases slightly with depth. This is explained by a slight increase in pH of the geothermal water during its rise in the well which lowers its corrosivity. Mackinawite scale thickness shows a similar pattern, being greater than that of dissolved iron for the first 10 years, after which time it becomes thinner. This is explained by the fact that the diffusional regime for precipitation is reached after only a few days whereas that for corrosion takes much longer. Figures 5 and 6 give an indication of the thicknesses of these two species as a function of time and for different depths.

Figure 7 shows the evolution of the casing diameter, which commonly decreases from 15.94 cm (nominal value) to about 15.916 cm after 380 days, and then increases to more than the nominal value (after 2100 days) due to the thin layer of mackinawite deposited compared to the thickness of iron dissolved. Consequently, the geothermal water flowrate also falls until day 380 and then rises again (Fig. 8).

Note: Simulation of deposition and scaling stops at 160 m, the depth of the submerged pump. This provides zero values (incorporated on the graph) for dissolved and deposited thicknesses, and nominal values for the casing diameter.

Figure 9 shows the evolution of pH in the fluid vein with depth and exploitation duration of the well. The pH rises slightly between the well bottom and the surface due to the drop in pressure which has an effect on chemical equilibria in solution. The drop in pH at 160 m is due to an increase in pressure at the pump. The pH evolution with time, which shows a marked drop at the beginning with a tendency to stabilize afterwards, is responsible for the evolution in the corrosion rate. At the beginning when the metal is bare, the thickness of the diffusion layer is restricted to that of the hydrodynamic layer, the H⁺ ions migrate easier towards the casing wall through this layer causing a high corrosion rate. As exploitation
duration increases, so does scale thickness, the diffusion layer is now made up of the hydrodynamic layer and the mackinawite scale (Abou Akar and Boens, 1995). Migration of the H\textsuperscript{+} ions through this layer via pores in the scale becomes increasingly difficult, which reduces the concentration of H\textsuperscript{+} ions on the casing wall (pH increase) and as a result, causes a lower corrosion rate (Fig. 2).

This pH increase on the casing wall which is shown in Figure 10, is very sharp initially (strong reduction in H\textsuperscript{+} ions) and then levels off.

Figure 11 shows the evolution of the content of total dissolved iron in the fluid vein with depth and for different exploitation lengths of the well. This content increases during the rise of geothermal water in the well due to the accumulation of iron injected into this fluid vein at each depth. It is reminded that the principle of simulating scale formation is the following: establishment of concentration gradients (Fe\textsuperscript{2+}, H\textsuperscript{+}, HS\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}) in the diffusion layer and injection of a determined quantity of iron per time and surface unit in the fluid vein according Fick's diffusion law, maintenance of the iron content on the casing wall in response to the solubility product $K_S$ of mackinawite, and calculation of the flux of iron precipitated as mackinawite on the wall. Figure 12 represents the concentration of free iron (Fe\textsuperscript{2+}) on the casing wall which increases as a function of time due to the pH increase (Fig. 10) and the decrease in the concentration of dissolved sulphides on this same wall (Fig. 13). Figure 13 also shows that the diffusional regime for precipitation is reached rapidly (HS\textsuperscript{-} concentration on the wall is about zero).

Figure 14 shows the evolution of the content of total dissolved iron in the fluid vein with exploitation duration and for different depths. This content rises sharply at first, reaches a maximum between 3 and 4 exploitation hours, and then falls gradually down to the end. This increase is explained by a very high corrosion rate at the beginning and a thin diffusion layer (reduced to the hydrodynamic layer) which enables the injection of a maximum of iron into the fluid vein. This is confirmed by H\textsuperscript{+} and HS\textsuperscript{-} activity on the wall, which is initially equal to that in the fluid vein meaning that iron saturation on the wall is reached quickly and as a consequence, the percentage of iron that precipitates (compared to total iron corroded) as mackinawite is reduced. After the curve maximum, the corrosion rate has already fallen considerably (Figs. 1 and 2), but an increase in the pH and the diffusional regime for mackinawite precipitation (HS\textsuperscript{-} $\approx$ 0) enables very high iron concentrations on the wall (Fig. 12). There is less precipitation but the percentage of iron precipitated increases and consequently, the percentage of iron injected in the fluid vein diminishes.

Figure 15 shows the evolution of the content of total dissolved sulphides in the fluid vein with depth for different exploitation durations. This content diminishes during the rise of geothermal water in the well due to the precipitation of mackinawite on the wall, and more specifically, falls sharply at the beginning of exploitation because the amount precipitated is high (even though percentage-wise the amount precipitated is lower). Figure 16 shows the evolution of the content of total dissolved sulphides in the fluid vein as a function of the well's exploitation duration and provides a better indication of the rapid gain of the quasi-steady state.
5.3. Second case: DEP2805D.CSV

This example relates to the second case cited above, i.e. no corrosion or mackinawite deposition in the rising pipe, precipitation without deposition of the five other mineral species in the rising pipe, and deposition of both mackinawite and the five other mineral species the length of the rest of the casing. Calculations show that only calcite and pyrrhotite reached saturation as defined previously (cf. § 4.6.5) and consequently, were the only species to precipitate. Calcite precipitates from the well bottom up to the surface and the volume precipitated increases in the direction of the rise. Its precipitation was based on elimination of CO$_3^{2-}$ excess, a very minor species compared to total carbonates or to calcium. This elimination is compensated at each stage of the rise by displacement of the chemical equilibria in favour of CO$_3^{2-}$, because of its consumption and the increase in pH of the geothermal water. This precipitation can be quite spectacular in certain cases (degassing of the fluid) but in the present study, the pressure is always greater than the degassing pressure. Pyrrhotite precipitates after the third stage and the quantity precipitated increases initially, then falls slowly before a sharp drop after the pump because corrosion stops. For all cases, the volume of pyrrhotite precipitated is always less than that of calcite, the ratio evolving between about 1:1 and 1:4.

Figures 17 and 18 show the evolution of the corrosion rate of the casing as a function of depth and exploitation duration of the well. The corrosion rate is very high at first on bare metal and drops from 10-11 mm/yr to about 2 mm/yr after the first day. It decreases quicker with time than for Figure 1 where only mackinawite scale is represented. This is because of the thicker scale in the present case which considerably slows down the migration of species through the diffusion layer and consequently, reduces the corrosion rate. Furthermore, the corrosion rate decreases between the well bottom and the surface which leads to a similar pattern for the thickness of dissolved iron (Figs. 19 and 20).

This drop in the corrosion rate between the well bottom and the surface is due to an increasing thickness of scale with the rise (Figs. 21 and 22) which, as has already been specified, is mainly due to increasing calcite precipitation in the present case.

Inversion in the volume of precipitated pyrrhotite is a result of the following phenomena:

Moving from the well bottom upwards, corrosion rate starts out high and there is only a thin layer of scale. This corresponds to a large flux of iron injected in the fluid vein and the iron content rises. Pyrrhotite becomes saturated and precipitates. However, calculations show that the free iron, which is the only species that can precipitate under our simulation conditions, is minor compared to iron complex compound (iron sulphides, carbonates and chlorides). There is therefore a large reserve of iron "ready for precipitation" in the fluid vein.

The drop in pyrrhotite solubility, addition of iron by corrosion and finally, compensation of precipitated iron (by displacement of the complexing equilibria in favour of free iron according to the Le Châtelier principle) lead to the continued precipitation and deposition of pyrrhotite during the rise in the well. As long as the supply of iron by corrosion is greater than the amount taken up by precipitation, there is an increase in the content of total iron in the fluid vein and consequently, of the volume of precipitated pyrrhotite. As the corrosion rate falls during the rise of the water and precipitation continues to take up iron from the iron complex compounds, the quantity of iron injected by corrosion will fall below that taken up.
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by precipitation, causing a downward bend in the curve of the content of total iron in the fluid vein (Fig. 23) and thus a decrease in the volume of precipitated pyrrhotite. This fall is accentuated in the rising pipe because corrosion stops.

This simulation method for the deposition of five mineral species, which consists of restoring (in the case of saturation) the saturation index of the fluid with respect to the mineral concerned to its value in the aquifer (cf. § 4.6.5), has proved to be the most coherent of the three methods tested. The method that restores saturation indexes to the value of 1 ended in clogging up of the well bottom (because of supersaturated species in the reservoir). Another simulation method, which consists of considering the ionic activity product of the reservoir as the solubility product, also provided incoherent results. A method that remains to be tested but which a priori gives more uniform scale thicknesses for corrosion products, is the present method applied to the precipitation of excess iron calculated with respect to total iron rather than to free iron. However, this method could lead to thick scale and, in the case of species not produced by the wall (e.g. CaCO₃, SiO₂), the excess would rapidly be used up and precipitation would stop, a phenomena observed in high-enthalpy geothermal wells for the precipitation and deposition of calcite after degassing of the geothermal water. The consequences of such an increase in scale thickness are a decreasing well diameter moving closer to the surface (Fig. 24) and a large drop in flowrate in the well (Fig. 25).

**Nb:** As for case No. 1, simulation of corrosion and scaling stops at 160 m depth, the location of the submerged pump.

Evolution of the pH in the fluid vein with depth and exploitation duration of the well is shown in Figure 26. This pH is slightly lower than for case No. 1 because there are less H⁺ ions to migrate towards the diffusion layer due to the thicker scale. Evolution of the pH on the casing wall (Fig. 27) shows a similar pattern to that of Figure 10 (case No. 1) but with stable values that are slightly higher (9.2 rather than 9.0). This caused iron concentration on the wall, also stable and higher (Fig. 28) than for Figure 12. Compared to case No. 1, the concentration in sulphides on the wall decreases more sharply (Fig. 29), the content of total iron in the fluid vein is lower (Fig. 30), and the content of total sulphides in the fluid vein reaches its bottom-hole value quicker (Figs. 31 and 32). This is due to thicker scale for the same length of simulation.

**6. CONCLUSION**

This report presents a program (MODEP) that enables simulation of corrosion and scaling phenomena in low-enthalpy geothermal wells. The simulation of casing corrosion is based on application of the Volmer-Heyrovski reactive mechanism. The calculations take into account Fick's diffusion laws, the variation of the thickness of the diffusion layer due to scale growth, and the porosity of the scale (assumed to be made up of mackinawite Fe₁₊ₓ S, the main scale constituent). The rate of mackinawite precipitation is calculated using the solubility product, Kₛ. These tests have enabled the calculation of chemical species concentrations on casing walls and the monitoring of the evolution of corrosion and mackinawite precipitation rates as a function of the main parameters and the duration of well-exploitation.
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Simulation of the behaviour of geothermal fluids in a well in the Paris basin using the MODEP code has enabled the study of the evolution of the major parameters as a function of the exploitation duration to be simulated and well depth.

As a function of time and depth, the use of the MODEP code, has revealed:

- The establishment of different kinetic regimes as a function of diffusion length.

- That the well is subjected to high corrosion at the beginning of its life. Inhibitor treatments must therefore be applied as soon as water flows through the well.

- That because of the simulation method chosen (increasing thickness of protector scale), the corrosion rate falls rapidly with time at the beginning of simulation. This reduction in corrosion becomes less marked when the scale is sufficiently thick. In addition, corrosion rates calculated are similar to those experimentally measured.

- A good correlation between the evolution of iron content (fluid vein and wall) and that of pH and sulphide content, and also between the evolution of casing diameter and production flowrate.

- The effect that the slightest variation in pH has on evolution of the corrosion rate of the casing.

This code also enables the simulation of mackinawite precipitation according to kinetic criteria, the precipitation and deposition of five other mineral species (depending on thermodynamic criteria) commonly encountered in scale in geothermal wells in the Paris basin, i.e. pyrrhotite Fe$_{1-x}$S, siderite FeCO$_3$, goethite FeOOH, calcite CaCO$_3$ and amorphous silica SiO$_2$. MODEP calculates the geothermal fluid flowrate and takes into account supplementary head losses due to installation of a well-bottom treatment tube (WBTT).

This is a simple model and certain phenomena are not taken into account. Nevertheless, this model could be improved by taking into consideration the reduction of chemical species other than $\text{H}^+$ such as $\text{HS}^-$ and $\text{HCO}_3^-$. Taking these two other species into account in the cathodic reduction reaction for the equilibration of iron corrosion formed the basis of a proposal at the European Union as part of the INCO COPERNICUS work programme this year.

However, certain phenomena are difficult to model:

- The possible precipitation or redissolution within the pores of the scale, which leads to a variation in porosity with time.

- The appearance of additional cathodic sites, where the protons would be reduced (the electrons produced during oxidation of iron can move around in the scale as it is conductive). It is no longer sufficient to only study the metal surface. The scale must be subdivided into thin layers (choice of the thickness of the layers, calculation of the total intensity of the corrosion current). The numerous problems to be overcome increase the calculation time considerably.

Certain phenomena are very difficult to model, such as the frequency of corrosion pitting at a given point of the casing. At the most, quantification of the influence of certain physical parameters on the probability of the appearance of pitting corrosion can be attempted.
Henceforth, the MODEP code can be used to calculate trends as a function of variations in the major parameters of the aquifer and/or the well. Results will be compared with corrosion measurements in the near future to provide an indication of the gap with reality and to enable calibration.

7. REFERENCES


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Fig. 1a - Evolution of corrosion rate (mm/year) with depth (m) and for different exploitation lengths (day).

Fig. 1b - Evolution of corrosion rate (mm/year) with depth (m) and for different exploitation lengths (day).
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Fig. 1c - Evolution of corrosion rate (mm/year) with depth (m) and for different exploitation lengths (day).

Fig. 2a - Evolution of corrosion rate (mm/year) with exploitation length (day) and for different depths (m).
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Fig. 2b - Evolution of corrosion rate (mm/year) with exploitation length (day) and for different depths (m).

Fig. 2c - Evolution of corrosion rate (mm/year) with exploitation length (day) and for different depths (m).
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Fig. 3a - Evolution of thickness of corroded iron (cm) with depth (m) and for different exploitation lengths (day).

Fig. 3b - Evolution of thickness of corroded iron (cm) with depth (m) and for different exploitation lengths (day).
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Fig. 4a - Evolution of thickness of deposited mackinawite on the well wall (cm) with depth (m) and for different exploitation lengths (day).

Fig. 4b - Evolution of thickness of deposited mackinawite on the well wall (cm) with depth (m) and for different exploitation lengths (day).
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Fig. 5a - Evolution of thickness of corroded iron (cm) with exploitation length (day) and for different depths (m).

Fig. 5b - Evolution of thickness of corroded iron (cm) with exploitation length (day) and for different depths (m).
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Fig. 6 - Evolution of thickness of deposited mackinawite (cm) with exploitation length (day) and for different depths (m).

Fig. 7a - Evolution of casing diameter (cm) with depth (m) and for different exploitation lengths (day).
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Fig. 7b - Evolution of casing diameter (cm) with exploitation length (day) and for different depths (m).

Fig. 8 - Evolution of flowrate (m³/h) with exploitation length (day).
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Fig. 9a - Evolution of the pH of the fluid vein with depth (m) and for different exploitation lengths (day).

Fig. 9b - Evolution of the pH of the fluid vein with depth (m) and for different exploitation lengths (day).
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Fig. 9c - Evolution of the pH of the fluid vein with depth (m) and for different exploitation lengths (day).

Fig. 10 - Evolution of the pH on the well wall with exploitation length (day) and for different depths (m).
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Fig. 11a - Evolution of the total iron concentration of the fluid vein (mg/kg water) with depth (m) and for different exploitation lengths (day).

Fig. 11b - Evolution of the total iron concentration of the fluid vein (mg/kg water) with depth (m) and for different exploitation lengths (day).
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Fig. 12 - Evolution of the free iron concentration ($\text{Fe}^{2+}$) on the well wall (mg/kg water) with exploitation length (day) and for different depths (m).

Fig. 13 - Evolution of the free sulphide concentration ($\text{HS}^-$) on the well wall (mg/kg water) with exploitation length (day) and for different depths (m).
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Fig. 14a - Evolution of the total iron concentration (Fe tot) of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).

Fig. 14b - Evolution of the total iron concentration (Fe tot) of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).
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Fig. 14c - Evolution of the total iron concentration (Fe tot) of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).

Fig. 14d - Evolution of the total iron concentration (Fe tot) of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).
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Fig. 15a - Evolution of the total sulphide concentration of the fluid vein (mg/kg water) with depth (m) and for different exploitation lengths (day).

Fig. 15b - Evolution of the total sulphide concentration of the fluid vein (mg/kg water) with depth (m) and for different exploitation lengths (day).
Fig. 16a - Evolution of the total sulphide concentration of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).

Fig. 16b - Evolution of the total sulphide concentration of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).
Fig. 17a - Evolution of corrosion rate (mm/year) with depth (m) and for different exploitation lengths (day).

Fig. 17a - Evolution of corrosion rate (mm/year) with depth (m) and for different exploitation lengths (day).
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Fig. 18a - Evolution of corrosion rate (mm/year) with exploitation length (day) and for different depths (m).

Fig. 18b - Evolution of corrosion rate (mm/year) with exploitation length (day) and for different depths (m).
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Fig. 18c - Evolution of corrosion rate (mm/year) with exploitation length (day) and for different depths (m).

Fig. 19 - Evolution of thickness of corroded iron (cm) with depth (m) and for different exploitation lengths (day).
Fig. 20 - Evolution of thickness of corroded iron (cm) with exploitation length (day) and for different depths (m).

Fig. 21 - Evolution of thickness of scale deposited (cm) with depth (m) and for different exploitation lengths (day).
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Fig. 22 - Evolution of thickness of scale deposited (cm) with exploitation length (day) and for different depths (m).

Fig. 23a - Evolution of the total iron concentration of the fluid vein (mg/kg water) with depth (m) and for different exploitation lengths (day).
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Fig. 23b - Evolution of the total iron concentration of the fluid vein (mg/kg water) with depth (m) and for different exploitation lengths (day).

Fig. 24a - Evolution of casing diameter (cm) with depth (m) and for different exploitation lengths (day).
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Fig. 24b - Evolution of casing diameter (cm) with exploitation length (day) and for different depths (m).

Fig. 25 - Evolution of flowrate (m³/h) with exploitation length (day).
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Fig. 26a - Evolution of the pH of the fluid vein with depth (m) and for different exploitation lengths (day).

Fig. 26b - Evolution of the pH of the fluid vein with depth (m) and for different exploitation lengths (day).
Fig. 26c - Evolution of the pH of the fluid vein with depth (m) and for different exploitation lengths (day).

Fig. 27a - Evolution of the pH on the well wall with exploitation length (day) and for different depths (m).
Fig. 27b - Evolution of the pH on the well wall with exploitation length (day) and for different depths (m).

Fig. 28a - Evolution of the free iron concentration ($Fe^{2+}$) on the well wall (mg/kg water) with exploitation length (day) and for different depths (m).
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**Fig. 28b** - Evolution of the free iron concentration ($Fe^{2+}$) on the well wall (mg/kg water) with exploitation length (day) and for different depths (m).

**Fig. 29** - Evolution of the free sulphide concentration ($HS^-$) on the well wall (mg/kg water) with exploitation length (day) and for different depths (m).
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Fig. 30a - Evolution of the total iron concentration (Fe tot) of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).

Fig. 30b - Evolution of the total iron concentration (Fe tot) of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).
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Fig. 30c - Evolution of the total iron concentration (Fe tot) of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).

Fig. 30d - Evolution of the total iron concentration (Fe tot) of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).
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Fig. 31a - Evolution of the total sulphide concentration of the fluid vein (mg/kg water) with depth (m) and for different exploitation lengths (day).

Fig. 31b - Evolution of the total sulphide concentration of the fluid vein (mg/kg water) with depth (m) and for different exploitation lengths (day).
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Fig. 32a - Evolution of the total sulphide concentration of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).

Fig. 32b - Evolution of the total sulphide concentration of the fluid vein (mg/kg water) with exploitation length (day) and for different depths (m).
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DESIGN OF A COMPUTER ASSISTED SYSTEM FOR CORROSION TESTS

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SUMMARY

The paper presents a corrosion monitoring system based on multi-electrode (matrix electrode) which gives simultaneous information about 50 samples under a corrosion test. The system can be used as well for monitoring the open-circuit potential ($I = 0$) or for monitoring the current distribution in the case of cathodic protection under external current source. The data acquisition board and the multiplexing system have been designed and produced by CAEL and allow extensions to different boards in use. Design details are given below particularly regarding the multiplexing system and the multi-electrode which constitute the object of the current research. The hardware is accompanied by a specific software component assisting in the CAEL experimental system.

The system was designed to monitor the corrosion process of different compositions of steel in geothermal water. The system was used to draw Evans' diagrams relative to the corrosion at the metal-metal interface (galvanic corrosion) in view to identify the opportunity of cathodic protection without an external current source.

1. INTRODUCTION

1.1. Data acquisition cards

For data acquisition field, the works of H. AUSTERLITZ (1991), are one of the relevant contribution together with the support of software technique under Windows environment (C. PETZOLD - 1992). Some dedicated journals or books, describes the new applications in the field of chemistry with important contribution of electrochemical aspects - H. A. STROBEL (1973), R.SCHROEDER and al. (1969), J.E.MUMBY and al. (1971), T.R. MUELLER and al. (1969).

Analog I/O cards are the most common form of data acquisition hardware for PCs. For the PC, two well known manufactures are present on the market: National Instruments and Keithley Metrabyte (1996). Usually, any card contain one or more ADCs for analog input and DACs for analog output, either on the same or separate cards. Usually, any card containing an ADC for analog input is considered a data acquisition card. Analog input cards typically contain one ADC IC or module along with one or more analog multiplexers. This enables several analog
signal sources (such as conditioned sensors) to be connected to one board at the same time. For example, multiple temperature sensors may be used in monitoring different portions of a piece of equipment under test. The multiplexer allows one of several analog inputs to be connected to the ADC at any given time. Commonly, commercial ADC cards have 8-32 analog input channels. These channels may be differential or just single ended. A complete chain of the computer aided experiment is present in Fig. 1. It contains: the transducers, signal condition block, data acquisition card and PC.

Figure 1 - Simplified block diagram of a data acquisition system

The resolution of the ADCs and DACs used range from 8 to 16 bits. Analog I/O boards with 12-bit resolution are the most common, at present. Another important parameter is the maximum conversion rate for analog input cards. This can range from only tens of samples/second on high resolution and/or low-cost cards to over 100,000 samples/second on high-speed data acquisition cards with DMA hardware. Cards with conversion rates as high as one million samples/second are also becoming common.

When looking at maximum conversion rates for these ADC cards, remember that the rate is usually specified for a single channel only. If there are need to measure several inputs simultaneously, the maximum conversion rate at any channel is the ADC's maximum rate divided by the number of multiplexed channels used.

Analog output cards usually contain one DAC per output channel. Occasionally, a card may contain one DAC and several analog output channels, employing a sample-and-hold (S&H) amplifier for each channel. S&H amplifiers “remember” a voltage level using a charged capacitor. Since the capacitor's charge slowly drops (due to its own leakage current and that of the surrounding circuitry), the S&H output “droops” with time. The S&H output must be continuously refreshed by recharging the capacitor, or the analog output will be valid only for a short period of time (usually on the order of milliseconds). Due to these drawbacks, this approach is not widely used. Most analog output boards have only a few channels, with an independent DAC for each.
Most analog I/O cards contain a timer/counter with multiple channels. This enables the card to perform conversions at a fixed rate, without any PC software overhead. It is common option for data conversion to be controlled either by an internal (on board) clock, an external clock, or PC software commands. Most analog input cards have hardware interrupt capability. This is a programmable option, used to generate an interrupt when the ADC is ready to be read. It is especially important when the ADC conversion rate is controlled by a clock and is essentially asynchronous to the control software running on the PC.

**Cards with DMA capability**

This allows data to be transferred between the data acquisition card and the PC at the fastest possible rate. It does require special software support. Only high-speed analog I/O cards use DMA, since for slower cards the analog data conversion speeds becomes the rate-limiting factor, not the data transfer rate.

Timer/counters are available on separate cards, typically in conjunction with digital I/O lines. Beside being used for controlling data conversion rates, they are also useful as general purpose clocks, frequency counters, and event counters. They usually have TTL compatible inputs, but with proper signal conditioning, such as an amplifier (to boost the signal level) and a comparator with hysteresis (to square up slow rise/fall times of a signal and convert it to TTL levels), analog signals can also be measured.

**Multifunction board**

This card contains, at a minimum, an ADC and digital I/O lines. A typical multifunction data acquisition card contains several analog input channels, one or more analog output channels, several digital I/O lines, DMA capability, local memory (as FIFO word) and several timer/counter channels. Some may even contain signal-conditioning circuitry, such as filters.

The following chapters will be dedicated to our original contribution of this work.

**1.2. About matrix electrode**

JIAN QI and al. (1990) have study the ionic mass transfer in a parallel plate electrochemical cell with an array electrode. The mass transfer coefficient measured for a fully development flow, was in a good agreement with Leveque equation. An array electrode, was used by A.A.WRAG and al. (1990), in order to study the the local mass transfer by using a cell in its baffled mode operation. A matrix electrode was used by F.B. LEITZ and al. (1977), in the study of mass transfer with turbulence promoters. U.Landau (1981) use the array electrode, for study the current distribution and local mass transfer. They use a name of segmented electrode (in stead of matrix electrode). A data acquisition system consists of a transducer with resistors of 10 kΩ each and a dedicated analog to digital converter. Woo S.Kim and al. (1981) describe a construction of a segmented electrode, which was used to study the local mass transfer. Unfortunately there are no so many study in the corrosion applications like in chemical engineering, for mass transfer.
The use of monitoring systems in the study of corrosion processes is aligned with the new concept called virtual instrumentation, launched by National Instruments. Such systems are based on two perfectly integrated resources of personal computers: A/D and D/A data acquisitions boards introduced in ISA or PCI buses on one hand, and a software environment including a powerful graphic interface associated with signal processing functions on the other hand. The software package Labview of National Instruments is now forcefully contested by products such as TestPoint. These are but two reference products among more than 20 similar packages to be used in different configurations and applications.

The investigation method proposed in the present paper is based on the scanning principle. A group of simultaneously tested samples is sequentially contacted in a periodic manner in a short time interval (about 50 milliseconds). There are different scanning systems of multiplexing type available on the market, usually presenting 8 differential inputs (E&G, Schlumberger, Gamry, etc.). The increase in the conversion rate of A/D converters and the reduction in amplifier noise allowed the simultaneous investigations of many electrodes. The multi-electrode concept (V. Cotarta, 1993,) can induce a confusing, since it can be associated with electrochemical systems where more than one reaction are active on the same electrode. From a terminology point of view the term of matrix (or array) electrode seems preferable. The advantages of this type of electrode can be summarized as follows:

- in situ measurements can be done;
- a simultaneous comparison between many samples operating in the same environment is possible;
- the influence of portions of corrosion inhibitors can be studied during their flow over a plane (matrix electrode) plate;
- the inclusion of a temperature sensor among the inputs allows the monitoring of the influence of this supplementary parameter on phenomena under consideration;
- the actual current distribution can be studied in electrochemical systems operating under external current sources.

The functions of the matrix electrode (multi-electrode)

The matrix electrode can be used in corrosion monitoring in the following applications:

- maximum number of electrodes = 50 (including the reference electrode);
- minimum number of electrodes = 2 (including the reference electrode);
- monitoring of the open-circuit (I = 0) electrode potential;
- monitoring of the galvanic corrosion (using a varying precision resistance);
- monitoring of the current distribution in systems with external current source.

The matrix electrode has been tested by all three methods. This type of electrode was integrated in an electrochemical system as a computer assisted measuring system. The main components of a computer assisted measuring chain is presented in Fig. 1.
2. ORIGINAL CONTRIBUTIONS

2.1. Brief description of the PC plug-in BP 100 board

The BP100 is an already done data acquisition board which was projected and tested in our laboratory (Fig. 2). The complete hardware system include both a multiplexer and a resistors boards discussed later in the next chapter and a multielectrode sensor. Further is a short description of this board that we used for data acquisition.

The BP100 is a high speed data acquisition plug-in board for the IBM PC/XT/AT and compatible computers. It features 12-bit A/D resolution and up to 100KHz throughput rate in DMA mode. The BP100 may be configured via switch setting for 16 single-ended or 8 differential analog input channels. To have a good noise immunity and higher A/D conversion accuracy, we selected differential mode. The BP100 board is designed with a programmable gain amplifier which can be configured for voltage gain of 1, 2, 4, and 8, with input ranges of +10V, +5V, +2.5V, +1.25V for unipolar and ±10V, ±5V, ±2.5V, ±1.25V for bipolar.

Three Kinds of A/D conversion speed are supported; low speed ADC, middle speed ADC and high speed ADC. The low speed ADC is initiated by software trigger. The middle speed ADC, with up to 3KHz A/D throughput, is triggered via interrupt. The high speed ADC, with up to 100KHz A/D throughput, is triggered by timer or external clock where the transfer of data is accomplished by DMA.

In addition to its analog input channels, the BP100 also provides two 12-bit analog output channels. The D/A converter, with internal reference voltage, uses programmable D/A code to output a voltage within the range of 0 to +5V.

Eight digital input and eight digital output lines are also available at the BP100’s 50 pin connector. These general purpose digital I/O lines are TTL/DTL compatible.

For timing functions, the BP100 uses 8254 chip to provide trigger pulses for A/D converter at any rate from 2.5MHz to 1 pulse/hr. The 8254 chip has three programmable counter/timer channels. Two of its channels are configured to fixed divider with 1MHz or 10MHz internal crystal clock. The third channel is configured as a gated 16-bit binary counter for user to use. In the Annex 1, the pin assignment connectors CN1 and CN2 for BP 100 are present.
2.2. Design of the multiplexer board

If data from many independent signal sources must be processed by the same computer, a multiplexer is usually introduced to couple the input signals into the AD converter in some sequence. Additional logic keeps track of which data source is coupled to the converter at any instant. The block diagram of the entire hardware system is presented in the Fig. 3.

---

**Figure 2** - Block diagram of the BP100 plug-in data acquisition board

**Figure 3** - Block diagram of the entire hardware system including the PC, BP100, Multiplexer board, Resistors board and the Multielectrod
A brief description of the operation of such a computer assisted measuring system is the following. The set of electric information produced by the matrix electrode is received by the data acquisition system (BP 100 board) via the multiplexor system. The electrical information is presented either directly or suitably amplified to the A/D board, where the continuously varying data are converted into digital (discrete varying) data, which is in turn presented to the PC computing system. This process is controlled by a dedicated software package which exchanges information with the matrix electrode. The experimental data can be either processed in real time or stored in view of subsequent processing using commercial software packages compatible with ASCII data files. The post-processing used in our study of corrosion processes was done on the ORIGIN software package.

The multielectrode could be useful in different electrochemical experiments, like measuring the current distribution in a cathodic protection application or potential distribution in a free system (without external source).

Since the data acquisition board measure voltages and not currents. For the current distribution applications, it need a current-voltage converter that is the resistors board. Because different current ranges could exist, several resistor boards are available. For the potential distribution applications simply connect the multielectrode to the multiplexer board. It is quite clear that is no way to fit 50 analog signals directly to the BP100 analog inputs. A multiplexer board was introduced with 7 analog multiplexers 8:1 (type HI508A HARRIS). The multiplexers inputs are selected via 3 digital lines provided by the output of the data acquisition card. Each 8 signals from the multielectrode are multiplexed so at the 7 of 8 analog inputs could be read 7x8=56 analog signals. For this moment only 50 are used. The 8-th analog input is available for a possible reference electrode voltage. On the BP100 board there is another 8:1 multiplexing level. For the on board multiplexers, the changing of data sources is done automatically without the soft interference. After reading the 8 channels (in the bipolar mode, 16 in the unipolar mode) the software must take care to change the multiplexers selection on the mux. board for seeking to the next 7 signals from the multielectrode, that is increasing the binary code present at the DO digital outputs. The HI508A chip was preferred considering his good features. The HI508A has input overvoltage protection. Analog input voltages may exceed either power supply voltage without damaging the device or disturbing the signal path of other channels. The protection circuitry assures that signal fidelity is maintained even under fault conditions that would destroy other multiplexers.

In order to avoid the electrical noise the mux. board is provided with ground planes and capacitors for power-supply decoupling. The complete electrical schematics of the multiplexer and resistors boards and also printed boards are presented in the Annex 2.

2.3. Software package LEAC

Leac is a software tool used to initialise and test the whole hardware system and also for data acquisition and management. Leac was designed to work under Microsoft Windows environment, thus it inherit many Windows advantages. For the user, Windows provides a multitasking, graphical-based windowing environment that runs programs especially designed for Windows. Such programs include Origin (scientific and technical graphics), Mathcad (mathematical calculations), Microsoft Excel (spreadsheet and business graphics), and many
others. Programs written for Windows have a consistent appearance and command structure and are thus often easier to learn and use than conventional MS-DOS programs. Users can easily switch among different Windows programs and exchange data between them.

Leac functions are initiated through the program menu. Below is a short description of the Leac main window (Fig. 4).

Leac main window looks typical for Windows programs. In the top of the main window are displayed the abbreviations of the channels to be acquired. At the run time, the most recent acquired dates will be written at the bottom of the main window. After one row has been completed the window content will scroll up one row. The scroll bar allows the window scrolling to the left and to the right in order to see all the 50 channels as well as the channel assigned to the reference electrode. By click with the mouse on the arrows at each end of the scroll bar or on the area between the arrows. Drag the thumb with the mouse to move to a particular location. If the mouse is missing the keyboard can be used: the arrows, the keys Page Up, Page Down to move faster or the keys Home, End to jump directly at the beginning or at the end of the window area.

The window’s menu bar is displayed immediately below the caption bar. Menu items listed in the top-level menu invoke drop-down menus. These items can see in Fig. 5.

- File
The File menu provides commands for saving data in the clipboard or in a file, and exiting the Leac.

After the acquisition is done or it was interrupted by the user the data can be saved the information either in the clipboard or in a file (Fig. 6). To save the data in the clipboard select the “Clipboard” command. To save the data in a file select the “Save as...” command and the following dialogue box will be displayed.

![Figure 6 - Save as...options dialogue box](image)

- Run (Fig. 7)

![Figure 7](image)

The Run menu provides commands for starting or stopping the data acquisition process.

- Options

The Options menu provides commands for choosing different data acquisition parameters (input voltage, acquisition speed, start channel and stop channel), selecting computer available hardware (IRQ number, DMA number, I/O port) and enabling or disabling the viewing of the new acquired data at the run time (Fig. 8 and 9).

![Figure 8](image)
Control of corrosion and scaling in geothermal systems

Selecting the Parameters command Leac will display the following dialog box:

![Parameters dialog box](image)

**Figure 9 - Parameters dialog box**

From the Input voltage radio buttons can be selected different gains. Usually the selection is ±1.25V because the signal is low-level.

![Hard dialog box](image)

**Figure 10 - Hard dialog box**

In the Samples/second control can be choose an integer that gives the acquisition speed. We tested the system on a 486-40MHz PC at a maximum rate of 3000 samples/second. The default values for Start and Stop channels are 0 and 7. The Hard command Leac use the dialog box from Fig. 10.

**I/O Port (HEX) selection**

BP100 use sixteen consecutive I/O port space, setting correct base address by the dip switch on the board will avoid contending other device. Let Leac now what is the base address choose by typing the correct hexadecimal number in the I/O Port (HEX) field. The default value is 300 h.
**DMA selection**

There are two DMA channels that can be hardware selected by BP100 for data transfer. Check the computer status before use DMA dip switch, avoiding crash the computer. Let Leac know what is the DMA channel that have been selected on the board by typing the correct number in the DMA Channel field. The default value is 3.

**IRQ selection**

The IRQ number is software programmable. Check the computer to see what are the free interrupt levels and type in the IRQ field one of them.

Enabling the Display option Leac will display the acquired data on the fly. At high speed acquisition the computer can’t display all the received data. Is better to simply don’t list them on the screen. To do this unchecked the Display option. For the notions that was used in this article, a glossary is available to the appendix.

**3. CONCLUSIONS**

- The matrix electrode (multi-electrode) is an extension of usual single-electrode electrochemical systems;
- The matrix electrode is particularly suited for corrosion monitoring in actual or micro-pilot systems;
- The matrix electrode can be used in studying the influence of flowing corrosion inhibitors over plane electrodes;
- The matrix electrode is a very flexible system, since it is computer assisted;
- The matrix electrode can be integrated in so called virtual instruments and can be operated in the frame of object type graphical programs;
- The matrix electrode reduces the measuring errors currently present in surface manufacturing by virtue of its very matrix structure;
- The matrix electrode can be used in electrochemical system with or without external current source;
- The system can be easily developed and oriented toward different data acquisition boards since a large part of it (electrode, multiplexor, software) is designed by CAEL;
- The matrix electrode is a monitoring system and as such it cannot be used properly in investigating surface phenomena associated with the first polarisation cycle;

NOTE. This work contains our contributions closed with the deliverables no.1, and the objectives no. 3.
4. REFERENCES


LABVIEW, is the trademark of National Instruments.


TESTPOINT, is the trademark of Capital Equipment Corporation - CEC.

V.COTARTA, (1993), Private seminar in INPG/CREM.GP-GRENoble and ENSIC - NANCY.

HOWARD A. STROBEL (1973) -"Chemical Instrumentation a systematic approach to instrumental analysis", Duke University, Addison-Wesley Publishing Company.


A.A.WRAG, A.A. LEONTARIDIS, (1990), In preceeding vol. of DEHEMA Symposium, 25-26 September.


5. ANNEX 1

Pin assignment of BP 100 for CN1 and CN2 connectors

**BP 100 board features**
- compatible with Keithley Metrabyte DAS-16G
- programmable gains 1, 2, 4, 8
- 16 S.E./8 DI. analog inputs with 12-bit resolution
- up to 100KHz sample rate through DMA mode operation
- programmable pacer clock initiates data conversions
- 2 channels of 12-bit analog output
- 8-bit TTL/DTL compatible digital inputs and outputs
- 1 channel counter/timer

<table>
<thead>
<tr>
<th>Pin assignment of BP 100 for CN1 and CN2 connectors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AI0</strong></td>
</tr>
<tr>
<td><strong>AI1</strong></td>
</tr>
<tr>
<td><strong>AI2</strong></td>
</tr>
<tr>
<td><strong>AI3</strong></td>
</tr>
<tr>
<td><strong>AI4</strong></td>
</tr>
<tr>
<td><strong>AI5</strong></td>
</tr>
<tr>
<td><strong>AI6</strong></td>
</tr>
<tr>
<td><strong>AI7</strong></td>
</tr>
<tr>
<td><strong>AGND</strong></td>
</tr>
<tr>
<td><strong>VDD</strong></td>
</tr>
<tr>
<td><strong>REF0</strong></td>
</tr>
<tr>
<td><strong>DA0</strong></td>
</tr>
<tr>
<td><strong>AGND</strong></td>
</tr>
<tr>
<td><strong>DO0</strong></td>
</tr>
<tr>
<td><strong>DO1</strong></td>
</tr>
<tr>
<td><strong>DO2</strong></td>
</tr>
<tr>
<td><strong>DO3</strong></td>
</tr>
<tr>
<td><strong>DGND</strong></td>
</tr>
<tr>
<td><strong>DO4</strong></td>
</tr>
<tr>
<td><strong>DO5</strong></td>
</tr>
<tr>
<td><strong>DO6</strong></td>
</tr>
<tr>
<td><strong>DO7</strong></td>
</tr>
<tr>
<td><strong>VCC</strong></td>
</tr>
<tr>
<td><strong>ETRG</strong></td>
</tr>
<tr>
<td><strong>DGND</strong></td>
</tr>
</tbody>
</table>

CN1
I/O functions for CN1 connector of BP100 board

<table>
<thead>
<tr>
<th>PIN</th>
<th>Name</th>
<th>I/O</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A10</td>
<td>Input</td>
<td>Analog input S.E.: Ch 0; DI: Ch 0 High</td>
</tr>
<tr>
<td>2</td>
<td>A18</td>
<td>Input</td>
<td>Analog input S.E.: Ch 8; DI: Ch 0 Low</td>
</tr>
<tr>
<td>3</td>
<td>A11</td>
<td>Input</td>
<td>Analog input S.E.: Ch 1; DI: Ch 1 High</td>
</tr>
<tr>
<td>4</td>
<td>A19</td>
<td>Input</td>
<td>Analog input S.E.: Ch 9; DI: Ch 1 Low</td>
</tr>
<tr>
<td>5</td>
<td>A12</td>
<td>Input</td>
<td>Analog input S.E.: Ch 2; DI: Ch 2 High</td>
</tr>
<tr>
<td>6</td>
<td>A110</td>
<td>Input</td>
<td>Analog input S.E.: Ch10; DI: Ch 2 Low</td>
</tr>
<tr>
<td>7</td>
<td>A13</td>
<td>Input</td>
<td>Analog input S.E.: Ch 3; DI: Ch 3 High</td>
</tr>
<tr>
<td>8</td>
<td>A111</td>
<td>Input</td>
<td>Analog input S.E.: Ch11; DI: Ch 3 Low</td>
</tr>
<tr>
<td>9</td>
<td>A14</td>
<td>Input</td>
<td>Analog input S.E.: Ch 4; DI: Ch 4 High</td>
</tr>
<tr>
<td>10</td>
<td>A112</td>
<td>Input</td>
<td>Analog input S.E.: Ch12; DI: Ch 4 Low</td>
</tr>
<tr>
<td>11</td>
<td>A15</td>
<td>Input</td>
<td>Analog input S.E.: Ch 5; DI: Ch 5 High</td>
</tr>
<tr>
<td>12</td>
<td>A113</td>
<td>Input</td>
<td>Analog input S.E.: Ch13; DI: Ch 5 Low</td>
</tr>
<tr>
<td>13</td>
<td>A16</td>
<td>Input</td>
<td>Analog input S.E.: Ch 6; DI: Ch 6 High</td>
</tr>
<tr>
<td>14</td>
<td>A114</td>
<td>Input</td>
<td>Analog input S.E.: Ch14; DI: Ch 6 Low</td>
</tr>
<tr>
<td>15</td>
<td>A17</td>
<td>Input</td>
<td>Analog input S.E.: Ch 7; DI: Ch 7 High</td>
</tr>
<tr>
<td>16</td>
<td>A115</td>
<td>Input</td>
<td>Analog input S.E.: Ch15; DI: Ch 7 Low</td>
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<td>17</td>
<td>AGND</td>
<td>Ground</td>
<td>Analog ground</td>
</tr>
<tr>
<td>18</td>
<td>-5VR</td>
<td>Output</td>
<td>-5V reference for REF0 and REF1</td>
</tr>
<tr>
<td>19</td>
<td>+15V</td>
<td>Source</td>
<td>Analog power</td>
</tr>
<tr>
<td>20</td>
<td>-15V</td>
<td>Source</td>
<td>Analog power</td>
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<tr>
<td>21</td>
<td>REF0</td>
<td>Input</td>
<td>D/A channel 0 reference voltage</td>
</tr>
<tr>
<td>22</td>
<td>REF1</td>
<td>Input</td>
<td>D/A channel 1 reference voltage</td>
</tr>
<tr>
<td>23</td>
<td>DA0</td>
<td>Output</td>
<td>D/A channel 0 voltage output</td>
</tr>
<tr>
<td>24</td>
<td>DA1</td>
<td>Output</td>
<td>D/A channel 0 voltage output</td>
</tr>
<tr>
<td>25-26</td>
<td>AGND</td>
<td>Ground</td>
<td>Analog ground</td>
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<tr>
<td>27</td>
<td>DO0</td>
<td>Output</td>
<td>Channel 0 digital output</td>
</tr>
<tr>
<td>28</td>
<td>DI0</td>
<td>Input</td>
<td>Channel 0 digital input</td>
</tr>
<tr>
<td>29</td>
<td>DO1</td>
<td>Output</td>
<td>Channel 1 digital output</td>
</tr>
<tr>
<td>30</td>
<td>DI1</td>
<td>Input</td>
<td>Channel 1 digital input</td>
</tr>
<tr>
<td>31</td>
<td>DO2</td>
<td>Output</td>
<td>Channel 2 digital output</td>
</tr>
<tr>
<td>32</td>
<td>DI2</td>
<td>Input</td>
<td>Channel 2 digital input</td>
</tr>
<tr>
<td>33</td>
<td>DO3</td>
<td>Output</td>
<td>Channel 3 digital output</td>
</tr>
<tr>
<td>34</td>
<td>DI3</td>
<td>Input</td>
<td>Channel 3 digital input</td>
</tr>
<tr>
<td>35-36</td>
<td>DGN7</td>
<td>Ground</td>
<td>Digital ground</td>
</tr>
<tr>
<td>37</td>
<td>DO4</td>
<td>Output</td>
<td>Channel 4 digital output</td>
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<tr>
<td>38</td>
<td>DI4</td>
<td>Input</td>
<td>Channel 4 digital input</td>
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<td>39</td>
<td>DO5</td>
<td>Output</td>
<td>Channel 5 digital output</td>
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<tr>
<td>40</td>
<td>DI5</td>
<td>Input</td>
<td>Channel 5 digital input</td>
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<tr>
<td>41</td>
<td>DO6</td>
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<td>Channel 6 digital output</td>
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<tr>
<td>42</td>
<td>DI6</td>
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<tr>
<td>43</td>
<td>DO7</td>
<td>Output</td>
<td>Channel 7 digital output</td>
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<tr>
<td>44</td>
<td>DI7</td>
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<td>Channel 7 digital input</td>
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<tr>
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<td>Source</td>
<td>PC +5V</td>
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<td>46</td>
<td>+12V</td>
<td>Source</td>
<td>PC +12V</td>
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<td>47</td>
<td>ETRG</td>
<td>Input</td>
<td>External trigger</td>
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<td>48</td>
<td>R/C</td>
<td>Output</td>
<td>Start conversion</td>
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<tr>
<td>49-50</td>
<td>DGN7</td>
<td>Ground</td>
<td>Digital ground</td>
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Pin assignment of CN2 connector

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<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>N/C</th>
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<tbody>
<tr>
<td>ECLK</td>
<td>3</td>
<td>4</td>
<td>N/C</td>
</tr>
<tr>
<td>OUT0</td>
<td>5</td>
<td>6</td>
<td>N/C</td>
</tr>
<tr>
<td>GO</td>
<td>7</td>
<td>8</td>
<td>N/C</td>
</tr>
<tr>
<td>OUT2</td>
<td>9</td>
<td>10</td>
<td>N/C</td>
</tr>
<tr>
<td>DGND</td>
<td>11</td>
<td>12</td>
<td>N/C</td>
</tr>
<tr>
<td>N/C</td>
<td>13</td>
<td>14</td>
<td>N/C</td>
</tr>
<tr>
<td>N/C</td>
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<td>16</td>
<td>N/C</td>
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<td>DGND</td>
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<td>18</td>
<td>N/C</td>
</tr>
<tr>
<td>+5V</td>
<td>19</td>
<td>20</td>
<td>N/C</td>
</tr>
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</table>

| ECLK | External clock for 8254 counter 0 |
| OUT0 | 8254 counter 0 output |
| GO | 8254 counter 0 gate |
| OUT 2 | 8254 counter 2 output |
6. ANNEX 2

Electrical diagrams of the multiplexer and resistors boards

MUXSOLD.HGL - multiplexer board layout

REZCOMP.HGL - resistor board layout
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MUXSILK.HGL - multiplexer board layout; silk screen component side

REZSOLD.HGL - resistor board layout
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REZ.HGL - resistor board; schematic design

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MUXCOMP.HGL - multiplexer board layout

REZSILK.HGL - resistor board layout

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TOP.HGL - multiplexer board

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7. ANNEX 3

Borland C v.4.5, code source for interrupt variables and handler

#include <interrupt.h>

void interrupt handler (__CPPARGS)
{
    disable();   //disable interrupts
    if(nGlobalContor == nBufferLenght)
    {
        outp(nIOPort+9,0); //stop acquisition
        asm mov dx,0x20     //specific EOI
        asm mov al,nIRQ
        asm or al,0x60
        asm out dx,al
    }
    else
    {
        switch (nAnalogIn)
        {
            case 7:
                nDigitalOut = 0;
                nAnalogIn   = 0;
                outp(nIOPort+2,0);
                outp(nIOPort+3,0);
                break;
            case 6:
                if(nDigitalOut == 1)
                {
                    nAnalogIn++;
                    asm mov al,nAnalogIn
                    asm mov ah,al
                    asm shl ah,4
                    asm or al,ah
                    asm mov dx,nIOPort
                    asm add dx,2
                }
        }
    }
}
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```c
asm out dx,al
}
default:
  nDigitalOut++;
  if(nDigitalOut == 8)
  {
    nDigitalOut = 0;
    nAnalogIn++;
    asm mov al,nAnalogIn
    asm mov ah,al
    asm shl ah,4
    asm or al,ah
    asm mov dx,nIOPort
    asm add dx,2
    asm out dx,al
  }
  outp(nIOPort+3,nDigitalOut);
}
asm mov dx,nIOPort
asm inc dx
asm in al,dx
asm mov ah,al
asm dec dx
asm in al,dx
asm mov nTemp,ax
*(lpwGlobalMemory+nGlobalContor) = nTemp;
nGlobalContor++;
asm mov dx,0x20                 //specific EOI
asm mov al,nIRQ
asm or al,0x60
asm out dx,al
outp(nIOPort+8,0);             //clear interrupt
}
enable();                      //enable interrupts
```
8. GLOSSARY

**Data Flow** - A model for programming in which instructions or operators execute only when all inputs are available. In this model, data flows into and out of operators.

**dB** - Decibel - The unit for expressing a logarithmic measure of the ratio of two signal levels: $dB = 20 \log_{10} \frac{V_1}{V_2}$, for signals in volts.

**DDE** - Dynamic Data Exchange - A standard software protocol in Microsoft Windows for interprocess communication. DDE is used when applications such as LabVIEW send messages to request and share data with other applications such as Microsoft Excel.

**Differential Input** - An analog input consisting of two terminals, both of which are isolated from computer ground, whose difference is measured.

**DIO** - Digital input/output.

**DLL** - Dynamic Link Library - A software module in Microsoft Windows containing executable code and data that can be called or used by Windows applications or other DLLs. Functions and data in a DLL are loaded and linked at run time when they are referenced by a Windows application or other DLLs.

**DMA** - Direct Memory Access - A method by which data can be transferred to/from computer memory from/to a device or memory on the bus while the processor does something else. DMA is the fastest method of transferring data to/from computer memory.

**Drivers** - Software that controls a specific hardware device such as a DAQ board or a GPIB interface board.

**DSP** - Digital signal processing.

**Dual-Access Memory** - Memory that can be sequentially accessed by more than one controller or processor but not simultaneously accessed. Also known as shared memory.

**External Trigger** - A voltage pulse from an external source that triggers an event such as A/D conversion.

**FIFO** - First-In First-out Memory Buffer - The first data stored is the first data sent to the acceptor.

**Flash ADC** - An ADC whose output code is determined in a single step by a bank of comparators and encoding logic.

**Floating-Point** - A format for processing or storing numbers in scientific exponential notation (digits multiplied by a power of 10).

**Gain** - The factor by which a signal is amplified, sometimes expressed in dB.

**GPIB** - General Purpose Interface bus, synonymous with HP-IB. The standard bus used for controlling electronic instruments with a computer. Also called IEEE 488 bus because it is defined by ANSI/IEEE Standards 488-1978, 488.1-1987, and 488.2-1987.

**GUI** - Graphical User Interface - An intuitive, easy-to-use means of communicating information to and from a computer program by means of graphical screen displays. GUIs can resemble the front panels of instruments or other objects associated with a computer program.

**Half-Flash ADC** - An ADC that determines its output code by digitally combining the results of two sequentially performed, lower-resolution flash conversions.

**Handler** - A device driver that is installed as part of the operating system of the computer.
Hardware - The physical components of a computer system, such as the circuit boards, plug-in boards, chassis, enclosures, peripherals, cables, and so on.


Instrumentation Amplifier - A circuit whose output voltage with respect to ground is proportional to the difference between the voltages at its two inputs.

Integrating ADC - An ADC whose output code represents the average value of the input voltage over a given time interval.

Interrupt - A computer signal indicating that the CPU should suspend its current task to service a designated activity.

I/O - Input/output - The transfer of data to/from a computer system involving communications channels, operator interface devices, and/or data acquisition and control interfaces.

k - kilo, the standard metric prefix for 1,000, or 103, used with units of measure such as volts, hertz, and meters.

kbytes/s - A unit for data transfer that means 1,000 or 103 bytes/s.

Multitasking - A property of an operating system in which several processes can be run simultaneously.

Mux - Multiplexer - A switching device with multiple inputs that sequentially connects each of its inputs to its output, typically at high speeds, in order to measure several signals with a single analog input channel.

Noise - An undesirable electrical signal - Noise comes from external sources such as the AC power line, motors, generators, transformers, fluorescent lights, soldering irons, CRT displays, computers, electrical storms, welders, radio transmitters, and internal sources such as semiconductors, resistors, and capacitors.

OLE - object Linking and Embedding - A set of system services that provides a means for applications to interact and interoperate. Based on the underlying Component Object Model, OLE is object-enabling system software. Through OLE Automation, an application can dynamically identify and use the services of other applications, to build powerful solutions using packaged software. OLE also makes it possible to create compound documents consisting of multiple sources of information from different applications.

PCI - Peripheral Component Interconnect - a high-performance expansion bus architecture originally developed by Intel to replace ISA and EISA. It is achieving widespread acceptance as a standard for PCs and work-stations; it offers a theoretical maximum transfer rate of 132 Mbytes/s.

Plug and Play ISA - A specification prepared by Microsoft, Intel, and other PC-related companies that will result in PCs with plug-in boards that can be fully configured in software, without jumpers or switches on the boards.

Port - A communications connection on a computer or a remote controller.

SE - Single-Ended - A term used to describe an analog input that is measured with respect to a common ground.

S/H - Sample-and-Hold - A circuit that acquires and stores an analog voltage on a capacitor for a short period of time.

Transfer Rate - The rate, measured in bytes/s, at which data is moved from source to destination after software initialization and set up.
**Unipolar** - A signal range operations; the maximum rate at which that is always positive (for hardware can operate. example, O to +10V).

**Virtual Instrument** - (1) A combination of hardware and/or software elements, typically used with a PC, that has the functionality of a classic stand-alone instrument; (2) A LabVIEW software module (VI), which consists of a front panel user interface and a block diagram program.
Control of corrosion and scaling in geothermal systems

CYLINDRICAL TANKS INNER CATHODICALLY PROTECTED
WITH EXTERNAL CURRENT SOURCE

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SUMMARY

The present paper deals with the modelling of active corrosion protection of tanks on the basis of solving Laplace’s equation according with formulations related to cylindrical and spherical co-ordinate systems. The solution of the simulated problem consists in the current density and potential distributions inside the tank filled with geothermal water, when a voltage is applied between a central positive submersed electrode and the negative metal wall electrode. Two programs were employed; one written by us the other being the MEGA package of the University of Bath.

The geometrical parameters which seem to be the most important are: L the liquid height in the cylindrical part; R the tank radius; L_e the electrode length; E_z the distance from the superior liquid level to the electrode. Also, in all cases the width of the electrode is considered negligible.

The linear discrete system was solved with the preconditioned GMRES (Saad and Schultz, 1986) method. GMRES is a generalised conjugated gradient algorithm belonging to the Petrov-Galerkin-Krilov class of methods.

1. INTRODUCTION

The anti-corrosion protection of large volume tanks where electrolyte solutions are stored still constitutes an important element influencing the cost of such units. The anti-corrosion can be realized by applying different methods. First, the inner wall surface can be diversely coated: thin film layer protection represented by dyes of diverse compositions, electrochemical thin film depositions of corrosion-resistant metals, plasma–jet ceramic oxide layer depositions, corrosion-resistant metal plating, polymer plating. Corrosion inhibitors can be added to the electrolyte itself. Finally, electrochemical protection can be used: cathodic protection without or with external current source, and anodic protection.

The high Cl^- contents in the chemical composition of geothermal water and its temperature drastically limit the efficiency of protection methods.
The cathodic protection with external current source supposes solving a field problem in an electrically conductive medium, described by Laplace's equation. The solution can be obtained either by analytic methods – in symmetrical configurations – or by numeric methods.

The analytic solution of Laplace's equation in different symmetric configuration is a largely known subject. The numerical solution of this equation can be applied to asymmetric configurations as well, and is now mostly done within the frame of dedicated software packages. E. McCafferty (1976) using an analytical form which include Bessel functions, have evaluating the current distribution in circular corrosion cell. Waber and al. (1954, 1955, 1956), use a bidimensional model with analytical solution. J.S.Newman (1973, 1962) have established the well known analytical form between medium current density and local value of de current density:

$$i = \frac{\Phi \, \text{ch} \, \Phi}{\sigma \, (\text{sh}^2 \, \Phi)} \left[ \text{sh}^2 \, \Phi - \text{sh}^2 \left( \frac{2x - L}{L} \right) \right]^{1/2}$$

The works of Gal-Or and al. 1973, extends the mathematical model to three dimensions treating semi-infinite parallel electrodes.

Numerical solution of Laplace equation of the corrosion problem can be seen in some contributions like the works of: R.S.Munn and al. (1991), which develop a numerical application for the galvanic corrosion using finite element method in order to solve the boundary value problem within an electrolyte medium. The group of the works of John W. Fu and al. (1984), using the finite element method of modelling localised corrosion cells. Other work reported by Albert W. Forrest and al. 1981, study with finite element cathodically protecting of bronze in water.

The methods based by numerically solving could be meet in the big software packages, for modelling electromagnetic field, like: Flux-expert of DT2i French company, for solving the partial derivative equations in 2D and 3D geometry or MEAGA package of the university of Bath. All the similar packages works only on the UNIX operation system, like HP, SUN, DIGITAL, CRAY with a very power hardware resources with RISC processor and 64 M RAM minimum. A high quality staff is another important demand.

An other direction is focused by using adimensional criteria like Wagner in order to establish the geometrically contribution, influence of electrolyte conductivity and polarisation resistance (N. Ibl 1983, 1976):

$$W_a = \sigma \frac{d i}{d \eta} \frac{1}{L}$$

2. MATHEMATICAL MODEL

The tank which is the subject of this work is presented in figure 1. The body of the tank is a cylinder while the bottom and the top have spherical form. The tank is partially filled with an electrolyte solution.
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The variations in composition of the electrolyte are neglected. In these conditions the potential distribution is the solution of the Laplace equation:

$$\Delta \Phi (x, y, z) = 0$$

Due to the electrode's position, the potential can be considered axisymmetric. In this situation the Laplace's equation becomes:

- the cylindrical part of the tank:

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Phi}{\partial r} \right) + \frac{\partial^2 \Phi}{\partial z^2} = 0$$

with the boundary conditions:

- on the electrode surface:

$$\Phi = \Phi_{\text{electrode}}$$

- on the axis of symmetry:

$$r = 0 \quad \frac{\partial \Phi}{\partial r} = 0$$

(1)

- at the liquid surface:

$$z = 0 \quad \frac{\partial \Phi}{\partial z} = 0$$

(2)

- at the tank wall:

$$r = R \quad -\sigma_c \frac{\partial \Phi}{\partial r} = \sigma_c \alpha \left( \Phi - \Phi^* \right)$$

(3)

where:

$$\alpha = \frac{1}{\delta}, \delta \text{ being the thickness of the coating}$$

$$\Phi^* = \text{potential in the metal}$$

$$\sigma_c = \text{the electrical conductivity of the electrolyte}$$

$$\sigma_c = \text{the electrical conductivity of the coating}$$

$$r = \text{cylindrical co-ordinate}$$

$$z = \text{cylindrical co-ordinate}$$

At the tank wall, in the coating layer, it is assumed that the potential breakdown is linear.

There are two possible situations for the metal potential:

(i) $$\Phi^* = \text{constant} = 0.0$$

or

(ii) $$\Phi^* = \text{variable and satisfying, in connection with (3), the relation of the normal current density continuity}$$
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\[
\sigma_e \frac{\partial \Phi}{\partial r} \bigg|_{r=R} = \sigma_m \frac{\partial \Phi^*}{\partial z} \bigg|_{z=0}
\]

where:
\[
\sigma_m = \text{the electrical conductivity of the metal wall}
\]

Elimination of \( \Phi^* \) from eqn. (4) gives:

\[
\frac{\sigma_e}{\alpha \sigma_c} \frac{\partial^2 \Phi}{\partial r \partial z} - \frac{\sigma_e}{\sigma_m} \frac{\partial \Phi}{\partial r} + \frac{\partial \Phi}{\partial z} = 0.0
\]

Because:
\[
\frac{\sigma_e}{\alpha \sigma_c} \ll 1 \text{ eqn. (5) becomes:}
\]

\[
-\frac{\sigma_e}{\sigma_m} \frac{\partial \Phi}{\partial r} + \frac{\partial \Phi}{\partial z} = 0.0
\]

which will be referred to as the oblique derivative boundary condition. Thinking to a thermal analogy, \( \Phi \) can be viewed as the temperature in a cylinder cooled by a peripherally flowing fluid with temperature \( \Phi^* \) assumed to be uniform across the flow. However, in the mathematical model solving, the oblique derivative boundary condition case is not take into account in this work.

In the spherical part of the tank, the Laplace equation can be written as:

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Phi}{\partial \theta} \right) = 0
\]

with the boundary conditions:

- at the sphere center
  \( r = 0 \) \( \Phi = \text{finite} \)

- at the tank wall:
  \( r = R \) \( -\sigma_c \frac{\partial \Phi}{\partial r} = \alpha \sigma_c (\Phi - \Phi^*) \)

or

\[
\frac{\sigma_e}{\sigma_m} \frac{\partial \Phi}{\partial r} + \frac{\partial \Phi}{\partial \theta} = 0.0
\]

- on the symmetry axis:
  \( \theta = \pi/2 \) \( \frac{\partial \Phi}{\partial \theta} = 0 \)

The solutions of the Laplace equations in the two co-ordinate frames are subjected to obvious continuity conditions of the potential and its normal derivative at the common boundary of the cylindrical and spherical domains:
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\[ \Phi_{\text{cylindrical}} \bigg|_{z=L} = \Phi_{\text{spherical}} \bigg|_{\theta=0}, \]

and

\[ \frac{\partial \Phi_{\text{cylindrical}}}{\partial z} \bigg|_{z=L} \frac{1}{r} \frac{\partial \Phi_{\text{spherical}}}{\partial \theta} \bigg|_{\theta=0}. \]

Defining the dimensionless parameters:

\[ a = \frac{r}{R}; \quad Z = \frac{\delta}{L} \quad \overline{\Phi} = \frac{\Phi}{\Phi_{\text{electrode}}} \]

the dimensionless form of the previous equations (only the case of constant metal potential is presented in detail) is:

- for the cylindrical part:

\[ k \frac{1}{a} \frac{\partial}{\partial a} \left( a \frac{\partial \overline{\Phi}}{\partial a} \right) + \frac{\partial^2 \overline{\Phi}}{\partial Z^2} = 0 \]

with the boundary conditions:

\[ a = 0 \quad \frac{\partial \overline{\Phi}}{\partial a} = 0 \]

\[ Z = 0 \quad \frac{\partial \overline{\Phi}}{\partial Z} = 0 \]

\[ a = 1 \quad -\frac{\partial \overline{\Phi}}{\partial a} = A \overline{\Phi} \]

where:

\[ k = \frac{L^2}{R^2} \quad \text{and} \quad A = \frac{\sigma_e}{\sigma_e} \]

- for spherical part:

\[ \frac{1}{\alpha^2} \frac{\partial}{\partial a} \left( a^2 \frac{\partial \overline{\Phi}}{\partial a} \right) + \frac{1}{a^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \overline{\Phi}}{\partial \theta} \right) = 0 \]

with the boundary conditions:

\[ a = 0 \quad \Phi = \text{finite} \]

\[ a = 1 \quad -\frac{\partial \overline{\Phi}}{\partial a} = A \overline{\Phi} \]

\[ \theta = \frac{\pi}{2} \quad \frac{\partial \overline{\Phi}}{\partial \theta} = 0 \]
3. METHOD OF SOLUTION

The mathematical model presented in the previous section was solved numerically. Two programs were employed; one written by us the other being the MEGA package of the University of Bath.

The program conceived by us used the finite difference method for discretization. The centred second order accurate finite difference scheme was employed in the both domains of the tank. For boundary grid point where only derivative conditions are available, the appropriate differential equation is suitably modified by incorporation of the boundary condition. At the cylinder and sphere center, the indetermination was solved using the L'Hopital rule. The procedure described in this paragraph being well known it is not necessary to insist supplementary on it.

The linear discrete system was solved with the preconditioned GMRES (Saad and Schultz 1986) method. GMRES is a generalised conjugated gradient algorithm belonging to the Petrov-Galerkin-Krilov class of methods. The convergence of the method requires the system matrix to be non singular. For the purpose of algorithm illustration, consider the general linear system:

\[ A \cdot x = b \]

and its left preconditioning by the matrix C.

Defined for practical calculation, the restarted m-version of the GMRES reads as:

1. Initialization: choose \( x_0 \) and a dimension of the Krylov subspaces;

2. Arnoldi process:
   - Compute \( r_0 = C^{-1} (b - A \cdot x_0) \), \( \beta = \| r_0 \| \) and \( v_1 = r_0 / \beta \);
   - for \( (j=1; \ j \leq m; \ j++) \{ \)
     - \( h_{ij} = < C^{-1} A \cdot v_j, A \cdot v_i > \), \( i = 1, \ldots, j \)
     - \( v_{j+1} = C^{-1} A \cdot v_j - \sum_{i=1}^{j} h_{ij} \cdot v_i \)
     - \( h_{j+1} = \| v_{j+1} \| \)
     - \( v_{j+1} = v_{j+1} / h_{j+1} \)
   - \}

3. Form the approximate solution:
   - Find the vector \( y_m \) which minimizes the function \( J(y) = \| \beta \cdot e_1 - H_m \cdot y \| \), where \( e_1 = [1,0,\ldots,0] \), among all vectors of \( \mathbb{R}^m \). Compute \( x_m = x_0 + v_m \cdot y_m \).

4. Restart:
   - if satisfied stop criterion out, else set \( x_0 \leftarrow x_m \) and goto 2.

The preconditioner employed is the incomplete LU factorisation of the coefficient matrix. The GMRES(m) algorithm is said to be convergent when the discrete Euclidean norm of the residuals is less than 1E-05, \( \| r_0 \| \). The results were obtained on a mesh having 65x65 points in each geometrical region of the tank.
The second package MEGA has been developed in the field of modelling electromagnetic device. The MEGA package is comprised of two programs: MEGAVIEW, which is the pre and post processor with an interactive environment to define, post process and edit electromagnetic models. MEGASOLVE is the solver which use the finite element method. It solve the problem in batch mode. MEGA can solve a wide variety of 2D and 3D problems. Some of the capabilities are: thermal diffusion equation coupled to electromagnetic solution.

4. RESULTS

The problem analysed in detail in this section refers to the influence of the electrode position, horizontal or vertical, on the potential distribution and the wall current. The geometrical parameters which seem to be the most important are:
- L the liquid height in the cylindrical part;
- R the tank radius;
- LE the electrode length;
- EZ the distance from the superior liquid level to the electrode.

Also, in all cases the width of the electrode is considered negligible. The values of the geometrical parameters for the case selected to be presented in detail here are depicted in table 1.

The influence of the electrode position on the potential distribution and the wall current is depicted in figures 2 to 5. Figures 2 and 4 show the potential distribution and the wall current for the case of the horizontal position. The situation when the electrode is vertical is shown in figures 3 and 5. The values considered for the electrical conductivity are: \( \sigma_L = 71 \text{ S/m} \) and \( \sigma_Z = 1.0E-04 \text{ S/m} \). The electrode potential value considered is 3 V. A good agreement was observed between the results provided by the two programs tested.

<table>
<thead>
<tr>
<th>L [m]</th>
<th>R [m]</th>
<th>LE [m]</th>
<th>EZ [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 1 - The values of the geometrical parameters

The results presented in figures 2 to 5 lead to the following statements:
- in both situations the potential breakdown is significant in the cylindrical region;
- the potential variation in the spherical is less significant;
- the current variation is also significant, in both cases, in the cylindrical domain;
- the horizontal position of the electrode provides higher values for the wall potential (the maximum value is approximately two times greater than the maximum value obtained in the case of vertical position);
- the wall current is higher in the case of horizontal position;
- the maximum wall current value in the case of horizontal position is approximately two times higher than the maximum wall current value of the vertical position.
In the protection of corrosion with external current source, the interface potential must be upper of the corrosion mix potential, and under the potential value of hydrogen evolution. For this reasons an uniformity of the potential on the inner surface is most important like the local maximum values.

In is not the aim of this study to analyse exhaustively the tank corrosion problem. The main task of this study is the development of the mathematical model and the programs necessary to solve the problem. Another important aspect is, as example, the influence of the distance between the liquid superior level and the electrode on the potential distribution and wall current values. However, moving the electrode in the liquid, the potential distribution and wall current changes are previsible.

5. CONCLUSIONS

A mathematical model for the analysis of active corrosion protection with external source of inner tanks was developed. The mathematical model was solved numerically. Two programs were employed; one written by us the other being the MEGA package of the University of Bath. The linear discrete system was solved, in our program, with the preconditioned GMRES (Saad and Schultz, 1986) method.

The results consist in the current density and potential distributions inside the tank filled with geothermal water, when a voltage is applied between a central positive submersed electrode and the negative metal wall electrode. The main aspect analysed was the influence of the electrode position, horizontal or vertical, on the potential distribution and the wall current values.

By the solving of Laplace’s equation, with the MEGA and CAEL software package, the vertical position of the anode seems to give much uniformity of the potential distribution, compared with the horizontally position.

REMARKS: This work is devoted to the CAEL objective no.1 and deliverables no. 1.

6. REFERENCES


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J.S. NEWMAN (1973) - Electrochemical Systems, Prentice Hall.


R.S. MUNN, O.F. DEVEREUX (1991) - Corrosion, 47, 8, 618.


ALBERT W. FORREST, R.T. BICICHI (1981) - Corrosion, 37, 6, 349.

FLUX EXPERT is trade mark of DT2i French - Company.

MEGA is a trade mark of University of Bath, UK.

7. CAPTIONS OF FIGURES

Figure 1 - The tank draft with the main geometrical characteristics.
Figure 2a - Potential distribution inside of the electrolyte in the cylindrical part. Electrode horizontal.

Figure 2b - Potential contour in the cylindrical part. Electrode horizontal.
Figure 2c - Potential distribution inside of the electrolyte in the spherical part. Electrode horizontal.

Figure 2d - Potential contour in the spherical part. Electrode horizontal.
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Figure 3a - Potential distribution inside of the electrolyte in the cylindrical part. Electrode vertical.

Figure 3b - Potential contour in the cylindrical part. Electrode vertical.
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Figure 3c - Potential distribution inside of the electrolyte in the spherical part. Electrode vertically.

Figure 3d - Potential contour in the spherical part. Electrode vertically.
Figure 4a - Current density variation with the length of the tank. Cylindrical part, horizontal electrode.

Figure 4b - Current density variation in the spherical part, horizontal electrode.
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Figure 5a - Current density variation with the length of the tank. Cylindrical part, vertical electrode.

Figure 5b - Current density variation in the spherical part, vertical electrode.
CATHODIC PROTECTION OF STEEL PIPES
WITHOUT EXTERNAL SOURCE

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SUMMARY

The paper presents the results of a laboratory study concerning the cathodic protection of metals (alloys) in geothermal water in the absence of external current sources. Metals/alloys like OL 37, OLCN 18-10, OLCN 18-20, OLC 17 and W 40, under zinc cathodic protection have been tested in geothermal water of different compositions, originating from Bihor area. The procedure used is based on Evans' diagrams, which allowed the computation of the degree of anodic, cathodic and ohmic control as well as the specific parameters such as the current and mixed corrosion potential. The relative value of the cathodic control imposes the stability order of steel varieties with respect to corrosion in geothermal water. The best behaviour among the steel varieties under study was exhibited by W 40 steel. The inner plating of low grade steel (OL 37) is seen as justified.

1. INTRODUCTION

The cathodic protection of steel structures using dummy anodes with no external current source is a common corrosion protection procedure used in ship building. The sea water is a medium of high corrosion action due to its high contents in salt, i.e., in Cl⁻ ions. The greatest part of the research regarding corrosion processes is focused in this area, which is explained by the impressive losses of about 2.6 billion US dollars annually in U.S.A. only (O. Chaix and al., 1995). The experimental studies are presently accompanied by theoretical studies and the modelling of corrosion processes based on the numerical solution of field problems using dedicated software packages.

Galvanic corrosion was investigated experimentally and by modelling. By using the experimental procedure O.Chaix and al. (1995), show that a technology involving localised impressed-current cathodic protection CP of the splash-zone region in association with conductive rubber anodes could be used in sea water. The initials study of Florida Department of Transportation, was focused upon a possible embattlement of tendons by CP (R.N. PARKINS and al., 1982; W.H. HARTT and al., 1993) and loss of bond to the concrete and then on durability and design of alternative anodes and CP systems (R.J.KESSELER and al., 1989). Steel inner covered with Zn was tested in sea water, by R.J.KESSELER and al. in 1990.
R.S. Munn and al. (1991) present in their work, a numerical modelling of galvanic corrosion system. The problem was solved in terms of the partial differential equation which describe the electrical fields in a conductive medium and the boundary conditions which describe the non-linear electrode kinetics of corroding metals.

The present paper is based on an experimental study of galvanic corrosion using the method of Evans' lines. The high HS- and polysulphur contents of geothermal water in Bihor (NW Romania) area is a remarkable feature of the active medium involved in corrosion processes. The initiation of the study was prompted by the fact that during the exploitation stage high temperature gradients and a scaling phenomenon induced by the chemical reaction against the steel pipe wall have been identified (I. Ignatidis and al., 1993). The behaviour of trivial steel such as OL 37 and allied steel: OLC 17, OLCN 18–20, W 40 under corrosion has been tested in geothermal water of diverse compositions originating from Bihor area (4195 Bors-source, 4797 Dublet-source, and 4619 Sacuieni wells). A zinc dummy anode has been used.

2. EXPERIMENTAL PROCEDURE

The procedure based on Evans' diagram was used with a view to detect and characterize galvanic corrosion phenomena due to the effect of short-circuited electrochemical cell. This effect is present at the interfaces in a metal/electrolyte/metal system. The galvanic corrosion has been simulated by short-circuiting the operating electrodes to the zinc anode via a controlled precision resistance. A new multi-electrode system was tested especially with this purpose (V. Cotarta and B. Petrescu, 1996, this issue). The matrix electrode consisted in 7 elements, of which 5 were operating electrodes made of steel specimens under study, one was the Zn anode, and one was the reference (SCE) electrode. The configuration of the matrix electrode is presented in Fig. 2, and a range of 10×100, 10×1000, and 5×10000 Ω resistance has been scanned using the multiplexing system previously presented (B. Petrescu and V. Cotarta, in this report). The electrochemical experiment was assisted by a dedicated LEAC acquisition software.

The measuring method consists in three steps:
- surface conditioning;
- experimental determinations;
- processing of experimental data.

Surface conditioning
The 1 cm² surface of each probe (steel and zinc) have been conditioned as follows:
- abrasive paper and aluminium oxide powder polishing;
- cleaning in trichloretylene;
- washing;
- drying.
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The open circuit potentials (at $I = 0$) are measured for both metals with respect to the calomel electrode. The closed circuit potentials are then measured for both metals along with the current intensity for each value of the resistance. The value of resistance was increased at a rate of 100 $\Omega$/min up to the steady state. The minimum current intensity is reached for the maximum value of the resistance.

The variation of anodic and cathodic potentials versus current density is drawn based on measured data, whence the maximum corrosion current $i_{\text{cor}}$ and the corrosion potential $\varepsilon_{\text{cor}}$ are determined. The procedure for the computation of the degree of anodic, cathodic and galvanic control is explained in Fig. 1.

The corrosion diagram presented in the figure above is used to compute the degree of anodic, cathodic and galvanic control, along with the relations:

$$c_a = \frac{\eta_a}{\eta_a + |\eta_c| + \Delta \varepsilon_R} \cdot 100 = \frac{\eta_a}{\varepsilon_{\text{cor},c} - \varepsilon_{\text{cor},a}} \cdot 100$$

$$c_c = \frac{|\eta_c|}{\eta_a + |\eta_c| + \Delta \varepsilon_R} \cdot 100 = \frac{|\eta_c|}{\varepsilon_{\text{cor},c} - \varepsilon_{\text{cor},a}} \cdot 100$$

$$c_R = \frac{\Delta \varepsilon_R}{\eta_a + |\eta_c| + \Delta \varepsilon_R} \cdot 100 = \frac{\Delta \varepsilon_R}{\varepsilon_{\text{cor},c} - \varepsilon_{\text{cor},a}} \cdot 100$$

The composition of electrodes used during experiments is given in Table 1.
Table 1 - Steel class and their main elements used in corrosion tests

<table>
<thead>
<tr>
<th>Steel class</th>
<th>% Cr</th>
<th>% Ni</th>
<th>% Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>W 40</td>
<td>13.3</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>CrNi 18-10</td>
<td>18</td>
<td>10</td>
<td>2.5</td>
</tr>
<tr>
<td>CrNi 18-20</td>
<td>18</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>OL 37</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr 17</td>
<td>17</td>
<td>0.44</td>
<td>1.8</td>
</tr>
</tbody>
</table>

3. RESULTS

The ORIGIN v.3.5 MICROCAL software package was used to process the experimental data. The Evans' line was drawn for each set of data based on a least mean square linear regression. The extrapolation of the curve resulted in the determination of the corrosion potential and maximum current.

The experimental results are summarised as follows: in the figures 3 (a...e) the behaviour of the steels in DUBLET geothermal water source; in the figures 4 (a...e) the behaviour of the same steel's composition in BORS water source. The effects of anodic, cathodic, and ohmic control for three steel compositions in DUBLET and BORS geothermal water are presented on a percentage basis in Figs. 5, 6 and 7 and table 2.

Table 2 - The degree of anodic, cathodic and ohmic control of the galvanic metals coupling.

<table>
<thead>
<tr>
<th>Coupling Metals in Galvanic corrosion</th>
<th>Romanian Water Source</th>
<th>Degree of the Anodic Control Ca [%]</th>
<th>Degree of the Cathodic Control Cc [%]</th>
<th>Degree of the Ohmic Control CR [%]</th>
<th>i cor μA/cm²</th>
<th>Ecorr V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn - W40</td>
<td>Dublet</td>
<td>10.97</td>
<td>85.6</td>
<td>3.43</td>
<td>27.7</td>
<td>-0.92</td>
</tr>
<tr>
<td>Zn - OLCN 18-20</td>
<td>Dublet</td>
<td>5.01</td>
<td>85.46</td>
<td>9.53</td>
<td>27.7</td>
<td>-0.956</td>
</tr>
<tr>
<td>Zn - OLCN 18-10</td>
<td>Dublet</td>
<td>19.57</td>
<td>49.6</td>
<td>19.53</td>
<td>79.46</td>
<td>-0.862</td>
</tr>
<tr>
<td>Zn - OL 37</td>
<td>Dublet</td>
<td>22.73</td>
<td>34.57</td>
<td>42.7</td>
<td>87.95</td>
<td>-0.856</td>
</tr>
<tr>
<td>Zn - OLC 17</td>
<td>Dublet</td>
<td>16.67</td>
<td>78.28</td>
<td>5.05</td>
<td>52.26</td>
<td>-0.889</td>
</tr>
<tr>
<td>Zn - W40</td>
<td>Bors</td>
<td>6.25</td>
<td>77.98</td>
<td>15.77</td>
<td>50.05</td>
<td>-0.996</td>
</tr>
<tr>
<td>Zn - OLCN 18-20</td>
<td>Bors</td>
<td>11.05</td>
<td>70.99</td>
<td>17.96</td>
<td>54.45</td>
<td>-0.55</td>
</tr>
<tr>
<td>Zn - OLCN 18-10</td>
<td>Bors</td>
<td>6.83</td>
<td>76.33</td>
<td>17.96</td>
<td>56</td>
<td>-0.962</td>
</tr>
<tr>
<td>Zn - OL 37</td>
<td>Bors</td>
<td>7.37</td>
<td>32.05</td>
<td>60.58</td>
<td>147.18</td>
<td>-0.971</td>
</tr>
<tr>
<td>Zn - OLC 17</td>
<td>Bors</td>
<td>3.77</td>
<td>39.78</td>
<td>56.45</td>
<td>207.16</td>
<td>-0.971</td>
</tr>
</tbody>
</table>

By using like stability criteria the cathodic control (reduction reaction could be blocking) in the table 3, are presented this order.
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Table 3 - Stability order of steel varieties under study according to the relative value of cathodic control.

<table>
<thead>
<tr>
<th>Stability order of steel</th>
<th>Geothermal water source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DUBLET</td>
</tr>
<tr>
<td>1.</td>
<td>INOX</td>
</tr>
<tr>
<td>2.</td>
<td>CrNi-18-10</td>
</tr>
<tr>
<td>3.</td>
<td>Cr 17</td>
</tr>
<tr>
<td>4.</td>
<td>CrNi 18-20</td>
</tr>
<tr>
<td>5.</td>
<td>OL 37</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The results concerning the ohmic control lead to the conclusion that in the case of trivial steel such as OL 37 the greatest values are attained. The explanation is that a high resistance film is grown at the steel/geothermal water interface. The black coloured film was detected by many partners in the present project. Local electrochemical microcells of anodic type are promoting the local passivation of the neighbouring surface and the presence of pitting corrosion phenomenon accompanied by cracks can be explained more easily.

The values of the anodic control are of approximately the same order for most of the steel compositions taken into consideration. The experiments show that the relative small anodic overvoltage results in the corrosion being controlled by the cathodic reaction as the engine of the process, for all steel types under study. The use of cathodic inhibitors instead of anodic or mixed inhibitors is to be considered. The explanation is that all steel has a cathodic behaviour with respect to zinc, in view of their more positive electrode potential.

The relative value of the cathodic control imposes the stability order of steel varieties with respect to corrosion in geothermal water. The best behaviour among the steel varieties under study was exhibited by W 40 steel. The inner plating of low grade steel (OL 37) is seen as justified. As well, it seems strange that crom and nickel allied steels do not exhibit important differences in corrosion behaviour as compared to trivial steel, so that their use seems not justified.

5. REFERENCES

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6. Caption of Figures

Figure 2 - Electrode matrix for galvanic corrosion

Figure 3a - Evans's lines for steel W 40 in DUBLET water source.
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Figure 3b - Evans's lines for steel Cr-Ni 18-20, in DUBLET water source

Figure 3c - Evans's lines for steel Cr-Ni 18-10, in DUBLET water source
Figure 3d - Evans's lines for steel OL 37, in DUBLET water source

Figure 3e - Evans's lines for steel Cr 17, in DUBLET water source
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Figure 4a - Evans's lines for steel INOX, in BORS water source

Figure 4b - Evans's lines for steel Cr-Ni 18-20, in BORS water source
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Figure 4c - Evans's lines for steel Cr-Ni 18-10, in BORS water source

Figure 4d - Evans's lines for steel OL 37, in BORS water source
Figure 4e - Evans's lines for steel Cr 17, in BORS water source

Figure 5 - Ohmic control degree of steels protected with Zn.
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Figure 6 - Anodic control degree of steels protected with Zn.

Figure 7 - Cathodic control degree of steels protected with Zn.
APPENDIX

Chemical composition of BORS water source

Source BORS 4159. Temperature = 92°C

<table>
<thead>
<tr>
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<th>U.M.</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>pH</td>
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</tr>
<tr>
<td>mineral</td>
<td>mg/l</td>
<td>14103.50</td>
</tr>
<tr>
<td>Na+</td>
<td>mg/l</td>
<td>4910.010</td>
</tr>
<tr>
<td>Ca++</td>
<td>mg/l</td>
<td>180.36</td>
</tr>
<tr>
<td>Mg+++</td>
<td>mg/l</td>
<td>97.28</td>
</tr>
<tr>
<td>Cl-</td>
<td>mg/l</td>
<td>7100.00</td>
</tr>
<tr>
<td>SO4-2</td>
<td>mg/l</td>
<td>125.9</td>
</tr>
<tr>
<td>HCO3-</td>
<td>mg/l</td>
<td>1686.65</td>
</tr>
<tr>
<td>H2S</td>
<td>mg/l</td>
<td>4.19</td>
</tr>
<tr>
<td>CO2</td>
<td>mg/l</td>
<td>72.69</td>
</tr>
<tr>
<td>O2</td>
<td>mg/l</td>
<td>3.34</td>
</tr>
<tr>
<td>NaCl</td>
<td>mg/l</td>
<td>1170.86</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm3</td>
<td>1.010</td>
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</table>

Source DUBLET 4797. Temperature: 70°C.

<table>
<thead>
<tr>
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<th>U.M.</th>
<th></th>
</tr>
</thead>
<tbody>
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<td>pH</td>
<td>unity pH</td>
<td>7.05</td>
</tr>
<tr>
<td>mineral</td>
<td>mg/l</td>
<td>1430.34</td>
</tr>
<tr>
<td>Na+</td>
<td>mg/l</td>
<td>34.14</td>
</tr>
<tr>
<td>Ca++</td>
<td>mg/l</td>
<td>292.58</td>
</tr>
<tr>
<td>Mg+++</td>
<td>mg/l</td>
<td>60.80</td>
</tr>
<tr>
<td>Cl-</td>
<td>mg/l</td>
<td>14.20</td>
</tr>
<tr>
<td>SO4-2</td>
<td>mg/l</td>
<td>876.54</td>
</tr>
<tr>
<td>HCO3-</td>
<td>mg/l</td>
<td>149.45</td>
</tr>
<tr>
<td>H2S</td>
<td>mg/l</td>
<td>1.05</td>
</tr>
<tr>
<td>CO2</td>
<td>mg/l</td>
<td>2.24</td>
</tr>
<tr>
<td>O2</td>
<td>mg/l</td>
<td>4.45</td>
</tr>
<tr>
<td>NaCl</td>
<td>mg/l</td>
<td>23.41</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm3</td>
<td>1.08</td>
</tr>
</tbody>
</table>
EXPERIMENTAL STUDY OF FLOW CHARACTERISTICS IN STRATIFIED/ATOMIZATION GAS/LIQUID FLOW

N.A. VLACHOS, S.V. PARAS and A.J. KARABELAS

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SUMMARY

New experiments, using an electrochemical technique, were conducted for measuring instantaneous axial liquid-to-wall shear stress, at different positions around the pipe circumference (every 22.5°). Measurements of liquid film thickness, pressure drop as well as visual observations were also made. In order to obtain this information a new horizontal flow loop (24 mm i.d.) together with specially designed test sections were constructed to accommodate parallel wire conductance probes, hot film probes and special electrodes suitable for the electrochemical technique.

Mean and RMS values and other useful statistical information were obtained from the analysis of the shear stress and film thickness records. Visual studies of the gas-liquid interface confirmed that its profile is concave rather than flat. Interpretation of the shear stress measurements, in the stratified-atomization regime, led to the conclusion that the mean shear stress tends to decrease in the lateral direction i.e. away from the pipe bottom where the liquid film gradually becomes thinner. Only for relatively low superficial gas velocities (e.g. \( U_g < 20 \text{ m/s} \)), the mean shear stress is almost constant up to \( \theta = 45^\circ \), where there is sufficient liquid in the film. Also by means of momentum balances and utilizing the above new data, the gas-liquid interfacial friction factor was determined with improved accuracy. Finally an equivalent gas-liquid interface roughness was expressed in terms of wave characteristics, i.e. wave intermittency and amplitude.

The analysis presented in this work is complemented by similar information obtained by Paras et al. (1994), from experiments conducted in a horizontal 50.8 mm i.d. flow loop, in the same flow regime examined here.

1. INTRODUCTION

Stratified/atomization flow regime is frequently encountered in various industrial processes (e.g. steam and water flow, natural gas and oil flow in pipelines etc.), including geothermal applications. In order to handle practical problems occurring in two-phase flows in pipes, such as friction losses, corrosion and scaling, experimental studies aim to gain better understanding of the characteristics (i.e. the wavy gas-liquid interface and its shape, the onset of droplet entrainment in the gas phase) and of the transport phenomena occurring in this particular flow regime. For modeling purposes it is necessary to be able to predict the interfacial and shear
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stresses by which momentum is transferred to the wall and from one phase to the other. This is required for developing reliable hold-up and pressure loss correlations.

The main objective of this work is to measure instantaneous axial liquid-to-wall shear stress, at different positions around the pipe circumference and to draw conclusions regarding flow characteristics. For this purpose an electrochemical (or electro-diffusion) technique was employed. This is a well known technique and in the past was used by numerous researchers (e.g. Reiss & Hanratty, 1962; Jolls & Hanratty 1969; Karabelas et al. 1971 etc.). The shear stress measurements are complemented by film thickness and pressure drop data and visual observations as well.

The assumption of a flat interface employed so far by various investigators (e.g. Agrawal et al. 1973; Taitel & Dukler 1976; Andritsos & Hanratty 1987) is not applicable to the stratified/atomization flow regime (Paras et al. 1994). Spedding & Hand (1995) evaluating various stratified flow models in predicting hold-up and pressure drop pointed out that the ARS (Apparent Rough Surface) model proposed by Hart et al. (1989) gave the best overall prediction due to a better estimation regarding the shape of the surface between the two phases. Hart et al. (1989) conducted experiments in a horizontal pipe loop of 51 mm i.d., with a small liquid holdup.

Shear stress measurements of some relevance to this work have been reported by Martin & Whalley (1983) and Govan et al. (1989), for vertical annular air-water flow and by Hagiwara et al. (1989), for horizontal wavy two-phase flow. Similar wall shear stress measurements have been carried out in a rectangular channel by Miya et al. (1971) and McCready & Hanratty (1985). These shear stress data have been obtained with the use of hot film probes.

Flush-mounted hot film probes were also employed by Kowalski (1987) and Paras et al. (1994), for performing wall shear stress measurements in horizontal gas-liquid flow in a 50.8 mm i.d. pipe loop. Of particular interest to this study is the analysis they presented, by means of flow momentum balances, for developing empirical correlations regarding the interfacial friction factor.

As reported previously, in this work, liquid-to-wall shear stress, at different pipe circumferential locations (using 12 electrodes over the pipe perimeter), was measured using the electrodiffusion technique rather than hot film probes. The latter are difficult to install and (due to their size) impossible to be placed very close to each other around the pipe circumference. On the other hand, regarding the electrochemical technique, very small (0.5 mm dia) circular electrodes were embedded every 22.5° at one pipe cross-section, without presenting special difficulties.

The electrochemical method was employed for wall shear stress measurements by Cognet et al. (1984) and Zabaras (1985) in vertical gas-liquid two-phase flows, in pipes of internal diameter 44 mm and 50.8 mm respectively, by Sobol’k et al. (1987) in flows of non-Newtonian liquids in wavy vertical films with free surface and by Rode et al. (1993) in experimental studies of liquid flow in packed beds.

Wall electrochemical microelectrodes distributed circumferentially in a 82 mm i.d. horizontal or slightly inclined pipe, were employed by Rosant (1993) for performing measurements of liquid-to-wall shear stress in stratified gas/liquid flow. Rosant compared the measured averaged
shear stress values to the calculated ones from one-dimensional phase momentum balances and found to overpredict them.

2. EXPERIMENTAL SETUP AND TECHNIQUES

The experiments were carried out very near atmospheric pressure, in a newly constructed horizontal flow loop, where two-phase flow developed in a 24 mm i.d. Plexiglas tube with a 5 m long straight section. A schematic layout of the flow loop is shown in figure 1. This setup is of smaller scale than an existing 50.8 mm i.d. pipe loop in order to better control the conditions of the electrochemical system and to reduce the volume of the photo-sensitive liquid inventory and of the possibly required nitrogen gas.

The liquid flow rate is measured using a set of 3 rotameters together with a low-flow paddle-wheel sensor. The electrochemical solution is collected in a 70 liter storage tank and is recirculated through the loop by means of a centrifugal chemical pump. Air is supplied by two compressors and its flow rate is measured by means of a calibrated rotameter and by a swirlmeter (used for relatively high air velocities). The superficial velocities were varied in the range \( \text{U}_L = 1-5 \) cm/s for the liquid (electrochemical solution) and \( \text{U}_G = 10-25 \) m/s for the air, where stratified atomization flow regime is developed.

Two specially designed test sections are positioned about 4 m downstream of the mixing section of the two phases. The first test section was designed to accommodate parallel wire conductance probes together with hot film probes for measuring instantaneous film thickness and wall shear stress respectively, at the pipe bottom. The conductance probes have two long parallel chromel wires 0.3 mm in diameter and 2 mm apart, covering the entire pipe diameter. The probes are part of an electronic circuit, comprised of a custom-made analyzer and a function generator with a 25 kHz carrier signal. Conductivity measurements of the electrochemical solution were made prior to and after each run, for eliminating the temperature effect on the wire probe conductance. A calibrated (in single phase flow) flush-mounted hot-film probe (DANTEC 55R46) was used for performing limited liquid-to-wall shear stress measurements, for reasons of comparison with the electrochemical technique, mainly employed in this work. Satisfactory agreement (of about 5-10%) was obtained between the two methods. The parallel wire conductance probe technique and the hot film anemometry are described in more detail elsewhere (Paras et al., 1994).

The second (downstream) test section was designed exclusively for shear stress measurements using the limiting current (or electrochemical) technique. In the electrochemical method, the diffusion limiting current which results from the transfer of ions to a small electrode (cathode), is controlled by hydrodynamic conditions. At high enough voltages the working electrodes are polarized, so that the reaction rate is fast and the process is controlled by the liquid-to-solid mass transfer rate. The space-averaged mass transfer coefficient is computed directly from the measured diffusional current and it is related to the local wall shear stress, at the surface of the probe (Reiss & Hauray 1962). Detailed review of this technique is presented by Selman & Tobias (1978).

A fluid mixture of potassium ferricyanide (0.01 M) and potassium ferrocyanide (0.05 M), with sodium hydroxide (1 M) acting as neutral electrolyte, was used. The same composition of the electrolytic solution was used by Tsochatzidis & Karabelas (1994) for measuring local liquid-
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The measured density of the solution was 1053 Kg/m³ whereas the viscosity was 1.24 x 10⁻² Kg/(m·s) at 20 °C. The latter was corrected for changes in temperature. The ferricyanide diffusivity was obtained by an equation proposed by Gordon et al. (1966). The solution was titrated prior to and after the experiments (following a procedure described in Vogel 1962) to determine the exact bulk concentration of the ferricyanide ions. During the experiments the solution in the tank was preserved in a nitrogen atmosphere, for protection from dissolved oxygen, whereas the Plexiglas tube was covered by aluminum foil to reduce light effects on the photo-sensitive electrolytic liquid. The latter has to be discarded after a short period of time (i.e. every 2-3 weeks).

The measuring section is instrumented with 10 isolated circular electrodes embedded around the pipe circumference, every 22.5° (electrodes #1 to #9), from the pipe bottom (at 0°) to the pipe top (at 180°), all located at one pipe cross section. Electrode #10 is positioned at 315° (at the same cross-section) i.e. symmetrically with the electrode #3, which is placed at 45°. At another cross-section of the pipe, located 2 cm upstream from the first, two more electrodes (i.e. #11 and #12) are positioned at 0° and 45° respectively. Each small electrode, made of nickel wire 0.5 mm in diameter, was mounted flush with the tube wall and very carefully polished. A thin nickel sheet (of 0.125 mm thickness), glued onto the tube inner surface, with a much greater surface area (~ 30 cm long), acts as an anode, about 30 cm downstream of the cathodes (small electrodes). The wall electrodes are calibrated in situ, in horizontal single-phase flow, to account for imperfections of their exposed surface. The calibration is carried out for each electrode prior to and after the main experiments.

Pressure drop measurements are carried out using an electronic differential pressure transmitter (series "DPX", Fischer & Porter) connected at two pressure taps. The two taps are 3 m apart and located at the pipe bottom. Special care is taken to purge, from air bubbles, the lines connecting the transmitter. Also visual observations were made with an angle gauge for measuring the angle θ (wetted wall fraction) over which the pipe walls were wetted by the liquid phase.

The diffusion limiting current (of each cathode separately) was converted to voltage, by means of precision resistances, amplified, fed to a 12 bit A/D converter (DT 2801-A, Data Translation Inc.) and stored in a PC 486 compatible, using a computer code developed in our laboratory. The analog output from the analyzer and the hot film anemometer unit were also digitized and recorded by the computer. Data sets of liquid-to-wall shear stress and film thickness were collected for a period of ~ 16.5 s with a sampling frequency of 500 Hz.

3. RESULTS

3.1. Film Thickness

Statistical analysis of film records at the pipe bottom (θ = 0°) has allowed the study of variation of time-averaged thickness and of RMS values. As one might have expected, the mean film thickness increases with liquid velocity whereas it tends to decrease with increasing gas velocity. As shown in figure 2, the RMS values of the film thickness vary with both superficial liquid and gas velocities. It is evident that by increasing gas velocity the RMS value decreases significantly, whereas it increases with liquid velocity.
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It should be pointed out that in some of the following figures data obtained by Paras et al. (1994) in a 50.8 mm i.d. horizontal pipe loop (in the stratified/atomization flow regime), with hot film probes, are included to check for consistency and to examine general trends.

The mean large wave amplitude (dH) is found to be a linear function of the RMS value of the film height (Figure 3); i.e. $dH = 2 \sqrt{2} \text{RMS}$. This type of expression is representative of sinusoidal wave motion and it seems to be applicable to the case of irregular large waves encountered in the stratified/atomization flow regime. Paras & Karabelas (1991) reported that the above mentioned expression fitted quite well their data obtained in the annular flow regime. For relatively low superficial gas velocities (i.e. $U_G < 20$ m/s) large wave intermittency $I$ (defined as the fraction of total sampling time corresponding to passage of large waves) increases with gas velocity whereas for $U_G$ above 20 m/s it has a value of about 0.3-0.4. Liquid flow rate seems to have no influence on the intermittency. Large wave height ($h_W$) tends to decrease with both superficial gas velocity and liquid flow rate, the former having a stronger influence (Figure 4). The aforementioned results are quite consistent with conclusions drawn by Paras et al. 1994), analyzing the same quantities. The approach followed for the determination of the large wave amplitude as well as its height and intermittency is presented in more detail by Paras & Karabelas (1991).

3.2. Wetted Wall Fraction

Hart et al. (1989) using their ARS model calculate the wetted wall fraction in terms of the angle $\theta$. Later Grolman & Fortuin (1995) present a Modified Apparent Rough Surface (MARS) model to extend it to cases of inclined flow. For cases where the inclination angle is $\beta = 0^\circ$, predictions based on their correlation for the wetted wall fraction are close to those obtained from the ARS model. The predicted values of $\theta$ (from this model), for the runs tested in this work and for experiments conducted earlier by Paras et al. (1994), are in fairly good agreement (max deviation ~ 20%) with the observed ones, as shown in figure 5. A few runs obtained in the annular flow regime are excluded from this figure.

As expected and confirmed by visual observations, the area of the interface tends to increase, with increasing gas velocity, and to deviate significantly from the flat (time averaged) shape, assumed in presently used computational procedures. It is also visually observed, that a continuous, quite thin liquid film, covers the lower part of the pipe circumference without any dry patches on the wetted portion of the tube walls. Similar observations regarding the gas-liquid interface, were made by Paras et al. (1994) in their 50.8 mm i.d. horizontal loop, in the stratified/atomization flow regime.

3.3. Liquid-to-wall shear stress

As mentioned above, axial liquid-to-wall shear stress was measured at different circumferential locations around the pipe (every 22.5°). It was found to increase with both gas and liquid superficial velocities, at all radial positions. In figure 6 time-averaged shear stress values obtained at 45°, for all runs, are compared to those obtained at 315°, at the same cross-section, and at 45°, at another cross-section 2 cm upstream from the first. The observed agreement gives
additional credit to the electrodiffusion method for obtaining reliable data of the mean local shear stress with the small circular probes.

In order to facilitate data interpretation, shear stress measurements obtained in the stratified/atomization flow regime, and a few in the annular regime (runs O, Q & R), are classified in two categories; i.e. for relatively low and relatively high superficial gas velocities (e.g. \( U_G < 20 \text{ m/s} \) and \( > 20 \text{ m/s} \) respectively). In the first category (i.e. for \( U_G < 20 \text{ m/s} \)), the mean shear stress is roughly constant up to \( 45^\circ \), where an adequate liquid film is present, and then reduces as the film diminishes to reach, at the angle \( \theta \), the value of the gas-to-wall shear stress (figure 7a). In the second category (i.e. for \( U_G > 20 \text{ m/s} \)), where the film is considered to be very thin, except perhaps at the pipe bottom, the time-averaged shear stress obtains its maximum value at \( \theta = 0^\circ \) (i.e. at the pipe bottom), having considerably smaller values at the other radial locations (figure 7b).

These results are in qualitative agreement with those reported by Paras et al. (1994), regarding the liquid-to-wall shear stress in a 50 mm i.d. pipe. On the contrary, in the model of Taitel & Dukler (1976), the wall shear stress is arbitrarily assumed to be circumferentially constant. Rosant (1993) reports that, in horizontal and slightly downward flows, by increasing the gas velocity so that the interface becomes wavy, the circumferential distribution of shear stress is roughly uniform. However, the scattering of his limited data is quite large and does not warrant a definitive conclusion.

3.4. Liquid-to-wall and gas-liquid friction factors

The new data reported here on instantaneous axial liquid-to-wall shear stress, at different locations around the pipe circumference, enable one to calculate more accurately an average value of \( \tau_{WL} \) using these data (i.e. at various radial positions) and the stress value at the angle \( \theta \), i.e. the limit of the wetted portion of the circumference. The latter was considered to be equal to the stress exerted by the gas flow on the solid wall (\( \tau_{WG} \)). Thus, the liquid-to-wall friction factor \( f_L \) is computed from the corresponding average values of shear stress \( \tau_{WL} \). In figure 8 friction factor data (except those obtained in the annular flow regime) are plotted versus liquid Reynolds number \( Re_{LF} \), based on actual liquid velocity and on mean film thickness at the pipe bottom, \( h_0 \). A quite satisfactory data correlation is obtained with the equation:

\[
f_L = 0.7 Re_{LF}^{-0.5}
\]

where

\[
Re_{LF} = \frac{U_L h_0}{\varepsilon_L \nu_L}
\]

with \( \varepsilon_L \): liquid holdup and \( \nu_L \): liquid kinematic viscosity.

Kowalski (1987) using a Reynolds number based on superficial liquid velocity correlated his data with a similar expression, also involving a -0.5 exponent.
Shear stress data combined with data on liquid film thickness at the pipe bottom and pressure drop led to an improved determination of the interfacial friction factor, by means of momentum balances. For the computational procedure the gas-liquid interface was considered to be concave, and not flat for reasons pointed out earlier.

The following equations were used, obtained from momentum balances for the liquid and the gas phase, respectively:

\[ -A_L \left( \frac{dP}{dx} \right) - \tau_w P_L + \tau_i S_i = 0 \]  
\[ -A_g \left( \frac{dP}{dx} \right) - \tau_w P_G - \tau_i S_i = 0 \]  

where the parameters \( A_L, A_G, P_L, P_G, S_i \) are defined in figure 9. These parameters are obtained from measured film thickness values at the pipe bottom, liquid hold-up values obtained by Hart et al. (1989) - their equation (19) and the visual observations of wetted wall fraction (angle \( \theta \)). The interfacial area \( S_i \) is approximated by taking the straight line segment CD instead of the arc CD (figure 9).

Having measured liquid film thickness and pressure drop \( (dP/dx) \), and calculated the average value of liquid-to-wall shear stress, the product \( \tau_i S_i \) can be obtained from (2).

The gas-wall shear stress is calculated using a friction factor \( (f_G) \) and the superficial gas velocity \( (U_G) \); i.e.

\[ \tau_G = f_G \frac{P_G U_G^2}{2} \]  

with

\[ f_G = 0.046 R_G^{0.2} \]  

Thus, the product \( \tau_i S_i \) was also calculated by using (3) and very good agreement was obtained between the two values (about 5% deviation). Finally, an average value of the quantity \( \tau_i S_i \) was employed for the determination of the interfacial shear stress \( (\tau_i) \). The latter is expressed in terms of an interfacial friction factor \( (f_i) \) and the superficial gas velocity \( (U_G) \):

\[ \tau_i = f_i \frac{P_G U_G^2}{2} \]  

Thus, the friction factor \( f_i \) is obtained, in the stratified/atomization flow regime, from (5) and found to be correlated quite well with the following expression, as shown in figure 10 (where \( f_i \) data obtained with the same procedure as in Paras et al. (1994) are also plotted):

\[ f_i = 0.03 \varepsilon_L^{0.56} R_G^{-0.038} R_L^{0.21} \]  

where \( \varepsilon_L \) is the liquid holdup and \( R_G \) and \( R_L \) the gas and liquid Reynolds numbers respectively, based on the actual phase velocities and the pipe diameter. In order to estimate \( f_i \), Kowalski (1987) proposed a similar power relation, based on the same terms (e.g. \( \varepsilon_L, R_G \) & \( R_L \)).
Another approach for calculating $f_t$ is to consider the well known resistance formula for the completely rough regime (Schlichting 1960):

$$f_t = \frac{0.25}{\left(2 \log_{10} \frac{R}{k_s} + 1.74\right)^2}$$

with $R$ being the tube radius and $k_s$ an apparent roughness.

Paras et al. (1994) determined an equivalent roughness for the gas/liquid interface by using independently obtained interfacial wave properties such as roll wave height, $h_w$, and intermittency, $I$. In the present work the calculated values of $k_s$, along with those obtained by Paras et al. (1994), normalized with respect to the pipe diameter, are fitted satisfactorily by the following correlation, as shown in figure 11 (where data obtained in the annular flow regime are excluded):

$$\frac{k_s}{D} = 2.85 \left(\frac{dH}{D}\right)^{0.17}$$

In the above expression the equivalent roughness is related to wave intermittency, $I$, and wave amplitude, $dH$, instead of the wave height, $h_w$. The quantity $dH$ is considered to represent more realistically, than $h_w$, the actual height of the protrusions introduced by the waves into the gas flow. It should be pointed out that this correlation goes through zero as it would be required on physical grounds.

4. CONCLUDING REMARKS

At relatively small liquid flow rates, when low viscosity fluids are employed, as is the electrochemical solution used in this work, by increasing the gas velocity above $10 \text{ m/s}$ the wavy stratified flow enters a transition regime i.e. stratified/atomization. The main features of this regime are the appearance of disturbance waves, with a characteristic frequency 1-10 Hz, the liquid droplets entrained in the gas phase and the drastic change of the average gas/liquid interface profile from flat to concave.

Special attention is paid to the lateral distribution of the liquid-to-wall shear stress by making measurements at different circumferential locations. An important result regarding the local time-averaged shear stress is that a significant lateral variation exists due to the decreasing liquid film thickness, away from the bottom of the pipe. Only in the case of relatively low superficial velocities (i.e. $U_G < 20 \text{ m/s}$), the mean shear stress is roughly constant up to $45^\circ$, where an adequate liquid film exists. Beyond that lateral position, shear stress tends to decrease as the film thickness decreases to reach, at the angle $\theta$, of the triple-point (solid/gas/liquid), the value of the gas-to-wall shear stress.
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By taking into account the correct shape of the gas/liquid interface and having the ability to calculate accurately a circumferentially averaged shear stress value (for each run), improved estimates of the interfacial friction factor $f_i$ are obtained. To calculate $f_i$, the film thickness, pressure drop and shear stress measurements are employed. Data on wave characteristics such as roll wave height ($h_w$), amplitude ($dH$) and intermittency ($I$) are computed and utilized in the analysis presented here. Finally an expression for an equivalent interface roughness is proposed.

5. REFERENCES


JOLLS K.R. & HANRATTY T.J. (1969) - Use of electrochemical techniques to study mass transfer rates and local skin friction to a sphere in a dumped bed. AIChe J. 15, p. 199-205.


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6. FIGURES

Fig. 1 - Schematic layout of the flow loop

Fig. 2 - The effect of superficial gas and liquid velocities on film thickness RMS values at \( \theta = 0^\circ \) (i.e. pipe bottom).
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Fig. 3 - Correlation of large wave amplitude as a function of film thickness RMS values at $\theta = 0^\circ$, (i.e. pipe bottom).

Fig. 4 - The influence of gas and liquid superficial velocities on large wave height at $\theta = 0^\circ$ (i.e. pipe bottom).
Fig. 5 - Wetted wall fraction data vs predicted values using the Hart et al. (1989) correlation.
Fig. 6 - Time-averaged $\tau_{WL}$ at $\theta = 45^\circ$ plotted against: a) $\tau_{WL}$ at $\theta = 135^\circ$, at the same cross-section and b) $\tau_{WL}$ at $\theta = 45^\circ$, at another cross-section 2 cm upstream.
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Fig. 7 - Circumferential distribution of normalized $\tau_{WL}$ with respect to $\tau_{WG}$: a) for relatively low superficial gas velocities (i.e. $U_G < 15$ m/s) and b) for relatively high superficial gas velocities (i.e. $U_G > 15$ m/s).
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Fig. 8 - Wall-to-liquid friction factor data plotted vs the corresponding liquid Re.

Fig. 9 - Schematic representation of horizontal gas-liquid stratified-atomization flow.
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Fig. 10 - Correlation of interfacial friction factor.

\[ f_i = e_L^{0.56} \Re_G^{-0.038} \Re_L^{0.21} \]

Fig. 11 - Apparent interface roughness \((k_s)\) data correlated with large wave amplitude \((dH)\) and intermittency \((I)\).

\[ k_s/D = (dH/D)^{0.17} \]
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QUANTITATIVE RELATIONSHIPS BETWEEN THE STRUCTURE AND ACTIVITY OF CORROSION INHIBITORS

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SUMMARY

Various N-acyloamino acids were synthesized and their inhibiting capacity was tested by using the potentiostatic method. The inhibiting efficiencies varied between 36 and 61%. The electronic properties obtained by using the AM1 quantum chemical approach, were correlated with experimental efficiencies and the best multiple correlation coefficient obtained was equal to 0.80. Due to these preliminary results, N-acylamino acids may form charge transfer complexes with the iron atoms on the metal surface.

1. INTRODUCTION

Quantitative Structure-Activity Relationships (QSAR) seem to become a useful approach, which may support researchers to find more effective corrosion inhibitors (1, 2, 3, 4). The approach is based on correlations derived between the dependent variable—in our case the efficiency \( \eta \) of inhibition of corrosion—and the set of independent variables, which account for some molecular properties. QSAR is basically a statistical approach, predictions are made on the basis of regressions derived in a series of compounds with known efficiencies. Most experiments are done in solutions with fixed inhibitor concentrations. Models were proposed, which account for the adsorption of the inhibitors on the metallic surface, and the results (that is the correlation) were improved by using adsorption models (5). QSAR were also used to the composition of inhibitor combinations (6).

In the present paper we report first preliminary results obtained for a series of N-acylamino acids. Significant correlation (R=0.80) has been found between the electronic structure of the molecules and the efficiency of inhibition.

2. EXPERIMENTAL

Chemicals used as inhibitors were synthesized in our laboratory, either by acylation of amino acids by Schotten-Baumann method. These chemicals differ in the chain length at the acyl moiety from \( C_5 \) to \( C_{16} \) in the alkyl series. In the other series there is phenyl ring which is attached directly to the CONH bond or is separated by a C=C from it. The modified amino acids are glycine, \( \beta \)-alanine and glutamic acid.
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The austenitic stainless steel was the type of AISI 304 (C:max. 0.12%; Si:max.2.0%; Mn:max.2.0%; Cr:max.17.0-19.0%; Ni:max.8.0-11.0%; S:max.0.030%; P:max.0.04%)

The electrochemical experiments were performed using a potentiostate (SOLARTRON 1286 ECI; scanning from -0.5 V to +0.5 V with the scan rate 10 mV/min. recorded; platinum/saturated calomel/cylindrically shaped corrosion test specimens fabricated from stainless steel of 0.78 cm²/specimen).

Corrosion rates of specimens exposed to inhibited or uninhibited model solution (0.47 g CaSO₄ x 2H₂O, 0.23 g MgSO₄ x 2H₂O, 0.11 g NaHCO₃, 0.13 g CaCl₂ x 2H₂O in one litre of distilled water, pH=7) were determined electrochemically by extrapolation of potentiostatic polarization curves.

The quantum chemical indices were calculated by using the AM1 method (7). The actual calculations were done by using the MOPAC 6.0 computer program with full optimization of all internal coordinates.

Table 1 - Experimental inhibitory efficiencies and calculated quantum chemical indices

<table>
<thead>
<tr>
<th>Molecule</th>
<th>EHOMO (eV)</th>
<th>ELUMO (eV)</th>
<th>Dipole moment</th>
<th>ηexp (%)</th>
<th>ηcalc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃(CH₂)⁴-CO-NH-CH(COOH)-CH₂-CH₂-COOH</td>
<td>-10.55</td>
<td>0.634</td>
<td>5.34</td>
<td>46</td>
<td>41</td>
</tr>
<tr>
<td>CH₃(CH₂)⁸-CO-NH-CH(COOH)-CH₂-CH₂-COOH</td>
<td>-10.55</td>
<td>0.634</td>
<td>5.37</td>
<td>50</td>
<td>41</td>
</tr>
<tr>
<td>CH₃(CH₂)¹⁴-CO-NH-CH(COOH)-CH₂-COOH</td>
<td>-10.38</td>
<td>0.790</td>
<td>4.33</td>
<td>31</td>
<td>36</td>
</tr>
<tr>
<td>(COOH)-CH₂-NH-CH(COOH)-CH₂-COOH</td>
<td>-11.14</td>
<td>0.044</td>
<td>4.92</td>
<td>65</td>
<td>61</td>
</tr>
<tr>
<td>OH-CH₂-NH-CH(COOH)-CH₂-COOH</td>
<td>-10.93</td>
<td>0.61</td>
<td>6.96</td>
<td>35</td>
<td>42</td>
</tr>
<tr>
<td>(COOH)-CH₂-NH-CH(COOH) (CH₂)2COOH</td>
<td>-10.97</td>
<td>0.23</td>
<td>5.68</td>
<td>46</td>
<td>54</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

The tested molecules and their experimental efficiencies and the calculated quantum chemical indices (EHOMO = energy of the highest occupied molecular orbital, ELUMO = energy of the lowest unoccupied molecular orbital) are shown in Table 1. The best regression equation found, is:

\[ \eta = -33 \cdot E_{\text{LUMO}} + 62 \]

R = 0.795, \quad s = 8.1, \quad F = -2.6

where R is the multiple correlation coefficient, s denotes the standard error of estimate and F is the result of Fisher’s F-test.

4. CONCLUSION

Our preliminary results indicate the importance of the ELUMO. Efficiency increases with decreasing values of ELUMO. The results seem to indicate, that charge transfer from the metal surface to the inhibitor takes place during the adsorption. The continuation of this investigations is in progress.
5. REFERENCES


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MECHANISM OF INHIBITION IN NEUTRAL SOLUTIONS

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SUMMARY

A stochastic mathematical model has been developed for a statistical description of corrosion process of metals and inhibition of corrosion by an adsorption mechanism. Based on the model, the dissolution of metals and the efficiency of inhibitors can be studied by computer simulation.

1. INTRODUCTION

The chemicals used in the inhibition of metal corrosion in nearly-neutral aqueous solutions can be classified as film-forming inhibitors. These chemicals are capable of depositing on metal surfaces, thus forming a three-dimensional protective-layer.

The relationship between the amount of substance adsorbed on unit area of the metal surface and the concentration of inhibitor molecules in the solution at given temperature is given by adsorption isotherm. The aim of our model calculations was to distinguish Langmuir, and Frumkin isotherms from each other by computer simulations.

2. THE MODEL

The total volume of the metal is divided into volume elements. The dissolution probability of each volume element depends on the number of free surface sites, the type of the metal and aggressiveness of the environment. In discrete time intervals the computer algorithm scans the whole surface of the metal and based on the given probability, a random number generator decides on the dissolution of each volume element with at least one surface site. During the dissolution in a volume element the number of free surface sites for neighbouring volume elements increases, which raises the probability of dissolution for those in the next time step.

The probability of dissolution in a volume element through one of its free surface sites is a function of solution parameters (chi, It, etc.),

\[ p_c = p(e_i, T_i, ...) \] (1)

The number of dissolved volume elements \( k_i \) is proportional to the number of free surface sites and to the probability of dissolution at the given surface site \( p_c \).
where \( N_i \) is the number of total and \( n_i \) is the number of blocked surface sites. \( A_i \) and \( A_0 \) are free and total areas of the surface, respectively.

The adsorption of the inhibitor compound on the free surface sites of a metal is characterized also by probability functions, depending on the inhibitor and the solution as in the case of the dissolution processes.

The probability of adsorption \( p_a \) is also a function of solution parameters. At equilibrium at any temperature and concentration a fraction \( \Theta \) of the sites is occupied by adsorbed molecules and a fraction \( 1-\Theta \) is not occupied. The probability of adsorption is the same for all sites and does not or does depend on the fraction covered for the Langmuir and Frumkin cases, respectively.

**Langmuir isotherm**

\[
b_i c = \frac{\Theta}{1-\Theta}
\]

**Frumkin isotherm**

\[
b_i c = \frac{\Theta}{1-\Theta} \exp(-a_i \Theta)
\]

The algorithm determines at each time step the number of blocked sites elements by means of a random number generator, which results in a decrease of the probability for the dissolution in the next time step. The time evaluation of the processes can be calculated by repeating each step.

If the number of dissolved volume elements is \( \chi_i \) at the \( i \)th time step, the corrosion rate \( c_v \) results in

\[
c_v = \frac{dM}{At} = \frac{\sum_i k_i r d\chi}{A \sum_i idt} \sim \frac{\sum_i k_i}{\sum_i}
\]

where \( \delta M \) is the loss of mass, \( \delta v \) is the volume of elementary cubes, \( A \) is the area and \( \rho \) is the density of the metal.

Thus the corrosion rate at the \( i \)th time step is proportional to the number of dissolved volume elements, i.e. \( c_v i_\chi \sim k_i \).

If the number of blocked surface sites is \( n_i \) and the number of free surface sites is \( N_i - n_i \) at each time step the fractional coverage is, simply,

\[
\Theta = \frac{n_i}{N_i} = p_a
\]

The probability of the adsorption is equal to the fractional coverage in the model. Thus, the corrosion rate in the presence of adsorption is expressed by the equation,
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\[ e_{nl} \sim \left( 1 - \frac{n_i}{N_i} \right) p_c = (1 - \Theta)p_c = (1 - p_a)p_c \]  

(7)

As a result of the above equation the efficiency due to adsorption is,

\[ IE = \frac{c_{n0} - c_{nl}}{c_{n0}} = \Theta = p_a \]  

(8)

3. COMPUTER SIMULATION

Two kinds of computer simulations have been carried out. In the first one the interaction between the blocked surface sites was excluded (Langmuir case). In the second one the interaction between the adsorbent with the already blocked nearest neighbour sites was taken into account by an simple algorithm (Frumkin case). The coordinates of all volume elements are stored in each time step (cycle). Originally the surface is smooth and the number of surface sites is actually 106. There is initially no blocked surface site \( n_0 = 0 \). The calculation consists of cycles, with each cycle having a dissolution and removes at random \( k_i \) volume elements with \( p_c \) probability. In the second adsorption step, the algorithm blocks \( n_i \) surface sites with \( p_a \) or \( p^*a \) probability for Langmuir or Frumkin type of adsorption, respectively. The input probabilities for the simulations are \( p_c \), \( p_a \) or \( p^*a \).

\( p_c \) is estimated form experimental corrosion rate without any inhibitor, i.e. \( p_c = \text{constant} \times \text{cv}0 \). The probability of adsorption \( p_a(c) \) for the Langmuir case is determined from the experimental efficiency as a function of inhibitor concentration for solution (A) \( p_a = IE \). The probability of adsorption \( p^*a \) for the simulation with interaction between the adsorbents is determined as follows. Substituting \( aI = 0 \) in the Frumkin isotherm (equation 4) fitted to experimental data (B) one can approximate the probability of adsorption in a free surface site \( p^*a \) if there are no blocked sites in the nearest neighbourhood,

\[ b_{1,c} = \frac{p_{a0}}{1 - p_{a0}} \]  

(9)

It corresponds to an adsorption event with no interactions. However, the probability of adsorption is increased to \( p^*a \) if there are already blocked sites in the nearest neighbourhood.

The \( p^*a \) is then determined as

\[ p^*a = nx0xp_{a0} \]  

(10)

if \( p^*a \leq 1 \), and \( p^*a = 1 \) for the cases when \( p^*a > 1 \), where \( n \) is the number of already blocked neighbouring surface sites (maximum 4) and \( \alpha \) is an adjustable parameter (\( \alpha = 1.4 \) for (B) solution).

As a result of the simulation, the average thickness of the model metal decreases and surface coverage changes. The corrosion rate of mild steel in solution A (without CaO) was 0.6 mm y\(^{-1} \). \( p_c \) was chosen so as to reduce the height by 60% in 1 year which means 90,000 cycles (1 cycle = 0.1 h, \( p_c = 4 \)).
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Figure 1 - Part of a metal surface at the beginning and at the end of the simulation with the probability of dissolution $p_c = 0.4$ and $0.8$ without an adsorption process.
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Figure 2 - Part of the metal surface at the end of simulation with dissolution probability $p_c = 0.8$ and probabilities of adsorption $p_a = 0.2$, $0.6$ and $0.8$, respectively.
4. RESULTS

Figure 1 shows the model metal surface at the beginning of the simulation and after 90,000 cycles without an adsorption process. The results of simulations for Langmuir type of adsorption with \( p_a = 0.2, 0.6, 0.8 \) and \( p_c = 0.8 \) can be seen in Fig. 2.

The reproduction of fractional coverages as a function of inhibitor concentration by simulating adsorption both without and with interaction of adsorbants for experimental data (A) and (B) is shown by circles in Fig. 3.

![Graph showing fractional coverage of carbon steel in NaClO4 solutions](image)

Figure 3 - Fractional coverage of carbon steel in NaClO4 solutions as a function of HEDP inhibitor concentration in the absence (A) and in the presence (B) of Ca ions. Starts and triangles stand for experimental data (A and B, respectively), full lines represent Langmuir and Frumkin isotherms fitted to Experimental data (A) and (B), respectively. Open circles are the results of computer simulations.

Comparing simulated and experimentally determined fractional coverages in this Fig. 3, one can see that a very simple model for interaction between the adsorbed species (equation 10) is able to distinguish between the Langmuir and Frumkin type of adsorption mechanisms.
MODELLING OF SCALE FORMATION FROM THERMAL WATER
and the Equilibrium Solubility Along the Well

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SUMMARY

Simulation of particle size evolution and of scale formation along the flow path is of
the great importance for data interpretation as well as for engineering application (e.g. minimization of the scale formation) in geothermal and hot water plants. In order
to construct a general model based on the kinetics, equilibrium and fluid dynamics to
describe the scale formation and deposition along the production tubing of geothermal
or thermal water wells we developed an equilibrium simulation algorithm and a
computer program for the determination of the partial pressures of the dissolved gases
(CO₂, CH₄, and N₂) and using the determined CO₂ partial pressures for the
determination of the CaCO₃ scale formation in Na-K-Mg-Ca-H-Ba-Sr-Cl-Br-SO₄-OH-
HCO₃-CO₃-CO₂-H₂O system along the well between the bubble point and the well
head.

1. INTRODUCTION

From the calcite dissolution equations (the CaCO₃-CO₂-H₂O system) it is quite clear that
removal of CO₂ to a steam phase during flashing leads to calcite supersaturation even though
the accompanying temperature drop itself leads to calcite saturation increase. Since most
reservoir fluids are close to saturation with calcite, carbonate scaling inside the well above
the bubble point depth and inside production casing is a possibility for all geothermal wells. The
solubility of calcium carbonate minerals in aqueous solution at any particular temperature
increases with increasing partial pressure of CO₂. Boiling leads to strong reduction in CO₂
partial pressure due to effective transfer of CO₂ into the steam phase. The presence of other
gases in the geothermal fluid, especially if less soluble in water then CO₂ will enhance
degassing of the CO₂ during boiling.

2. DETERMINATION OF THE PARTIAL PRESSURE AT A GIVEN DEPTH

During the last period we have developed a modeling algorithm and a program to compute the
bubble point pressure and the corresponding depth. In the next step we combined this algorithm
with the earlier developed multicomponent equilibrium solubility algorithm. The basic idea of
this combination is the fact that scaling starts only above the bubble point, so we have to
describe the precipitation and dissolution processes between the bubble point depth and the well head. Using the available gas separation and chemical analysis data for a given well one can determine the bubble point pressure (and the partial pressures of the three gas components). Moving in the direction upward of the well head it is possible to determine the new gas pressures, temperature the liquid/gas phase ratio at this new depth value.

In our simulation model we used a method similar to the Kocsis method [1] for the determination of the equilibrium gas pressures and temperature between the bubble point and well head depths. The method is based on the assumption that in the pressure range of these pressures the chemical activity of the components in the liquid phase equals one.

Formulating this model for an aqueous electrolyte system the following steps of computation is to be completed:

- the determination of the separated and dissolved gas-water ratio for the gases N\textsubscript{2}, CH\textsubscript{4}, CO\textsubscript{2} using the measured values of the separated gas-water ratio (GWR\textsubscript{sep}), the dissolved gas-water ratio (GWR\textsubscript{dis}) and the volumetric concentrations for these three gas components in the separated and dissolved fractions (V\textsubscript{X\textsubscript{i}}, V\textsubscript{Y\textsubscript{i}})

\[
GWR_{\text{sep},i} = \frac{GWR_{\text{sep}} V_{Xi}}{100} \\
GWR_{\text{dis},i} = \frac{GWR_{\text{dis}} V_{Yi}}{100}
\]  

(1)

where:

- GWR\textsubscript{sep} is the separated gas-water ratio (Nm\textsuperscript{3}/m\textsuperscript{3})
- GWR\textsubscript{dis} is the dissolved gas-water ratio (Nm\textsuperscript{3}/m\textsuperscript{3})
- V\textsubscript{X\textsubscript{i}} is the volumetric concentration of the i-th gas in the separated fraction (vol\%)
- V\textsubscript{Y\textsubscript{i}} is the volumetric concentration of the i-th gas in the dissolved fraction (vol\%)

- the determination of the total (separated+dissolved) gas-water ratios for the three gas components

\[
GWR_{\text{tot},i} = GWR_{\text{sep},i} + GWR_{\text{dis},i}
\]  

(2)

- The determination of the number of moles of various gases and the total number of moles of the gases in 1 m thermal water

\[
n_i = GWR_{\text{tot},i} * 0.01 / 22.41383
\]

\[
n_{\text{sum}} = \sum_{i=1}^{3} n_i
\]  

(3)

where:

- ni is the number of moles of a gas component (mol/m\textsuperscript{3})

- The determination of number of moles of the gas components in 1 mol water

\[
m_i = n_i / (\rho_{\text{water}} 10^6 / 18.167 + n_{\text{sum}})
\]  

(4)

where:

- mi is the number of moles of the gas component in 1 mole water
- \rho\text{\textsubscript{w}} is the density of the thermal water (g/cm\textsuperscript{3})
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- the determination of the equilibrium constant for the dissolved gases in saline water

\[
K_i^* = K_i \cdot 10^{n \cdot \text{Sechenov}}
\]  
(5)

where \( K_i^* \) is the equilibrium constant of the gas component in saline water,
\( K_i \) is the Henry equilibrium constant of the gas component in water,
\( K_{\text{Sechenov}} \) is the Sechenov equilibrium constant of the gas component in saline water,
\( n \) is the total dissolved salt content as NaCl in the solution (mol/dm³).

- The determination of the mole fraction of the gas components in the water

\[
X_i = \frac{m_i}{F + (1 - F)K_i^*}
\]

where \( F \) is the mole fraction of the liquid phase.

The sum of products of equilibrium constants and of mole fractions of the dissolved gases should be one within a prescribed tolerance.

\[
\sum_{i=1}^{3} (K_i^* X_i) = 1 \pm \varepsilon
\]  
(6)

where \( \varepsilon \) is the tolerance level.

The set of equations may be solved using iteration technique. During the iteration one should increase the \( F \) (the mole fraction of the fluid phase) if the result of Equation 6 is greater than one and decrease in the opposite case. The resulted mole fractions of the gas components can be used for the determination of the partial pressures.

\[
P_i = K_i^* X_i P_{\text{tot}}
\]

\[
P_{\text{tot}} = H \frac{dP}{dH}
\]

where \( P_i \) is the partial pressure of the given gas component at the depth \( H \) (bar),
\( P_{\text{tot}} \) is the total pressure at the depth \( H \) (bar),
\( H \) is the given depth between the bubble point and the well head depths (m),
\( dP/dH \) is the pressure gradient (bar/m).

The computation is started after the input of the gas separation and chemical analysis data with the determination of the bubble point. Decreasing this pressure by sufficiently small value, using this new total pressure (\( P_{\text{new}} \)) we can determine the new depth (\( H_{\text{new}} \)) from the equation:

\[
H_{\text{new}} = \frac{P_{\text{new}}}{dP/dH}
\]  
(8)

At this depth the partial pressures of the gas components can be determined. Repeating this procedure results the partial pressures profiles.
3. CALCULATION OF THE CALCITE SOLUBILITY ALONG THE WELL

The resulted partial pressure, temperature profiles can serve as input data for the computation of the equilibrium solubility of calcite at a given vertical depth of the well between the bubble point and well head depths. The starting concentration values at the bubble point depth can be determined using the surface analysis data. For this process we compute the separated steam fraction \( y \) using steam tables fitted functions between the enthalpy values and temperature

\[
y = \frac{H_0 - H_{\text{liq}}}{H_{\text{vap}} - H_{\text{liq}}}
\]

where
- \( y \) is the separated steam fraction
- \( H_0 \) is the enthalpy of the liquid at the temperature in the deep (kJ/kg)
- \( H_{\text{liq}} \) is the enthalpy of the liquid phase at the separation temperature in surface (kJ/kg)
- \( H_{\text{vap}} \) is the enthalpy of the vapor phase at the separation temperature in surface (kJ/kg)

Using this \( y \) value the original deep water concentrations for the non volatile components:

\[
C_{i0} = (1 - y)C_i
\]

where
- \( C_{i0} \) is the starting concentration of a non volatile component \( i \) at the bubble point (mol/kg water)
- \( C_i \) is the concentration of a non volatile component at the surface analysis (mol/kg water)

and for the volatile (CO2) components:

\[
C_{i0} = C_{\text{vap}}(y + \frac{1-y}{B_i}) = C_{\text{liq}}(1 + y(B_i - 1))
\]

where
- \( C_{i0} \) is the starting concentration of a volatile component \( i \) at the bubble point (mol/kg water)
- \( C_{\text{vap}} \) is the concentration of a volatile component in the vapor phase at the surface analysis (mol/kg water)
- \( C_{\text{liq}} \) is the concentration of a volatile component in the liquid phase at the surface analysis (mol/kg water)
- \( B_i \) is the inverse value of the mass distribution coefficient of a volatile component (determined by the equation given by Nicholson [2])

The computation starts with the calculation of the bubble point depth concentration input values for volatile and non volatile components. Computing the equilibrium solubility at this depth one can move upwards to the next depth using input concentrations determined at the previous depth.
4. RESULTS

In order to test and to check the developed model we computed the bubble points for several Hungarian thermal water wells and compared the results of computations with the measured values. The results of computation are shown in table 1. The fit seems to be quite good.

Table 1 - The measured and computed bubble point depths for several Hungarian thermal water wells

<table>
<thead>
<tr>
<th>Name of the well</th>
<th>measured bubble point depth (m)</th>
<th>computed bubble point depth (m)</th>
<th>difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Szeged Uj Elet Tsz. 3.</td>
<td>110</td>
<td>104</td>
<td>5.45</td>
</tr>
<tr>
<td>Szeged Uj Elet Tsz. DC9</td>
<td>85</td>
<td>87</td>
<td>2.35</td>
</tr>
<tr>
<td>Apátfalva Aranykalász Tsz</td>
<td>80</td>
<td>84</td>
<td>5.00</td>
</tr>
<tr>
<td>Acs Ernő major</td>
<td>20</td>
<td>21</td>
<td>5.00</td>
</tr>
<tr>
<td>Csorna Petőfi termál</td>
<td>240</td>
<td>237</td>
<td>1.25</td>
</tr>
<tr>
<td>Szeged Kilińska 1.</td>
<td>100</td>
<td>112</td>
<td>12.00</td>
</tr>
</tbody>
</table>

The determined partial pressure and temperature profiles for three wells are shown in Figures 1 to 3.
Control of corrosion and scaling in geothermal systems

Figure 2 - The partial pressure profiles along the well Csorna Petőfi termál

![Partial pressure profiles along the well Csorna Petőfi termál](image)

Figure 3 - The partial pressure profiles along the well Ács Ernő major

![Partial pressure profiles along the well Ács Ernő major](image)

In figure 4, we show the computed Ca²⁺ solubility profile in well Szeged Uj Élet Tsz 3.
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Figure 4 - The Ca²⁺ Solubility Profile in well Szeged Uj Élet Tsz 3

The computations suggest that there is a calcite precipitation between the bubble point depth 104 m and 92 m. The solubility decreases in this section from 3.382 mmol/kg to 2.842 mmol/kg. Higher to the well head a slow dissolution is predicted (the partial pressure of CO₂ slowly increases and at 4m starts again a supersaturation a precipitation can occur at well head.

CONCLUSIONS

An equilibrium simulation algorithm and a computer program were developed for the determination of the bubble point, the partial pressure profiles and the corresponding equilibrium solubility in a thermal or geothermal well. The developed program computes the bubble point and the profiles using the measured gas separation and other data. The computer program was written in FORTRAN and consists of 6 modules.

REFERENCES


IRON SULFIDE SCALE FORMATION AND IMPLICATIONS ON CORROSION OF STEEL ALLOYS IN GEOTHERMAL SYSTEMS

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SUMMARY

In the present report, we have investigated the mechanism of the formation of iron sulfide scale deposits in high ionic strength solutions both at high and low temperatures. Polymer additives were tested as scale formation inhibitors for the iron sulfide system under similar conditions. These compounds were also tested for their inhibition properties on the calcium carbonate system and for their effect on the corrosion behaviour of carbon steel in NaCl containing aqueous media in the presence and absence of sulfides.

Nucleation and growth of iron sulfide was investigated over the temperature range between 25 °C and 80 °C as a function of the solution supersaturation using the constant supersaturation experimental approach. At 25 °C and pH 6.5 the ionic strength irrespective of the background electrolyte did not affect the nature of the phase forming (which was found in all cases to be amorphous FeS). The rate of the mineral formation showed a third order dependence on the relative solution supersaturation. The tested additives were polymer and copolymer derivatives of malonic acid. At 80 °C and at concentration levels of 5 ppm they showed a considerable reduction of the rates and the volume of the precipitates formed. The inhibitor with code name ATP 6.2 at a concentration level of 5 ppm caused a 77% reduction in the rate of amorphous FeS precipitation.

The effectiveness of commercially available water soluble additives, namely Solamine 129®, Aquaprox MDC1300® and Norust 491® as corrosion inhibitors, was tested by DC and AC electrochemical measurements. The malonic acid polymeric derivatives, in addition to their antiscaling efficiency were also tested as potential corrosion inhibitors. From the compounds tested, only Solamine 129® had satisfactory performance as corrosion inhibitor. The rest of the chemicals examined, were either ineffective or even in some cases enhanced the rates of corrosion of carbon steel.

The polymeric compounds tested were found to be highly effective inhibitors of calcium carbonate scale formation at concentrations as low as 0.3 ppm proved by seeded growth experiments at conditions of sustained supersaturation. From the commercially available corrosion inhibitors only Aquaprox MDC 1300 was found to be a very effective scale inhibitor for calcium carbonate formation under the same conditions as in the case of polymeric compounds.
INTRODUCTION

Exploitation of geothermal resources has for many years been one of the most widely used alternatives for confronting energy problems all around the world. However, many problems related with the utilization of this natural energy resource have not been completely overcome yet. Two of the most often encountered problems are corrosion and scaling, processes that may occur concurrently on the saline hot water handling equipment. The nature of the solids forming depends on the chemical composition of the bulk fluids pumped from the production wells. A wide variety of insoluble salts is encountered in geothermal systems including among others, calcium carbonates, silicates and metal sulfides. The formation of these salts mostly follows the steps of a heterogeneous process including:

- Development of supersaturation.
- Bulk diffusion of the growth units of the forming salts onto the heterogeneous surface (pipe walls, suspended particles, pumps and valves).
- Surface diffusion on the active sites of the growing crystals.
- Dehydration and integration of the growth units into the lattice of the growing crystal.

Very often between the development of supersaturation and the formation of the first macroscopic crystal there is a time lapse defined as the induction period, $\tau$. This time period corresponds to the formation of the critical nucleus which then grows further to form the crystalline deposits. The slowest of the above steps determines the overall rate of the process. For each salt forming however, the mechanism of formation may be completely different and has to be studied separately. Parameters such as temperature, supersaturation and ionic strength have to be investigated regarding their effect on the insoluble salt formation. Precipitation kinetics should also be measured in order to understand the mechanism of scale formation. In several cases, kinetics rather than thermodynamics may control nucleation and crystallization phenomena.

Scaling is often very closely related to corrosion. Chloride ions, contained in most natural geothermal fluids along with the often-encountered sulfide ions and the conditions existing in these brines (high pressure, dissolved gases, alkaline $\text{pH}$) are mostly responsible for the high corrosion rate of the carbon steel pipe walls used in most of the geothermal installations. In the vicinity of the sites where corrosion occurs, iron concentration may reach high levels giving rise to the supersaturation with respect to iron sulfides. As a consequence a non protective layer of precipitate may form on the pipe wall at considerably high rates.

The main task of the work of our group in the frame of this project was to provide information on the fundamental aspects of iron sulfide formation encountered in the sulfide containing brines of the European geothermal fields. We have also investigated the corrosion of carbon steel in relation to the conditions existing in the aqueous environment. Moreover our research group tested the effectiveness of various water soluble chemical substances, both commercially available and synthesized in the laboratory regarding protection against both corrosion and scaling phenomena in high salinity aqueous environments.
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The spontaneous precipitation of Iron Sulfide in aqueous media was investigated by experiments in unstable solutions at high salinity both at 25 and 80 °C. The kinetics of precipitation was investigated both in the absence and in the presence of water soluble compounds in order to assess their potential use as inhibitors of the formation of FeS scale deposits. Their effect towards corrosion of carbon steel, a material commonly used in the various equipment utilized for geothermal brine handling, was also examined.

The following tasks have been accomplished:

(i) Study of spontaneous precipitation of iron sulfides in unstable solutions of high salinity (25°C, I=0.4 M using (NH₄)₂SO₄ as inert electrolyte), at conditions of constant supersaturation.

(ii) Study of the process of pyrite formation by refluxing amorphous FeS suspensions for extended time periods.

(iii) Inhibition of the spontaneous precipitation of iron sulfide at 80 °C and I = 0.4 M using NaCl, in the presence of the additives AP 28.52.1, AV 142.52.1, ATP 6.2, Solamine® and Aquaprox MMC7300®. Code numbers refer to polymeric water soluble additives prepared by BBPDICM.

(iv) Inhibition of calcium carbonate scale formation by the water soluble polymers prepared by BBPDICM and by commercially available corrosion inhibitors (Solamine® Aquaprox and Norust®).

(v) Electrochemical investigations of the anti-corrosive properties of the additives prepared by BBPDICM, organophosphorus compounds, organic aromatic compounds and already used commercial corrosion inhibitors on carbon steel in NaCl containing media.

EXPERIMENTAL

i. Spontaneous precipitation experiments at 25 °C in high salinity solutions

A double walled, water-jacketed reactor vessel of 250 ml total volume was used for these experiments. The temperature was kept constant at 25 ± 0.1 °C by circulating water from a constant temperature water bath. A magnetic stirrer was used for the stirring of the working solution. Before each experiment fresh stock solutions of Fe²⁺ and S²⁻ ions were prepared with triply distilled water, deaerated with N₂ gas bubbling for at least 30 minutes. Crystalline (NH₄)₂Fe(SO₄)₂ (Merck) and (NH₄)₂S 20 % solution (Ferrak) were used for the preparation of the stock solutions as described in the previous reports. Analytical grade crystalline (NH₄)₂SO₄ (Merck) was used for the preparation of the inert electrolyte stock solution utilized for the creation of high ionic strength conditions. (NH₄)₂SO₄ was used here instead of NaCl so as not to introduce foreign ions in the working solution (other than those already existing) and to take advantage of the rather reducing character of the NH₄⁺ ion, thus minimizing oxidation phenomena.
Control of corrosion and scaling in geothermal systems

All working solutions were supersaturated with respect to amorphous FeS, otherwise no precipitation occurred for adequately long time periods (48 h). Equal volumes (100 ml each) of iron (II) and sulfide solutions were directly mixed into the reactor vessel under vigorous stirring. The required quantity of (NH₄)₂SO₄ stock solution was included in the iron (II) solution along with a small quantity of H₂SO₄ (determined by initial trial and error experiments) so that the pH value of the supersaturated working solution would reach a value of about 6.5. Following mixing of the component solutions in the reactor was done through an opening on the reactor lid which was sealed and made airtight immediately after the mixing. A slight overpressure of water vapor saturated nitrogen gas was maintained to ensure inert atmosphere above the working solution. A combination Glass difficult electrode was used for monitoring the working solution pH throughout each experiment.

Following the preparation of the supersaturated solutions a computer controlled, automatic system was used to maintain the solution supersaturation constant at the initial level where precipitation started. The constant supersaturation experimental approach used can be briefly described as follows:

The precipitation of FeS is accompanied by the release of protons according to the reaction:

\[ xFe^{2+} + yH_2S + zHS^- + uS^{2-} \rightarrow FeS_{(s)} + mh^+ \]

A decrease in the solution pH as small as 0.001 units triggered the addition of concentrated Fe²⁺ and S²⁻ solutions contained in the syringes, so as to keep pH, iron and sulfide activities in the supersaturated solutions constant.

The concentrations for the titrant solutions were calculated as follows: Assuming CFe and CS the initial iron and sulfide concentrations in the working solution respectively, then the concentration in each syringe was:

- Syringe 1: \( n \times C_{Fe} + 2 \times C_{Fe} = (n+2) \times C_{Fe} \) (M in Fe²⁺)
- Syringe 2: \( n \times C_{S} + 2 \times C_{S} = (n+2) \times C \) (M in S²⁻)

The n factor varied depending on the velocity of iron sulfide precipitation and was determined from preliminary experiments. The factor 2 corresponds to the dilution anticipated by the addition of solutions from the two syringes. In the experiments where pH was adjusted using acid, a concentration of 2Cacid was required in the syringe containing the iron solution. To avoid changes in ionic strength due to dilution, a concentration of nCFe inert electrolyte (NH₄)₂SO₄ had to be added in the working solution.

To verify that solution supersaturation was kept constant and consequently that the precipitating phase had the assumed stoichiometry of Fe:S (1:1 in the experiments presented here), samples were withdrawn from the working solution at regular time intervals, were filtered through membrane filters (0.2 μ) and the filtrates analyzed for iron (by atomic absorption spectroscopy, Perkin Elmer 305A) and sulfide.

During each experiment, the automatic system continuously recorded the solution pH value and the volume of titrants added as a function of time. The data were translated into moles of iron sulfide precipitated as a function of time and the rates of precipitation of the crystalline phase forming, were easily obtained by curve fitting numerical methods. For each experiment all data
Control of corrosion and scaling in geothermal systems

points up to the formation of 1 mg of solid were taken into consideration for the fitting procedure for the calculation of the rates of precipitation.

After sufficiently long time periods, the solids were collected on membrane filters, dried at 25 °C in a desiccator under inert atmosphere and kept to be analyzed with powder X-ray diffraction (Philips PW 1840) and Scanning Electron Microscopy (Jeol JSM-5200).

ii. Study of the process of pyrite formation by refluxing amorphous FeS suspensions for extended time periods

As it has been stated in the 4th report, our group had managed to prepare pure pyrite crystals by refluxing amorphous FeS suspensions for 10 days in moderately acidic (with addition of HClO₄) solutions. In continuation of these efforts, we have modified this initial successful preparation method with respect to two factors: First we carried out the same procedure without the addition of HClO₄ in the suspension to be refluxed. In the next attempt we did not add HClO₄ but the ionic strength of the suspension was adjusted to I = 0.4 M by adding the appropriate quantity of concentrated NaCl solution.

Moreover, we monitored the process of pyrite formation by taking samples from the refluxing suspension at regular time intervals. The preparation lasted 15 days. The solids' examination was done by powder X-ray diffraction and scanning electron microscopy. All solids, including the final product, were collected on 0.2μ cellulose membrane filters and dried under vacuum for at least 24 hours before they were analyzed.

iii. Study of the inhibiting properties of various additives (AP 28.52.1, AV 142.52.1 and ATP 6.2, Solamine®, Aquaprox MMC7300®) on the spontaneous precipitation of iron sulfide at 80 °C and I = 0.4 M

The experimental setup and the methodology used has been described in previous reports. The additives were tested at concentration levels of 5 ppm. Their addition in the working solution was done before the reactor assembly (at 25°C), thus attaining a homogeneous distribution of the compound prior to the addition of sulfide stock solution (at 80°C). Continuing the experimental work presented in our previous report and in order to compare the experimental findings from the on-site experiments at Melun l' Almont site (France), we carried out experiments testing the same additives prepared by BBPDICM that were tested in France plus two commercial ones (also tested in France) for comparison purposes.

Samples were withdrawn from the working solution with the same frequency as in the on-site experiments at the early stages of each experiment. The precipitation experiments were however allowed to proceed for considerably longer time periods. The data obtained from sample analysis for total iron as a function of time, were used to calculate the precipitation rates. The solids collected after the end of each experiment were treated and analyzed the same way as the solids collected from the 25 °C experiments.
iv. Investigation of polymer additives as scale inhibitors in the precipitation of calcium carbonate from aqueous solutions using the constant composition method

The experiments described herein were done at 25 °C in a 600 ml, double walled Pyrex vessel thermostated by circulating water from a thermostat. The supersaturated solutions of total volume 500 ml, were prepared in the reaction vessel by the careful mixing of known volumes of calcium nitrate, sodium bicarbonate, sodium nitrate and additive stock solutions. The pH of the solution was subsequently adjusted to 8.50 by the addition of 0.1M standard sodium hydroxide solution (Merck, Titrisol). The pH of the solution was measured by a combination pH electrode (INGOLD, Type 405-60-57/120) standardized before each experiment with NBS Buffer solutions (pH 4.008 and 9.180 at 25°C). The solutions were stirred by a magnetic stirrer with a Teflon-coated stirring bar.

The initial solution conditions for the experiments were:

- Total Calcium, \( C_{Ca} \) = Total Carbonate, \( C_{CO_3} \) = 2.5 mM
- Total Sodium Nitrate = 0.025M
- \( \text{pH} = 8.50 \) and \( \text{Temperature} = 25 ^\circ \text{C} \).

At these initial conditions the working solutions were stable for period exceeding 48h and were supersaturated with respect to all calcium carbonate polymorphs. After pH adjustment, an exactly weighted amount of calcite seed crystals (ca. 20 mg) was introduced in the supersaturated working solutions. The pH of the supersaturated solutions was recorded with the aid of a data acquisition card (PCL-812PG, ADVANTECH) connected to a personal computer (AT-80286). The solution pH decreased with the onset of calcium carbonate precipitation, accompanied by proton release in the bulk solution. A pH drop as small as 0.005 pH units triggered the addition of titrant solutions from two mechanically coupled syringes of a computer controlled titrator through the appropriate software. The titrant solutions were prepared as follows:

- Titrant 1 : 30mM \( \text{Ca(NO}_3\text{)}_2 \)
- Titrant 2 : 5mM \( \text{NaHCO}_3 \) + 25mM \( \text{Na}_2\text{CO}_3 \) + \( 2 * C_{IN} \)

where \( C_{IN} \) is the concentration of the additive tested in the working solution. The added amounts of total calcium and total carbonate from titrant solutions were according to the stoichiometry (1:1) of the precipitating calcium carbonate.

The titrant concentrations were determined from preliminary experiments. Sodium nitrate was added in the working solution for keeping the ionic strength of the working solution constant during the addition of the titrants. Throughout the course of the experiments the pH of the working solution and the added volume of titrants as a function of time were recorded and stored in computer for further analysis. Samples were withdrawn during the experiments and filtered through membrane filters (Millipore, 0.2 μ). The filtrates were analyzed for calcium by atomic absorption spectroscopy (Perkin Elmer 305) in order to confirm the constant solution composition. In all experiments the analysis showed that the calcium concentration remained constant to within ± 2 %. The working solutions after the end of the experiments were filtered as previously described and the solids dried and analyzed by powder X-ray diffraction.
The precipitation rates (in the presence and in the absence of additives) were determined from the curves of added titrants versus time using curve fitting software. The additives tested in these experiments were Solamine 129®, Aquaprox MDC 1300®, Norust 491®, AP 28.52.1, AP 28.2, AS 11.2 and AV 142.1. The exact formulae for the first three additives are commercial secrets. These additives are used as corrosion inhibitors in the geothermal wells in the Paris-Basin in France. The last four additives were prepared by BBPDICM and their formulae have been reported.

v. Electrochemical Measurements

The following water-soluble compounds were examined with respect to their potential as corrosion inhibitors:

1. Organophosphorus compounds:
   - ENTMP (N,N,N',N' - ethylenediaminetetra (methylene phosphonic) acid, Monsanto) and NTMP (Nitritoltri (methylene phosphonic) acid, Monsanto)

2. Commercial products:
   - Solamine 129® (SEPPIC, Paris, France),
   - Norust 491® (CECA, La Defense, France) and
   - Aquaprox MDC 1300® (PROTEX, Levallois, France),

3. Polymeric additives:
   prepared by BBPDICM

4. Organic Aromatic compounds:
   - Picric Acid (C₆H₃(OH)(NO₂)₃),
   - Sodium Benzonate (C₆H₅COONa) and
   - p-Hydroxy Benzoic Acid (C₆H₄(OH)COOH),

The corrosion of carbon steel in corrosive media (NaCl) and in the absence of sulfide ions included two kinds of experiments:

a) DC measurements: Open Circuit Potential measurement vs. Time and potentiodynamic scans (Log(I) vs. Applied potential).

b) AC measurements (Impedance Spectroscopy).

The DC measurements (Open Circuit Potential and Potentiodynamic Scans) were done in an electrochemical cell consisting of a 0.6 dm³ thermostated glass vessel, magnetically stirred, and equipped with the appropriate electrodes. The cell was sealed with a polyamide lid equipped with ports accommodating a graphite counter electrode, a reference (Ag/AgCl/KCl(sat)) electrode with a salt bridge and the working electrode. The steel examined was embedded in an otherwise chemically inactive resin matrix in the form of rods.

The specimens used as working electrodes were shaped in the form of plates. The electrodes were connected to a Potentiostat (PGS-151, INTERTECH). The function of potentiostat (OCP and potentiodynamic scans) was selected by the appropriate switch.
The potentiostat employed for the measurements has two outputs, one for measuring voltage, another one for the measurements of the current and one input for external scan voltage. The potentiostat has also the capability to be controlled from Digital Input/Output ports of computer data acquisition cards using the appropriate software.

The total surface area exposed in the solution was 1 cm² and was polished before each experiment with a series of silicon carbide papers up to 1000 grit. After polishing, the surface was thoroughly washed with triply distilled water and dried with distilled acetone.

Following the immersion of the specimen in the corrosive media, the open circuit potential (OCP) with respect to the reference electrode was measured for at least ten hours. The potentiodynamic scans were done after the measurement of the OCP starting from the cathodic region, at potentials about $E_{OCP} - 200 \text{ mV}$ and ended to the anodic region at potentials $E_{OCP} + 150 \text{ mV}$ or at current equal to 1 mA for carbon steel with a scan rate 0.167 mV/s (ASTM standard).

The measurements were done using a combination of data acquisition cards (PCL-812PG and PCL-726, ADVANTECH) and an AT-386DX personal computer with the appropriate connections with the potentiostat. The data were collected by the computer and were stored in files for further treatment. The measurement of the OCP and the potentiodynamic scans of the steel specimens were done in non-aerated, stirred solutions in:

- The absence of sulfide ions in the solution and any deposits on the specimen surface.
- The presence of commercial products and organic aromatic compounds in the solution and absence of any deposits on the specimen surface.

The pH of the solutions in the above experiments was adjusted at approximately 6.0 to 6.5 by the addition of standard 0.1M HCl or 0.1M NaOH solutions as needed. The polarization resistance was calculated from the slope of the curve of the measured current versus the applied potential in the vicinity of the OCP ($OCP - 15 \text{ mV}$ to $OCP + 15 \text{ mV}$).

The AC measurements were done in an identical thermostated vessel using an Electrochemical Impedance Analyzer (Model 6310, EG&G). The Electrochemical Impedance Analyzer was connected to the computer via a GPIB expansion card (PC-AT National Instruments) and the impedance measurements were done using the corresponding software.

The AC measurements included impedance measurements of carbon steel specimens in deaerated (with N₂ purging), stirred solutions from an initial frequency of 10 mHz to a final frequency of 100 KHz with AC-Voltage amplitude 5.00 mV RMS with respect to the OCP and:

- in the absence of sulfide ions at various time periods,
- in the presence of commercial products at various time periods (at least 16 h).

The polarization resistance was calculated from the Nyquist plots using appropriate semicircle fit after subtraction of the solution resistance. The solution resistance was calculated from the same plot and was found to be about 10 Ω for a 0.1M NaCl solution.
RESULTS AND DISCUSSION

The solution speciation and the calculation of the relative solution supersaturation was done using the HYDRAQL program as described in the previous reports. The expressions and values for the solubility products of the various iron sulfides used for calculations, are stated below.

The equilibrium between the sulfides and the aqueous phase may be described by the equation:

\[
\text{Fe}_y\text{S}_x\text{S}_y(s) + xH^+ = x\text{Fe}^{2+} + x\text{HS}^- + yS_s(s)
\]  

(1)

The corresponding expression for the thermodynamic solubility product shall therefore be:

\[
K = \frac{(\text{Fe}^{2+})^x(\text{HS}^-)^x}{(H^+)}
\]

(2)

From the equilibrium:

\[
\text{HS}^- \leftrightarrow H^+ + S^{2-}
\]

with

\[
K_2 = \frac{(H^+)(S^{2-})}{(\text{HS}^-)} \quad \text{and} \quad \frac{(\text{HS}^-)}{(H^+)} = \frac{(S^{2-})}{K_2}
\]

(3)

it follows that:

\[
K = \frac{1}{K_2^x} (\text{Fe}^{2+})^x(S^{2-})^x
\]

(4)

and

\[
K_{2p} = KK_2^x = (\text{Fe}^{2+})^x(S^{2-})^x
\]

(5)

The thermodynamic solubility products considered in our calculations are summarized in table 1.

Table 1 - Thermodynamic solubility products of the various iron sulfides forming in aqueous media; logK = log \{ (\text{Fe}^{2+})^x(\text{HS}^-)^x / H^+ \}. From M. A. A. Schoonen, H. L. Barnes, Geochim. Cosmochim. Acta, 55, 1495-1504 (1991).

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>logK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>FeS</td>
<td>-2.99</td>
</tr>
<tr>
<td>Mackinawite</td>
<td>FeS</td>
<td>-3.60</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Fe0.98S</td>
<td>-4.95</td>
</tr>
<tr>
<td>Troilite</td>
<td>α-FeS</td>
<td>-7.94</td>
</tr>
<tr>
<td>Greigite</td>
<td>Fe3S4</td>
<td>-12.85</td>
</tr>
<tr>
<td>Marcasite</td>
<td>FeS2</td>
<td>-16.04</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS2</td>
<td>-16.35</td>
</tr>
</tbody>
</table>

Kinetics data from the constant supersaturation experiments was fitted to the semi-empirical equation.
Control of corrosion and scaling in geothermal systems

\[ R_p = k_g \sigma^m \]  

where \( R_p \) is the measured rate of precipitation, \( k_g \) the reaction constant, \( m \) the apparent order of precipitation and \( \sigma \) the relative supersaturation with respect to the solid phase forming defined as

\[ \sigma = \left[ \frac{(Fe^{2+})(S^{2-})}{K_{s\text{,solid}}} \right]^{1/2} - 1 = \Omega^{1/2}_{s\text{,solid}} - 1 \]  

Experiments at 25 °C, \( I = 0.4 \text{ M } (\text{NH}_4)_2\text{SO}_4 \)

Continuing the investigation of iron sulfide precipitation in high salinity solutions (\( I = 0.4 \text{ M} \)), we carried out these experiments in a pH region close to neutral (\( \approx 6.5 \)), which is the mean pH value for most natural geothermal waters in northern France. The solid that precipitated under the conditions specified, was amorphous with respect to x-rays, and had the characteristic texture of iron monosulfides when examined in a scanning electron microscope. This once more indicated that only iron monosulfides can be precipitated at low temperature and verified the finding presented in the previous report, that high ionic strength alone cannot induce pyrite formation.

The rates of precipitation were proportional to the solution supersaturation. The experimental conditions and the rates measured are summarized in table 2. The kinetics plot according to the power law (eq. 7) is shown in figure 1. The apparent rate order found is equal to 3 suggesting that the rate determining step is diffusion of the growth units on the surface of the growing crystals. This value is differentiated from the value of 1 found for iron monosulfide precipitation, a fact that has to be more closely examined.

Table 2 - Experimental conditions for the precipitation of amorphous FeS at 25 °C, \( I = 0.4 \text{ M } ((\text{NH}_4)_2\text{SO}_4) \).

<table>
<thead>
<tr>
<th>Exp No</th>
<th>[Fe]_i[S] (x 10^4 M)</th>
<th>Product</th>
<th>( \sigma_{am} ) (x 10^1)</th>
<th>Rate (mole FeS l^-1 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F147</td>
<td>6.0</td>
<td>Amorphous</td>
<td>1.953</td>
<td>2.40\times10^{-7}</td>
</tr>
<tr>
<td>F144</td>
<td>5.0</td>
<td>Amorphous</td>
<td>1.694</td>
<td>1.37\times10^{-7}</td>
</tr>
<tr>
<td>F143</td>
<td>4.0</td>
<td>Amorphous</td>
<td>1.408</td>
<td>6.86\times10^{-8}</td>
</tr>
<tr>
<td>F149</td>
<td>3.0</td>
<td>Amorphous</td>
<td>1.081</td>
<td>3.65\times10^{-8}</td>
</tr>
</tbody>
</table>
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Figure 1 - Kinetics of amorphous FeS precipitation at 25 °C, I = 0.4 M ((NH₄)₂SO₄).

Study of the process of pyrite formation by refluxing amorphous FeS suspensions for extended time periods

Both attempts for preparing pyrite under the new sets of conditions described were successful. Pyrite was in both cases the final product, having the same properties with that prepared in previous attempts.

We present here the evolution of the texture and crystallinity of the solid during the preparation process. As may be seen in figure 2a, in combination with the X-ray diffractogram in figure 3a, the initial solid was amorphous FeS. After 1 day of refluxing the change in texture was striking (fig. 2b) and the characteristic pyrite peaks appeared in the x-ray diffractogram (fig. 3b). After 5 days of refluxing the spherullitic texture of pyrite was clearer and the peaks sharper (figs 2c and 3c). As refluxing proceeded, the spherical pyrite crystals grew in size and the diffraction peaks increased in relative intensity and sharpness. The texture of the final product (after 15 days of refluxing) with spherical crystals of uniform size about 1μm typical for synthetic pyrite may be seen in figure 2d and the corresponding diffractogram in figure 3d.
Figure 2 a,b - SEM micrographs of synthetic iron sulfides.
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Figure 2 c,d - SEM micrographs of synthetic pyrite.
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The same trend was followed in both cases of pyrite preparation. From this finding we have assumed that at elevated temperatures the solid forming at the very early stages of the experiment was amorphous iron monosulfide which transformed very rapidly to pyrite by gradual loss of Fe or addition of S.

Testing of the inhibition effect of various additives on the crystal growth of iron sulfide at 80 °C, I = 0.4 M (NaCl)

The additives prepared by BBPDICM group were tested in a high salinity aqueous environment created by NaCl addition. Na⁺ and Cl⁻ are predominant species in natural hot waters as proved by the chemical analyses of the geothermal fluids from wells in northern France. The supersaturation created to cause onset of spontaneous precipitation, was comparable with the supersaturations created at the on-site experiments carried out in France. The additives tested here were again used at 5 ppm concentration.

We carried out a series of experiments at one level of supersaturation so that the rates of precipitation measured could be directly compared with each other. The additives tested showed a remarkably good inhibition effect, by considerably lowering the rates of iron sulfide precipitation in comparison with blank experiments where no additive was used. The relative inhibition was defined as
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Relative Inhibition \( \% = \frac{R_i}{R_o} \times 100 \)

where \( R_o \), \( R_i \) are the rates measured in the absence and in the presence of the inhibitors respectively. In table 3 the rates measured for each experiment and the percent reduction of the precipitation rates calculated are presented.

Table 3 - Rates measured and calculated inhibition for iron sulfide precipitation experiments at 80 °C, \( I = 0.4 \text{M} \), in the presence of various additives at 5 ppm.

<table>
<thead>
<tr>
<th>Additive Name</th>
<th>Rate measured ( \text{mol l}^{-1} \text{min}^{-1} )</th>
<th>Relative Inhibition %</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>( 1.9746 \times 10^{-4} )</td>
<td>-</td>
</tr>
<tr>
<td>AV 142.52.1</td>
<td>( 1.1750 \times 10^{-4} )</td>
<td>40.49</td>
</tr>
<tr>
<td>AP 28.52.1</td>
<td>( 8.6200 \times 10^{-5} )</td>
<td>56.44</td>
</tr>
<tr>
<td>ATP 6.2</td>
<td>( 4.5200 \times 10^{-5} )</td>
<td>77.11</td>
</tr>
<tr>
<td>Solamine</td>
<td>( 2.1450 \times 10^{-4} )</td>
<td>-8.62</td>
</tr>
<tr>
<td>Aquaprox MMC 7300</td>
<td>( 1.1130 \times 10^{-4} )</td>
<td>43.63</td>
</tr>
</tbody>
</table>

As may be seen, all additives except for Solamine\textsuperscript{®}, show significant inhibition effect on the spontaneous precipitation of iron sulfide at 80 °C. ATP 6.2 which showed good inhibiting properties at on-site experiments, proved also to be the most effective compound in the in vitro experiments. It should be noted however that the concentration level of 5 ppm that the compounds were used, refers to the functional group of the additives prepared by BBPDICM, while for the two commercial additives applies to the gross mass of the compound. This is because for the latter we cannot have any information about their composition or the active substances they comprise as they are patent protected.

Investigation of additives as Calcium Carbonate scale inhibitors

In the seeded growth experiments without additive (blank), precipitation started immediately after the addition of seed crystals. In the presence of polymeric additives at concentrations lower than 0.3 ppm the precipitation process proceeded without any inhibition. At concentrations greater than 0.3 ppm no precipitation was observed except in the presence of AS 11.2. On the contrary, AS 11.2 was found to inhibit completely the precipitation at concentration of 3ppm. The inhibition probably was due to the blocking of the active growth sites of the seed crystals by the copolymer molecules. Most probably, the responsible group in the copolymer molecule for the adsorption and blocking processes are the carboxylate groups. The presence of other groups in the copolymer molecules may alter the degree of adsorption. The behaviour of AS 11.2 was probably due to the more hydrophobic character of styrene groups in comparison with other groups contained in the tested additives. A similar behaviour was found in previous experiments for the spontaneous precipitation of calcium carbonate as described in our last report. The only phase forming in all experiments was calcite, as identified by x-ray analysis. The percentage of inhibition as a function of additive concentration for the tested additives is presented in Table 4.
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More specifically the percentage inhibition of AP 28.2 is graphically represented versus AP 28.2 concentration in Fig. 4, where $R_i$ and $R_o$ are the precipitation rates in the presence of inhibitor and in the absence of inhibitor respectively. The percentage inhibition was found to have a linear dependence on AP 28.2 concentration. The kinetic analysis showed that the absorption of AP 28.2 on the surface of calcite crystals follows the Langmuir model. This analysis is shown in Fig. 5, where the term $R_o / (R_o - R_i)$ is represented versus $1/C$ where $C$ is the AP 28.2 concentration (ppm). The ordinate was found lower than 1. This value suggested complete inhibition at concentrations below the concentration corresponding to complete coverage of crystal surface with a monolayer of additive molecules. The same behaviour has been quoted in the literature for the organophosphorus compounds tested in this report, for many salts of alkaline earth metals.

Table 4 - Inhibition percentage versus additive concentration for tested additives.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration of Additive /ppm</th>
<th>Relative Inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP 28.52.1</td>
<td>0.10</td>
<td>44.0</td>
</tr>
<tr>
<td>AP 28.52.1</td>
<td>0.15</td>
<td>62.6</td>
</tr>
<tr>
<td>AP 28.52.1</td>
<td>0.20</td>
<td>91.8</td>
</tr>
<tr>
<td>AP 28.52.1</td>
<td>0.25</td>
<td>100</td>
</tr>
<tr>
<td>AS 11.2</td>
<td>0.05</td>
<td>13.8</td>
</tr>
<tr>
<td>AS 11.2</td>
<td>0.10</td>
<td>55.0</td>
</tr>
<tr>
<td>AS 11.2</td>
<td>0.20</td>
<td>86.0</td>
</tr>
<tr>
<td>AS 11.2</td>
<td>3.00</td>
<td>100</td>
</tr>
<tr>
<td>AP 28.2</td>
<td>0.05</td>
<td>7.20</td>
</tr>
<tr>
<td>AP 28.2</td>
<td>0.10</td>
<td>42.2</td>
</tr>
<tr>
<td>AP 28.2</td>
<td>0.15</td>
<td>54.2</td>
</tr>
<tr>
<td>AP 28.2</td>
<td>0.20</td>
<td>83.4</td>
</tr>
<tr>
<td>AP 28.2</td>
<td>0.25</td>
<td>100</td>
</tr>
<tr>
<td>AV 142.1</td>
<td>0.01</td>
<td>14.7</td>
</tr>
<tr>
<td>AV 142.1</td>
<td>0.05</td>
<td>41.3</td>
</tr>
<tr>
<td>AV 142.1</td>
<td>0.10</td>
<td>78.3</td>
</tr>
<tr>
<td>AV 142.1</td>
<td>0.20</td>
<td>100</td>
</tr>
<tr>
<td>Solamine 129</td>
<td>1.00</td>
<td>60</td>
</tr>
<tr>
<td>Solamine 129</td>
<td>2.50</td>
<td>58</td>
</tr>
<tr>
<td>Solamine 129</td>
<td>5.00</td>
<td>58</td>
</tr>
<tr>
<td>Solamine 129</td>
<td>10.00</td>
<td>60</td>
</tr>
<tr>
<td>Norust 491</td>
<td>5.00</td>
<td>0</td>
</tr>
<tr>
<td>Aquaprox MDC 1300</td>
<td>0.50</td>
<td>100</td>
</tr>
<tr>
<td>Aquaprox MDC 1300</td>
<td>1.00</td>
<td>100</td>
</tr>
<tr>
<td>Aquaprox MDC 1300</td>
<td>5.00</td>
<td>100</td>
</tr>
</tbody>
</table>
Control of corrosion and scaling in geothermal systems

Figure 4 - Percentage of AP 28.2 inhibition versus its concentration in seeded growth experiments for Calcium Carbonate system at constant composition conditions.

Figure 5 - Kinetic Analysis for AP 28.2 - Kinetic Langmuir Isotherm.
A different behaviour was observed for the commercial corrosion inhibitors. In the presence of Norust 491® no inhibition was measured. The precipitation rate was the same as in the blank experiment. The concentration of Norust 491® is equal to the concentration used for the treatment of geothermal wells (5 ppm). On the contrary, in all experiments with Aquaprox MDC 1300®, complete inhibition was found at concentrations lower than those usually used in geothermal wells. In the experiments with Solamine 125® the inhibition was rather strong (~60%) even at concentration levels twice that used in the treatment of geothermal wells. This was probably due to the partial blocking of the crystal growth active sites. Further analysis of the exact inhibition mechanism of the commercial corrosion inhibitors cannot be done because their chemical composition is a commercial secret.

**Electrochemical measurements**

Measurements of the open circuit potential (OCP) in the presence of Picric Acid, p-Hydroxybenzoic Acid and Sodium Benzonate in non-aerated sodium chloride aqueous solutions showed that the OCP is shifted to more negative values (in almost all cases) in comparison with the OCP measured in the absence of additives. The potentiodynamic curves in the presence of the previously reported compounds are almost similar (slightly lower current in the anodic branch of the potentiodynamic curve) to the potentiodynamic curve in the absence of additive. The potentiodynamic scans after the lapse of 18h in the presence and in the absence of 5ppm picric acid are shown in Figure 6. We tested these compounds because substituted aromatic compounds have been reported as corrosion inhibitors in the literature (Corrosion Inhibitors, Nathan C.C., ed. NACE, 1973, p.20).

![Polarization curves](image-url)

Figure 6 - Polarization curves (shifted to the same OCP) for carbon steel specimens in the presence of 5 ppm Picric Acid and in the absence of it in 0.1 M NaCl, pH = 6.5 and 25 °C.
Measurements of the open circuit potential in the presence of commercial additives Solamine 129®, Norust 491® and Aquaprox MDC1300® in deaerated sodium chloride solutions showed that the OCP is shifted to more positive values for Norust 491 (~ 40 mV) and Solamine 129 (~ 10 mV) and slightly more negative values for Aquaprox MDC 1300 (~ -5 mV) in comparison with the OCP measured in the absence of additives after the lapse of 18 h of specimen immersion in the aqueous media. The variation of OCP vs. time in the presence of 5 ppm of each additive and in their absence respectively is shown in Fig.7. In the presence of 10 ppm of commercial additives all of OCP shifts were found positive and larger in comparison with the respective OCP at 5 ppm. This shift of OCP to more positive values in the presence of additives in comparison with OCP measured in the blank experiments suggested increased protection of the specimen in this aqueous environment but this is not adequate proof for the effectiveness of the additive as reported in our previous semiannual report. A more reliable criterion for the effectiveness of an additive as corrosion inhibitor is the measurement of the polarization resistance. The polarization resistance is related directly with corrosion current and consequently with the corrosion rate.

![Figure 7](image)

**Figure 7** - Open Circuit Potential (OCP) evolution with time for a carbon steel specimen in the presence and in the absence of commercial additives in 0.1 M NaCl, pH = 6.5 and 25 °C.

The specimen surface after the lapse of 18h in the presence of commercial additives did not show any graphitization or other solid formation but it stayed clear as it was after polishing. In the absence of commercial additives and in the presence of all other examined compounds graphitization appeared in various degrees (whole or partial coverage of specimen surface).
As shown in table 5, the polarization resistance measured for the commercial additives over the entire concentration range was larger in comparison with the polarization resistance in their absence. This was verified in the potentiodynamic plots where the currents measured and the current at OCP in the presence of additives were lower in comparison with the measured currents in the absence of them. The anodic branch of the potentiodynamic curves in the presence of additives had a slightly larger Tafel slope in comparison with their absence except for the 5 ppm concentration of Solamine 129®. The polarization curves of carbon steel specimen in the presence of 5ppm commercial additives and the polarization curve in the absence of additives are presented in Fig. 8. The polarization curves in the presence of various concentrations of commercial additives and in their absence are shown in Figures 9, 10 and 11 respectively.

Table 5 - Anodic Tafel slope ($B_a$), Cathodic Tafel slope ($B_c$), Corrosion Current ($i_{corr}$) and Polarization Resistance ($R_p$) at Open circuit potential calculated from the potentiodynamic curves (Log(I) vs. Overpotential) in the absence and in the presence of commercial corrosion inhibitors.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration (ppm)</th>
<th>$B_a$ / mV</th>
<th>$B_c$ / mV</th>
<th>$i_{corr}$ /μA</th>
<th>Polarization Resistance/Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>83</td>
<td>285.0</td>
<td>17.9</td>
<td>1106</td>
</tr>
<tr>
<td>Solamine</td>
<td>2</td>
<td>84.8</td>
<td>156.0</td>
<td>8.2</td>
<td>2326</td>
</tr>
<tr>
<td>Solamine</td>
<td>5</td>
<td>49.0</td>
<td>171.0</td>
<td>3.5</td>
<td>5433</td>
</tr>
<tr>
<td>Solamine</td>
<td>10</td>
<td>87.0</td>
<td>117.3</td>
<td>10.2</td>
<td>2038</td>
</tr>
<tr>
<td>Norust</td>
<td>2</td>
<td>112</td>
<td>134.2</td>
<td>7.1</td>
<td>3348</td>
</tr>
<tr>
<td>Norust</td>
<td>5</td>
<td>88.7</td>
<td>207.9</td>
<td>11.5</td>
<td>2050</td>
</tr>
<tr>
<td>Norust</td>
<td>10</td>
<td>100</td>
<td>157.0</td>
<td>7.1</td>
<td>2827</td>
</tr>
<tr>
<td>Aquaprox</td>
<td>2</td>
<td>98.6</td>
<td>130.4</td>
<td>10.7</td>
<td>1934</td>
</tr>
<tr>
<td>Aquaprox</td>
<td>5</td>
<td>97.2</td>
<td>158.0</td>
<td>10.2</td>
<td>2356</td>
</tr>
<tr>
<td>Aquaprox</td>
<td>10</td>
<td>107</td>
<td>135.0</td>
<td>8.8</td>
<td>2520</td>
</tr>
</tbody>
</table>

In Figure 12, the variation of the polarization resistance with time in the presence of commercial additives at concentration of 5 ppm and the variation of polarization resistance with time in the absence of additives are shown. The polarization resistance in the presence of commercial additives was found to be larger than in their absence for the duration of measurements. More specifically, Solamine 129® yielded the higher polarization resistance in comparison with the other two additives. Initially, the polarization resistance showed a sharp increase while later on it showed a tendency to level off. The polarization resistance of Aquaprox MDC 1300 increased slowly with time during the course of the measurements. On the contrary, the polarization resistance in the presence of Norust 491® remained almost constant over this time period.
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Figure 8 - Polarization curves (shifted to the same OCP) for carbon steel specimens in the presence and in the absence of commercial additives in 0.1 M NaCl, pH = 6.5 and 25 °C.

Figure 9 - Polarization curves (shifted to the same OCP) for carbon steel specimens in the presence and in the absence of various concentrations of AQUAPROX MDC 1300 in 0.1 M NaCl, pH = 6.5 and 25°C.
Figure 10 - Polarization curves (shifted to the same OCP) for carbon steel specimens in the presence and in the absence of various conditions of SOLAMINE 129 in 0.1 M NaCl, pH = 6.5 and 25°C.

Figure 11 - Polarization curves (shifted to the same OCP) for carbon steel specimens in the presence and in the absence of various conditions of NORUST 491 in 0.1 M NaCl, pH = 6.5 and 25°C.
In Figure 13, the variation of polarization resistance of carbon steel in the presence of various concentrations of Solamine 129 and in the absence of Solamine 129 with time is presented. The polarization resistance increased with the Solamine 129 concentration, from 2 to 5 ppm but remained almost stable from 5 to 10 ppm after the lapse 10 h of specimen immersion into the inhibitor containing medium. This was probably due to the absorption kinetics of Solamine 129 on the specimen surface. The exact adsorption mechanism of Solamine 129 is not known.

Finally, in the presence of ENTMP and NTMP over a wide concentration range ($10^{-5}$ to $10^{3}$ M) the polarization resistance of carbon steel was found lower than the polarization resistance measured in the absence of these compounds. Increasing ENTMP and NTMP concentrations above $2\times10^{-4}$ M the polarization resistance of carbon steel decreased. This was probably due to the formation of complexes between iron and phosphonate ions. Similar effect was observed for HEDP as reported in the literature (Kalman E. et al in J. Electrochem. Soc., Vol. 141(12), 1994, 3357). Also, for concentrations lower than $2\times10^{-4}$M the polarization resistance of carbon steel decreased. This was probably due to the formation of complexes between iron and phosphonate ions. Similar effect was observed for HEDP as reported in the literature (Kalman E. et al in J. Electrochem. Soc., Vol. 141(12), 1994, 3357). Also, for concentrations lower than $2\times10^{-4}$ M the OCP was more positive than OCP measured in the absence of these compounds. If the concentration exceeded this value, the OCP shifted to more negative values in comparison with OCP measured in their absence. In the presence of Sulfide ions the polarization resistance was also lower. The same behaviour of ENTMP and NTMP was found in the A.C. Impedance measurements.

Figure 12 - Polarization resistance vs. Time for corrosion of carbon steel in the presence and in the absence of commercial additives (at condition: 5 ppm) in 0.1 M NaCl, pH = 6.5 and 25°C.
CONCLUSIONS

From the experimental results presented above the following may be concluded:

1. The iron sulfide precipitating at pH 6.5, 25°C and I = 0.4 M in aqueous supersaturated solutions is amorphous FeS. The apparent rate order found for the kinetics of formation was equal to 3 suggesting a surface controlled mechanism.

2. Pyrite formation at high temperatures was achieved through refluxing of amorphous FeS suspensions under various conditions of acidity and ionic strength. Amorphous FeS particles transform gradually to spherical pyrite particles.

3. The additives tested were found to be from moderately to highly effective on the lowering of the iron sulfide precipitation velocity at 80°C at a concentration level of 5 ppm. No additive was capable of completely impeding iron sulfide formation under these conditions.

4. Polymeric additives, derivatives of maleic anhydride showed very good behaviour in most cases as scale inhibitors in the calcium carbonate system. Reduction up to 100 % in the crystallization rates were obtained.

5. From the examined additives for corrosion inhibition only the commercial products showed a satisfactory behaviour. Solamine 129 showed the best behaviour in sodium chloride aqueous media. All the other additives tested either they did not affect the corrosion of carbon steel, or they enhanced the corrosion process.
THE STUDY OF THE GEOThERMAL WATER CORROSIVENESS WITH MOLYeLECTROLYTE ADDITION: COPOLYMERS OF MALEIC ACID AND N-VINILPIROLIDINA WITH PIPERAZINE AND ITS DERIVATES

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I.C.P.E. SA, Electrochemical technologies and active anticorrosive protections laboratory, Splaiul Unirii no. 315, sector 3 - Bucharest, Romania

SUMMARY

It is known the control method with corrosion inhibitor addition in electrolystables mediums. These inhibitors have efficiency only if they are added quantitatively and qualitatively accordingly.

Also it is known the quality of some polyelectrolyte to diminish - control the scale formation - a specific phenomena at the metal geothermal water interface.

In this paper, it were investigated from corrosion point of view three polyelectrolytes: copolymers of maleic acid and N-vinilpirolidone with piperazine and its derivatives synthesized at "Petru Poni" Institute of Macromolecular Chemistry by A. Carpov and co., polyelectrolytes with known antiscalling effect.

From our experimental determination, based on the draw of the polarization curves with a slow scan rate (0.5 mV/s) and also on the impedance analysis (alternative current polarography) its results that in synthetic geothermal waters the electrolytes act only about on the partial cathodic process, respectively remove E0 to more negative values and reduce -brake the cathodic reaction (reducing ik) a more pronounced effect having polyelectrolyte APP-1. The polyelectrolyte APAEP-1 brakes the anodic reaction and also the cathodic one with a displacement of E0 to more positive values and reduces the corrosion currents over four times to a concentration of 14 ppm.

1. INTRODUCTION

The control of corrosion and scaling in the geothermal systems has a great practice and economical importance. Because of the special water of the geothermal electrolyte the geothermal water systems represent a complex theoretic problem.

The technical-economic optimization of this control suppose a continuous dosing - with automatic control in close-loop, of inhibitors (1) and (2), eventually with cumulative effect corrosion and scaling.
1.1. General context

The inhibitor effect of corrosion for polyelectrolytes based on maleic acid, respectively the salts of Na, k, Zn, were studied in our papers (4).

Also, polyelectrolytes of maleic acid respectively salts with triethanolamine were studied through polarization method (13).

1.2. Purpose

This paper has to study through impedance analysis method as so as the steady state polarization curves method too, of the inhibition effect for carbon steel R 37 in synthetic geothermal water in addition with the copolymers of maleic acid and N-Vinilpiolidone with piperazine and its derivates.

2. SHORT THEORY

The study of the corrosion phenomenology through the classic method of the steady state polarization curves is very common, well known and much applied.

Also it is known the fact that though of this method results the kinetic global parameters \( J_0, b_A, b_K, E_0 \) of the corrosion reaction, the method gives not any information with regard to the process which take place in the vicinity of the corrosion potential \( E_0 \), information which in the presence of the corrosion inhibitor can be decisive and it helps to take a correct decision to select them.

2.1. The equivalent circuit of the electrochemical cell

In the case of the simple processes when the diffusive process and especially the formation of isolated films are neglected it is shown in fig.1. For diffusive processes the equivalent electric scheme becomes as it is shown in Fig. 2 in which the Warburg impedance characterize the diffusive process.

2.2. The principle of the impedance analysis method

This method requires to overlap, over a electrochemical cell potentiostatically controlled at \( E_0 \) value, a low amplitude signal with variable frequency, recording in time the response in current of the system.

The method introduced in electrochemistry by Epelboin (6), is new, modern and much used in the last years.

Processing the very vast references in the field (for example: 5-17) was made the table 1 which contains the correlation between the kinetic parameters \( (b_A, b_K \) and \( J_{on} \)), and the resistance of the pure charge transfer \( (R_{ds}) \) for different mechanisms, partially anodics and cathodies.
3. EXPERIMENTAL SET- UP

To determine the inhibition effect of corrosion and also of the action mechanism for some addition of polyelectrolytes in synthetic geothermal water, have been drawn the steady state polarization curves (\(\log I = f(E)\)).

Also, the kinetic of the corrosion and the mechanism of electrochemical were studied through the method of electrochemical spectroscopy in alternative current - impedance analysis.

The synthetic geothermal water was prepared in the laboratory and its composition is:

\[
\begin{align*}
\text{MgSO}_4 &: 0.088; \\
\text{CaSO}_4 &: 0.563; \\
\text{CaCl}_2 &: 0.362; \\
\text{NaCl} &: 10.440 \text{ and NaHCO}_3 &: 2.302 \text{ [in g/l]},
\end{align*}
\]

respectively:

\[
\begin{align*}
\text{Na}^+: 4.740; \\
\text{Ca}^{2+}: 0.147; \\
\text{Mg}^{2+}: 0.018; \\
\text{Cl}^-: 6.567; \\
\text{SO}_{4}^{2-}: 0.111 \text{ and HCO}_3^-: 1.671 \text{ [m g/l]}. 
\end{align*}
\]

The observation were obtained at a temperature of 60±1°C with a thermostat type MLW (with oil). As reference electrode was utilized an SCE the working electrode has been done of carbon steel R37 with a total surface of 17 cm², and the secondary electrodes of spectral graphite (200 cm²).

The potentiostatically determinations were done with a potentiostat type SYCOPEL SCIENTIFIC - "SCANNING MINISTAT" the output signal - current - was processed through a logarithmic electronic amplifier described in (8). The records was achieved with a recorder X-Y, type ENDIM 620.02. The scheme was presented in Fig. 3.

The scanning was made in the range (-1.1 - -0.5) V_{SCE} with scan rate of 0.5 mV/s. Thus, the polarization curves specifically for the interface carbon steel R37 / synthetic geothermal water with and without three types of polyelectrolytes - copolymers of maleic acid and N-vinilpirolidone with piperazine and its derivates, have been drawn in the range of concentration 1-14 ppm.

The determination through electrochemical spectroscopy in alternative current impedance analyze were achieved on the electrochemical cell described above with a specialized equipment SYCOPEL SCIENTIFIC -type TFA 2000 A- connected to a computer (PC) and using the proper software the signal in a.c. overlap was of 10 mV peak to peak.

The frequency range was 1 kHz - 0.01 Hz. The recording and graphic processing of the obtained values were done utilizing a computer. The data was pick up at 1 hour after the addition of inhibitor.

4. RESULTS AND DISCUSSIONS

The steady state polarization curves for the three types of polyelectrolytes are presented in Fig. 4, 5 and 6. Comparing the three families of curves the result is that the polyelectrolytes APP-1 and APHEP-1 (Fig. 4 and 5) have the same behaviour, respectively the addition of them break only the cathodic process (APP-1 more pronouncing).
By Fig. 6. results that the polyelectrolyte APEP-1 reduce the rate of the cathodic process and especially the anodic one, giving a slowly movement to a more positive value of EO. It can be explained this behaviour through the fact that the polyelectrolyte APEP-1 has a lateral aminic group by comparison With APP-1 and APHEP-1 polyelectrolytes.

It is interesting to compare the data obtained on the potentiostatic way (Fig. 4, 5 and 6) of the data obtained through the method of electrochemical polarography in a.c.. Thus, for the three polyelectrolytes added in 1,5 and 14 ppm concentration, the Nyquist diagrams \( Z_r = f(Z_f) \) are presented in Fig. 7, 8 and 9. From Nyquist diagrams analyses it results that electrolyte resistance (geothermal water at 60°C) is about 20-25 \( \Omega \)cm\(^2\)and the corrosion process of carbon steel R 37 is a pure kinetically one (pure charge transfer - the slope of the line at low frequencies is about n/4 rad. it means 45°) and the polarization resistance is 250 \( \Omega \)cm\(^2\) (Rp).

After addition polyelectrolytes it can be observed that the concentration of very small for them (1 ppm) in the zone of small frequencies (<10 Hz) these produce an increasing of the capacitance and implicitly the increasing of impedance and polarization resistance. It is interesting to notice that in the range of the studied concentrations (1-14 ppm) the kinetic process (pure charge transfer) is decisive. The rate of pure charge transfer did not change when the concentration of the polyelectrolytes is increasing. Through this method, too it can be distinguished the diverse behaviour of APAEP-1 even for small concentration. It almost produces the doubling of the value of polarization resistance and to the maximum concentration (14 ppm) the increasing of polarization is almost 4 times.

All these results are in concordance with those obtained by Mr. I. Ignatidis (19) on divers types of commercial inhibitors.

The evolution of the polarization impedances is presented in Fig. 10, 11 and 12. The obtained values are in respect with the data previously presented. By comparison of these data it result that the polyelectrolytes - the copolymers of maleic acid, vinilpirolidone with piperazine and its derivates are inhibitors of corrosion. They act by reducing the rate of pure charge transfer in anodic processes and also cathodics, in the presence of lateral aminic groups, and only cathodics in the absences of these groups. It can be distinguished the big efficiency of these inhibitors even at 1 ppm, efficiency which is felt very fast (about 1 hour after the application of the inhibitor).

5. CONCLUSIONS

The inhibition of corrosion effect was tested for carbon steel R 37 in synthetic geothermal water at temperature of 60 ± 1°C with some polyelectrolytes - copolymers of maleic acid, N-vinilpirolidone with piperazine and its derivates, synthesized at "Petru Poni" Institute from Iasi.

The tests were realized through the methods of steady state polarization curves and impedance spectroscopy in a.c. - impedance analyses.
By analyzing the data it results that:

- the polyelectrolytes copolymers of maleic acid and N-vinilpirolidone with piperazine and its derivates, are joint inhibitors respectively they reduce the rate of pure charge transfer for anodic and cathodic reaction if their structures have lateral aminic groups;

- in absence of lateral aminic groups polyelectrolytes reduce the rate of pure charge transfer only for the cathodic reaction;

- the tested electrolytes have a fast effect, so only 1 hour after the addition of inhibitors the corrosion rate is reduced about 2 to 4 times;

- maximum inhibitions effect is achieved with the polyelectrolyte APAEP-1 which has a lateral aminic group and it has a combined action (cathodic and anodic).

6. REFERENCES

1) **LINGVAY I., CHEFNEUX M., STANCIU V. (1995); "Study of Monitoring Possibility of Corrosion or/and Scaling Rate in Geothermal Systems", in EEC-DGXII - JOU2-CT92-0108 - 6th periodic report, 275-292.**


Table 1 - Theoretical relations between the corrosion current, pure charge transfer resistance and polarization resistance for different anodic and cathodic kinetics

<table>
<thead>
<tr>
<th>Kinetic control of anodic reactions</th>
<th>Kinetic control of cathodic reaction</th>
<th>The relation between corrosion current I_{cor} and polarization resistance R_{p}</th>
<th>The relation between corrosion current I_{cor} and pure charge transfer resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>One stage, electronic transfer type Tafel</td>
<td>One stage, electronic transfer type Tafel</td>
<td>( b_{d} b_{k} / [2.303 (b_{a} + b_{k}) l_{cor}] )</td>
<td>( b_{d} b_{k} / [2.303 (b_{a} + b_{k}) l_{cor}] )</td>
</tr>
<tr>
<td>One stage, electronic transfer type Tafel</td>
<td>Pure diffusive</td>
<td>( b_{d} / 2.303 l_{cor} )</td>
<td>( b_{d} b_{k} / [2.303 (b_{a} + b_{k}) l_{cor}] )</td>
</tr>
<tr>
<td>One stage, electronic transfer type Tafel</td>
<td>Joint control, partial diffusive</td>
<td>Intricate equations depending on the control of diffusion degree</td>
<td>( b_{d} b_{k} / [2.303 (b_{a} + b_{k}) l_{cor}] )</td>
</tr>
<tr>
<td>na consecutive, irreversible stages type Tafel (b_{hi})</td>
<td>na consecutive, irreversible stages type Tafel (b_{ki})</td>
<td>Intricate equations depending on rate constants</td>
<td>( 1/[2.303 (n_{a} - \sum b_{a-j} + n_{k-j} \sum b_{k-c}) l_{cor}] )</td>
</tr>
<tr>
<td>Passive dissolution</td>
<td>Irreversible transfer type Tafel on the passive surface</td>
<td>( b_{k} / 2.303 l_{cor} )</td>
<td>Intricate equations depending on the dissolution and passivation kinetic</td>
</tr>
</tbody>
</table>

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Figure 1 - Equivalent circuit for a simple corrosion system
RΩ: electrolyte resistance; Rp: polarization resistance; Cd: the capacity of double layer

Figure 2 - Equivalent circuit for a diffusion process.
RTS: pure charge transfer resistance; W: Warburg impedance; Cd: the capacity of double layer; RΩ: electrolyte resistance.
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Figure 3 - Schema of the circuit utilised for polarisation curves plotting
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![Polarization curves](image)

**Figure 4** - Polarization curves of the interface R37 steel/synthetic geothermal water with and without addition of polyelectrolyte type APHEP1. T=60±1°C

<table>
<thead>
<tr>
<th>Condition</th>
<th>$b_A$</th>
<th>$b_K$</th>
<th>$j_0 [A/m^2]$</th>
<th>$E_0 [V_{ESC}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>without</td>
<td>0.11</td>
<td>0.30</td>
<td>0.537</td>
<td>-0.770</td>
</tr>
<tr>
<td>with 5 ppm</td>
<td>0.11</td>
<td>0.28</td>
<td>0.398</td>
<td>-0.785</td>
</tr>
<tr>
<td>with 14 ppm</td>
<td>0.11</td>
<td>0.25</td>
<td>0.301</td>
<td>-0.795</td>
</tr>
</tbody>
</table>
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Figure 5 - Polarization curves to the interface R37 steel/synthetic geothermal water with and without addition of polyelectrolyte type APP1. T=60±1°C.

<table>
<thead>
<tr>
<th>Condition</th>
<th>b_A</th>
<th>b_K</th>
<th>j_0 [A/m²]</th>
<th>E₀ [VESC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>without</td>
<td>0.11</td>
<td>0.30</td>
<td>0.537</td>
<td>-0.770</td>
</tr>
<tr>
<td>with 5 ppm</td>
<td>0.11</td>
<td>0.26</td>
<td>0.331</td>
<td>-0.795</td>
</tr>
<tr>
<td>with 14 ppm</td>
<td>0.11</td>
<td>0.23</td>
<td>0.214</td>
<td>-0.820</td>
</tr>
</tbody>
</table>
Figure 6 - Polarization curves to the interface R37 steel/synthetic geothermal water with and without addition of polyelectrolyte type APAEP1. T=60±1°C.
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Figure 7 - The Nyquist diagrams at one hour after addition of APHEP 1 Inhibitor

Figure 8 - The Nyquist diagrams at one hour after addition of APP 1 Inhibitor
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Figure 9 - The Nyquist diagrams at one hour after addition of APAEP 1 Inhibitor

Figure 10 - The diagrams of polarization impedances at one hour after addition of APP1 inhibitor
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Figure 11 - The diagrams of polarization impedances at one hour after addition of APHEP1 inhibitor.

Figure 12 - The diagrams of polarization impedances at one hour after addition of APAEP1 inhibitor.
THE STUDY OF THE GEOTHERMAL WATER CORROSIVENESS WITH POLYELECTROLYTE ADDITION: COPOLYMERS OF MALEIC ACID WITH AROMATICAL AIMINES

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ICPE S.A., Electrochemical technologies and active anticorrosive protections laboratory, Splaiul Unirii no. 315, sector 3 - BUCHAREST, ROMANIA

SUMMARY

It is known the control method with corrosion inhibitor addition in electrolysables mediums. These inhibitors have efficiency only if they are added quantitatively and qualitatively accordingly.

Also it is known the quality of some polyelectrolyte to diminish - control the scale formation - a specific phenomena at the metal/geothermal water interface.

In this paper it were investigated from corrosion point of view three polyelectrolytes: copolymers of maleic acid and piperazine with aromatical amines synthesized at "Petru Poni" Institute of Macromolecular Chemistry by A.Carpov and co., polyelectrolytes with known antiscalling effect.

From our determinations it results that the more pronouncing effect of inhibition at the temperature of 50°C and also for 80°C is given by polyelectrolyte type SAPOT 1.2 and APOT 1, respectively at one hour after addition (concentration 4 ppm) these are reducing the corrosion of about four times. The results for SAPA 2.2 inhibitor are not so significant - respectively it reduce the corrosion rate of approximative two times (at 4 ppm).

1. INTRODUCTION

The control of corrosion and scaling in the geothermal systems has a great practice and economical importance. Because of the special water of the geothermal electrolyte the geothermal water systems represent a complex theoretic problem.

The technical-economic optimization of this control suppose a continuous dosing with automatic control in close-loop, of inhibitors (1) and (2), eventually with cumulative effect corrosion and scaling.
1.1. General context

The inhibitor effect of corrosion for polyelectrolytes based on maleic acid, respectively the salts of Na, K, Zn, were studied in our papers (4).

Also, polyelectrolytes of maleic acid respectively, salts with triethanolamine were studied through polarization method (3).

The anticorrosive effect of the polyelectrolytes - copolymers of maleic acid with piperazine and its derivate, as studied by un in (20).

1.2. Purpose

This paper has to study through the impedance analysis method as so as the steady state polarization curves method too, of the inhibition effect for carbon steel R 37 in synthetic geothermal water in addition with the copolymers of maleic acid and piperazine with aromatical amines.

2. EXPERIMENTAL SET-UP

The methodology of work, the electrical devices and the chemical substances used for these experiments were presented in (20). The determinations with the polyelectrolytes type SAPOT 1.2, APOT 1 and SAPA2.2 -synthesized at "Petru Poni" Institute, Iasi - ROMANIA, by A. Carpov and co., were tested at 50°C as so as at 80°C, too.

3. RESULTS AND DISCUSSIONS

The steady states polarization curves for different concentrations of the polyelectrolyte type SAPOT 1.1 at 50°C, are presented in fig. 1 and at 80°C in figure 2. From these graphics it results that at 50°C and also at 80°C this product, after one hour, inhibit the corrosion reaction by reducing the rate of the charge transfer-in the anodic stage and also in the catholic one. So at one hour after addition of inhibitor at 4 ppm, \(j_0\) decrease about four times. When the addition is of 14 ppm the behaviour relatively to the temperature is differently. So at 50°C the corrosion rate decrease of 9.5 times and at 80°C of only 7.6 times.

For this copolymer (SAPOT 1.2) the results obtained through the method of electrochemical spectroscopy - impedance analysis are presented in figure 7 (for 50°C) and in figure 8 (for 80°C). The behaviour of the curves from figures 7 and 8 demonstrates the kinetical control (charge transfer) of the corrosion reaction and also indicates that polyelectrolyte is absorbed on the surface, where it creates a capacitive layer having a bad tg \(\delta\). This layer brakes substantially the charge transfer at the interface metal/electrolyte. The Nyquist diagrams presented in figures 8 and 9 also demonstrates the efficiency of this product as inhibitor.
An interesting behaviour it can be observed for the product type APOT 1, which at a temperature of 50°C (fig. 3) and also of 80°C (fig. 4) act by modifying the Tafel slopes-differently of SAPOT 1.2 for which the slopes are the same. In the case of APOT b$_A$ and b$_K$ have a big decreasing-. The relation for the Tafel slope is (1).

(1) \[ b = \frac{RT}{\alpha ZF} \]

in which

- R: the constant of perfect gases;
- T: the temperature [K]
- \( \alpha \): transfer coefficient introduced in Electrochemistry, by Erdey, Gruz and Volmer (21)
- Z: the valence
- F: the constant of Faraday

It can be observed that in the presence of the polyelectrolyte type APOT, \( \alpha \) has a great modifying- so implicitly the isotherm of absorption. The conclusion is that APOT act primarily by modifying the transfer coefficient and secondary by braking the charge transfer. The same conclusion it can be obtained if we analyze the Nyquist diagrams (fig. 9 for 50°C and fig. 10 for 80°C); here it can be observed a great capacitance (absorbed latter) only for low frequencies.

The product type SAPA 2.2 has the same behaviour as APHEP 1 and APP 1 presented in our previously paper (20). It can be ascertained that the inhibition efficacy is a modest one and has only a cathodic effect (see fig.5, 6, 11, 12). But we notice that the cathodic action is determined by the absorption of the product (\( b_k \) is modifying its value)- absorption which is not identified on the anodic part.

We consider that these observation regarding the acting mechanism of the inhibitors (polyelectrolytes) could be important to conceive the molecular formula of its structures. So we consider that the ideal product (inhibitor) must to:
- modify \( b_A \) and \( b_K \) simultaneous (by reducing its as much as possible) APOT 1;
- to brake the charge transfer rate as niuch as possible (SAPOT 1.2; APAEP 1 from (20)).

We hope that these informations will be helpfully for future to conceive the molecular structure of the polyelectrolyes destined for reducing the corrosion.

4. CONCLUSIONS

The inhibition of corrosion effect was tested for carbon steel R37 in synthetic geothermal water at temperature of 50 and 80 ±1°C with some polyelectrolytes-copolymers of maleic acid, piperazine with aromatical amines. The tests were realized through the methods of steady state polarization curves and impedance spectroscopy in a.c. - impedance analyses.

By analyzing the data it results that:
- the product type SAPOT 1.2. presents a high efficiency at 50°C and also at 80°C (at 4 ppm).
  In one hour it reduces the corrosion rate more then four times. The action of this polyelectrolyte consists primarily in the braking of the charge transfer and secondary by modifying the transfer coefficient (21);
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- the product type APOT 1 has also a great efficiency at low temperatures (50°C) at 4 ppm - in one hour it reduced the corrosion rate of 4-5 times and at 14 ppm over ten times at 50°C and over eight times at 80°C. This product act through the modifying of α (21), and the absorption is a few, diminuated at highest temperatures;

- the product type SAPA 2.2 has action only about of the partial cathodic reaction through modifying the coefficient α. The effect of this inhibitor is not an important one (it reduces the corrosion rate only of 1.5-2 times).

Making the correlation between the obtained results for anticorrosive efficiency with the molecular structure - respectively the content in lateral groups of the studied polyelectrolytes, our opinion is that in can be produced polyelectrolytes having a more accentuate efficiency.

5. REFERENCES


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Figure 1 - Polarization curves to the interface R37 steel/synthetic geothermal water with and without addition of polyelectrite type SAPOT 1.2, T=50°C.
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Figure 2 - Polarization curves to the interface R37 steel/synthetic geothermal water with and without addition of polyelectrite type SAPOT 1.2, T=80°C.
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Figure 3 - Polarization curves to the interface R37 steel/synthetic geothermal water with and without addition of polyelectrite type APOT 1, T=50°C.

<table>
<thead>
<tr>
<th>Condition</th>
<th>b_A</th>
<th>b_K</th>
<th>j_0 [A/m²]</th>
<th>E_0 [VESC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>without</td>
<td>0.11</td>
<td>0.30</td>
<td>0.290</td>
<td>-0.705</td>
</tr>
<tr>
<td>with 5 ppm</td>
<td>0.05</td>
<td>0.16</td>
<td>0.058</td>
<td>-0.710</td>
</tr>
<tr>
<td>with 14 ppm</td>
<td>0.05</td>
<td>0.15</td>
<td>0.027</td>
<td>-0.705</td>
</tr>
</tbody>
</table>
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Figure 4 - Polarization curves to the interface R37 steel/synthetic geothermal water with and without addition of polyelectrite type APOT 1, T=80°C.

<table>
<thead>
<tr>
<th>Type</th>
<th>b_A</th>
<th>b_K</th>
<th>j_0 [A/m²]</th>
<th>E_0 [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>without</td>
<td>0.10</td>
<td>0.25</td>
<td>0.705</td>
<td>-0.800</td>
</tr>
<tr>
<td>with 5 ppm</td>
<td>0.05</td>
<td>0.16</td>
<td>0.199</td>
<td>-0.795</td>
</tr>
<tr>
<td>with 14 ppm</td>
<td>0.05</td>
<td>0.15</td>
<td>0.089</td>
<td>-0.800</td>
</tr>
</tbody>
</table>
Figure 5 - Polarization curves to the interface R37 steel/synthetic geothermal water with and without addition of polyelectrite type SAPA 2.2, T=50°C.
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Figure 6 - Polarization curves to the interface R37 steel/synthetic geothermal water with and without addition of polyelectrite type SAPA 2.2, T=50°C.

<table>
<thead>
<tr>
<th>Condition</th>
<th>b_A</th>
<th>b_K</th>
<th>j_f[A/m²]</th>
<th>E_0[V ESC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>without</td>
<td>0.10</td>
<td>0.25</td>
<td>0.705</td>
<td>-0.800</td>
</tr>
<tr>
<td>with 5ppm</td>
<td>0.08</td>
<td>0.19</td>
<td>0.416</td>
<td>-0.810</td>
</tr>
<tr>
<td>with 14ppm</td>
<td>0.08</td>
<td>0.19</td>
<td>0.316</td>
<td>-0.805</td>
</tr>
</tbody>
</table>
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Figure 7 - The Nyquist diagrams at one hour after addition of SAPOT 1.2 inhibitor (T=50°C).

Figure 8 - The Nyquist diagrams at one hour after addition of SAPOT 1.2 inhibitor (T=80°C).
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Figure 9 - The Nyquist diagrams at one hour after addition of APOT 1 inhibitor (T=50°C).

Figure 10 - The Nyquist diagrams at one hour after addition of APOT 1 inhibitor (T=80°C).
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Figure 11 - The Nyquist diagrams at one hour after addition of SAPA 2.2 inhibitor (T=50°C).

Figure 12 - The Nyquist diagrams at one hour after addition of SAPA 2.2 inhibitor (T=80°C).
STUDY OF MONITORING POSSIBILITY OF SCALING RATE IN GEOTHERMAL SYSTEMS

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I.C.P.E. SA, Splaiul Unirii 313, Sector 3, Bucharest, ROMANIA

ABSTRACT

It was studied the possibility of monitoring of the scale deposition through measuring in the installation of the geothermal well No.4159 from ORADEA-ROMANIA. For this aim, it was supervising in time the value of the measured impedance with a special transducer which was concepted for the presence and also the absence of a polyelectrolyte based on maleic acid. From our experiments was resulting that at the studied well, in the presence of the inhibitor, the scale deposition is starting after a germination period of about 10 minutes, and after it increase in time with a speed of roughly $1.10^{-3}$ m/h.

1. GENERAL CONTEXT

In our previous paper (1), it was conceived and realized the model of a multifunctional transducer for simultaneous and in situ monitoring of the corrosion, scaling and of the temperature range in the geothermal systems. For the design and the build of the device, versus the scale deposition, it was considered that due to the low electrical conduction for the scale, in its presence, the electrical impedance of two plane-parallel electrodes it must have a big increasing which is determined by the thickness of the scale deposition.

2. THE AIM OF THE STUDY

The aim of this paper is to define the condition for in situ determination of scaling rate, respectively the testing of the multifunctional transducer achieved by us (1).

3. EXPERIMENTAL TESTS

For the supervision of the impedance cell, which have two plane-parallel electrodes, immersed in geothermal water, it was realized the assembly presented in fig. 1. Thus, it was injected a current, by the current generator of a.c. -100 Hz, between the two electrodes, supervising the voltage (in a.c.) which appears.

The apparatus for current measurement is a multimeter type VOLTCAST-M-3850 (AC-mA). The voltage between the two electrodes was readed on a multimeter type PHILIPS-PM.
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2718/02-rms. The current generator is our conception and it is able to give at its output currents in the range of 1-100 mA with constant amplitude - indifferently of the variation of the cell impedance, obviously in the voltage range of 0-48 V peak to peak. The electrochemical cell was described in (1) and it has two plane-parallel electrodes with the total surface of 2 x 12 cm², distanced at 1.8 cm.

In the first stage, the multifunctional transducer was mounted at the top of the well - but due to the high content of gases - so a pronounced biphasic character - the impedance variations were important and it has been analyzed only the minimal values of the voltage - corresponding to the moments when the electrodes are completely covered with electrolyte.

In the second stage, the transducer was mounted after the vessel of degazation - so it was eliminated the disturbings caused by the biphasic character of the geothermal water. The electrodes were cleaned between the tests. The thickness of the scale deposition was measured with the gauge. The determinations were done with and without addition of polyelectrolyte type PONILIT-GT 1TM (2).

4. RESULTS AND DISCUSSIONS

In figure 1, are presented the values of the obtained impedances \( Z = \Delta U/I \), respectively the evolution in time of its and the resulted thickness of scale deposit.

If we consider the nature of the geothermal water from the studied well, respectively the content of \( \text{HCO}_3^- \) and \( \text{Ca}^{2+} \). It results that the scale deposition has as origin the carbonates. The electrical resistivity of the scale deposit, was calculated from the experimental data and its value is about 120 \( \Omega \)m.

In the case of injection of polyelectrolyte type PONILIT-GT 1TM, having a concentration of 1 ppm, the curve \( Z = f(t) \) shows that at this concentration (fig. 2), the scaling rate is about 10 times smaller. The formation of scale completely disappear when the polyelectrolyte has a concentration of 10 ppm.

5. CONCLUSION

It was experimentally demonstrated the possibility of monitoring the scaling rate by measuring the impedance of some special designed electrodes. It was designed, built and tested the proper device.

From our determination, it results that:
- the formation of scale can be monitored by measuring the impedance using an adequate transducer;
- the signal given by the transducer, in the case of scales of \( \text{CaCO}_3 \) is about 200 \( \Omega \)/mm, so with a not very intricate device it can be detected the variation of scaling of 10-15 \( \mu \)m;
- the resistivity of scale (\( \text{CaCO}_3 \)) resulted from geothermal water of the well No 4159 from ORADEA, ROMANIA is about 120 \( \Omega \)m.

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Considering the ideas presented previously, the conclusion are that the multifunctional transducer described in (1) can give at its output a signal which is substantial sufficient to control an automatic injection system of inhibitor.

6. REFERENCES


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**Figure 1 - Electric scheme**

- 1 - geothermal well
- 2 - parallel electrodes
- 3 - multifunctional transducer
- 4 - current generator (a.c. - 100 Hz)
Figure 2. The impedance cell evolution in time relatively to the thickness of the scale.

Well No. 4109 - ORADEA

T = 98°C

- x - without inhibitor
- o - 1 ppm - PONILIT GT-1 TM
- - 10 ppm - PONILIT GT-1 TM
EQCM STUDY OF IRON CORROSION IN GEOTHERMAL FLUID FROM WEST-LITHUANIA AQUIFERS

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SUMMARY

This report gives the results of iron corrosion investigations in geothermal fluids Vidmantai 1 and Vidmantai 2 obtained by electrochemical quartz crystal microgravimetry (EQCM) measurements. The EQCM data were analysed in terms of oxide layer formation, precipitation of scarcely soluble compounds on the electrode, and iron corrosive dissolution. The investigations in synthesised solutions were conducted as well.

1. INTRODUCTION

The task of our work was a study of iron corrosion in the geothermal fluids Vidmantai 1 and Vidmantai 2 by means of electrochemical quartz crystal microgravimetry (EQCM). This was a last task of our investigations carried out under the Contract.

Since quartz crystal microbalance estimates the changes of electrode mass very sensitively (in nanograms/cm²) the method is a very useful tool for in situ corrosion investigations [1-4]. The method can supply also a significant information about interphase layer formation. In our case this is essential because an interphase layer plays an important part in iron corrosion in geothermal fluids [5].

EQCM technique was widely applied to electrochemical measurements in situ in the last decade. Advantages of the method include such properties as extremely high sensitivity, continuity of information, coupling possibility with other measurements techniques etc. For instance, a large quantity of information may be obtained by coupling EQCM with dc and/or ac voltammetry as well as with spectroscopy.

The EQCM method is based on linear relationships between changes in quartz oscillation frequencies (Δf) and a mass change (Δm). According to [6] a relationship between the above parameters is

\[
\Delta f = \frac{2\Delta mf^2}{A(\mu q)^{1/2}},
\]

(1)
where \( n \) is the order of the oscillation harmonic, \( A \) the geometric area of the active surface, \( \rho q \) the density of quartz, and \( \mu q \) its shear modulus. A theoretical proportional coefficient between the frequency and the mass is approximately equal to 18 ng Hz\(^{-1}\) cm\(^{-2}\) when the main resonance frequency is 5 MHz.

### 2. MATERIALS AND METHODS

Quartz discs were used, their fundamental frequency being \( f_0 = 5 \) and 6 MHz, and \( r = 15 \) mm (produced by *Quarzverarbeitung, Neckarbischofsheim*, Germany and by *Intellometrics Ltd, Clydebank G 81 2 LA, UK*). Both quartz sides were plated with gold 200 nm thick using the standard vacuum thermal evaporation technique (*Edward's Coating*). To improve adhesion a chromium sublayer 5 nm thick was evaporated on quartz surfaces. To improve the compactness of the layer a 1\( \mu \)m gold coating was deposited from a cyanide gold plating bath. The iron was plated on the above gold coating using plasma-coating equipment *Alcatel SCM 850* (France). The coating procedure was the subject of our investigations in the sixth semester and the results were in details presented in the Sixth Periodic Report [7].

A special electrochemical cell was designed for EQCM measurements. It is possible to mount the crystals on the side of the glass cell thus enabling the solution to be changed without disturbing the crystal. The EQCM device was constructed according to the CAMAC standard (IEEE 583) which allowed the frequency to be measured at 0.01 s intervals (resolution of 0.1 Hz) and the results to be stored on a PC. The 4.9152 MHz quartz was used as a reference in the oscillating circuit.

### 3. RESULTS AND DISCUSSION

EQCM data obtained in the geothermal fluids *Vidmantai 1* and *Vidmantai 2* are depicted in figures 1 an 2. The investigations were conducted in both naturally aerated and deaerated solutions. The measurements in CO\(_2\) saturated fluids were carried out as well. The curves represent oscillation frequency change in the course of corrosion. Frequency data can be easily transformed into mass values (eq. 1) taking into account the factor of proportionality \( C = 18 \text{ ng Hz}^{-1}\text{ cm}^{-2}\) [6]. In principle, frequency increase means mass decrease.

The data obtained show that electrode mass growth is preferential in the first stages of corrosion. The effect can be attributed to significant surface blocking by corrosion products. The interphase layer should be sufficient compact otherwise it could not affect a quartz oscillation frequency. The mass gain stops after a certain time and a further mass decrease is observed. This is indicative that the interphase layer reaches its maximal thick and further mass lost is preferential occurring as a result of the corrosive iron dissolution. The mass of the layer developed in the naturally aerated geothermal fluid *Vidmantai 1* can be estimated by \( m = 18 \text{ ng Hz}^{-1}\text{ cm}^{-2} \times 360 \text{ Hz} = 6.48 \times 10^{-6} \text{ g/cm}^2\).

The most thick layer is observed in the naturally aerated solution. The layer developed in the CO\(_2\) saturated fluid is significant thinner. Thus, it is obvious that dissolved oxygen favours the oxide/hydroxide layer formation. Reduction of dissolved oxygen in the aerated solution may proceed according reactions:
Both of reactions cause a pH increase in the vicinity of electrode. This may favour a precipitation of scarcely soluble compounds on the iron surface.

Corrosion current densities may be calculated on the basis of frequency data using the ratio [2]:

\[
jc = \left( zF \frac{C}{M} \right) \frac{df}{di}
\]  

(3)

where \( z \) is the number of electrons, \( F \) the Faraday constant, and \( M \) the molar mass of the corrosion product. This ratio gives accurate results when corrosive dissolution of metals proceed without an accumulation of scarcely soluble compounds on the electrode surface.

For instance, corrosion currents of cadmium in an acid media were determined according to the above ratio in [2]. Under our conditions, the accumulation mentioned takes place. Thus, to obtain exact values of corrosion rate the chemical composition of the surface layer must be well defined.

The conclusions about chemical composition of surface layer on iron are unequivocal. It was concluded that passivation layer on iron is formed mainly from \( \text{Fe}_2\text{O}_3 \) [8]. Authors of [9-13] supposed presence of \( \text{Fe}_3\text{O}_4 \) in the interface zone "iron/oxide" however this compound has been not found during the ellipsometrical investigations [14]. The authors of [15] use the formula \( \text{Fe}_{2.67}\text{O}_4 \) discussing the phenomenon of passivity of iron in acid solutions. Presence of \( \text{Fe} \text{(OH)}_2 \) can be supposed as well. Certainly, in our conditions the passivation layer can be even more complex because the solution contains a great amount of various salts.

The initial slope of the curve in aerated fluid Vidmantai 1 is \( \frac{df}{dt} = -0.22 \) Hz/s. The value of \( jc = 0.96 \text{ mA cm}^{-2} \) was obtained according to the ratio (1) presuming \( \text{Fe}_2\text{O}_3 \) a main corrosion product on the surface. The analogous values for \( \text{Fe}_3\text{O}_4 \) and \( \text{Fe} \text{(OH)}_2 \) are \( j_c = 0.99 \) and \( j_c = 0.85 \text{ mA cm}^{-2} \), respectively. The real corrosion rate should be even higher because some iron transfer into solution should occurs and it must be accounted. (To be exact, a dissolution of the interphase layer must be accounted as well; however this aspect can be neglected in a rough estimations).

It should be emphasised that above calculated values of \( jc \) for the system under study are extremely high. For instance, the corrosion current densities determined in the fluid Vidmantai 1 by polarisations resistance method after 15 min immersion was much lower ( \( 0.08 \text{ mA cm}^{-2} \) ) [15]. Three main reasons can be presumed to explain such a difference:

i) a pH increase in the vicinity of electrode occurs because of hydrogen and oxygen reduction and it favours a precipitation of solution components on the electrode in the form of scarcely soluble compounds;

ii) initial electrode activity is high and it decreases in the course of corrosion; iii) a depletion layer with pH gradient is thinner at the first stages, consequently, reduction rate of depolarisers is much higher. The first hypothesis corresponds well with the results of oxide layer investigations by x-ray photoelectron spectroscopy etching surface with ionised argon [5]. Calcium, magnesium, iodine, and nitrogen were found in the surface layer by this mean.
It was concluded in [15] that corrosion process is inhibited in a synthesised solution which contain such a high concentration of chloride like the real geothermal fluid, i.e. 100 g/l. The same conclusion can be made in the current work on the basis of EQCM data (Fig. 3). The initial electrode mass growth in the NaCl solution is suppressed comparing it with the chloride-free solution. Therefore, the oxide layer in chloride-free solution should be thicker. Despite this the rate of mass decrease (the corrosion rate) in chloride-free solution is higher.

The initial slope of the curve in chloride free solution (Fig. 3) is high as well ($df/dt = 11$ Hz/s). According the above calculations this value corresponds to an extremely high corrosion current density. This can be explained in terms of high electrode activity as well as high reduction rate of depolariser. The hypothesis of precipitation of solution components is not true in this case because the solution does not contains the components which are able to precipitate.

4. CONCLUSIONS

1. An electrode mass growth occurs in the first stages of iron corrosion in geothermal fluids Vidmantai 1 and Vidmantai 2. The effect was attributed to surface blocking by scarcely soluble compounds. The interphase layer should be sufficient compact otherwise it could not affect a quartz oscillation frequency.

2. The solution oxygen favours an oxide/hydroxide layer formation on the interface. CO$_2$ has an inhibiting effect on the layer formation.

3. The mass gain rate at the initial stages of corrosion is extremely high. This indicates the high corrosion rate. Three main reasons can be presumed to explain such a result:
   i) an high initial electrode activity;
   ii) a thin depletion layer with pH gradient at the first stages, consequently, high reduction rate of depolarisers;
   iii) a precipitation of solution components simultaneously with corrosion products precipitation;

4. The oxide layer developed in the first stages of corrosion in the synthesised solution containing 100 g/l NaCl is more thin comparing with the chloride-free solution. Despite this, the corrosion rate in the chloride-free solution is higher.
5. REFERENCES


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Fig. 1 - Frequency change vs time for iron electrode immersed in geothermal fluid Vidmantai1.

Fig. 2 - Frequency change vs time for iron electrode immersed in geothermal fluid Vidmantai2.
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Fig. 3 - Frequency change vs time for iron electrode immersed in H$_2$SO$_4$ (pH 3) and when added 10 and 100 g/l NaCl.  

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STEAM WASHING IN THE WELL

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1 Introduction

In high enthalpy geothermal power plants a steam washing operation is usually performed to eliminate acid compounds, particularly HCl. Usually this is done by injecting a cold NaOH solution 0.2 - 0.3 N directly into the transportation line in order to neutralize the acidity of the condensate before the turbine.

Injecting the alkaline solution at the bottom of the well could turn in the twofold advantage of protecting from corrosion both the well and the transportation pipe. In this situation, and under a broad range of operational conditions, annular flow regime is established in the well. The washing solution (which may be assumed having the same physical properties of water) is introduced at the bottom of the well and produces a mist, in thermodynamic equilibrium with the steam, which starts depositing on the well lining. The pressure gradient in the well drives the two phase flow up to the surface.

To understand the fluid dynamics, the following picture of the washing process can be useful: the liquid is injected from a nozzle at the bottom of the well under the high pressure, maintained by a valve, given by the piezometric head (roughly 200 \( \cdot 10^5 \) Pa, assuming a well depth of about 2000 m). The pressure of the high temperature (about 490 K) steam at the bottom of the well is roughly 20 \( \cdot 10^5 \) Pa: therefore, the liquid undergoes a flash vaporization to reach the equilibrium conditions under which most of the liquid is vaporized and the rest is in the form of a droplet dispersion. These droplets will start depositing onto the wall and flowing as a film, from which, in turn, other droplet will be entrained by the gas shearing action in a dynamical balance. Since pressure and temperature conditions vary along the well (heat losses from the bottom to the well surface), the quality of the flowing mixture changes in different regions of the pipe as well as the ratio of liquid and steam.

The objective of this work is to determine the operational conditions under which the existence of concurrent upward annular flow in the well is ensured. Indeed, the annular flow regime presents the advantages of having a liquid film flowing over the well lining, thus preserving it from corrosion, and droplets entrained by the gas core, which ensure a high ratio between transfer area and entrained mass. However, some limits exist to the variation of the injected liquid flowrate: as a matter of fact, the larger is the liquid feed, the larger will be the pressure drop. On the other hand, a minimum amount of liquid necessary to wet the pipe is required to prevent corrosion and the forming of soda scaling.

Models for annular flow are based on balance equations for gas, liquid flowing at the wall and entrained droplets. Information on droplet dynamics, size distribution, generation mechanisms is relevant to know mass exchange and momentum exchange: ultimately, to design the washing system. However, information regarding the detailed structure of droplet flow is usually lacking.

In this work, a physical approach to model droplet interchange and dynamics is presented and used to develop the annular flow model. The developed model is assessed against experimental data and is subsequently used to evaluate the typical operational conditions of geothermal wells.
Considering the well depth, it has been decided that any computation of HCl transfer between the vapour phase and the caustic solution is not necessary, as equilibrium conditions are likely to be reached in a pipe length which is two orders of magnitude less than the well depth. Therefore present computations are only relevant for determining the flow structure and the pressure drops in the well.

![Diagram of annular flow](image)

**Figure 1: Schematics of annular flow.**

1.1 Flow Conditions

The operational conditions described would be ensured by the liquid and the vapour flowing concurrently upward in annular flow regime as shown schematically in Figure 1. However, conditions may exist under which the vapour flowrate is not sufficient to drag the liquid upward: the vapour flowrate might be just enough to hold the liquid film (*flooding*) or not even enough to prevent the liquid from flowing downward.

In the following part of the section, existing and newly developed models will be described to examine:

1. The conditions under which the injected liquid flowrate can be transported upward.
2. The conditions for the existence along the wall of a thin layer of liquid which will prevent the corrosion of the pipe lining.
3. The pressure drop along the pipe and its variation with gas and liquid flowrates.

1.1.1 Flooding and Flow Reversal

Considering a vertical pipe with gas flowing upward and liquid fed from a slot on the wall at a certain intermediate height, at low gas flowrates pressure drops are small and the liquid flows countercurrent, as a film going downward on the pipe wall. Increasing the gas flowrate the interfacial shear is increased and also increased is the size of the wave structure on the liquid surface. A value of the gas flowrate is reached at which the shear is enough to stop a wave from going downward (*standing wave*), and some liquid is transported upward. This is the *flooding* point characterized by a sharp increase of pressure drops. Just above the flooding point
(identified by a flooding velocity), there is a region in which film flow occurs both upward and downward. Now, let us suppose to have a high gas flow rate able to transport all the liquid film upward: decreasing the gas flow rate, the flow reversal point is reached (identified by a flow reversal velocity) when the liquid just begins to fall. Flooding and flow reversal transitions are rather sharp, however, such phenomena are characterized by some hysteresis. Indeed, the gas flowrate necessary to reestablish countercurrent flow is much lower than the flowrate at which flooding occurred. Similarly, the gas flowrate necessary to reestablish upward concurrent flow is higher than that at which flow reversal occurred.

Turning back to the problem of annular flow in the well, it is to be verified that the operational conditions are above the flow reversal point. Indeed, only in this condition all the injected liquid will be transported upward avoiding a decrease of the washing efficiency and a dangerous flooding of the well. Wallis (1969) proposed the following correlation to evaluate the flow reversal velocity:

\[ u_{SG}^* = C, \]

where \( u_{SG}^* \) is the dimensionless superficial gas velocity defined as:

\[ u_{SG}^* = u_{SG} \sqrt{\frac{\rho_G}{gD(\rho_L - \rho_G)}}, \]

and \( C \) is a constant in the range of 0.8 – 0.9. From experiments with pipe diameters up to 300 mm, Pushkina and Sorokin (1969) proposed a correlation based on the Kutateladze number, \( K \), defined as:

\[ K = \frac{\rho_L^2}{g\sigma(\rho_L - \rho_G)}. \]

The flow reversal point is characterized by \( K = 3.2 \). Both correlations indicate the flow reversal point to be independent of the liquid flow rate. Wallis and Makkenchery (1974) showed that Eq. 1 is better for small diameter pipes whereas Eq. 3 is more accurate for pipes with diameters larger than 50 mm. For the considered system, the value \( K = 3.2 \) predicts a flow reversal velocity of 4.6 m/s, corresponding to a steam flow rate of 2.2 kg/s, sufficiently less than the operational value of 5.6 kg/s. In such conditions, the presence of a climbing liquid film flowing at the wall is ensured.

1.2 Annular Flow

A model for annular flow will be developed on the basis of mass and momentum balance equations. The closure laws necessary to calculate the pressure drop along the pipe have been developed onto well grounded physical hypotheses developing some original correlations which were assessed against experimental data obtained in laboratory scale facilities.

1.2.1 Balance Equations

In annular flow, the liquid flows as a thin film at the wall and as a dispersion of drops in the center of the pipe. Balance equations for the annular flow system may be written for the
three fluid system liquid film—gas core—entrained drops. Balance equations will be written for a segment of a pipe over which the hypotheses of steady state conditions and negligible mass transfer between gas and liquid are satisfied. Pressure and temperature influence on the quality of the flowing mixture will be accounted for considering several pipe segments each at uniform pressure and temperature. The mass conservation for the gas, liquid film and entrained drops are, respectively:

\[ \frac{d}{dz} (\alpha_G u_G) = 0 \quad , \quad (4) \]

\[ \rho_L \frac{d}{dz} (\alpha_F u_F) + (R_A - R_D) \frac{P_F}{A} = 0 \quad , \quad (5) \]

\[ \rho_L \frac{d}{dz} (\alpha_D u_D) + (R_A - R_D) \frac{P_F}{A} = 0 \quad . \quad (6) \]

The conservation of momentum is expressed as:

\[ \alpha_G \frac{dP}{dz} + \frac{d}{dz} (\alpha_G \rho_G u_G^2) + \tau_i \frac{P_F}{A} = 0 \quad , \quad (7) \]

\[ \alpha_F \frac{dP}{dz} + \frac{d}{dz} (\alpha_F \rho_L u_F^2) + \tau_w \frac{4}{A} - \tau_i \frac{P_F}{A} + R_A \frac{P_F}{A} u_{FD} - R_D \frac{P_F}{A} u_{DF} = 0 \quad , \quad (8) \]

\[ \alpha_D \frac{dP}{dz} + \frac{d}{dz} (\alpha_D \rho_L u_D^2) - F_D - R_A \frac{P_F}{A} u_{FD} + R_D \frac{P_F}{A} u_{DF} = 0 \quad , \quad (9) \]

respectively for gas core, liquid film and entrained drops. If we assume that entrained droplets travel at the gas velocity and we add Eqs. 8 to 9, we obtain:

\[ (\alpha_G + \alpha_D) \frac{dP}{dz} + \frac{d}{dz} (\alpha_D \rho_L u_D^2 + \alpha_G \rho_G u_G^2) + \tau_i \frac{P_F}{A} - R_A \frac{P_F}{A} u_{FD} + R_D \frac{P_F}{A} u_{DF} = 0 \quad . \quad (10) \]

The volume conservation equation,

\[ \alpha_G + \alpha_D + \alpha_F = 1 \quad , \quad (11) \]

completes the set of equations. In order to solve Eqs. 4 — 11 for given liquid and gas flow rates, and pipe diameter, closure relations for the parameters \( \tau_i \), \( \tau_w \), \( R_A \), \( R_D \), \( u_{FD} \) and \( u_{DF} \) are required. In particular, difficulties arise when modelling the exchange terms due to droplet dynamics, given the uncertainties in determining droplet size and droplet size distribution, droplet generation and deposition mechanisms.

The issues relative to the determination of the closure relations will be addressed in the following paragraphs. The terms \( u_{DF} \) and \( u_{FD} \) represent the first the average velocity of the entrained droplets, and the second the ejection velocity of the droplet from the film: they will be analyzed in the paragraph relative to the entrainment model.
1.2.2 Interfacial Friction and Wall Friction

The wall stress and the interfacial stress may be expressed as function of gas and liquid film velocity and and some suitable friction factors. Thus we have:

\[ \tau_i = f_i \frac{1}{2} \rho G (u_G - u_L)^2 \]  

\[ \tau_w = f_w \frac{1}{2} \rho L u_L^2 \]  

Therefore, the issue is now the evaluation of the two friction factors, \( f_i \) and \( f_w \).

The wall friction factor is customary calculated using the well assessed Colebrook expression for turbulent flow in rough pipes:

\[ \frac{1}{\sqrt{f_w}} = 2.28 - 1.7 \ln \left( \frac{k}{D} + \frac{4.67}{Re_F \sqrt{f_w}} \right) \]  

If the flow is laminar, the Hagen-Poiseuille relationship, \( f_w = 16/Re_F \), is employed.

The film Reynolds number, \( Re_F \), is defined as:

\[ Re_F = \frac{u_F \alpha_F \rho L D}{\mu_L} \]  

About the interfacial friction factor, experimental observations show that:

1. Disturbances of the liquid film (ripples, waves, surface oscillations) are perceived as roughness elements by the flowing gas. Gas pressure drops in annular flow are higher than in a smooth pipe flow, even for no entrainment.

2. The interfacial friction factor decreases for decreasing film thickness. Under a limiting value of the film thickness, \( f_i \) is equal to the smooth pipe friction factor, \( f_s \).

3. A linear dependence of \( f_i \) on the film thickness is often observed.

On the basis of such observations, Asali et al. (1985) proposed a correlation with the following form:

\[ f_i = f_s \left[ 1 + 0.45 Re_G^{-0.2} \left( m_G^+ - 4.0 \right) \right] \]  

where, the smooth pipe friction factor, \( f_s \), is calculated as:

\[ f_s = 0.046 Re_G^{-0.2} \]  

and the dimensionless liquid film thickness, \( m_G^+ \), is calculated as:

\[ m_G^+ = 0.19 Re_F^{0.7} \frac{\nu L}{\rho G} \sqrt{\frac{\rho_L}{\rho_G}} \]
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1.2.3 Interchange Model: the Entrained Fraction

One of the most successful correlations to predict the entrainment fraction in annular flow is the one developed by Oliemans et al. (1986), which is based on all flow variables and was fitted over a large data bank with the aid of seven parameters. However, such a correlation is not grounded on a physical basis and does not appear capable of predicting other sets of experimental data (Willets, 1987).

A physical approach appears more reasonable and is followed in this work. Considering vertical annular flow, droplets are continuously generated at the liquid surface and continuously deposit back onto the film in a dynamical balance as sketched in Figure 2. A mass balance for the liquid phase yields:

$$\frac{dW_F}{dz} = \pi D (R_D - R_A) \quad ,$$

where, $W_F$ is the liquid film flowrate, $z$ is the axial coordinate, and $D$ is the pipe diameter. If the rate of atomization, $R_A$, equals the rate of deposition, $R_D$, the flow is fully developed, while developing flows occur in the other cases. The deposition rate may be expressed as:

$$R_D = k C_E \quad ,$$

where $k$ is the deposition coefficient and $C_E$ is the droplet concentration in the gas core. In the hypothesis of fully developed flow conditions ($R_D = R_A$), the following relation holds:

$$C_E = \frac{R_A}{k} \quad .$$

Figure 2: Control volume for the interchange model.
The entrainment fraction can be calculated from the values of droplet concentration and droplet mean velocity. Therefore, via the modelling of atomization and deposition mechanisms the entrainment fraction may be obtained.

1.2.4 Rate of Entrainment

The physical mechanism which seems responsible for droplet generation in the case of a low viscosity fluid like water is the shearing off of the roll wave crests. Therefore, the dimensionless rate of entrainment, $\bar{R}_A$, defined as:

$$\bar{R}_A = \frac{R_A}{\sqrt{\rho G u_G}}$$

(22)

is related to the dimensionless roll wave frequency, $\tilde{I}$, and to a function of the liquid film thickness, $m$, and surface tension, $\sigma$. This last function is the Weber number based on the film thickness (Willets, 1987), $We = \rho_G u_G^2 m / \sigma$, raised to some exponent $\beta$. In these formulas, $\rho_G$ and $\rho_l$ are the gas and liquid density, and $u_G^*$ is the gas shear velocity$^1$. The roll wave frequency is modelled following the criteria suggested by Schadel and Hanratty (1989).

For the rate of the entrainment, the following relation is proposed (See also Schadel and Hanratty, 1989, for a similar model):

$$\bar{R}_A = 0.0033 \ I^{1.3} \ We^{0.6}$$

(23)

1.2.5 Rate of Deposition

Once droplets are entrained in the gas core, they deposit either by diffusion mechanisms, if their motion is dominated by turbulent fluctuations (small droplets), or by impaction deposition, if their motion is trajectory wise and scarcely affected by the gas turbulence (large droplets). Furthermore, the motion of all droplets is influenced by droplet concentration: the larger is droplet concentration the more frequent are collisions and coalescence phenomena among droplets. Droplets entrained in the gas core may undergo two different types of interactions. A large, accelerating drop moves through the gas core slower than the gas and slower than smaller entrained droplets. Such drop may interact with smaller droplets in a sweeping action, thus gaining axial momentum (axial interaction). A drop may also interact with other drops which move at about the same axial velocity but along different chords in the cross section (lateral interaction). This may be the case for small droplets fully entrained by the gas, which move at about the same axial velocity and are subject to lateral displacements. These phenomena ultimately reduce deposition rates as discussed in Soldati and Andreussi (1996).

The effect of coalescence may be characterized by the interaction probability, which is defined as

$$p_i = \frac{S_{OD}}{\rho l} \ \frac{D}{d_{32}}$$

(24)

$^1$The gas shear velocity is defined as:

$$u_G^* = \sqrt{\frac{\tau_l}{\rho_G}}$$
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where $S$ is the slip ratio between gas and droplets, $\alpha_D$ is the liquid entrainment fraction, and $d_{32}$ is the droplet Sauter mean diameter, which is calculated using the correlation proposed by Ambrosini et al. (1991). The correlation has the following form:

$$\frac{d_{32}}{h_f} = x_1 \sqrt{\frac{\sigma}{\rho_g u_f^2 h_f}} \left( \frac{\rho_g}{\rho_l} \right)^{z_2} \exp \left[ x_3 p_i + \frac{x_4}{W_e} \right], \tag{25}$$

where $\sigma$ is the liquid surface tension, $h_f$ is the liquid film thickness, $f_i$ is the interfacial friction factor and $W_e$ is the Weber number based on the pipe diameter, $W_e = \rho_g u_f^2 D/\sigma$. The four parameters appearing in Eq. 25 have the optimized values: $x_1 = 22.0$, $x_2 = 0.83$, $x_3 = 0.6$ and $x_4 = 99.0$. This correlation, validated against a large set of data (Jepson et al., 1989, among others), introduces the effect of coalescence through the correction factor $\exp[x_3 p_i]$, which depends on the interaction probability.

In their work, Soldati and Andreussi (1996) give a detailed description of droplet dynamics in annular flow. They also supply a correlation for the deposition coefficient, $k$, which is well suited to predict experimental data in downward annular flow. However, such model is far too cumbersome to be applied for practical design purposes and a simpler model, based on the same approach, will be developed here.

Andreussi (1983) found the deposition coefficient to depend inversely on droplet concentration. Soldati and Andreussi (1996) found that the deposition coefficient may be represented better by an inverse dependance on the interaction probability. On such basis, the deposition coefficient may be calculated as:

$$\bar{k} = \frac{k^0}{1. + 4.505 \rho_i}, \tag{26}$$

where, $k^0$, the asymptotic value for $k$ in the limit of no coalescence, is expressed as:

$$k^0 = (1 - V_I)k_d^0 + V_I k_f^0. \tag{27}$$

In this equation, $V_I$ is the volumetric fraction of droplets depositing by impaction calculated with the following equation, as proposed by Andreussi and Azzopardi (1983),

$$V_I = \exp \left[ -\left( \frac{1}{2} \frac{d_c}{d_{32}} \right)^2 \right], \tag{28}$$

where $d_c$ is the critical drop diameter at the transition between the two transfer mechanisms, and $d_{32}$ is the Sauter mean diameter calculated adopting the correlation proposed by Ambrosini et al. (1991). Droplets with diameter smaller than the critical diameter move following diffusion mechanisms, and droplets with diameter larger move along a trajectory. The critical diameter may be calculated as (see Soldati and Andreussi, 1996):

$$d_c = \left[ 0.9 D 18.5 \left( \frac{\nu G}{u^*} \right)^{0.61} \right]^{5/3}, \tag{29}$$

where the droplet radial ejection velocity, $u_i$ is defined following Andreussi and Azzopardi (1984) as $u_i = 12u^* \sqrt{\rho_G/\rho_L}$. The dimensionless diffusion deposition coefficient, $k_d^0$, has the optimized
value of $\tilde{k}_d^0 = 0.164$, while the dimensionless impact deposition coefficient is calculated as:

$$\tilde{k}_d^0 = \frac{1}{u_r} \frac{u_G D}{4 C_0 \bar{x}_d} .$$  (30)

The coefficient $C_0 = 0.62$ accounts for averaging procedures to obtain Eq. 30, and the axial distance covered by the mean size drop, $\bar{x}_d$, is calculated solving a simplified equation of motion for the droplet. The equation is two-dimensional (radial and axial dimensions) and only the inertial and drag forces are supposed to act. $d_I$ is the volume median diameter of the fraction $V_I$ of droplets which deposit by impaction. The equation of motion for the droplet is:

$$\frac{d\bar{u}_d}{dt} = \frac{3}{4} C_D \frac{\rho G}{d_I \rho_l} (\bar{u}_G - \bar{u}_d) \left| \bar{u}_G - \bar{u}_d \right| ,$$  (31)

where, $C_D = 18.5/R_e^{0.6}$. To solve this equation, it has been assumed that the mean radial path covered by the droplet is $\bar{x}_d = 0.7D$, as suggested by Andreussi and Azzopardi (1983). The axial distance covered by the characteristic droplet of diameter $d_I$ is

$$\bar{x}_d = \frac{5 u_G^{3/5}}{2 A} \left[ \left( 1 - \frac{3}{5} \bar{s}_d A \frac{u_G^{2/5}}{v_i} \right)^{-2/3} - 1 \right] - \frac{u_G \bar{s}_d}{v_i} ,$$  (32)

where $v_i$ is the radial ejection velocity of the droplet, and $A = \frac{3}{4} \rho G / \rho_l 18.5 v_G^{0.6}$.

1.3 Results

1.3.1 Annular Flow Model

On the basis of the equations developed in section 1.2 a model for annular flow was set up and compared against existing experimental data obtained in experimental facilities. Such comparison is presented in paragraphs 1.3.3 and 1.3.4.

The mixture flowing in the well is composed by steam and liquid, leaving the bottom of the well at high temperature (above 480 K) and under a pressure of about $20 \cdot 10^5$ Pa. Over the length of the well, there are some heat losses which cool the mixture. Some condensation, is expected. Temperature variations are of the order of 20 K over the the whole pipe if a sensible value of linear heat flux of about $0.4 \cdot 10^5$ W/m is assumed. Therefore, the model is based on the following hypotheses:

1. The well is subdivided into a number of segments sufficiently small to be considered at thermodynamic equilibrium.

2. The annular flow model as presented in section 1.2 is used to calculate the flow variables on the segment.

3. Steam water tables are used to compute temperature and enthalpy for each of the segments considering also the presence of some non condensible gas such as CO$_2$, the amount of which is estimated around 7%.
The developed model was used as a subroutine of the existing code HORF (1990), which was assembled as a design tool for steam water pipelines and was able to simulate stratified flow, slug flow and dispersed flow.

The annular flow model was assessed against an experimental database obtained in laboratory scale facilities. The fluid dynamic model for the well was used to examine the features of the flow in the well.

1.3.2 Experimental Database

The model was compared against a database obtained in previous experiments. The following data have been used:

1. data by Jepson et al. (1990) obtained for upward air-water annular flow in a 10.26 mm internal diameter tube.

2. data by Azzopardi et al. (1991) obtained for upward air-water annular flow in a 20. mm internal diameter tube.

3. data by Andreussi (1983) obtained for downward air-water annular flow in a 24. mm internal diameter tube.

4. data by Fore and Dukler (1995) obtained for upward air-water annular flow in a 50.8 mm internal diameter tube.
In particular, the use of data obtained by Fore and Dukler (1995) was extremely significant since they were obtained for low values of the gas velocity, very similar to the ones characterizing annular flow in the well.

1.3.3 Validation of the Annular Flow Model

The model developed in the previous section was validated against existing experimental data. In the first place, rates of entrainment and deposition were assessed. In Figure 3, the entrained flowrate, $W_t$, calculated with the model is compared against the experimental data obtained by Jepson et al. (1990) and by Azzopardi et al. (1991), and the result is rather satisfactory. At the equilibrium, the rate of deposition is equal to the rate of entrainment and directly related to the entrainment flowrate. The calculated rate of deposition is compared against experimental data obtained by Andreussi (1983) and by Fore and Dukler (1995) in Figure 4. Since data by Andreussi is obtained for downward annular flow, flowrates are much higher and plotting this last comparison also in Figure 3 would have made more difficult the examination of the result. As from Figures 3 and 4, the models proposed for deposition rate and entrainment rate appear capable of covering satisfactorily a rather broad range of values.

The prediction of the pressure gradient is of particular interest. Annular flows which may occur into a geothermal well are characterized by a small gas superficial velocity, almost at the boundary with flow reversal conditions. In the literature, available data of this kind are provided by Fore and Dukler (1995) who also supplied pressure drop measurements. Pressure drops are not usually reported in many investigations. However, Andreussi (1983) presents pressure drop data for downward annular flow. Such case is of limited interest for annular flow in the well, since liquid film thickness and flowrates may be much larger than for the corresponding upward
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Figure 5: Comparison of the model for pressure drop against experimental data by Andreussi (1983) and by Fore and Dukler (1995).

Yet, it is relevant to assess the validity of the model for a broad range of application. In Figure 5, calculated and measured pressure drops are presented. The agreement is definitely good, especially for the data by Fore and Dukler (1995).

1.3.4 Entry Length in Annular Flow

It is important to determine the length necessary to obtain fully developed flow. The hypotheses under which the annular flow model was developed include fully developed conditions. However, if the differential term in Eq. 19 is not zero, inlet conditions may not be represented by such model. Ishii and Mishima (1989) proposed to use equations for fully developed flow after the

<table>
<thead>
<tr>
<th>Variable</th>
<th>Case 1: saturated vapour</th>
<th>Case 2: wet vapour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inlet</td>
<td>Outlet</td>
</tr>
<tr>
<td>Temperature</td>
<td>484.5 K</td>
<td>466.9 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>20 \cdot 10^5 Pa</td>
<td>14.05 \cdot 10^5 Pa</td>
</tr>
<tr>
<td>Quality</td>
<td>\approx 1</td>
<td>0.945</td>
</tr>
<tr>
<td>Gas Flowrate</td>
<td>8.9 kg/s</td>
<td>8.47 kg/s</td>
</tr>
<tr>
<td>Liquid Flowrate</td>
<td>0.0085 kg/s</td>
<td>0.46 kg/s</td>
</tr>
<tr>
<td>\textit{CO}_2</td>
<td>7%</td>
<td>7%</td>
</tr>
</tbody>
</table>

Table 1: Flow variables at the top and at the bottom of the pipe for Case 1, with saturated vapour at the bottom of the pipe, and for case 2, with minimum liquid flowrate to ensure the presence of a film wetting the pipe at the inlet.
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Figure 6: Evaluation of the transient region. Attainment of fully developed flow is shown for experimental data obtained at a) \( u_{GS} = 43. m/s \), Andreussi (1983), b) \( u_{GS} = 29. m/s \), Jepson et al. (1990), c) \( u_{GS} = 16. m/s \), Fore and Dukler (1995).

Entry length \( z_t \), calculated as:

\[
z_t = 600D \sqrt{u_G \left( \frac{\sigma g (\rho_L - \rho_G)}{\rho_G^2} \left( \frac{\rho_G}{\rho_L - \rho_G} \right)^{2/3} \right)^{1/4}}
\]

(33)

Using such equations, we obtain values in the range \([100D - 300D]\) for the experiments by Fore and Dukler (1995), Jepson et al. (1989) and Andreussi (1983). However, the differential term in Eq. 19 may be calculated directly using Eqs. 22 and 23 for the entrainment rate and Eqs. 26 - 32 for the deposition rate. In Figure 6 a), b) and c) the attainment of fully developed conditions is presented for the different experimental data. Particular attention should be given to data by Fore and Dukler (1995), obtained for conditions very similar to those expected in geothermal wells. Entrainment rate and deposition rate become equal after 200 D and before 400 D. Fully developed conditions are attained before if the liquid flowrate is lower. The developing length appears independent of the gas flowrate. Such estimate is slightly conservative if
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Figure 7: Behaviour of vapour quality along the well for the flow conditions summarized in Table 1.

compared against the relationship presented by Ishii and Mishima (1989). However, considering the dimensions of a geothermal well, the flow is fully developed over almost all the length of the pipe.

1.3.5 Characteristics of the Flow in the Well

The model was used to investigate on the characteristics of the flow occurring in the well. Since heat is lost to the neighbouring ground along the well, the vapour loses enthalpy and there might be condensation. Indeed, as vapour enters the well almost at saturation temperature, liquid is condensed along the pipe. The minimum liquid flowrate necessary to cool down the superheated steam to saturated conditions was calculated with a simple enthalpy balance supposing the liquid descending in the coil always in thermal equilibrium with the mixture flowing upward. Calculations have been made for the limiting case of injected flowrate just enough to obtain saturated vapour entering (case 1). However, in this case the presence of a liquid film wetting the wall from the beginning of the pipe is not ensured.

Experimental observations suggested that a minimum value of the liquid film Reynolds number sufficient to ensure the wetting of the wall is about 300. Therefore, another case was run injecting at the bottom of the well a liquid flowrate large enough to guarantee such value for the liquid film Reynolds number (case 2).

The length necessary to obtain fully developed conditions is approximately equal to 125 D, which corresponds to about 30 m. The model was used dividing the pipe into 100 intervals after an analysis of sensitivity to the grid. The well is 2000 m deep and its diameter is \(D = 0.25\) m. The heat loss per meter of pipe is 400 W/m. In Table 1, the inlet and outlet conditions for some variables are reported for the two cases studied in Figures 7 - 11. In Figure 7, the behaviour of the quality along the pipe for the two calculated cases is reported. Due to the heat loss, there is a small decrease of the steam flowrate and some condensation occurs. The heat loss is towards the neighbouring ground, but there is some heat required to bring the descending liquid to thermal equilibrium with the gas. Such heat loss is small. The behaviour of the liquid flowrate along the well is reported in Figure 8, where the liquid split into entrained fraction and

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Figure 8: Behaviour of the liquid flowrate along the well.

Figure 9: Pressure drop in the well as a function of the vapour flowrate.

The liquid film is reported also. The liquid flowrate increases toward the surface, as expected. The entrainment as well changes going upward, due to the different shear conditions. This Figure refers just to Case 1. The trend observed for the liquid flowrates in Case 2 are substantially the same. Figure 9 shows an analysis of the variation of the pressure drop as a function of the inlet vapour flowrate. In this analysis, the inlet liquid flowrate was kept constant and therefore the enthalpy of the inlet mixture varies in the plot.

The pressure gradient variation in the well is reported in 10 as a function of the height: the increase of the pressure gradient is due to the increase of the liquid flowrate toward the surface.

The liquid film Reynolds number is shown in 11 as a function of the height for the two cases treated: even for the case relative to low inlet liquid flowrate, case 1, the Reynolds number quickly reaches the conditions for complete wetting of the pipe.
Figure 10: Pressure gradient in the well.

Figure 11: Liquid film Reynolds number in the well.

2 Conclusions

The proposed solution of washing the geothermal steam directly in the well has been theoretically examined and a model for the study of the problem was set up. Geothermal steam rises upward from the bottom of the well where its conditions are superheated steam or almost saturated steam at about $2 \times 10^5$ Pa and 490 K. Some percentage 7% of CO$_2$ is present as well. The injection of some high pressure liquid water ensures the cooling down of the steam to the saturation point and the presence of some drops which may start the washing process and the corrosion protection depositing on the well lining. In such conditions, annular flow regime is established in the well.

Existing models have been used to verify that, indeed, annular flow is established in the well, and there is no flow reversal situation. Furthermore, a new model for calculating pressure drop in annular flow was set up and compared with experimental data. The model was proven to
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predict accurately liquid entrainment rates, liquid deposition rates and pressure drops. Finally, such model was used to verify that fully developed conditions are quickly attained in the well and to investigate on the features of the fluid dynamics of the well.

Notation

\[ A = \text{area } [m \cdot s^{-1}] \]
\[ C_D = \text{drag coefficient} \]
\[ C_E = \text{droplet concentration } [kg \cdot m^{-3}] \]
\[ d_c = \text{droplet diameter at the transition } [m] \]
\[ d_I = \text{mean diameter of impact depositing droplets } [m] \]
\[ d_{32} = \text{droplet Sauter mean diameter } [m] \]
\[ D = \text{pipe diameter } [m] \]
\[ f_i = \text{interfacial friction factor} \]
\[ f_s = \text{smooth pipe friction factor} \]
\[ f_w = \text{wall friction factor} \]
\[ g = \text{gravity acceleration } [m \cdot s^{-2}] \]
\[ h_f = \text{film thickness } [m] \]
\[ K = \text{Kutateladze number} \]
\[ k = \text{deposition coefficient } [m \cdot s^{-1}] \]
\[ k_d = \text{diffusional deposition coefficient } [m \cdot s^{-1}] \]
\[ k_I = \text{impact deposition coefficient } [m \cdot s^{-1}] \]
\[ I = \text{wave intermittancy} \]
\[ m_d = \text{droplet mass } [kg] \]
\[ m^+_D = \text{dimensionless film thickness} \]
\[ P = \text{pressure } [Pa] \]
\[ P_F = \text{liquid film inner perimeter } [m] \]
\[ p_i = \text{interaction probability per unit length } [m^{-1}] \]
\[ R_D = \text{deposition rate } [kg \cdot m^{-2} \cdot s^{-1}] \]
\[ R_A = \text{atomization rate } [kg \cdot m^{-2} \cdot s^{-1}] \]
\[ Re = \text{Reynolds number} \]
\[ S = \text{slip velocity} \]
\[ t = \text{time } [s] \]
\[ u = \text{velocity } [m \cdot s^{-1}] \]
\[ u_{DF} = \text{velocity of droplets relative to the film } [m \cdot s^{-1}] \]
\[ u_{FD} = \text{velocity of the film relative to droplets } [m \cdot s^{-1}] \]
\[ u_{SG} = \text{gas superficial velocity } [m \cdot s^{-1}] \]
\[ u_{SL} = \text{liquid superficial velocity } [m \cdot s^{-1}] \]
\[ u_s = \text{shear velocity } [m \cdot s^{-1}] \]
\[ u_i = \text{droplet ejection velocity } [m \cdot s^{-1}] \]
\[ V = \text{droplet volume fraction} \]
\[ W = \text{mass flowrate } [kg/s] \]
\[ We = \text{Droplet Weber number} \]
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\[ z = \text{axial coordinate} \]
\[ z_d = \text{droplet axial path [m]} \]

Greek Letters

\[ \alpha_D = \text{volume fraction of entrained liquid} \]
\[ \alpha_F = \text{volume fraction of the film} \]
\[ \alpha_G = \text{volume fraction of the gas} \]
\[ \mu = \text{fluid viscosity [kg m}^{-1}s^{-1}] \]
\[ \nu = \text{fluid kinematic viscosity [m}^2s^{-1}] \]
\[ \rho = \text{density [kg m}^{-3}] \]
\[ \sigma = \text{surface tension [kg m}^{-1}s^{-2}] \]
\[ \tau_i = \text{interfacial shear stress [Pa]} \]
\[ \tau_w = \text{wall shear stress [Pa]} \]

Superscripts

\[ ^0 = \text{no coalescence effect} \]
\[ ^\sim = \text{dimensionless (for the deposition coefficient)} \]
\[ ^- = \text{average} \]

Subscripts

\[ F = \text{liquid film} \]
\[ D = \text{entrained droplets} \]
\[ G = \text{gas core} \]
\[ L = \text{liquid} \]
\[ p = \text{particle, droplet} \]
\[ ^\sim = \text{dimensionless (for the deposition coefficient)} \]
\[ ^- = \text{average} \]

References


SIMULATION OF CHEMICAL EQUILIBRIA IN THE EQUIPMENT OF A GEOGHERMAL POWER PLANT: THE GEA (GEOTHERMAL EQUILIBRIA ASSESSMENT) CODE

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CONSORZIO PISA RICERCHE, Centro per le Tecnologie Energetiche Ambientali

1. INTRODUCTION

Geothermal steam generally contains chemical species different from water that cause problems during the exploitation cycle. These species may in fact precipitate causing scaling or may interact with steel causing corrosion.

The understanding of the chemical behaviour of geothermal fluid during its utilization cycle became, therefore, of crucial importance to properly design equipment and to properly select the best methodology to reduce pollution problems.

This document describes the activities carried out to prepare the computation code GEA (Geothermal Equilibria Assessment) needed to evaluate the equilibrium partitioning of the most common chemical species in geothermal fluids.

These computer programs represent in fact the first step for defining the best operating conditions to be maintained during geothermal power plant operation.

The programs can be used to predict the chemical composition of the cooling tower water, to calculate how much hydrogen sulfide is expelled from the compressor outlet and how much is absorbed in the condensate, and to calculate the amounts of additives that may be needed to condition the cooling tower water (pH adjustment) and to absorb the hydrogen sulfide from gas streams leaving geothermal power plants.

This work is thus the logical continuation, expansion and integration of the work previously performed to calculate the partitioning of chemical compounds in a reboiler plant. It is proposed as a useful design tool for the entire condensation/cooling circuit of geothermal power plants.
2. CONCEPTUAL MODEL USED

The studied system is diagrammed in Figure 2.1. As can be seen, the plant is made up by a condenser and a cooling tower. The condenser receives the spent steam, whose composition is known, and the recirculating water from the cooling tower, whose composition depends on the composition of the geothermal steam and the atmospheric conditions (evaporation rate in the tower).

The study examined the behavior of the compounds CO₂, H₂S, NH₃, SiO₂, H₃BO₃, HCl and NaCl, although at the condenser operating temperatures (about 40°C) only CO₂, H₂S and NH₃ enter the vapor phase in significant amounts.

The study did not consider elements such as Mg⁺, Ca⁺ and Fe⁺⁺, which, together with silica, come from solid-phase entrainment and corrosion in the coding circuit (pipeline and cooling tower). This was because these elements should not greatly modify the liquid-vapor equilibrium conditions, while as we shall see below, they can significantly influence the pH of the cooling tower water.

The amounts of H₂O, CO₂, H₂S and NH₃ in gaseous form depend on condenser temperature and pressure, the composition of the geothermal inlet steam and the flow rate of cooling water entering the condenser. The pH of the condensate is therefore fixed since the mass and charge balances must be respected. The water leaving the condenser is sent to the cooling tower, which for the purposes of chemical equilibria acts as a stripping tower in an air stream, causing the water to evaporate and the volatile compounds (CO₂, H₂S and NH₃) to pass to the gas phase. Part of this water is sent back to the condenser, and part is reinjected (surplus water).

In order to solve the problem of determining the distribution of the different species between liquid phase and gas phase and then calculate the mass balances and pH of the surplus water and the condensate, the thermodynamic conditions of the model must be defined.

2.1 CONDENSER

The condenser was likened to an isothermal, isobaric system whose total pressure and temperature are fixed. It was hypothesized that the different substances considered are in thermodynamic equilibrium with each other at the mean between the cooling water inlet and outlet temperatures.

A condenser model with N equilibrium stages was also developed.
Figure 2.1 Diagram of a geothermal power plant with indication of streams
However, this model creates considerable complications and delays the coming together of the whole calculation system (as will be clarified below). It was therefore decided to simplify the model in order to facilitate use of the computer programs.

Since the condensate comes from the cooling tower and is therefore aerated, oxygen was also considered among the reactive species. In the event that H$_2$S is present, a redox reaction occurs between oxygen and H$_2$S with the formation of colloidal sulfur according to the equation

$$\text{H}_2\text{S} (\text{aq}) + \frac{1}{2} \text{O}_2 (\text{aq}) \rightarrow \text{S}^0 + \text{H}_2\text{O}$$

The numeric model must therefore take into account not only the partitioning of H$_2$S and O$_2$ between the liquid and gas phases, but also of the reaction described above. Experimental studies performed on the chemical composition of the waters leaving the condenser (Mroczek et al., 1995) show that the oxygen concentration in the condensate has higher values than those that would be expected from the thermodynamic calculations. For this reason a parameter was introduced that takes into account the fact that only part of the oxygen contained in the water reacts to form colloidal sulfur.

2.2 COOLING TOWER

Studies carried out by Glover (Glover R.B., 1979) showed that degassing occurs at the top of the cooling tower with a stripping mechanism whose kinetics is controlled by the liquid phase chemical reaction. In other words, the molecular species take lesser time to migrate in the gas phase than that needed to equilibrate the solution.

The solution then reaches the equilibrium conditions at the temperature of the cooling tower. The constraint of equilibrium of CO$_2$ at atmospheric P$_{CO2}$ was therefore not set.

The total sulfide remaining, equal to the sum of the ionic species HS$^-$ and S$^{2-}$, oxidizes to sulfate upon contact with the atmospheric oxygen. The thermodynamic conditions in the cooling tower do not allow the formation of colloidal sulfur (Stumm and Morgan, 1970).
3. **CALCULATION ALGORITHMS USED**

3.1 **GENERAL**

Once the physicochemical conditions of the outlet steam and the amount of surplus water have been defined, it is possible to set up the equations that make it possible to redetermine the chemical composition of the different streams of the system.

It must be pointed out that the system is complicated by the fact that the composition of the water flowing into the condenser is unknown and must be calculated.

By making the initial concentration values of the cooling water equal to 0, it can be demonstrated that an iterative process converges toward the solution (Guidi et al. 1996).

For the sake of simplicity, let us consider the case in which there is just one substance. Let:

- $C_1$ be the concentration in the inlet steam,
- $Q_1$ be the flow rate of the inlet steam,
- $C_2$ be the concentration in the outlet gaseous stream,
- $Q_2$ be the flow rate of the gaseous stream,
- $C_3$ be the concentration in the water at the condenser outlet,
- $Q_3$ be the flow rate of the water at the condenser outlet,
- $C_4(c)$ be the concentration of the cooling water at the condenser inlet,
- $Q_4$ be the flow rate of the water at the condenser inlet,
- $C_4$ be the concentration of the surplus water,
- $Q_5$ be the flow rate of the surplus water,
- $C_6$ the concentration in the steam leaving the cooling tower,
- $Q_6$ be the flow rate of the steam leaving the cooling tower.
- $B_c = C_2/C_3$ be the partition coefficient of the substance between the gas and liquid phases in the condenser,
- $B_t = C_6/C_4$ be the partition coefficient of the substance between the liquid and gas phases in the cooling tower.

$C_4(c)$ and $C_4$ are obviously identical in the final conditions, that is, at convergence. Since the final value is unknown in the calculation scheme used, however, $C_4(c)$ represents the tentative value used for the $n$th iteration and $C_4$ represents the result of the $n$th iteration, which is also the tentative value for the $(n+1)$-th iteration, and so on.

We therefore have:

$$C_4(c)[n] = C_4[n-1]$$

for $n = 0, 1, ..., N$ where $n$ indicates the number of iterations.
The following mass balances are valid for the condenser and the cooling tower, respectively:

\[ Q_1 + C_4[n]*Q_4 = C_2 + Q_2 + C_3*Q_3 \]

\[ C_3*Q_3 = Q_4*C_4[n+1] + Q_5*C_4[n+1] + Q_6*C_6 \]

In addition, we have

\[ C_2 = Bc*C_3 \]

and

\[ C_6 = Bt*C_4[n+1] \]

Be and Bt are not just functions of the temperature; for substances present in ionic form in the aqueous phase, they also depend on the pH.

By substituting we obtain

\[ C_{4[n+1]} = Q_4*C_{4[n]}/[(1+Bc*Q_2/Q_3)\*(Q_4+Q_5+Bt*Q_6)] + Q_1*C_1/[(1+Bc*Q_2/Q_3)\*(Q_4+Q_5+Bt*Q_6)] \]

If we indicate the denominator of the recursive formula with the symbol DEN, that is:

\[ \text{DEN} = (1+Bc*Q_2/Q_3)\*(Q_4+Q_5+Bt*Q_6) \]

we obtain

\[ C_{4[1]} = Q_4*C_{4[0]}/\text{DEN} + Q_1*C_1/\text{DEN} \]

\[ C_{4[2]} = Q_4[Q_4*C_{4[0]}/\text{DEN} + Q_1*C_1/\text{DEN}]\text{DEN} + Q_1*C_1/\text{DEN} \]

Therefore, after \( n \) iterations

\[ C_{4[n]} = (Q_4/\text{DEN})^{n-1}C_{4[0]} + (Q_1*C_1/\text{DEN})*\sum_{i=0}^{n-1} (Q_4/\text{DEN})^i \]

The term \( Q_4/\text{DEN} \) is < 1 since DEN is greater than \( Q_4 \), so that the term \((Q_4/\text{DEN})^n\) becomes smaller the larger \( n \) becomes.

The summation represents a geometric series of ratio \((Q_4/\text{DEN})\). Remembering that the sum of \( n \) terms of a geometric progression is given by \( S_n = (1-r^n)/(1-r) \), where \( r = (Q_4/\text{DEN}) \) is the ratio of the progression, we have:

\[ \lim_{n \to \infty} S_n = 1/(1-r) \]

for \( n \to \infty \)
so that the term \( \sum_{i=0}^{n-1} (Q_4/DEN)^i \) for the number of iterations which tends to infinity is

\[
\frac{1}{1-Q_4/DEN}
\]

that is

\[
\frac{DEN}{DEN-Q_4}
\]

and therefore

\[
C_{4[\infty]} = Q_1 \cdot C_1/(DEN-Q_4)
\]

Substituting once again the complete expression for DEN we obtain

\[
C_{[\infty]} = Q_1 \cdot C_1/[(1+Bc*Q_2/Q_3)*(Q_4+Q_5+Bt*Q_6)-Q_4]
\]

In the case of substances that do not pass in the vapor phase, we have

\[
C_{[\infty]} = Q_1 \cdot C_1/Q_5
\]

These expressions make it possible to find the starting tentative solution rather easily.

The calculation algorithms used for the condenser and the cooling tower are different from each other. In the first case one must calculate, besides the mass flow rates of the substances, also the flow rates of liquid water and steam; in the second case the water flow rates are fixed. Furthermore, in the condenser the distribution of a substance between the two phases occurs at equilibrium, while in the cooling tower the process is unaffected by the water-gas distribution coefficients.

The general scheme used to calculate the compositions of the gaseous stream leaving the condenser and the surplus water is schematized in the block diagram of Figure 3.1.

The starting data are the flow rates and composition of the inlet steam (flow 1 in Figure 2.1) and of the condensate, condenser temperature and pressure, flow rate of surplus water, and cooling tower temperature.

The convergence criterion adopted is naturally based on verification of the following mass balance

\[
Q_{1i} = Q_{2i} + Q_{5i} + Q_{6i}
\]

where \( Q_{1i} \) is the mass flow rate of the i-th substance entering the system and \( Q_{2i}, Q_{5i} \) and \( Q_{6i} \) are those leaving it.
Input data:
Mass flow rates in 1 of incoming substances
(see Fig. 2.1)
flow rate of condensate
flow rate of surplus water

Tentative composition of surplus water

Calculation of mass flow rates
and composition
of water and steam
leaving the condenser

Calculation of mass flow rates
leaving the cooling tower
and composition
of surplus water

\[ Q_{1i} = Q_{2i} + Q_{4i} + Q_{6i} \]

Figure 3.1 Block diagram of calculation algorithm
3.2  **Calculation algorithm used for the condenser**

Two algorithms were developed, one iterative, the other based on the solution of a polynomial equation of degree \( n \) to verify the computer program results. The procedures and hypotheses made to reach the desired solution are with the iterative algorithm indicated below.

3.2.1  **Iterative algorithm**

We shall first develop the case in which there are no reactions among the different species present in the condenser except acid-base reactions (dissociation and neutralization). Later we will introduce the case of a redox reaction between oxygen and \( \text{H}_2\text{S} \) with formation of \( \text{S}^0 \).

The scheme for calculating the flow rates and composition of the steam and water leaving the condenser can be schematized as follows:

- having fixed the tentative pH, on the basis of the values of the Henry constants and the partial pressure of water at the condenser temperature, it is possible to calculate the mass flow rates of the different substances in both the water and vapor phases, as well as their total concentrations;
- from these, by applying the electroneutrality principle, it is possible to calculate the new pH of the water. With this new value it is thus possible to evaluate the mass flow rates, and so on until convergence.

The calculation algorithm of the condenser can therefore be broken down into two parts: an algorithm to calculate the flow rates and total concentrations in the aqueous phase, with an assigned pH, and a second algorithm to calculate the pH of the aqueous phase given the total concentration values of the different substances.

3.2.1.1  **Case without reaction between \( \text{H}_2\text{S} \) and oxygen**.

Let:

- \( N_{\text{tw}} \) be the number of moles of water that enter (spent steam from the turbine + cooling water) in the condenser,
- \( N_i \) be the total number of moles of species \( i \) entering the condenser,
- \( N_{\text{vw}} \) be the number of moles of steam leaving the condenser,
- \( N_{\text{vi}} \) be the total number of moles of species \( i \) in the vapor phase leaving the condenser,
- \( N_{\text{lw}} \) be the total number of moles of liquid water leaving the condenser,
- \( N_{\text{li}} \) be the total number of moles of species \( i \) in the aqueous phase leaving the condenser,
- \( P_i \) be the partial pressure of substance \( i \),
- \( K_H \) be the Henry constant of substance \( i \),
- \( P \) be the total pressure in the condenser,
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- \( P_{H_2O} \) be the vapor pressure of the water in the condenser.
- \( \alpha_i(pH) \) be the ratio between the concentration of species \( i \) in its molecular form and the total concentration of species \( i \). In the case of species that dissociate in the aqueous phase this ratio is a function of the pH.
- \( \Sigma N_{vi} \) be the sum of the moles of species other than water in the gas phase,
- \( \Sigma N_{li} \) be the sum of the moles of species other than water in the aqueous phase.

The following mass balances hold:

\[
N_{tW} = N_{vw} + N_{lw}
\]

\[
N_{li} = N_{vi} + N_{li}
\]

On the basis of Dalton’s and Henry’s laws it is useful to define the following partition coefficient:

\[
N_{vi}/N_{li} = K_{Hi} \cdot \alpha_i(pH) \cdot N_{vw}/(P_{H_2O} \cdot N_{lw})
\]

By appropriately manipulating Dalton’s law we obtain:

\[
N_{vw} = \Sigma N_{vi} \cdot (P_{H_2O}/(P - P_{H_2O}))
\]

From these relationships, solving with respect to \( N_{vw} \), one would obtain an equation of a degree equal to the number of substances other than water present in the system.

The algorithm that we chose for the numerical calculation is different and does not require writing the resolvent polynomial.

From the above equations it is easily obtained that

\[
N_{ti} = N_{li} \cdot (N_{vw} \cdot K_{Hi} \cdot \alpha_i(pH)/(N_{lw} \cdot P_{H_2O}) + 1)
\]

Hence, putting

\[
\delta_i = N_{vw} \cdot K_{Hi} \cdot \alpha_i(pH)/(N_{lw} \cdot P_{H_2O}) + 1
\]

we obtain

\[
N_{li} = N_{ti}/\delta_i
\]

and

\[
N_{vi} = N_{ti} \cdot (1 - 1/\delta_i)
\]

Remembering that

\[
N_{tW} = N_{vw} + N_{lw}
\]

we have

\[
\delta_i = [N_{tW} \cdot K_{Hi} \cdot \alpha_i(pH) + N_{lw} \cdot (P_{H_2O} - K_{Hi} \cdot \alpha_i(pH))]/(N_{lw} \cdot P_{H_2O}) (1)
\]
Moreover, since

\[ N_{vw} = \Sigma N_{vi} * P_{H2O} / (P_{H2O}) \]

we obtain

\[ N_{lw} = N_{lw} - \Sigma N_{vi} * P_{H2O} / (P_{H2O}) \]

Substituting this expression in (1) we obtain:

\[ \delta_i = \frac{N_{lw} * K_{Hi}*c_i(pH)+\left[ N_{lw} - \Sigma N_{vi} * P_{H2O} / (P_{H2O})\right] * (P_{H2O}- K_{Hi}*c_i(pH))}{\left[ N_{lw} - \Sigma N_{vi} * P_{H2O} / (P_{H2O})\right] * P_{H2O}} \]

To obtain the solution with a numerical method it is convenient to follow the following procedure:

- fix a tentative pH,
- calculate \( \alpha_i(pH) \),
- calculate tentative \( N_{vi} \)
- calculate \( \delta_i \)
- calculate \( N_{H} \)
- calculate tentative \( N_{vw} \)
- calculate tentative \( N_{lw} \)
- calculate the new \( N_{vi} \) and so on.

### 3.2.1.2 Case with reaction between H\(_2\)S and oxygen.

In the case where the reaction between H\(_2\)S and oxygen is considered, the formulas for determining these two species must of course be modified.

In addition to the symbols already introduced above, let:

- \( K_{ox} \) be the constant of the redox reaction

\[ H_2S \text{ (acq)} + \frac{1}{2} O_2 \text{ (acq)} = S^0 \]

- \( K'_{ox} \) be the apparent constant of the considered reaction,
- \([a]\) be the concentration of species \( a \),
- \( N_{tO2} \) be the total number of moles of \( O_2 \) that enter the system overall (steam from the turbine + cooling water),
- \( N_{vO2} \) be the number of moles of \( O_2 \) in the gas phase leaving the condenser,
- \( N_{lO2} \) be the number of moles of \( O_2 \) in the aqueous phase leaving the condenser,
- \( N_{tH2S} \) be the number of moles of H\(_2\)S entering the condenser overall,
- \( N_{vH2S} \) be the total number of moles of H\(_2\)S in the gas phase leaving the condenser,
- \( N_{lH2S} \) be the total number of moles of H\(_2\)S in the aqueous phase leaving the condenser,
- \( N_S \) be the number of moles of colloidal sulfur formed in the condenser.
The following relations hold:

\[
[H_2S]_{acq} = \frac{N_I[H_2S]}{N_I} \quad [O_2]_{acq} = \frac{N_I[O_2]}{N_I} \\
[H_2S]_{acq}[O_2]_{acq}^{1/2} = 1/K_{ox}
\]

\[
N_{tH_2S} = N_I[H_2S] + N_{vH_2S} + N_S \\
N_{tO_2} = N_I[O_2] + N_{vO_2} + 0.5*N_S
\]

Also valid are

\[
N_{vH_2S} = N_I[H_2S] \cdot K_{H_2S} \cdot \alpha_{H_2S}(pH) \cdot N_{vw}/(N_{lw} \cdot P_{H_2O})
\]

and

\[
N_{vO_2} = N_I[O_2] \cdot K_{HO_2} \cdot N_{vw}/(N_{lw} \cdot P_{H_2O})
\]

Since

\[
N_S = N_{tH_2S} - N_I[H_2S] - N_{vH_2S}
\]

we have

\[
N_{tO_2} = N_I[O_2] + N_{vO_2} + 0.5*N_{tH_2S} - 0.5*N_{I[H_2S]} - 0.5*N_{vH_2S}
\]

from which, after a few simple substitutions, we obtain:

\[
N_{tO_2} - 0.5*N_{tH_2S} = N_I[O_2] + N_{vO_2} \cdot K_{HO_2} \cdot N_{vw}/(N_{lw} \cdot P_{H_2O}) - 0.5*N_{I[H_2S]} - N_{tH_2S} \cdot K_{H_2S} \cdot \alpha_{H_2S}(pH) \cdot N_{vw}/(2*N_{lw} \cdot P_{H_2O})
\]

### 3.2.2 Algorithm for solving a polynomial of degree n

#### 3.2.2.1 Case without oxygen

To illustrate, we shall consider a system formed by the species CO₂, NH₃, H₂S, Cl (HCl) and H₂O.

Supposing that the partition coefficient of HCl between the steam and aqueous phases is nil at the low temperatures considered, the species to be considered in the vapor phase are CO₂, NH₃, H₂S and H₂O, and CO₂, NH₃, H₂S, H₂O and Cl(HCl/Cl⁻ complex compounds) in the aqueous phase.

Furthermore, let:

- \(N_{IW}\) be the total number of moles of water entering the system,
- \(N_{IC}\) be the total number of moles of CO₂ entering the system,
- \(N_{IS}\) be the total number of moles of H₂S entering the system,
- \(N_{IN}\) be the total number of moles of NH₃ entering the system,
- \(N_{ICl}\) be the total number of moles of Cl entering the system,
- \(N_{vW}\) be the number of moles of water in the gas phase,
- \(N_{vC}\) be the number of moles of CO₂ in the gas phase,
- \(N_{vN}\) be the total number of moles of NH₃ in the gas phase,
- \(N_{vS}\) be the total number of moles of H₂S in the gas phase,
- \(N_{lW}\) be the number of moles of liquid water,
- \(N_{IC}\) be the total number of moles of CO₂ (CO₂+H₂CO₃+HCO₃+CO₃⁻ complex compounds) in the aqueous phase,
- \(N_{IS}\) be the total number of moles of H₂S in the aqueous phase,
- \(N_{IN}\) be the total number of moles of NH₃ in the aqueous phase,
- \(N_{ICl}\) be the total number of moles of Cl in the aqueous phase,
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- $P_{CO2}$ be the partial pressure of $CO_2$,
- $P_{NH3}$ be the partial pressure of $NH_3$,
- $P_{H2S}$ be the partial pressure of $H_2S$,
- $P_{H2O}$ be the partial pressure of the water, which we consider only as a function of the temperature,
- $K_{HCO2}$ be the Henry constant of $CO_2$,
- $K_{HNH3}$ be the Henry constant of $NH_3$,
- $K_{HH2S}$ be the Henry constant of $H_2S$,
- $P$ be the total pressure in the condenser,
- $\alpha_i(pH)$ be the ratio between the concentration of species $i$ in its molecular form and the total concentration of species $i$. In the case of species that dissociate in the aqueous phase this ratio is a function of the pH.

It is possible to write the following relations:

\begin{align*}
N_{iW} &= N_{iC} + N_{iN} \\
N_{iC} &= N_{iC} + N_{iI} \\
N_{iN} &= N_{iN} + N_{iN} \\
N_{iS} &= N_{iS} + N_{iS} \\
N_{iCl} &= N_{iCl} \\
N_{iC}/N_{iW} &= K_{iHCO2} \cdot \alpha_i CO2(pH) \cdot N_{iCl}/(P_{H2O} \cdot N_{iW}) \\
N_{iS}/N_{iW} &= K_{iH2S} \cdot \alpha_i H2S(pH) \cdot N_{iS}/(P_{H2O} \cdot N_{iW}) \\
N_{iN}/N_{iW} &= K_{iHNH3} \cdot \alpha_i NH3(pH) \cdot N_{iN}/(P_{H2O} \cdot N_{iW}) \\
\end{align*}

In addition, the following hold:

\begin{align*}
P_{H2O} + P_{H2S} + P_{NH3} + P_{CO2} &= P \\
P_{H2S}/P_{H2O} &= N_{iS}/N_{iW} \\
P_{CO2}/P_{H2O} &= N_{iC}/N_{iW} \\
P_{NH3}/P_{H2O} &= N_{iN}/N_{iW} \\
\end{align*}

The following expression can be derived:

\[
(N_{iC} + N_{iS} + N_{iN})/N_{iW} = (P - P_{H2O})/P_{H2O}
\]

By defining $K_C$, $K_S$ and $K_N$ as:

\[
K_C = K_{iHCO2} \cdot \alpha_i CO2(pH)/P_{H2O} \\
K_S = K_{iH2S} \cdot \alpha_i H2S(pH) / P_{H2O} \\
K_N = K_{iHNH3} \cdot \alpha_i NH3(pH)/P_{H2O}
\]

relations (6), (7) and (8) can be reformulated as follows:

\begin{align*}
N_{iC}/N_{iW} &= K_C \cdot N_{iC}/N_{iW} \\
N_{iN}/N_{iW} &= K_N \cdot N_{iN}/N_{iW} \\
N_{iS}/N_{iW} &= K_S \cdot N_{iS}/N_{iW} \\
\end{align*}

and hence

\[
N_{iC}(N_{iC} - N_{iC}) = K_C \cdot N_{iC}/(N_{iW} - N_{iW})
\]
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\[ N_{vN}/(N_{tN}-N_{vN})=K_{N}^*N_{vW}/(N_{tW}-N_{vW}) \]
\[ N_{vS}/(N_{tS}-N_{vS})=K_{S}^*N_{vW}/(N_{tW}-N_{vW}) \]

From which

\[ N_{vC}=N_{tC}^*K_{C}^*N_{vW}/(N_{vW}^*(K_{C}-1)+N_{tW}) \]  \hspace{1cm} (14)
\[ N_{vN}=N_{tN}^*K_{N}^*N_{vW}/(N_{vW}^*(K_{N}-1)+N_{tW}) \]  \hspace{1cm} (15)
\[ N_{vS}=N_{tS}^*K_{S}^*N_{vW}/(N_{vW}^*(K_{S}-1)+N_{tW}) \]  \hspace{1cm} (16)

Indicating with

\[ P_{R}=P_{PH2O}/P_{H2O} \]
\[ K_{C1}=K_{C-1} \]
\[ K_{S1}=K_{S-1} \]
\[ K_{N1}=K_{N-1} \]

and substituting (14), (15) and (16) in expression (13), we obtain

\[ N_{tC}^*K_{C}^*N_{vW}/(N_{vW}^*K_{C1}+N_{tW})+N_{tS}^*K_{S}^*N_{vW}/(N_{vW}^*K_{S1}+N_{tW})+ \]
\[ N_{tN}^*K_{N}^*N_{vW}/(N_{vW}^*K_{N1}+N_{tW})=P_{R}^*N_{vW} \]  \hspace{1cm} (17)

From (17), with appropriate passages, we obtain the cubic equation in \( N_{vW} \) of the form \( AX^3+BX^2+CX+D=0 \), where:

\[ A=-P_{R}^*K_{C1}^*K_{S1}^*K_{N1} \]
\[ B=N_{tC}^*K_{C}^*K_{S1}^*K_{N1}+N_{tS}^*K_{S}^*K_{C1}^*K_{N1}+N_{tN}^*K_{N}^*K_{S1}^*K_{C1}^*- \]
\[ -P_{R}^*N_{tW}^*K_{N1}^*(K_{S1}+K_{C1})-P_{R}^*N_{tW}^*K_{C1}^*K_{S1} \]
\[ C=N_{tC}^*N_{tW}^*K_{C}^*(K_{S1}+K_{N1})+N_{tS}^*N_{tW}^*K_{S}^*(K_{C1}+K_{N1})+ \]
\[ N_{tN}^*N_{tW}^*K_{N}^*(K_{S1}+K_{C1})-P_{R}^*N_{tW}^*(K_{N1}+K_{C1}+K_{S1}) \]
\[ D=N_{tW}^2(N_{tC}^*K_{C}^*+N_{tS}^*K_{S}^*+N_{tN}^*K_{N})-P_{R}^*N_{tW}^3 \]

Once \( N_{vW} \) is found, it is possible to determine all the other unknowns.

3.2.2.2 Case with reaction between \( H_2S \) and oxygen

The very high value of the constant \( K_{OX} (> 10^{10}) \) and the relatively high values of the inlet concentrations of \( O_2 \) and \( H_2S \), permits us to assume the complete consumption of substoichiometric the specie. Three cases are possible:

1) \( H_2S < 2*O_2 \)
2) \( H_2S > 2*O_2 \)
3) Some authors (Mrockez E., Glover R.B., Webster J. (1995)) have hypothesized that the kinetics of the redox reaction is slower than that of partitioning between water and vapor of \( H_2S \) and \( O_2 \). This implies that only part of the oxygen reacts with \( H_2S \), so in the gas phase \( H_2S \) and oxygen can coexist. In this case the resolvent polynomial is no longer cubic, but quartic.
Discussion of first case

Without committing large errors we can assume that all the H$_2$S present oxides completely to colloidal sulfur. The remaining oxygen that will partition between the water and gas phase is:

$$N_{tO} = N_{tO0} + 0.5 * N_{tS}$$

where $N_{tS}$ is the total amount of H$_2$S that enters the system and $N_{tO0}$ is the initial amount of oxygen contained in the cooling water.

The algorithm illustrated earlier still holds. It is sufficient to substitute the oxygen data for the H$_2$S data. The polynomial is still cubic.

Discussion of second case

In this case the oxygen is completely consumed, and it holds that

$$N_{tS} = N_{tS0} - 2 * N_{tO}$$

where $N_{tO}$ is the amount of oxygen that enters the system and $N_{tS0}$ is the initial amount, before the reaction. Obviously, the algorithm used earlier still holds, it is sufficient to use the value of $N_{tS}$ after the reaction has occurred.

Discussion of partial oxidation of H$_2$S to S(c)

Let:

- $N_{tO0}$ be the amount of oxygen initially present in the cooling water,
- F be the fraction of oxygen that reacts,
- $N_{tO}$ be the amount of oxygen present after the reaction.

If

$$N_{tS} > 2 * N_{tO0} * F$$

then all the "reactive oxygen" is consumed, and hence

$$N_{tO} = N_{tO0} * (1 - F)$$

and

$$N_{tS} = N_{tS0} - 2 * N_{tO0} * F$$

If

$$N_{tS} \leq 2 * N_{tO0} * F$$

all the H$_2$S is consumed and the excess "reactive oxygen" remains.

Therefore the following hold:

$$N_{tO} = N_{tO0} - 0.5 * N_{tS0}$$

$$N_{tS} = 0$$

This second case has already been treated. In the following we shall consider the simultaneous presence of H$_2$S and O$_2$ in the vapor phase.
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Since the scheme used is analogous to what was discussed above, we shall only report the final solution.

The polynomial to be solved is quartic in the unknown $X = N_1 W$.

The form of the polynomial is $AX^4 + BX^3 + CX^2 + DX + F = 0$, where

$$A = \prod \left( \frac{K_{S1} \cdot K_{O1} \cdot K_{C1} \cdot K_{N1}}{N_1} \right)$$

$$B = \prod \left( \frac{K_{S1} \cdot K_{N1} \cdot K_{O1}}{N_2} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{N1}}{N_3} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{O1}}{N_4} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{N1}}{N_5} \right)$$

$$C = \prod \left( \frac{K_{S1} \cdot K_{O1} \cdot K_{C1} \cdot K_{N1}}{N_6} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{O1}}{N_7} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{N1}}{N_8} \right)$$

$$D = \prod \left( \frac{K_{S1} \cdot K_{O1} \cdot K_{C1}}{N_9} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{O1}}{N_10} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{N1}}{N_11} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{N1}}{N_12} \right)$$

$$E = \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{N1} \cdot K_{O1} \cdot K_{C1} \cdot K_{N1}}{N_13} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{N1} \cdot K_{O1} \cdot K_{C1} \cdot K_{N1}}{N_14} \right) + \prod \left( \frac{K_{S1} \cdot K_{C1} \cdot K_{N1} \cdot K_{O1} \cdot K_{C1} \cdot K_{N1}}{N_15} \right)$$

\[3.2.3\] Calculation of pH with assigned total concentrations of the different substances

Once the mass flow rates and therefore the total concentrations of the considered species have been calculated, it is possible to calculate the pH of the solution and the concentrations of the various ionic species.

The species considered in the aqueous phase are $H^+$, $H_2CO_3^-$, $HCO_3^-$, $CO_3^{2-}$, $H_2S^-$, $HS^-$, $S^{2-}$, $H_3BO_3^-$, $H_2BO_3^-$, $H_4SiO_4^-$, $H_3SiO_4^-$, $H_2SiO_4^{2-}$, $HCl^-$, $Cl^-$, $NH_3^+$, $NH_4^+$, $Na^+$, $NaOH^-$, $NaCO_3^-$, $NaCl^-$, $NaHCO_3^-$, $B2(OH)_7^-$, $B3(OH)_{10}^-$, $B5(OH)_{14}^-$, $CaCO_3^-$, $CaHCO_3^-$, $CaCO_3^+$, $CaSO_4^-$, $CaOH^-$, $KCl^-$, $KSO_4^-$, $MgCO_3^-$, $MgHCO_3^-$, $MgSO_4^-$, $MgOH^-$, $Ca^{2+}$, $Mg^{2+}$, $K^+$, $SO_4^{2-}$.

The speciation reactions considered are reported in section 4.1.

Each substance when dissolved will form $N_i$ species. If we indicate with $C_{ji}$ the concentration of species $j$ of substance $i$, it obviously holds that

$$\sum_{j=1}^{N_i} C_{ji} = C_{ti}$$

For each species $j$ it is possible to define the quantity $\alpha_{ji}$

$$\alpha_{ji} = C_{ji}/C_{ti}$$

which is a function of the pH and of the speciation constants.
Having fixed a tentative pH it is possible to calculate \( \alpha_j \), then the values of \( C_j \) and lastly the sum of the total positive and negative charges. Naturally the mass balance must hold; if this does not occur it means the pH value must be changed until convergence is reached.

Once the pH that satisfies this condition is found one can calculate the ionic strength and then repeat the cycle until convergence on the pH and the ionic strength.

### 3.3 Calculation algorithm used for the cooling tower

Experimental studies (Glover 1979) make it possible to affirm the following:

- the gas escaping from the solution by stripping in the cooling tower can be considered to be the gas present in molecular form in the water entering the tower;
- the hydrogen sulfide that remains in the liquid phase after stripping is completely oxidized to sulfate.

For this reason the calculation algorithm for the cooling tower was subdivided into two distinct parts: in the first the stripping of the gases is simulated, in the second the pH is calculated considering that the total concentrations of the different species are varied because of stripping, steam loss and oxidation of the remaining sulfide to sulfate.

By defining

- \( C_{\text{li}} \) as the total concentration of the volatile substance \( i \) in the water entering the tower
- \( C_{\text{Oi}} \) as the concentration of the neutral molecular form of substance \( i \) in the water entering the tower,
- \( C_{\text{bi}} \) as the total concentration of substance \( i \) after stripping, that is, in the water leaving the tower
- \( Q_{\text{tw}} \) as the flow rate of water entering the tower,
- \( Q_{\text{ow}} \) as the flow rate of water leaving the tower,

we have

\[
C_{\text{bi}} \cdot Q_{\text{ow}} = (C_{\text{li}} - C_{\text{Oi}}) \cdot Q_{\text{tw}}
\]

from which

\[
C_{\text{bi}} = (C_{\text{li}} - C_{\text{Oi}}) \cdot Q_{\text{tw}} / Q_{\text{ow}}
\]

For the nonvolatile substances it obviously holds that

\[
C_{\text{bi}} = C_{\text{li}} \cdot Q_{\text{tw}} / Q_{\text{ow}}
\]

After calculating the concentrations \( C_{\text{bi}} \) it is possible to determine the pH with the same algorithm used for the condenser, described in section 3.2.2.
3.4 REMARKS ON ALGORITHM CONVERGENCE

As stated in the preceding sections, it is generally possible to reach at the final solution by successive iterations, but this procedure is very slow and several hundred iterations would be needed. However, it has been demonstrated that for species that do not partition in the vapor phase the final solution can be easily calculated with the formula

$$C_F = \frac{Q_I}{W_E}$$

where

- $C_F$ is the final concentration of the species,
- $Q_I$ is the inlet flow rate and
- $W_E$ is the flow rate of the surplus water.

The formula is not applicable to species that partition in the vapor phase. In this case important roles are played by the water-vapor partition coefficient and the pH of the solution, which is a function of the concentration of the species present in solution and in particular of the amount of weak acids and bases present. Since partitioning occurs in both the condenser and the cooling tower, it is not possible to find a simple relation that allows coming up with an algorithm for rapid convergence.

The best solution found is that of supplying interactively for each run the concentration values of CO$_2$, NH$_3$, and SO$_4$ in the surplus water and verifying the mass balances with the solutions obtained from the approximate values supplied.

Given the low volatility of NH$_4$, at least in the range of pH the geothermal solutions, the initial tentative value of NH$_4$ is calculated with the formula shown above. The value of SO$_4$ is approximately set to one-half the concentration of ammonium ion.

Despite these stratagems, convergence problems can arise, especially in calculating the mass balances of the condenser. The problems occur when the ammonium in the surplus water is in excess with respect to the sulfate and hence the pH of the solution in the condenser may exceed 8 units.

One observes in this case, as can be logically expected, that the solution oscillates between two values. This being so, after 50 iterations the operator can provide new surplus water composition values.
4 THERMODYNAMIC DATA USED

4.1 WEAK ACIDS AND BASES

For the dissociation constants of the weak acids and the complex sodic species, reference was made to numerous bibliographic sources (Arnorsson et al., 1982; Glover, 1982; Helgeson, 1969; Kharaka and Barnes, 1973; Wolery, 1979).

Where the data are reported for discrete temperature values (Glover, 1982; Helgeson, 1969; Kharaka and Barnes, 1973; Wolery, 1979), multiple regression analysis was applied stepwise to obtain suitable functions of log K vs T (K).

These functions are reported below.

\[
\begin{align*}
\text{H}_2\text{O}^\circ & \Rightarrow \text{H}^+ + \text{OH}^- \quad \text{(Glover, 1982)} \\
\log K_w & = -35.5726 + 0.55982 T + 5706.6/T - 0.000045699 T^2 - 906062/T^2
\\
\text{H}_2\text{CO}_3^\circ & \Rightarrow \text{H}^+ + \text{HCO}_3^- \quad \text{(Glover, 1982)} \\
\log K_{\text{HCO}_3^-} & = 10.6177 - 0.035342 T - 1841.4/T + 0.0001522 T^2 - 143947/T^2
\\
\text{H}_2\text{CO}_3^\circ & \Rightarrow 2\text{H}^+ + \text{CO}_3^{2-} \quad \text{(Glover, 1982)} \\
\log K_{\text{CO}_3^{2-}} & = -0.4702 - 0.032428 T + 0.0000713 T^2 - 993177/T^2
\\
\text{H}_2\text{S}^\circ & \Rightarrow \text{H}^+ + \text{HS}^- \quad \text{(Glover, 1982)} \\
\log K_{\text{HS}^-} & = 6.7135 - 0.032128 T + 0.0001565 T^2 - 489195/T^2
\\
\text{H}_2\text{S}^\circ & \Rightarrow 2\text{H}^+ + \text{S}^{2-} \quad \text{(Glover, 1982; Wolery, 1979)} \\
\log K_{\text{S}^{2-}} & = -27.6311 + 0.054986 T - 0.0006840 T^2 - 609990/T^2
\\
\text{H}_3\text{BO}_3^\circ & \Rightarrow \text{H}^+ + \text{H}_2\text{BO}_3^- \quad \text{(Glover, 1982)} \\
\log K_{\text{H}_2\text{BO}_3^-} & = -58.4854 - 0.83540 T + 33844/T - 0.00002021 T^2 - 2248173/T^2 + 90.5844 lnT
\\
\text{H}_4\text{SiO}_4^\circ & \Rightarrow \text{H}^+ + \text{H}_3\text{SiO}_4^- \quad \text{(Arnorsson et al., 1982)} \\
\log K_{\text{H}_3\text{SiO}_4^-} & = -2549/T + 0.0001536 T^2
\\
\text{H}_4\text{SiO}_4^\circ & \Rightarrow 2\text{H}^+ + \text{H}_2\text{SiO}_4^{2-} \quad \text{(Arnorsson et al., 1982)} \\
\log K_{\text{H}_2\text{SiO}_4^{2-}} & = 5.37 - 0.2000 T - 3320/T
\\
\text{NH}_3^\circ & \Rightarrow \text{H}^+ + \text{NH}_3^\circ \quad \text{(Glover, 1982)} \\
\log K_{\text{NH}_3^\circ} & = -10.0569 + 0.14471 T - 0.00006234 T^2 - 262230/T^2
\\
\text{NaCl}^\circ & \Rightarrow \text{Na}^+ + \text{Cl}^- \quad \text{(Kharaka and Barnes, 1973)} \\
\log K_{\text{NaCl}^\circ} & = 78.4643 + 0.098530 T - 0.000072432 T^2 - 17.6473 lnT
\\
\text{NaOH}^\circ & \Rightarrow \text{Na}^+ + \text{OH}^- \quad \text{(Wolery, 1979)} \\
\log K_{\text{NaOH}^\circ} & = 633.8541 + 0.318190 T - 14297/T - 0.000146748 T^2 - 17.6473 lnT
\end{align*}
\]
Control of corrosion and scaling in geothermal systems

\[ \text{NaCO}_3^- = \text{Na}^+ + \text{CO}_3^{2-} \quad (\text{Wolery, 1979}) \]

\[
\log K_{\text{NaCO}_3} = 5.7406947 + 1.821097 T - 231803/T - 0.000641675 T^2 + 10236241/T - 976.7727 \ln T
\]

\[ \text{NaH}_2\text{SiO}_4^2- = \text{Na}^+ + \text{H}_2\text{SiO}_4^- \quad (\text{Arnorsson et al., 1982}) \]

\[
\log K_{\text{NaH}_2\text{SiO}_4} = -270/T - 0.0000271 T^2
\]

4.2 HYDROCHLORIC ACID

The hydrochloric acid contained in geothermal steam plays an important part in corrosion and scaling processes in well casings, steam pipelines and turbine blades. The origin and transport of HCl in geothermal environments has therefore received considerable attention (see, for example, Andreussi et al., 1994, and related bibliography). Insight into these phenomena is made even more difficult by the lack of sure data on the dissociation constant of aqueous HCl as well as of experimental data on the solubility of gaseous HCl at high temperature. This second gap was recently filled by Simonson and Palmer (1993), who measured HCl partitioning between liquid and vapor phases from 50 to 350°C, at 50°C intervals. The dissociation constant of dissolved HCl is still uncertain, however, particularly at low temperatures. For instance, at 25°C, the common logarithm of this constant could be 6.1 (Reed, 1991), or 0.67 (Ruaya and Seward, 1987), or 0.20 (Glover, 1982).

Due to these uncertainties regarding the dissociation constant of aqueous HCl, Simonson and Palmer (1993) decided to take into consideration the total stoichiometric molalities of aqueous HCl, which they measured in liquid and vapor phases presumably in equilibrium \( (m_{\text{HCl},l} \text{ and } m_{\text{HCl},v}) \), respectively, and the stoichiometric activity coefficient in the liquid phase \( (\Gamma_{\text{HCl},l}) \) to calculate the global distribution coefficient:

\[
K = \frac{m_{\text{HCl},v}}{(m_{\text{HCl},l} \Gamma_{\text{HCl},l})^2} \quad (1)
\]

According to Simonson and Palmer (1993), their experimental results and the previous data are described by the following function:

\[
\log K = -13.4944 - 934.466/T - 11.0029 \log \rho + 5.4847 \log T \quad (2)
\]

where the temperature \( T \) is in degrees Kelvin and the water density \( \rho \) is in \( \text{g/cm}^3 \).

The experimental work of Simonson and Palmer (1993) is extremely important. However, their global distribution coefficient \( K \) cannot be used to calculate HCl distribution between multicomponent aqueous solutions and coexisting vapors. We therefore decided to process the experimental data of Simonson and Palmer (1993) to calculate a distribution coefficient of HCl between liquid and vapor phases, \( B_{\text{HCl}} \), which would be of general use, accepting the introduction of the uncertainties obviously connected with the dissociation constant of aqueous
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Figure 4.1 Partition coefficient of HCl as a function of temperature

4.3 ACTIVITY COEFFICIENTS

The individual activity coefficients of ionic solutes, $\gamma_i$, are calculated using the extended Debye-Hückel formula (Helgeson, 1969):

$$ \log \gamma_i = -[(A z_i^2 I^{1/2})/(1 + \delta_i B I^{1/2})] + C I $$

where:
- the coefficients $A$, $B$ and $C$ are functions of temperature (Helgeson, 1969; Helgeson and Kirkham, 1974);
- $\delta_i$ is the "distance of closest approach" of the ions in solution, whose dependence on temperature is unfortunately not known (Helgeson, 1969); the values at 25°C, reported by various authors (such as Fritz, 1981) are therefore used;
- $I$ is the true ionic strength, defined by the relation:
  $$ I = 0.5 \Sigma m_i z_i^2 $$

The activity coefficients of species with zero charge are considered equal to those of CO$_2$, reported by Helgeson (1969) for different values of $T$ and $I$. 
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Finally, to calculate the values of $B_{HCl}$ it is necessary to consider the dissociation constant of $HCl^o$:

$$K_{HCl^o} = (m_{H^+} m_{Cl^-} \gamma_{H^+} \gamma_{Cl^-})/(m_{HCl^o} \gamma_{HCl^o})$$ (3)

and the mass balance:

$$m_{HCl^1} = m_{HCl^o} + m_{Cl^-}$$ (4)

where $\gamma_i$ identifies the individual activity coefficient of the aqueous species $i$.

The values of $\gamma_i$ are calculated using the extended Debye-Hückel expression (Helgeson, 1969):

$$\log \gamma_i = -\left(A z_i^2 (1/2)/(1 + \frac{\tilde{a}_i B 1/2)} + C I\right)$$ (5)

where:

- $A$ and $B$ are parameters of the solvent, that is, they depend on the density and the dielectric constant of pure water and on the temperature (Helgeson and Kirkham, 1974);
- $\tilde{a}_i$ is the distance of closest approach between one ion and another of opposite charge. Since its dependence on temperature is unknown (Helgeson, 1969), the values of $\tilde{a}_i$ at 25°C are generally used at any temperature. The values of $\tilde{a}_i$ at 25°C are 9.0 $10^{-8}$ cm for $H^+$ and 3.5 $10^{-8}$ cm for $Cl^-;
- $C$ is a function of temperature (Helgeson, 1969);
- $I$ is the true ionic strength, which is defined by the following equation:

$$I = 0.5 \Sigma m_i z_i^2$$ (6)

The individual activity coefficients of the neutral aqueous species, such as $HCl^o$, are usually considered equal to those of $CO_2$. The latter are reported by Helgeson (1969) for different values of $T$ and $I$.

By substituting (4) in (3) the following equation is obtained:

$$(m_{Cl^-})^2(\gamma_{H^+} + \gamma_{Cl^-})/(\gamma_{HCl^o}) + m_{Cl^-} K_{HCl^o} - m_{HCl^1} K_{HCl^o} = 0$$ (7)

which is easily solved to $m_{Cl^-}$ by iterating on the ionic strength. The value of $m_{HCl^o}$ is then calculated by inserting $m_{Cl^-}$ in equation (3). Lastly, the liquid-vapor distribution coefficient is calculated using the following expression:

$$B_{HCl} = m_{HCl^v}/m_{HCl^o}$$ (8)

The results of the 9 experimental tests of Simonson and Palmer (1993) with high values of $m_{HCl^1}$ (4.2-4.9 mol/kg) were not considered because the extended Debye-Hückel expression cannot be applied to such highly concentrated aqueous solutions. The results of the other 56 experimental tests of Simonson and Palmer (1993) make it possible to obtain the values of $B_{HCl}$ represented in Figure 4.1.
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The calculations were performed twice, taking into consideration different values of the dissociation constant of aqueous HCl: the asterisks and squares identify the values of $B_{HCl}$ obtained by referring to $K_{HCl}$ of Glover (1982) and Reed (1991), respectively. The dependence of $K_{HCl}$ on temperature is given by the following expression, according to Glover (1982):

$$\log K_{HCl}^\circ = 5191.1685 + 1.572626 \frac{T}{T-215414/T} - 0.00529035 T^2 + 9792563/T^2 - 877.6468 \ln T$$ (9)

while Reed (1991) has:

$$\log K_{HCl}^\circ = 7.1913 - 0.042377 (T-273.15) - 0.68516E-4 (T-273.15)^2 + 0.75865E-6 (T-273.15)^3 - 0.12389E-8 (T-273.15)^4$$ (10)

Although some scattering is observed in Figure 4.1, the $B_{HCl}$ values obtained referring to the $K_{HCl}$ of Glover (1982) are satisfactorily represented by the following function:

$$\log B_{HCl} = -2.74437 + 0.0174508 (T-273.15) - 2.34326E-5 (T-273.15)^2$$ (11)

whereas the $B_{HCl}$ values obtained referring to the $K_{HCl}$ values of Reed (1991) agree with the following equation:

$$\log B_{HCl} = 5.29026 - 0.0549219 (T-273.15) + 1.87451E-4 (T-273.15)^2 - 1.96095E-7 (T-273.15)^3$$ (12)

Finally, it must be stressed that functions (11) and (12) yield similar values of $B_{HCl}$ in the 220-350°C range, while they diverge significantly at temperatures below 220°C.
5.

APPLICATIONS AND DISCUSSION OF MODEL

The computer program is suitable to be used in simulating the chemical behavior of the geothermal fluid within the exploitation cycle.

The hypotheses made here should be checked with a series of campaigns to measure the chemical composition of the cooling tower water and the inlet steam.

The subsequent work examined a few cases of chemical composition of inlet steam in order to identify the control parameters of the reaction mechanisms and to identify possible directions for future study, even though the number of cases, due to obvious time limitations, was restricted to only a few conditions.

The program was used to simulate the conditions of pH and composition in the case reported in Table 5.1.

Table 5.1. Input data for the condenser/cooling tower system

| Steam flow rate entering the condenser (t/h) | 104.83 |
| Water flow rate entering the condenser (t/h) | 5300 |
| CO2 flow rate entering the condenser (kg/h) | 5075 |
| H2S flow rate entering the condenser (kg/h) | 77.52 |
| NH3 flow rate entering the condenser (kg/h) | 15.73 |
| Total pressure of condenser (bar) | 0.0750 |
| Condensation temperature (°C) | 27 |
| Water temperature leaving cooling tower (°C) | 25 |
| Steam composition, in moles/kg: | |
| CO2 | 1.10 |
| H2S | 2.17E-2 |
| NH3 | 8.81E-3 |

Keeping the above conditions fixed, the system behavior was studied by varying the flow rate of the surplus water, supposing oxidation of H2S to colloidal sulfur in the condenser and hypothesizing the presence of variable amounts of HCl.

The obtained results are shown in Tables 5.2, 5.3, and 5.4.
Table 5.2. Material balances and composition of cooling tower water vs flow rate and oxidation of H2S

<table>
<thead>
<tr>
<th>INPUT</th>
<th>OUTPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONDENSER</td>
<td>CONDENSER STEAM</td>
</tr>
<tr>
<td>H2O (t/h)</td>
<td>104.83</td>
</tr>
<tr>
<td>CO2 (kg/h)</td>
<td>5075</td>
</tr>
<tr>
<td>H2S (kg/h)</td>
<td>77.5</td>
</tr>
<tr>
<td>NH3 (kg/h)</td>
<td>15.7</td>
</tr>
<tr>
<td>HCl (kg/h)</td>
<td>0</td>
</tr>
<tr>
<td>SO4</td>
<td>3.95</td>
</tr>
<tr>
<td>O2 (kg/h)</td>
<td>53</td>
</tr>
<tr>
<td>SO (kg/h)</td>
<td>77.5</td>
</tr>
<tr>
<td>O2 consumed (kg/h)</td>
<td>36.29</td>
</tr>
<tr>
<td>O2 (mg/l)</td>
<td>0.0075</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CONDENSER</th>
<th>SURPLUS WATER</th>
<th>CONCENTRATIONS IN SURPLUS WATER (moles/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O (t/h)</td>
<td>104.83</td>
<td>4.32E-03</td>
</tr>
<tr>
<td>CO2 (kg/h)</td>
<td>5075</td>
<td>8.3E-03</td>
</tr>
<tr>
<td>H2S (kg/h)</td>
<td>77.5</td>
<td>15.73</td>
</tr>
<tr>
<td>NH3 (kg/h)</td>
<td>15.7</td>
<td>15.73</td>
</tr>
<tr>
<td>HCl (kg/h)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SO4</td>
<td>8.32E-03</td>
<td>2.8E-01</td>
</tr>
<tr>
<td>O2 (kg/h)</td>
<td>53</td>
<td>3.97</td>
</tr>
<tr>
<td>SO (kg/h)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2 consumed (kg/h)</td>
<td>15.73</td>
<td>15.29</td>
</tr>
<tr>
<td>O2 (mg/l)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

30, 60 and 80 are the surplus water flow rates in t/h
Sox = without oxidation of sulfides to colloidal S in condenser
ox = with oxidation of sulfides to colloidal S in condenser
Tabella 5.3. Effect of the presence of HCl on material balances for some surplus water flow rate values.

<table>
<thead>
<tr>
<th>INPUT</th>
<th>OUTPUT</th>
<th>Condenser steam</th>
<th>Cooling tower steam</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Condenser steam</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Sox</td>
<td>ox</td>
<td>Sox</td>
</tr>
<tr>
<td>H2O (l/h)</td>
<td>104.83</td>
<td></td>
<td>1798</td>
</tr>
<tr>
<td>CO2 (kg/h)</td>
<td>5075</td>
<td></td>
<td>4770</td>
</tr>
<tr>
<td>H2S (kg/h)</td>
<td>77.5</td>
<td></td>
<td>65.3</td>
</tr>
<tr>
<td>NH3 (kg/h)</td>
<td>15.73</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HCl (kg/h)</td>
<td>1.61679</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SO4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 (kg/h)</td>
<td>53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 consumed (kg/h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 (mg/l)</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>INPUT</th>
<th>OUTPUT</th>
<th>Surplus water</th>
<th>Concentrations in surplus water (mole/l)</th>
</tr>
</thead>
<tbody>
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<td>Superfis water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Sox</td>
<td>ox</td>
<td>Sox</td>
</tr>
<tr>
<td>H2O (l/h)</td>
<td>104.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2 (kg/h)</td>
<td>5075</td>
<td>0.00E+00</td>
<td>1.20E-01</td>
</tr>
<tr>
<td>H2S (kg/h)</td>
<td>77.5</td>
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<td>0</td>
</tr>
<tr>
<td>NH3 (kg/h)</td>
<td>15.73</td>
<td>15.72</td>
<td>15.52</td>
</tr>
<tr>
<td>HCl (kg/h)</td>
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<td>1.61</td>
<td>1.61</td>
</tr>
<tr>
<td>SO4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 (kg/h)</td>
<td>53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 consumed (kg/h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 (mg/l)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

30 and 80 are the surplus water flow rates in l/h
Sox = without oxidation of sulfides to colloidal S in condenser
ox = with oxidation of sulfides to colloidal S in condenser
Table 5.4. Material balances and composition of cooling tower water as a function of efficiency of the redox reaction between H2S and O2

<table>
<thead>
<tr>
<th>INPUT</th>
<th>Condenser water</th>
<th>Condenser steam</th>
<th>Condenser steam</th>
<th>Cooling tower steam</th>
<th>Cooling tower steam</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Condenser steam</td>
<td>Condenser steam</td>
<td>Condenser steam</td>
<td>Cooling tower steam</td>
<td>Cooling tower steam</td>
</tr>
<tr>
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<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>H2O (t/h)</td>
<td>104.83</td>
<td>1.774</td>
<td>1.769</td>
<td>1800</td>
<td>1816.2</td>
</tr>
<tr>
<td>CO2 (kg/h)</td>
<td>5075</td>
<td>4766</td>
<td>4762</td>
<td>4767</td>
<td>4769</td>
</tr>
<tr>
<td>H2S (kg/h)</td>
<td>77.5</td>
<td>0</td>
<td>12.98</td>
<td>52.11</td>
<td>64.8</td>
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<tr>
<td>NH3 (kg/h)</td>
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<td>0.00165</td>
<td>0.00072</td>
<td>3.50E-04</td>
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</tr>
<tr>
<td>HCl (kg/h)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2 consumed (kg/h)</td>
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<td>4.7</td>
<td>4.39</td>
<td>3.95</td>
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<td>0</td>
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<tr>
<td>O2 (mg/l)</td>
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<td>0.010872</td>
<td>0.0204</td>
<td>0.02318</td>
<td>0.0075</td>
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</table>

<table>
<thead>
<tr>
<th>INPUT</th>
<th>OUTPUT</th>
<th>Surplus water</th>
<th>Concentrations in surplus water (moles/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Condenser</td>
<td>Surplus water</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Surplus water</td>
<td>Surplus water</td>
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</tr>
<tr>
<td></td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>H2O (t/h)</td>
<td>104.83</td>
<td>1.774</td>
<td>1.769</td>
</tr>
<tr>
<td>CO2 (kg/h)</td>
<td>5075</td>
<td>4766</td>
<td>4762</td>
</tr>
<tr>
<td>H2S (kg/h)</td>
<td>77.5</td>
<td>0</td>
<td>12.98</td>
</tr>
<tr>
<td>NH3 (kg/h)</td>
<td>15.73</td>
<td>0.00165</td>
<td>0.00072</td>
</tr>
<tr>
<td>HCl (kg/h)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2 consumed (kg/h)</td>
<td>53</td>
<td>5.12</td>
<td>4.7</td>
</tr>
<tr>
<td>pH</td>
<td>53</td>
<td>16.6</td>
<td>23.9</td>
</tr>
<tr>
<td>SO4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2 (mg/l)</td>
<td>0.0075</td>
<td>0.010872</td>
<td>0.0204</td>
</tr>
</tbody>
</table>

The surplus water flow rate is 30 t/h.
F is the fraction of H2S that oxidizes.
Table 5.2 shows the effect that the surplus water flow rate has in the hypothesis of total oxidation of sulfides to colloidal sulfur and of non-oxidation, assuming the complete absence of hydrochloric acid in the inlet stream.

Table 5.3 shows the effect of hydrochloric acid for the same conditions as Table 5.2.

Table 5.4 shows the effect of different degrees of hydrogen sulfide oxidation on the chemical composition of the streams.

The following is observed:

- Over 94% of the CO₂ present in the steam at the condenser inlet is expelled in all cases through the gas extractor while only a tiny part, about 0.02%, remains dissolved in the surplus water. This condition seems quite unaffected by variations in the composition of the inlet steam.
- Some 98-99.93% of the NH₃ present in the steam is found in the surplus water while only a modest amount remains in the gas to the extractors.
- Similar remarks to those made for CO₂ would also apply to the H₂S present in the steam if the oxidation phenomena caused by the oxygen in the condensate were excluded.
- Owing to the oxidation of sulfides to colloidal sulfur, the H₂S content dispersed through the cooling towers could decrease considerably because in conditions of complete oxidation of H₂S in the condenser, the hydrogen sulfide dispersed through the towers would be virtually nil. Indeed, the formation of colloidal sulfur was observed in the water leaving the condenser; the chemical processes do not occur at equilibrium, however, as attested by the oxygen concentration measured during experimental testing of chemical equilibrium calculation models (Glover R.B., Mrockez E. (1995), Mrockez E., Glover R.B., Webster J. (1995)). The measured concentration was too high (about 2 mg/l) in relation to the expected concentration, which should range between 0.0075 and 0.023 mg/l if even partial oxidation of hydrogen sulfide occurred.
- Having supposed that the sulfide ion that remains, even in very small amounts, in the discharge water from the condenser oxidizes completely to sulfate, the composition of the surplus water is basically "ammonium sulfate water." Small excess amounts of ammonia or sulfate thus cause the pH variations of the surplus water and the content in carbonate species. Due to the composition of the inlet steam the pH of the surplus water stays acid and varies between 3.97 and 5.1 depending on the surplus water flow rate. The fraction of H₂S oxidized in the condenser also influences the pH.
- The presence of HCl in the steam makes the circulating fluids more acid, but does not substantially modify the partitioning between the gas and aqueous phases of the different species.
- The pH variations of the surplus water are greatly influenced by the concentration ratio and the oxidation of sulfides to colloidal sulfur.

The chemical data on the surplus water obtained with the model and the values measured, even if not entirely satisfactorily, by ENEL, are in good agreement with regard to chemical classification of the type of water, since the cooling tower surplus water is of the ammonium sulfate type. However, the measured pH is generally slightly basic and the waters display 2-3 meq of alkalinity.
Even if the $H_2S/NH_3$ ratio in the inlet steam were modified, important variations would not be observed in the calculated pH trends.

The measured pH values, higher than those predicted by the model, could also be explained by considering the dissolution of carbonate species (the cement of the cooling tower tanks) by acid waters from the condenser.

However, it was decided to investigate the topic further, so the model of $H_2S$ stripping in the cooling tower was modified.

We point out that in the adopted model, only molecular $H_2S$ passes into the gas phase, $HS^-$ does not have time to be transformed to $H_2S$ and be liberated. In other words, the speed of oxidation of $HS^-$ was considered to be faster than the speed at which aqueous $H_2S$ and then gaseous $H_2S$ form. However, if we consider the exact opposite to be true, that is, that the stripping involves the sum of the $H_2S+HS^-$ species, an increase in the pH of the surplus water is observed.

The comparison data are contained in Table 5.5, showing the possible effect of the hypothesis of stripping in the cooling tower not only of the molecular hydrogen sulfide but also of $HS^-$ ion.

The above underscores the importance of having a correct model of gas stripping in the cooling tower in order to be able to reconstruct the fluid composition in the condenser/cooling tower system as exactly as possible.

Nevertheless, despite the uncertainties the proposed model may have, one interesting result must be emphasized: if the oxygen present in the cooling tower condensate reacted with the $H_2S$ present to form colloidal $S$, it would abate much of the hydrogen sulfide, eliminating the need for the techniques being studied to remove $H_2S$ from the aqueous phase (acid injection, surface condenser).

The experimental data collected (Mrockez E., Glover R.B., Webster J. (1995) demonstrate that kinetic factors make the efficiencies of the reaction very low. This might instead play an important role in sulfide abatement.
Table 5.5. Material balances and composition of cooling tower water as a function of model of cooling tower stripping

<table>
<thead>
<tr>
<th>INPUT</th>
<th>OUTPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Condenser</td>
</tr>
<tr>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>H2O (t/h)</td>
<td>104.83</td>
</tr>
<tr>
<td>CO2 (kg/h)</td>
<td>5075</td>
</tr>
<tr>
<td>H2S (kg/h)</td>
<td>77.5</td>
</tr>
<tr>
<td>NH3 (kg/h)</td>
<td>15.7</td>
</tr>
<tr>
<td>HCl (kg/h)</td>
<td>0</td>
</tr>
<tr>
<td>SO4</td>
<td>53</td>
</tr>
<tr>
<td>O2 (kg/h)</td>
<td>2</td>
</tr>
<tr>
<td>S0 (kg/h)</td>
<td>53</td>
</tr>
<tr>
<td>O2 consumed (kg/h)</td>
<td>0</td>
</tr>
<tr>
<td>O2 (mg/l)</td>
<td>30</td>
</tr>
</tbody>
</table>

(1) = stripping only of molecular H2S present in solution
(2) = stripping of molecular H2S + HS present in solution
CONCLUSIONS

A model was developed to calculate the chemical composition of the liquid and gas streams that form a conventional geothermal power plant with an assigned chemical composition of the turbine inlet steam.

The model showed how changing the hypotheses regarding the kinetics of the chemical reactions in the different plant components substantially influences the chemical composition and pH of the solutions.

In particular, it was shown that the pH levels both in the condenser and of the surplus water are acid unless one hypothesizes complete stripping of HS' ion in the cooling tower. It was also shown that complete oxidation of hydrogen sulfide in the condenser is possible and would result in complete elimination of the sulfurous species in the cooling tower.

A number of directions in which additional work could be done are:

- a campaign to measure the chemical composition of the steam, the surplus water and their flow rates. Such a measuring campaign would make it possible to identify calculation hypotheses that would come closer to the physical reality and to develop a more reliable calculation model.

- verification of the oxygen content in the condenser and study of design modifications on the direct-contact condenser in order to promote complete oxidation of hydrogen sulfide. This would make it possible not only to eliminate hydrogen sulfide in the cooling tower water but also to raise the pH, resulting in reduced corrosion problems in the cooling water circuit.

- developing a "kinetic" model of the cooling tower to evaluate the phenomena controlling the CO₂ and H₂S stripping process.
APPENDIX 1. SHORT GUIDE TO USE OF THE COMPUTER PROGRAMS

The program is written in Quik-Basic and is organized interactively. From the operator's standpoint, the program can be thought of as subdivided into three sections: entry of system chemical and physicochemical data, entry of the necessary thermodynamic data, and approximate solutions. For each approximate solution that is supplied the program prints out the mass balances. When convergence is reached it is possible to have as output the pH and concentration values of the surplus and condenser water and the mass flow rates of the different components leaving the condenser and cooling tower as gas.

A.1. ENTRY OF CHEMICAL AND PHYSICAL DATA

The prompt "WORKING DIRECTORY?" first appears on the screen. The operator must type in the path of the working directory where the files containing the thermodynamic data will be located. The data files must instead be located in the current working directory. This is immediately followed on the screen by the query "ARE DATA ON FILE?" The operator can respond "y" or "n" depending on the case.

A.1.1. Procedure to follow if data are on file

If the data are already on file the prompt "Filename" will appear. When the file has been read the prompt "Print initial data? (y/n)" appears. Answering "y" will cause the data to be printed.

A.1.2. Procedure to follow for data entry from keyboard

If the data are not on file the operator can follow the cues given by the program. The data are subdivided into physical data and chemical data. The first thing requested is the physical data of the condenser:
- cooling water flow rate (t/h)
- inlet steam flow rate (t/h)
- condenser pressure (bars)
- condenser temperature (°C)

The program then asks for the tentative composition of the surplus water, equal to the composition of the cooling water. The data can be supplied in moles/kg of water. The values are requested in the following order:
- CO₂ tot
- H₂S tot
- NH₃ tot
- SiO₂
- H₃BO₃
- Cl
- Na
- Ca
- Mg
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- SO₄
- K
- O₂

In view of what was said in the report, the tentative values can be set at 0. For oxygen the program assigns a default value of 0.000313 moles/kg of water (10 ppm of oxygen). If no data are provided for SiO₂, H₃BO₃, and Cl, the program automatically assigns the convergence value.

Next the program requests the data on the steam composition, expressed in moles/kg. In the following order, the program asks about
- CO₂ tot
- H₂S tot
- NH₃ tot
- SiO₂
- H₃BO₃
- HCl
- NaCl
- O₂

The last data requested are the temperature of the cooling tower water (°C) and the flow rate of the surplus water (v/h).

The program allows the entered data to be stored. After the data have been entered the prompt "Save data? (y/n)" appears. If the answer is "y", the program requests the filename. The data will be saved in the current working directory.

Obviously, also in this case it is possible to print out the data supplied to the computer.

A2. PROCEDURE FOR ENTERING TENTATIVE DATA AND VERIFICATION OF CONVERGENCE OF MASS BALANCES

Convergence is verified on the net mass balances of the system. Therefore, the mass balance must hold i.e. mass flowrate that enters the condenser from the turbine (thereby excluding from the balances the cooling water entering the condenser) must be equal to that which leaves the cooling tower as surplus water and that which leaves the condenser and the cooling tower in the form of vapor. Since it is assumed that only CO₂, H₂S and NH₃ partition at the condenser and cooling tower temperatures in the vapor phase, and that all the H₂S oxidizes to SO₄²⁻ in the cooling tower, the only species for which tentative concentration values must be provided are CO₂, NH₃ and SO₄²⁻.

For each tentative solution, the screen will display the material unbalances for the species of interest, expressed as absolute difference in the number of moles between inlet and outlet. If the unbalance is positive it will generally be necessary to increase the amount of the species in the surplus water, if it is negative this amount will have to be reduced. If the unbalance is considered small enough the operator can print out the definitive results.
REFERENCES


SYNTHESIS OF MALEIC COPOLYMERS CONTAINING:
A) PIPERAZINE OR ITS DERIVATIVES, B) AROMATIC AMINES

A. CARPOV, G.C. CHITANU, L.I. ZAHARIA, A.G. ANGHELESCU-DOGARU

"Petru Poni" Institute of Macromolecular Chemistry, BBPDICM

SUMMARY

Several derivatives of maleic anhydride copolymer with piperazine or N-substituted piperazine were synthesized by our laboratory and tested by ICPE C-60 as corrosion inhibitors. They exhibit very good properties in corrosion inhibition and also an excellent behaviour as calcium carbonate precipitation inhibitors (laboratory tests, BBPDICM).

Another class of maleic derivatives were obtained by reaction with aromatic amines. Such samples were synthesized by BBPDICM and tested by ICPE C-60 as corrosion inhibitors and showed also a good activity.

In this report are also presented the results obtained by ICE/HT, BRGM and CPERI concerning the ability of some maleic copolymers to reduce to a certain extent the iron sulphide precipitation, the excellent behaviour of several maleic copolymers as calcium carbonate scale inhibitors and the uneffectiveness of some maleic copolymers to control the corrosion in natural geothermal environment.

1. INTRODUCTION

In the fourth report the objectives and deliverables are the same as in the other three previous reports.

In the first report were presented the following results:
- study of the synthesis of monoesters of maleic anhydride copolymers with different OH-containing reaction partners (Romanian Patent Appl. C/1366/12.08.1994)
- synthesis of samples of NH4+, Na+, Zn2+ or Na+/Zn2+ salts of different maleic acid copolymers to be tested as corrosion inhibitors by our contract partner ICPE C-60 (encouraging results)
- synthesis of pilot scale samples of NH4+, Na+ and Na+/Zn2+ salts of maleic acid-vinyl acetate copolymers to be tested in the geothermal wells in Oradea Region of Western Romania.
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In the second report we have presented:
- studies concerning the obtaining of inorganic salts of different binary or ternary maleic acid copolymers (Romanian Patent Appl. S/00308/1995)
- preliminary experiments about the obtaining of salts of maleic acid copolymers with organic cations and the synthesis of monoamides of maleic copolymers;
- synthesis of maleic polyelectrolyte samples to be tested by our colleagues by ICE/HT Patras, ICPE C-60 Bucharest, CPERI Thessaloniki, CRIC Budapest and ICVL Vilnius.

In the third report were presented following results:
- study of the synthesis of new binary and ternary copolymers of maleic anhydride with N-vinylpyrrolidone (Romanian Patent Appl. C/01004/06.05.1996)
- study of the synthesis of salts of maleic acid copolymers with organic cations (Romanian Patent Appl. C/01060/23.05.1996)
- experiments concerning the reaction of maleic anhydride copolymers with aliphatic amines and with monoethers of ethylene glycol. A patent application concerning this topic will be claimed in the near future.
- synthesis of a pilot sample of Na+/Zn2+ salt of maleic acid - vinyl acetate copolymer to be tested in geothermal plants.

In the fourth report will be presented our activities concerning the literature documentation and the experimental work during the period November 1, 1995 - May 31, 1996.

2. DOCUMENTATION

It was continued our usual literature search concerning the synthesis, characterisation and applications of maleic copolymers and about the use of water-soluble polymers as scale and corrosion inhibitors. This activity allowed us to have a general approach of this topic and to target our experiments to the optimum ways to obtain the most efficient products.

3. EXPERIMENTAL WORK

Our experimental effort was focused on the synthesis of two classes of products:
- reaction products of maleic anhydride copolymers with piperazine and its derivatives
- monoamides of maleic anhydride copolymers with aromatic amines as aniline or o-toluidine.

3.1. Synthesis of maleic copolymers containing piperazine or its derivatives.

It is known the corrosion activity of some amines as fatty, heterocyclic or aromatic ones [1, 2]. On the other hand, the preliminary results obtained by our contract partners ICPE C-60 and ICE/HT emphasized a good efficiency of some maleic copolymers, especially the ones based on maleic acid-alt-N-vinylpyrrolidone copolymer (MA-NVP) as corrosion inhibitors in synthetic sea water or geothermal brine. Consequently, we have studied the reaction between the maleic anhydride-alt-N-vinylpyrrolidone copolymer and a heterocyclic saturated amine - piperazine or its derivatives: N-(2-hydroxyethyl)piperazine and N-(2-aminoethyl)piperazine. The piperazine derivatives of MA-NVP copolymer were tested as scale inhibitors using two
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methods available in our laboratory: the precipitation test and the Hampshire test. Their corrosion inhibition effect was tested by our colleagues at ICPE C-60 Bucharest using the impedance analysis method and the steady state polarization curves method for a synthetic geothermal water with a composition similar to the Romanian geothermal water with a carbon steel R 37 sample.

Materials and methods

A maleic anhydride - alt - N-vinylpyrrolidone (MA-NVP) copolymer was synthesized by radical copolymerization using our method described in Rom. Pat. Appl. C/1004/1996 [3], with the chemical formula depicted in the Scheme 1.

\[ \text{Scheme 1 - Chemical formula of MA-NVP copolymer} \]

Maleic anhydride was twice recrystallized from dry chloroform; N-vinylpyrrolidone was twice distilled at reduced pressure and the fraction with \( nD_{20} = 1.5075 \) was used. The catalyst azobisisobutyronitrile was recrystallized from anhydrous methanol. The other solvents used for copolymerization or for subsequent reactions on MA-NVP copolymer were p.a. grade. Piperazine, N-(2-hydroxyethyl)piperazine and N-(2-aminoethyl)piperazine were p.a. reagents obtained from BASF - Germany.

MA-NVP copolymer was characterized by conductometric titration with 0.1 N aqueous NaOH in a 1:1 mixture acetone-water. Its acidity number \( I_a \) was 351.6 mg NaOH/g, corresponding to a molar ratio MA:NVP = 1:1.16. The molecular weight, estimated from viscometric measurements in aqueous acidic solution (pH=2.1), using the values \( K=3.25 \times 10^{-4} \text{ dL/g}, \alpha=0.62 \) [4], was 16 000.

The products of reaction between MA-NVP copolymer and piperazine or its derivatives were characterized by conductometric titration as described elsewhere and by IR spectra, recorded with a Perkin-Elmer 577 spectrophotometer in KBr pellets. From \( I_a \) the conversion can be estimated.

The conductivity of polyelectrolyte solutions was measured with a Radiometer Copenhagen conductivity meter type CDM 2d, and the surface tension was determined with a K 300 surface tensiometer (A. Krüss, Germany).

The scale inhibition ability of piperazine-maleic derivatives was checked by precipitation test [5] in comparison with the Hampshire test [6]. In the precipitation test two chemically incompatible solutions are combined: a brine containing CaCl₂, MgCl₂ and NaCl is mixed with a brine containing NaHCO₃, Na₂SO₄ and NaCl in a glass test cell (4 oz square bottle
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with screw lid is recommended; instead we used 4 oz round bottles with screw lid). The brine samples added with inhibitors and two control samples were kept in a water bath at 71 °C for 72 hours, then the Ca²⁺ content in the supernatant solution was measured by titration with a standard EDTA solution. The unprecipitated calcium carbonate is a measure for the scale inhibition ability of the maleic polymer.

The Hampshire test consists of the following: 2g polymer is weighed and dissolved in 50 mL twice distilled water. 10 mL 2% Na₂CO₃ is added, the pH is brought at 11-12 with NaOH 1N and water is added up to 100 mL. This solution is titrated with aqueous 0.25M calcium acetate solution as far as a pronounced, stable turbidity is developed. The calcium acetate consumption is a measure of the calcium carbonate retained in solution.

Results and discussion

The possible reactions between the MA-NVP copolymer and piperazine (Pp), N-(2-hydroxyethyl)piperazine (HEP) or N-(2-aminoethyl)piperazine (AEP) are presented in the Scheme 2a, 2b, 2c, respectively. It can be observed that these compounds are di- or tri-functional and, consequently can be obtained insoluble reaction products.

The conditions of synthesis and the characteristics of reaction products are summarized in the Table 1. All reactions were performed in an organic aprotic dipolar solvent.

Table 1 - The synthesis of piperazine covalent derivatives of a maleic anhydride-alt-N-vinylpyrrolidone copolymer.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Reactant (R), MA-NVP:R</th>
<th>MA-NVP/solvent ratio</th>
<th>Reaction time</th>
<th>Solubility</th>
<th>Iₐ,g</th>
<th>Conversion (X)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ratio, moles</td>
<td>g:mL</td>
<td>hours</td>
<td>acetone</td>
<td>water</td>
<td>copolymer %</td>
</tr>
<tr>
<td>SAPAEP 1</td>
<td>AEP, 1:1</td>
<td>1:10</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SAPAEP 2</td>
<td>AEP, 1:0.5</td>
<td>1:10</td>
<td>4</td>
<td>-</td>
<td>+</td>
<td>0.122 93.0</td>
</tr>
<tr>
<td>SEPHEP 1</td>
<td>HEP, 1:1</td>
<td>1:10</td>
<td>6</td>
<td>-</td>
<td>+</td>
<td>0.132 88.0</td>
</tr>
<tr>
<td>SEPHEP 2</td>
<td>HEP, 1:1</td>
<td>1:10</td>
<td>4.5</td>
<td>-</td>
<td>+</td>
<td>0.133 86.0</td>
</tr>
<tr>
<td>SEPHEP 3</td>
<td>HEP, 1:1</td>
<td>1:10</td>
<td>4</td>
<td>-</td>
<td>+</td>
<td>0.133 86.0</td>
</tr>
<tr>
<td>SAPP 1</td>
<td>Pp, 1:1</td>
<td>1:11.5</td>
<td>4.5</td>
<td>±</td>
<td>±</td>
<td>0.117 105.0</td>
</tr>
<tr>
<td>SAPP 2</td>
<td>Pp, 1:0.25</td>
<td>1:5.5</td>
<td>4.5</td>
<td>±</td>
<td>±</td>
<td>0.171 74.0</td>
</tr>
</tbody>
</table>

\[
X_{SAPHEP} = \frac{80 - 244.76 \times I_a}{40 + 112 \times I_a} \cdot 100\%; \quad X_{SAPP} = \frac{80 - 231.2 \times I_a}{40 + 86 \times I_a} \cdot 100\%
\]
Scheme 2 - Reactions of maleic anhydride-alt-N-vinylpyrrolidone copolymer with piperazine and its derivatives.

2a. with piperazine

2b. with N-(2-hydroxyethyl) piperazine
2e. with N-(2-aminoethyl)piperazine

The conditions of synthesis of piperazine salts of MA-NVP copolymer are presented in Table 2. All these reactions were carried out in water, at room temperature, 4-5 hours.

Table 2 - The synthesis salts of MA-NVP copolymer with piperazine and its derivatives.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Reactant (R), MA-NVP:R ratio, moles</th>
<th>Reaction time, hours</th>
<th>pH of final solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>APAEP 1</td>
<td>AEP, 1:2</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>APAEP 2</td>
<td>AEP, 3:2</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>APHEP 1</td>
<td>HEP, 1:1</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>APP 1</td>
<td>Pp, 1:1</td>
<td>5</td>
<td>7</td>
</tr>
</tbody>
</table>

It can be observed that, due to the polyfunctionality of piperazine and AEP the reaction products are insoluble, even at smaller ratio polymer:amine. Water-soluble products are obtained only with HEP, probably due to the fact that the monoesterification with the OH group takes place more rapidly than the monoamidation with NH group from the piperazine ring. The monoesterification is quite reproducible, the conversion being between 86 and 93%. For the samples SAPP 1 and SAPP 2 the conversion estimated from conductometric titration is more than 100%. We suppose that this is due to a supplementary cross-linking between the –COOH groups arisen during the amidation and the amino groups of piperazine; however the sample SAPP 2 is partially soluble.

The polyfunctionality of some piperazine derivatives is manifested also in the salt formation with the MA-NVP copolymer. Thus, the results presented in Table 2 show that a molar ratio of 1:1 between the copolymer and the amine is enough to assure the electroneutrality (pH=7) of the reaction product. In the case of AEP, a molar ratio of 3:2

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<table>
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<th>Reactant (R), MA-NVP:R ratio, moles</th>
<th>Reaction time, hours</th>
<th>pH of final solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>APAEP 1</td>
<td>AEP, 1:2</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>APAEP 2</td>
<td>AEP, 3:2</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>APHEP 1</td>
<td>HEP, 1:1</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>APP 1</td>
<td>Pp, 1:1</td>
<td>5</td>
<td>7</td>
</tr>
</tbody>
</table>

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(moles) between the copolymer and the amine provides the electroneutrality, corresponding to the three amino groups from AEP molecule. The addition of a amine quantity corresponding to a 1:1 molar ratio induces a pH over 12.

The characterization of the reaction products of MA-NVP copolymer with piperazine was made by conductometric titration and IR spectra. In Figure 1 are presented the titration curves for the copolymer MA-NVP, for the monoester samples SEPHEP 1 and SEPHEP 2 and for the monoamide sample SAPP 2.

![Conductometric titration of a MA-NVP copolymer (P 36) and its reaction products with Pp, (SAPP 2) and HEP, conversion 93%, (SEPHEP 1) and 88% (SEPHEP 2).](image)

There is a visible difference between MA-NVP copolymer and its reaction products. The last ones show typical curves for the titration of a weak acid with a strong base. Unlike these, the copolymer presents a small part corresponding to a strong acid behaviour (it is known that the first carboxylic group of maleic acid in its copolymers behaves as a strong acid).

The IR spectra presented in Figure 2 are in agreement with the results obtained from conductometric titration.

The bands at 1780 and 1850 cm–1 characteristic for maleic anhydride rings are very pronounced in the original copolymer (1). For the sample SAPP 2 and the monoester sample SAPHEP 1 these bands are almost disappeared.
The behaviour of piperazine derivatives of MA-NVP copolymer in aqueous solution was checked by means of conductivity and surface tension measurements. Figures 3a and 3b show the surface tension and the conductivity of APP 1, APHEP 1, and APAEP 1 samples, at different polyelectrolyte concentrations, in the range where they have proved a good corrosion inhibition activity (see later). It can be observed that the conductivity of all samples is very low, corresponding to the small values of concentration (from 1 to 30 ppm, i.e. approximately 10^-6 - 10^-4 M). The concentration dependence of the conductivity is quite flat, same as for the surface tension.

For the sample APP 1 however some variation is visible for both properties when the concentration increases. A similar behaviour can be seen for the sample SEPHEP 2 (Figures 4a and 4b), in which the HEP is covalently bounded, unlike the sample APHEP 2 where the HEP is retained by electrostatic interactions.
Figure 3 - Surface tension (3a) and conductivity (3b) of APP 1, APHEP 1 and APAEP 1 samples.
Figure 4 - Surface tension (4a) and conductivity (4b) of APHEP 1 and SEPHEP 2 samples.
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Figure 5 - Surface tension (5a) and conductivity (5b) of AP 36.0, AP 36.2, APP 1 and piperazine (Pp).
In Figures 5a and 5b are collected the values of surface tension and conductivity respectively, for four products: the copolymer maleic acid-N-vinylpyrrolidone (MAc-NVP), its sodium salt, the salt of the copolymer with piperazine and the piperazine itself. The higher values of conductivity for piperazine solution compared to those of APP 1 copolymer support the fact that the piperazinium ion is strongly bounded to the polyanion, in agreement with the theoretical data concerning ion binding to the polyelectrolytes. The surface tension of the polyanion, piperazine and their salt APP 1 are not very different, that is the surface activity is an intrinsic property of the copolymer, too. The sodium salt of MAC-NVP copolymer behaves similarly with the other samples.

The values of surface activity for all studied samples are very low and less dependent of the concentration. That is in agreement with the few data appeared hitherto [7]. The low values of the surface tension of vinyl-type synthetic polyelectrolytes, like our samples, are ascribed to the fact that their conformations are inadequate to separate their groups sterically to hydrophilic and hydrophobic parts at the air-water interface. It is not negligible nevertheless to note that the concentration range of our experiments is far from the one used in [7]: $10^{-6}$-$10^{-4}$ M in our case compared with $10^{-2}$-$10^{-1}$ M in the cited case.

The scale inhibition of the maleic acid copolymers containing piperazine was evaluated by means of precipitation test and Hampshire test, the latest being taken from the detergent chemistry because our products are polyelectrolytes and we consider it is appropriate for a comparison with the results of the precipitation test. Also for comparison reasons it was synthesized other maleic acid copolymers presented in Table 3. These polyelectrolytes are binary or ternary copolymers of maleic acid with different comonomers as vinyl acetate, N-vinylpyrrolidone, methyl methacrylate and were obtained by our own methods [3, 8, 9]. There were selected according to a preliminary examination [10].

Table 3 - Other maleic polyelectrolytes used as scale inhibitors according to the precipitation test and Hampshire test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inhibitor code</th>
<th>Chemical structure</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>AP 36.2</td>
<td>sodium salt of a maleic acid (MAc)-alt-N-vinylpyrrolidone (NVP) copolymer</td>
<td>15 000</td>
</tr>
<tr>
<td>2.</td>
<td>AV 153.2</td>
<td>sodium salt of a maleic acid (MAc)-alt-vinyl acetate (VA) copolymer</td>
<td>112 000</td>
</tr>
<tr>
<td>3.</td>
<td>ATP 3.2</td>
<td>sodium salt of a MAc-NVP-VA copolymer, MAc:NVP:VA=1:0,75:0,5 (moles)</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>AM 77.2</td>
<td>sodium salt of a MAc-methyl methacrylate (MMA) copolymer, MAc:MMA=1:1 (moles)</td>
<td>70 000</td>
</tr>
<tr>
<td>5.</td>
<td>ASAP 1.2</td>
<td>sodium salt of monoamide of a maleic anhydride-NVP copolymer with butylamine</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>AP 36.0</td>
<td>maleic acid-alt-N-vinylpyrrolidone copolymer</td>
<td>16 000</td>
</tr>
</tbody>
</table>

* All inhibitors were obtained as aqueous solutions with the concentration between 9.60 and 23.00 % (g/g). The pH of solutions was about 7.00, except AM 77.2, whose pH = 10.00.

The results of the precipitation test are collected in the Table 4.
Table 4 - Results of the precipitation test for different maleic acid copolymers and derivatives.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Inhibitor code</th>
<th>Polymer dose, mg/L</th>
<th>EDTA 10−2 M consumption, mL</th>
<th>Calcium carbonate retained in solution, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>APAEP 1</td>
<td>14.85</td>
<td>4.300</td>
<td>4300</td>
</tr>
<tr>
<td>2</td>
<td>APHEP 1</td>
<td>15.04</td>
<td>4.325</td>
<td>4325</td>
</tr>
<tr>
<td>3</td>
<td>SEPHEP 2</td>
<td>14.92</td>
<td>4.200</td>
<td>4200</td>
</tr>
<tr>
<td>4</td>
<td>APP 1</td>
<td>14.79</td>
<td>4.225</td>
<td>4225</td>
</tr>
<tr>
<td>5</td>
<td>SAPOT 1.2</td>
<td>15.03</td>
<td>4.250</td>
<td>4250</td>
</tr>
<tr>
<td>6</td>
<td>SAP 2.2</td>
<td>14.93</td>
<td>4.300</td>
<td>4300</td>
</tr>
<tr>
<td>7</td>
<td>ASAP 1.2</td>
<td>15.08</td>
<td>4.100</td>
<td>4100</td>
</tr>
<tr>
<td>8</td>
<td>AP 36.2</td>
<td>15.30</td>
<td>4.275</td>
<td>4275</td>
</tr>
<tr>
<td>9</td>
<td>AV 153.2</td>
<td>15.00</td>
<td>4.250</td>
<td>4250</td>
</tr>
<tr>
<td>10</td>
<td>ATP 3.2</td>
<td>15.02</td>
<td>4.275</td>
<td>4275</td>
</tr>
<tr>
<td>11</td>
<td>AM 77.2</td>
<td>15.01</td>
<td>4.300</td>
<td>4300</td>
</tr>
<tr>
<td>12</td>
<td>control sample 1</td>
<td>_</td>
<td>3.425</td>
<td>3425</td>
</tr>
<tr>
<td>13</td>
<td>control sample 2</td>
<td>_</td>
<td>3.325</td>
<td>3325</td>
</tr>
<tr>
<td>14</td>
<td>control sample 3</td>
<td>_</td>
<td>3.275</td>
<td>3275</td>
</tr>
</tbody>
</table>

Note: In sample 11 an opalescence was observed by mixing the inhibitor with brine A (containing CaCl2 and MgCl2).

For the simplicity reasons in this table are also presented the results obtained using the maleic acid copolymer derivatives with aromatic amines. They will be discussed in the chapter concerning these products. All the inhibitors were added to attain a polymer content in solution around 15 ppm (mg/L). Almost all inhibitors show a good antiscale efficiency, the values of CaCO3 retained in solution (R) being between 4100 and 4375 mg/L compared with 3275 - 3425 mg/L retained in the blanks. Several observations can be made concerning the relationship between the chemical structure of the inhibitor and its antiscale activity. First, there are quite small differences between R values obtained with salts with piperazine, with substituted piperazine or with sodium, however it can be noted that the highest value of R is attained with salts of N-substituted piperazine.
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(samples 1, 2). Second, it can be observed a difference between R values when HEP is covalently bounded or forms a salt with MA-NVP copolymer (samples 3 and 2, respectively). Third, the efficiency of a maleic polyelectrolyte is dependent on the nature of the comonomer (samples 8-11), but not in a pronounced extent. At last, the nature of the aromatic amine in the monoamides of MA-NVP copolymer induces a change in their antiscale efficiency (samples 5, 6).

The results obtained using Hampshire test are presented in Table 5.

Table 5 - Results of Hampshire test for different maleic acid copolymers and derivatives. EDTA=disodium salt of ethylenediaminetetraacetic acid; NTA=nitrilotriacetic acid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inhibitor code</th>
<th>Ca(OOCCH3)2 0.25 M consumption, mg/L</th>
<th>Calcium carbonate retained in solution, mg/g inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>APAEP 1</td>
<td>19.6</td>
<td>930</td>
</tr>
<tr>
<td>2.</td>
<td>APHEP 1</td>
<td>19.3</td>
<td>965</td>
</tr>
<tr>
<td>3.</td>
<td>SEPHEP 2</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>4.</td>
<td>APP 1</td>
<td>25.5</td>
<td>1275</td>
</tr>
<tr>
<td>5.</td>
<td>SAPOT 1.2</td>
<td>26.3</td>
<td>1315</td>
</tr>
<tr>
<td>6.</td>
<td>SAP 2.2</td>
<td>24.7</td>
<td>1235</td>
</tr>
<tr>
<td>7.</td>
<td>ASAP 1.2</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>8.</td>
<td>AP 36.2</td>
<td>19.5</td>
<td>975</td>
</tr>
<tr>
<td>9.</td>
<td>AV 153.2</td>
<td>15.0</td>
<td>750</td>
</tr>
<tr>
<td>10.</td>
<td>ATP 3.2</td>
<td>29.3</td>
<td>1465</td>
</tr>
<tr>
<td>11.</td>
<td>AM 77.2</td>
<td>5.0</td>
<td>250</td>
</tr>
<tr>
<td>12.</td>
<td>EDTA</td>
<td>7.1</td>
<td>355</td>
</tr>
<tr>
<td>13.</td>
<td>NTA</td>
<td>13.4</td>
<td>670</td>
</tr>
</tbody>
</table>

* It was impossible to observe a sharp alteration of solution by addition of Ca(OOCCH3)2. For sample 3 however a significant alteration was observed after 1 hour by adding more than 50 mL Ca(OOCCH3)2.

As a general observation, the values obtained for our products are very high. We consider that this fact can occur because the inhibitor quantities used in our experiments were smaller (0.5 g instead of 2 g), thus the polymer concentration in the test solutions being smaller. All inhibitors studied exhibit high and very high values for R.

The antiscale activity of some maleic polyelectrolytes was checked also by our colleagues from ICE/HT Patras and BRGM Orléans. In Table 6 are summarized the results obtained by our colleagues from Patras, Greece concerning the inhibition of calcium carbonate, received at 31.10.1995 by fax.
Table 6 - Results concerning the inhibition of CaCO3 precipitation using maleic polyelectrolytes. MAC=maleic acid.

<table>
<thead>
<tr>
<th>Exp. code</th>
<th>Inhibitor code</th>
<th>Chemical structure of the inhibitor</th>
<th>Result</th>
<th>pHfin</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. AP 27.7.1</td>
<td>1 triethanolamine salt of MAC-NVP copolymer</td>
<td>No precipitation for 3 hours</td>
<td>TCa=TCO3=3.0x10⁻³ M</td>
<td>pH=8.50, v=10, 25°C</td>
<td></td>
</tr>
<tr>
<td>2. AP 27.7.1</td>
<td>1 triethanolamine salt of MAC-NVP copolymer</td>
<td>No precipitation for 3 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. AV 142.1</td>
<td>1 ammonium salt of MAC-VA copolymer</td>
<td>No precipitation for 3 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. AV 142.7.1</td>
<td>1 triethanolamine salt of MAC-VA copolymer</td>
<td>No precipitation for 3 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. AV 142.52.1</td>
<td>1 Na/Zn salt of MAC-VA copolymer</td>
<td>No precipitation for 3 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. AV 142.10</td>
<td>1 benzyltrimethylammonium salt of MAC-VA copolymer</td>
<td>No precipitation for 3 hours</td>
<td>20 mg Calcite (seeded growth)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. AS 11.2</td>
<td>1 sodium salt of MAC-styrene (St) copolymer</td>
<td>No precipitation for 3 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. AM 76.2</td>
<td>1 sodium salt of MAC-MMA copolymer</td>
<td>No precipitation for 3 hours</td>
<td>30 mg Calcite (8.51→8.45) fin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. AP 28.10</td>
<td>1 benzyltrimethylammonium salt of MAC-NVP copolymer</td>
<td>No precipitation for 3 hours</td>
<td>31 mg Calcite (8.51→8.45) fin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. ATPS 5.2</td>
<td>1 sodium salt of MAC-NVP-St ternary copolymer</td>
<td>No precipitation for 3 hours</td>
<td>33.1 mg Calcite (8.52→8.45) fin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. ATP 6.2</td>
<td>1 sodium salt of MAC-NVP-VA ternary copolymer</td>
<td>No precipitation for 3 hours</td>
<td>37.2 mg Calcite (8.51→8.49) fin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. AP 28.52.1</td>
<td>1 Na/Zn salt of MAC-NVP copolymer</td>
<td>No precipitation for 3 hours</td>
<td>36.2 mg Calcite (8.52→8.50) fin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. AP 28.2</td>
<td>1 sodium salt of MAC-NVP copolymer</td>
<td>No precipitation for 3 hours</td>
<td>38.5 mg Calcite (fin pH=8.50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. Blank exp.</td>
<td></td>
<td>Precipitation after 3600 s</td>
<td>pHfin=7.73 (total time 16000 s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15. Blank exp.</td>
<td></td>
<td>Seed crystals 29.1 mg</td>
<td>pHfin=7.76 (4h)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It is concluded that inhibitors 9-13, especially 11-13 showed excellent behaviour with respect to the inhibition of calcium carbonate formation. At the same time our colleagues have stated that the polyelectrolytes 9-13 show also a good corrosion inhibition activity in laboratory experiments: they have shifted the open circuit potential to more anodic values and reduced the rates of corrosion.

In Table 7 are briefly presented the results obtained by our colleagues from BRGM Orléans using maleic polyelectrolytes sent by us at Patras in March, 1995 to reduce the rate of FeS precipitation[13]. The results were received in June 1996.

Table 7 - Results concerning the effectiveness of maleic polyelectrolytes in reducing the FeS precipitation.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Qmack</th>
<th>Additive (5 mg/L)</th>
<th>Chemical structure of the inhibitor</th>
<th>Sd</th>
<th>B×10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.10</td>
<td>AP 28.52.1</td>
<td>Na/Zn salt of MA-NVP copolymer</td>
<td>43.15</td>
<td>1.4960</td>
</tr>
<tr>
<td>19</td>
<td>5.82</td>
<td>AP 28.52.1</td>
<td>Na/Zn salt of MA-NVP copolymer</td>
<td>43.26</td>
<td>3.5500</td>
</tr>
<tr>
<td>18</td>
<td>15.60</td>
<td>AP 28.52.1</td>
<td>Na/Zn salt of MA-NVP copolymer</td>
<td>58.55</td>
<td>5.5400</td>
</tr>
<tr>
<td>23</td>
<td>2.10</td>
<td>AV 142.52.1</td>
<td>Na/Zn salt of MA-VA copolymer</td>
<td>47.28</td>
<td>1.4960</td>
</tr>
<tr>
<td>24</td>
<td>7.40</td>
<td>AV 142.52.1</td>
<td>Na/Zn salt of MA-VA copolymer</td>
<td>40.93</td>
<td>4.0370</td>
</tr>
<tr>
<td>25</td>
<td>16.60</td>
<td>AV 142.52.1</td>
<td>Na/Zn salt of MA-VA copolymer</td>
<td>42.10</td>
<td>5.6600</td>
</tr>
<tr>
<td>28</td>
<td>2.43</td>
<td>ATP 6.2</td>
<td>Na salt of MA-VA-NVP copolymer</td>
<td>13.59</td>
<td>1.7900</td>
</tr>
<tr>
<td>27</td>
<td>6.86</td>
<td>ATP 6.2</td>
<td>Na salt of MA-VA-NVP copolymer</td>
<td>9.10</td>
<td>3.8800</td>
</tr>
<tr>
<td>26</td>
<td>20.20</td>
<td>ATP 6.2</td>
<td>Na salt of MA-VA-NVP copolymer</td>
<td>44.53</td>
<td>6.0000</td>
</tr>
<tr>
<td>2</td>
<td>2.37</td>
<td>-</td>
<td>-</td>
<td>38.46</td>
<td>1.7400</td>
</tr>
<tr>
<td>3</td>
<td>7.22</td>
<td>-</td>
<td>-</td>
<td>60.71</td>
<td>3.9870</td>
</tr>
<tr>
<td>4</td>
<td>17.50</td>
<td>-</td>
<td>-</td>
<td>44.54</td>
<td>5.7700</td>
</tr>
</tbody>
</table>

Sd = the dimensionless growth rate; B = the dimensionless driving force.

It was concluded that the maleic polyelectrolytes studied like other commercially available additives were not adequately effective, the only substance found to exhibit significant inhibition effectiveness in solutions of low supersaturation is ATP 6.2.

Several tests concerning the corrosion inhibition of control steel in a natural geothermal environment were performed by BRGM Orléans [14], using maleic copolymers and some other commercial products. All series of electrochemical tests provided data which
allowed to determine which inhibitor is best adapted to a given metallic material in a given environment. The results obtained showed that the maleic copolymers have not presented a significant activity as corrosion inhibitors. At this moment we have no explanation for this fact.

The piperazine derivatives of MA-NVP copolymer were also tested as corrosion inhibitors by ICPE C-60 Bucharest by means of the impedance analysis method as so as the steady state polarization curves method [11]. The polymer dose was between 1 and 14 ppm. It was stated that the samples APP 1, APHEP 1 and APAEP 1 show good activity as corrosion inhibitors. The inhibitor APAEP 1 reduces the charge transfer rate in the anodic stage and also in the cathodic one. The other two have only a cathodic effect. These inhibitors act relatively quick, thus, after only 1 hour they reduce the corrosion rate about 2-4 times at a polymer dose of 1 ppm. These results suggest that the favourable effect of N-vinylpyrrolidone ring in the macromolecule of the inhibitor is increased by the piperazine derivatives. These results have to be compared with the ones obtained with Na+ or Na+/Zn+ salt of the same copolymer, to identify the contribution of piperazine and/or of free amino groups in the side chain. It is a new topic to study the relationship chemical structure - anticorrosion activity.

3.2. Synthesis of maleic copolymers containing aromatic amines.

The aromatic amines are known, like other amines, as corrosion inhibitors. For the aromatic and the heterocyclic aromatic amines it was established the so called “ortho effect” [2], that is, the introduction of alkyl group at the benzene ring of aniline, for example, leads to better inhibition. The methyl group is considered to have its main effect on the strength of the chemosorption bond on the metallic surface, that is due qualitatively to its ability to supply electrons to the ring, increasing electron density on the nitrogen atom. It was found the following order for the anticorrosion effectiveness:

\[
\text{NH}_2 < \text{NH}_2 \text{CH}_3 < \text{NH}_2 \text{CH}_3 < \text{NH}_2 \text{CH}_3
\]

aniline meta-toluidine para-toluidine ortho-toluidine

Considering these data, our effort was focused to synthesize some maleic copolymer derivatives containing aniline and o-toluidine by monoamidation of maleic anhydride -alt-N-vinylpyrrolidone copolymer (MA-NVP) with aniline or o-toluidine.
Scheme 3 - Reaction of maleic anhydride-alt-N-vinylpyrrolidone copolymer with aromatic amines.

Materials and methods

For the reasons presented in the part 3.1 the copolymer MA-NVP was selected as maleic anhydride copolymer. It was synthesized and characterized in the same way, using purified monomers, catalyst and solvents. The amines used were aniline of technical grade, twice distilled at normal pressure and o-toluidine from BASF-Germany. The reaction of MA-NVP copolymer with aromatic amines was performed in organic solvent, without catalyst, at different temperatures. The reaction products were characterized by conductometric titration and IR spectra, as described earlier. Their scale inhibition ability was tested in our laboratory by the precipitation and Hampshire tests, and the corrosion inhibition power was investigated by our colleagues from ICPE C-60 Bucharest.

Results and discussion

The possible reactions between MA-NVP copolymer and aromatic amines are shown in Scheme 3.

In Table 8 are summarized the reaction conditions for obtaining the maleic copolymer derivatives with aromatic amines.
Table 8 - Reaction products of MA-NVP copolymer with aromatic amines.

ADS = aprotic dipolar solvent; RT = room temperature.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample code</th>
<th>Reactant (R), MA-NVP: R ratio, moles</th>
<th>Solvent (S), MA-NVP: S ratio, moles</th>
<th>Temperature, °C</th>
<th>Time, hours</th>
<th>NaOH, g</th>
<th>Conversion (X) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SAP 2</td>
<td>aniline, 1:10</td>
<td>ADS, 1:5</td>
<td>RT</td>
<td>8</td>
<td>0.153</td>
<td>89</td>
</tr>
<tr>
<td>2.</td>
<td>SAPOT 1</td>
<td>o-toluidine, 1:1</td>
<td>ADS, 1:10</td>
<td>over 25</td>
<td>4</td>
<td>0.184</td>
<td>63</td>
</tr>
<tr>
<td>3.</td>
<td>APOT 1</td>
<td>o-toluidine, water, 1:5</td>
<td>RT</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\[
X_{SAP} = \frac{80 - 209 \times I_a}{40 + 93 \times I_a} \times 100\%
\]

\[
X_{SAPOT} = \frac{80 - 2312 \times I_a}{40 + 107 \times I_a} \times 100\%
\]

The titration data (Figure 6) allowed us to estimate the conversion, that is over 60%, being higher for aniline compared to o-toluidine. IR spectra presented in Figure 7 are in agreement with the conversion obtained by conductometric titration.

The behaviour in aqueous solution was investigated by surface tension and conductivity measurements. In Figure 8a and 8b can be observed that, like the other maleic copolymer derivatives, the values of \( \sigma \) and \( c \) are low and their concentration dependence is flat. The explanation of this behaviour is the same as for the piperazine derivatives of maleic copolymers presented in chapter 3.2.

![Figure 6](image-url) - Conductometric titration of a MA-NVP copolymer (P 36) and its reaction products with aniline (SAP 2) and o-toluidine (SAPOT 1).
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The results concerning the antiscale activity of SAF' 2.2 and SAF'OT 1.2 estimated by precipitation test was presented previously in Table 4, while the results of Hampshire test were shown in Table 5. Both polymers exhibit good effectiveness as scale inhibitor, comparable to those of piperazine derivatives of MA-NVP copolymers.

The corrosion inhibition activity of samples SAP 2.2 and SAPOT 1.2, as so of APOT 1 sample were tested by ICPE C-60 Bucharest [12]. It was concluded that the more pronounced effect of inhibition at 50 °C and also at 80 °C is attained with samples SAPOT 1.2 and APOT 1. At one hour after addition (polymer dose 4 ppm) they reduce the corrosion of about four times, while the SAP 2.2 sample reduced the corrosion of approximately two times at 4 ppm polymer dose. Taking into account the effectiveness as corrosion inhibitor of about all the maleic polymer derivatives containing piperazines or aromatic amines and their low surface tensions, we suggest that the corrosion inhibition effect is not due to the formation of a polymer protecting film. The difference observed between the samples SAPOT 1.2 and SAP 2.2, which are monoamides of MA-NVP copolymer with o-toluidine and respectively aniline is in good agreement with the "ortho effect" observed for the amines themselves. Of course, it is imperatively necessary a systematically study of corrosion inhibition activity of aromatic amines and their polymer derivatives compared with piperazines and their polymer derivatives, eventually with other amines. We propose to continue this work in collaboration with our colleagues from ICPE C-60 and eventually other colleagues interested in this work.

Figure 7 -IR spectra of a MA-NVP copolymer (1) and its reaction product with o-toluidine (2).
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Figure 8 - Surface tension (8a) and conductivity (8b) of SAPOT 1.2 and SAP 2.2 samples.
CONCLUSIONS

1. It was synthesized several derivatives of maleic anhydride copolymers with piperazine or N-substituted piperazine by neutralization, esterification or amination reactions. These samples were tested by ICPE C-60 as corrosion inhibitors and it was observed a good anticorrosion activity, especially the salt of a maleic acid-alt-N-vinylpyrrolidone with N-(2-aminoethyl) piperazine.

2. We have also obtained maleic copolymer derivatives containing aromatic amines as aniline or ortho-toluidine. The tests performed by ICPE C-60 show a good behaviour of these products as corrosion inhibitors. Furthermore, the “ortho effect” observed by some aromatic amines was identified also by derivatives of maleic copolymer with aromatic amines with respect to their anticorrosion activity.

3. The inhibition of calcium carbonate precipitation was tested by BBPDICM using the precipitation and Hampshire tests. The results exhibit that these products act as calcium carbonate scale inhibitors, in agreement with some results obtained by ICE/HT.

4. In this report are also commented the results obtained by ICE/HT, BRGM and CPERI regarding the ability of some maleic copolymers to reduce to a certain extent the iron sulphide precipitation.

5. Tests of some maleic copolymers concerning their anticorrosion activity in a natural geothermal environment were also performed by BRGM Orléans and ICE/HT, but did not show a favourable effect.

FUTURE WORK

* It is imperatively necessary a systematic study of corrosion inhibition activity of aromatic amines and their polymer derivatives compared to piperazines and their polymer derivatives, eventually with other amines. We propose to continue this work in collaboration with other colleagues from ICPE C-60 and other colleagues interested in this subject.

* It will be claimed several Romanian Patent Applications concerning synthesis if maleic anhydride derivatives.

* The investigation of maleic polyelectrolytes behaviour in aqueous solution will be performed using potentiometric (pH-metric) and turbidimetric measurements, including different titrations.

REFERENCES


5. NACE Standard TM-03-74 “Laboratory screening tests to determine the ability of scale inhibitors to prevent the precipitation of calcium sulfate and calcium carbonate from solution”.


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