



Ademe



INSTITUT MIXTE
DE RECHERCHES GÉOTHERMIQUES

study of corrosion and scaling in low enthalpy geothermal system

document public

Research funded in part by the
Commission of the European Communities
Non-nuclear Energy R&D Programme
(Geothermal Energy)

Final report of the JOULE
contract n°JOUG-0005-C

*A. Boisdet
*P. Bray
*I. Ignatiadis
*A. Abou Akar
**I. Lambert
***P. Iris

Contribution of :
IMRG/BRGM Orléans (FR)
CEA Fontenay-aux-Roses (FR)
ARMINES Fontainebleau (FR)

October 1992
R 36 103

*IMRG
**CEA
***ARMINES

BRGM - IMRG

B.P. 6009 - 45060 ORLÉANS CEDEX 2 - France - Tél. : (33) 38.64.31.72

ABSTRACT

The results of research carried out by IMRG and its sub contractors (CEA and ARMINES) within the framework of CEC Joule contract n° JOUG-0005-C are presented here in two main parts following the introduction which gives the context of the geothermal problems at the origin of the proposed research.

The first part examines the nature of corrosion and scaling phenomena in low enthalpy geothermal plants, in particular, those in the French Paris basin.

The corrosion and scaling phenomena in the monophasic and the diphasic zones of the geothermal plants are studied and a preliminary model of these phenomena is proposed. This model is a computer code (MODEP) which allows us to predict the amount of well wall scale by mackinawite, the main iron sulphide encountered. The solubility of this mineral was studied by the CEA in order to determine thermodynamic constants at temperatures and pH values adapted to geothermal conditions. A detailed report of this last study is given in appendix 1 of this report.

In order to gain a better knowledge of the characteristics of the geothermal fluid of the aquifer (Dogger) responsible for the corrosion and scaling, a new bottom hole fluid sampler was designed and used in the Ris Orangis geothermal production well. The use of an composite tube inside the production well for the sampling of the fluid coming from the aquifer was tested in the Orly geothermal plant. These experiments allowed us to estimate that iron concentrations of the Dogger aquifer were higher than before imagined (iron in equilibrium with the pyrite of the reservoir). The origin of the increased dissolved sulphide concentrations of some geothermal fluids were determined. Studies using isotopic methods reveal that bacterial activity (sulphate reducing bacteria) in the well and even in the aquifer near the well bottom is responsible.

The second part of this report deals with anti-corrosion and anti-scaling methods and is made up of two main paragraphs.

The organic inhibitors, now being used in the Paris geothermal plants are studied in the first paragraph. These studies deal with the optimisation of their use in geothermal plants (methods for measuring their concentrations in the geothermal fluid, criteria for choosing inhibitor, action of the inhibitor on iron sulphide scale), their long term effects on the aquifer at the injection well (percolation experiments through cores)

In the second paragraph, four new processes for the protection of geothermal doublets are studied.

The first one deals with the chemical cleaning of geothermal wells: laboratory experiments show that a mixture of hydrochloric acid and organic corrosion inhibitor can eliminate iron sulphide scale without causing exaggerated corrosion of the iron so cleaned.

The second one is the treatment of geothermal fluid by chemical oxidation of the dissolved sulphides and the use of cross-flow microfiltration of the geothermal water before re-injection, for the elimination of the sulphur produced.

The third is the use of solid inhibitors instead of the present well bottom additive injection tube system (this part, carried out by ARMINES, is discussed in detail in appendix 2).

The fourth deals with the use of mineral corrosion inhibitors: after determining the best inhibitor with regard to the geothermal conditions, the results of the laboratory and on site experiments are given.

The conclusions summarise the main results of this research and propose further work, in particular, the determination of the iron sulphide growth mode and formation kinetics, the modelling of other scale formation (including kinetic aspects), the capacity of corrosion inhibitor to protect iron recovered by scale and the evaluation of the risks of pitting corrosion caused by the presence of an organic inhibitor.

SUMMARY

1. INTRODUCTION	9
2. UNDERSTANDING OF CORROSION AND SCALING PHENOMENA IN LOW ENTHALPY GEOTHERMAL SYSTEMS	11
2.1. Analysis of the corrosion and scaling phenomena on the iron well wall	11
2.1.1 Description of the phenomena	12
2.1.1.1. Characterization of the monophasic zone phenomena	12
2.1.1.2. The diphasic zone case	17
2.1.1.3. Study of the solubility of mackinawite (CEA-FR)	23
2.1.2. Modelling of scaling phenomena	24
2.1.2.1. Introduction	24
2.1.2.2. State of progress	24
2.1.2.3. MODEP organization chart	31
2.1.2.4. Results and discussion	33
2.1.2.5. Conclusion	41
2.2. Researchs about iron and sulphides concentrations of the Dogger geothermal fluid	42
2.2.1. Introduction	42
2.2.2. Construction of the "PRINPIMO" down hole fluid sampler	42
2.2.2.1. The specifications	42
2.2.2.2. The chosen solutions	43
2.2.2.3. Operating principle	45
2.2.2.4. Capacities of the implement at the present developpement stage	45
2.2.3. Sampling of fluid at the well bottom with the "PRINPIMO" sown hole sampler	46
2.2.4. Sampling of fluid at the well bottom with a special composite tubing	47
2.2.5. Mapping of sulphide concentrations	51
2.2.5.1. Description of a method for sulphide analysis	51
2.2.5.2. Mapping of sulphide concentrations	52
2.2.6. Analysis of the present bacterial contribution to the increase of sulphide concentrations in the geothermal fluid	53
2.2.6.1. By a the flowrate variation method	53
2.2.6.2. By isotopic analysis	61

3. PROCESSES FOR A RELIABLE EXPLOITATION OF GEOTHERMAL DOUBLET	69
3.1. Organic inhibitors use optimization in geothermal systems	69
3.1.1. Organic inhibitors description and use	70
3.1.2. Practical use of inhibitors	72
3.1.2.1. Choice of the inhibitors	72
3.1.2.2. Processes for injection	74
3.1.2.3. Measuring concentrations of organic surfactants	75
3.1.2.4. Long term effects of reinjection of inhibitor on the reservoir	76
3.1.2.5. Assessing the action of an inhibitor on scale	81
3.2. New processes for the geothermal doublets protection	84
3.2.1. Chemical cleaning of geothermal wells	84
3.2.1.1. Introduction	84
3.2.1.2. Preliminary studies	85
3.2.1.3. Experimental results and discussion	88
3.2.1.4. Conclusion	95
3.2.2. New geothermal fluid treatments	96
3.2.2.1. Treatment by chemical oxidation of dissolved sulphides and cross-flow microfiltration	96
3.2.2.2. Study of solid inhibitors for the treatment of the geothermal wells (ARMINES-FR)	105
3.2.3. Mineral corrosion inhibitors	107
3.2.3.1. Investigations of different mineral inhibitors	107
3.2.3.2. Anti-corrosion treatment of a carbon steel using sodium silicate to deposit a silica film. Analysis of films by photo-electron spectroscopy (ESCA)	109
3.2.3.3. In situ studies (in actual geothermal media) of anti-corrosion treatment of a carbon steel using sodium silicate to deposit a silica film	114
4. CONCLUSIONS	125
5. REFERENCES	127
6. LIST OF THE FIGURES	135
7. LIST OF THE TABLES	139

Appendix n°1:	CEA report : Study of the solubility of the mackinawite.	141
Appendix n°2:	ARMINES report: Study of the faisability of using solid inhibitors in geothermal wells.	143
Appendix n° 3:	TPDEGAZ code - reactions and thermodynamic data	145
Appendix n°4:	List of reports and thesis	147
Appendix n°5:	List of publications	149

1. INTRODUCTION

The research program described in this report was undertaken as a result of problems encountered in the fifty-odd geothermal projects in the Paris region.

The water extracted from the Paris Basin Dogger aquifer transports chemicals that make it corrosive for the steels used in the wells and surface installations. The concentrations of these compounds - mainly dissolved salts, H_2S and CO_2 - vary from place to place and, in some cases (sulphides), over time. This causes clogging of the wells by iron sulphide scale. However, since the iron involved comes from the casing steel and since the iron sulphides formed (mainly mackinawite) are not protective, the process could go as far as to completely eat away the casing steel.

After a diagnostic phase during the early years of the wells (1980-1986), testing of a new method for treating the geothermal fluid, by injecting an organic corrosion inhibitor into the production pump, was begun in 1986. Since 1989, inhibitor injection systems have been installed at the well bottoms so as to protect the entire doublet.

Treatment methods must enable the wells to operate long enough to pay off the considerable investments involved, in the best conditions.

The objective of the research program was to increase knowledge and control of corrosion and scaling in low enthalpy geothermal systems, such as those found in the Paris Basin Dogger aquifer.

The project included studies of the following five aspects:

- corrosion and scaling in the steel casings
- chemical characterization of the reservoir fluid
- the use of organic corrosion inhibitors
- elimination of sulphides
- possible use of mineral inhibitors

As a part of the program, sub-contractor CEA, of Fontenay aux Roses (FR), studied mineral inhibitors and the solubility of mackinawite, which is the main iron sulphide encountered in the scale extracted from geothermal wells exploiting the Dogger (see appendix 1).

ARMINES, also a sub-contractor, studied the possibility of using inhibitors in the form of weighted granules or pellets introduced at the production wellhead, making it unnecessary to use an injection tube to inject the inhibitor directly at the well bottom (see appendix 2).

Without the help of the geothermal well operators, the studies could not have been carried out. The operators kindly placed at our disposal, for the whole duration of the experiments, a

part of the geothermal fluid extracted and, when fluid had to be sampled at well bottoms, even provided access to production wells free of all pumping equipment.

The present report is divided into two parts.

The first part deals with corrosion and scaling phenomena in low enthalpy geothermal wells, where the study of corrosion and scaling in the steel casings and the chemical characterization of the reservoir fluid are discussed together.

The second part deals with the processes for combatting corrosion and scaling in such wells, such as the chemical cleaning of the well wall, the use of organic corrosion inhibitors, the elimination of dissolved sulphides by oxidation, the use of solid inhibitors and the study of mineral inhibitors.

Lists of the reports and theses written in the course of the program are found in appendix 4. Readers can turn to these for more detailed information.

A list of conference papers and publications concerning the studies carried out under this programme can also be found in appendix 5.

2. UNDERSTANDING OF CORROSION AND SCALING PHENOMENA IN LOW ENTHALPY GEOTHERMAL SYSTEMS

Corrosion of the carbon steel casing used in geothermal wells, and the scale formed by the products of this corrosion, proceed at a rate that can oblige operators to halt the use of the system long before their investments have been fully paid off.

There is also a danger that the corrosion may pierce the casing and establish a contact between two different aquifers. This can have important consequences if the aquifers concerned are used for drinking water supplies.

The aim of the research we carried out under contract with the CEC's DG XII was to understand these phenomena and to develop methods of prediction.

With these goals in view, we set about improving our knowledge of the characteristics of the fluid from the Dogger reservoir, identifying the reactions involved in the corrosion and scaling, and designing a computer code for predicting the growth of scale on well casing walls.

2.1. ANALYSIS OF THE CORROSION AND SCALING PHENOMENA ON THE IRON WELL WALL

Without inhibitor treatment the geothermal power plants in the Paris region are encountering corrosion problems because of the aggressivity of geothermal fluids which lack oxygen and are, because of their overall characteristics, potentially highly corrosive. In the geothermal fluid corrosivity classification system established by Ellis P.E. (1981), they can be classed as V-a. The Ellis scale contains six classes (I to VI) and class V is broken down into two sub-classes, V-a and V-b. According to Ellis, the corrosion observed on carbon steel exposed to this anaerobic geothermal environment (V-a) is:

- a) a uniform corrosion of 0.2 to 0.4 mm/y,
- b) a corrosion by scaling of more than 2 mm/y. In addition, according to Ellis, the variation in the hydrogen sulphide concentration from 0.03 to 5 mg/l has very little effect on steel corrosion.

According to measurements carried out by the IMRG and by site operators, the average corrosion rate of geothermal well casing in the Dogger without treatment is estimated to be around 0.4 to 0.6 mm/y, considerably reducing the life span of geothermal plants originally conceived to operate for more than 20 years.

The first problem encountered was the clogging of geothermal wells due to deposits which formed on the casing walls. Evidence of corrosion of the casing was then revealed and the

first treatments using additives were begun. Within the framework of a contract with the CEC DGXII, the IMRG proposed to determine the reactions involved in corrosion and deposition phenomena and to develop a computer code which would predict the growth of corrosion deposits on the casing walls.

2.1.1. Description of the phenomena

Like all industrial systems, corrosion affects low-enthalpy geothermal exploitations. This study aims to characterize and quantify the various types of corrosion affecting the different equipment in low-enthalpy geothermal loops, with a view to optimising the choice of solutions.

2.1.1.1. Characterization of the monophasic zone phenomena

Several parallel approaches have been taken. The study is based on :

- the international bibliography on corrosion
- actual problems and their qualitative analysis
- the measurement and evaluation of corrosion on carbon steel specimens (coupons, electrochemical probes) in reconstituted or real geothermal environments.
- corrosion rate measurements based on the iron and hydrogen sulphide analyses in the fluids.

International bibliography on corrosion

In spite of the vast amount of research on corrosion which has been carried out and published in the international bibliography, no study has yet been done on a corrosive environment identical to that of the Dogger aquifer in the Paris Basin: 5 to 35 g/l salinity, presence of gases such as H₂S and CO₂, pH between 6.1 and 6.8, temperatures from 47 to 87°C, pressure of 1 to 220 bars, carbon steel casings. Indeed, the fluid composition is extremely variable, its salts and gases are among the most corrosive and are, moreover, among the most difficult to reproduce in the laboratory. We have limited our review to a relatively exhaustive bibliography of the subject in an effort to deal mainly with studies related to preoccupations and problems most similar to ours.

Studies have been carried out by the IMRG, the Compagnie Française de la Géothermie and the French Atomic Energy Department in order to understand corrosion mechanisms in the absence and in the presence of a corrosion inhibitor in various exploitation sites and on different metallic and/or composite materials. A study of the behaviour of metallic materials in the low enthalpy geothermal environment of the Dogger aquifer has been published by the IMRG (Honneger J.L. et al., 1986).

The bibliographic reviews carried out by the IMRG on this theme have been published in various reports listed in the appendix and, in particular, in a bibliographic and synthesis report by Amalhay M. and Ignatiadis I. (1992) in which the authors gathered and analysed current knowledge on corrosion/deposition problems which have arisen in the geothermal plants exploiting the Dogger aquifer. The authors explain the origin of the corrosivity of the geothermal fluids by identifying the action of each corrosion factor. An attempt is made to explain further corrosion under scaling.

Amalhay M. and Ignatiadis I. (1992) list as factors essential for corrosion (factors having a direct effect on the form and rate of corrosion): chloride ions, hydrogen sulphide, carbon dioxide, non-protective deposits present on the metal and sulphate reducing bacteria present in the environment and on the casing walls. Carbon dioxide and hydrogen sulphide have an effect on both the pH of the aqueous medium and the corrosion of steel.

Actual problems and their qualitative analysis

Three distinct phenomena were noted :

- a) generalised (uniform) corrosion of carbon steel casings or pipes, identified at the surface (and within the wells through logging),
- b) very localised attacks on carbon steel casings or pipes revealed by fluid losses or inflows (and by logs),
- c) localised corrosion (pitting, crevices) of stainless steel or of metallurgical alloys in immersed pumps, surface pumps, heat exchangers, water gates and sampling valves.

In the first case (a), the corrosivity of the fluid itself is enough to explain why corrosion occurs. However, differences in the rate of corrosion measured from one installation to another are not only linked to physico-chemical differences between the fluids (salinity, hydrogen sulphide and carbon dioxide content, temperature, diphasic flow), but also to very specific conditions of deposition. Logging measurements carried out on doublets in the Paris Basin where the fluid is weakly mineralised and contains little dissolved sulphide, have revealed no substantial corrosion of casings (less than 10% of the initial thickness of the metal, after 5-8 years of exploitation). At the Seine-St-Denis installation however, this type of corrosion can be much greater (the La Courneuve Nord well for example, where a 17% reduction in thickness in 4 years has been noted) (Sainson S. and Honneger J.L., 1987).

Generalised corrosion itself is not enough to explain case (b). Other causes must also be investigated. Among these are causes of chemical, electrical and mechanical origin.

Causes of chemical origin:

Besides corrosion in the strict sense (case (a)), by hydrolysis of metal ions and acidification, local conditions of deposition or of fluid composition play an important part in the corrosion of carbon and stainless steel, notably in fluid cells isolated by scale (differential aeration cell for example) or zones of contact between fluid, gas and metal.

Causes of electrical origin:

Electrical currents can flow in well casings. The urban and industrial zones in which these geothermal doublets are drilled, are undoubtedly subject to these poorly understood phenomena, which are poorly controlled at great depths. The fact that electric pumps are immersed in relatively conductive fluids is another penalising factor.

Causes of mechanical origin:

These can be linked to stress (tension) or twisting (torsion) of the casing (often very slight with regard to their mechanical properties). Possible contact between the suspended immersed pumps and the casing may also be involved. Dilatation, vibration and water hammer damping can also cause stress in pipes, such as at well-head elbow joints and connecting-pipes to pumps.

Case (c) is even more complicated than the first two, in that materials used because of their mechanical properties as well as for their resistance to generalised corrosion, are much more sensitive to localised corrosion. On supposedly stainless steels in fact, only one of the three causes is sufficient to locally destroy the passive film characteristic of this type of steel, and to cause pitting. Although weight losses are usually negligible, perforations in pipes or ruptures of mechanical parts can appear very rapidly. The presence of chlorides, sulphides or even oxygen (when the pipes are emptied for example), causes a great deal of damage to this type of material. The choice of material (stainless steel and alloys) should depend not only on the environment and the mechanical stresses applied, but also on operating conditions. The poor resistivity of the fluids provides many possibilities of galvanic cells between different alloys and within the alloys themselves.

Measurement and evaluation of corrosion on carbon steel specimens (coupons, electrochemical probes) in reconstituted or actual geothermal environments.

The design itself of geothermal installations, with casings of the order of 1800 m deep, cemented to the rock, prevents direct analyses of the behaviour of the material.

Even for the most accessible equipment (surface installations, immersed pumps) direct analyses are not possible due to exploitation conditions, but more specific and complex evaluations can be made.

The procedure for measuring the corrosion rate in the artificial or natural geothermal environments included both weight loss and electrochemical methods.

The conventional technique of corrosion tests on carbon steel API K55 coupons (the same iron used for the well casings), was used for specific identifications of the corrosivity of the fluids with respect to carbon steel. But the electrochemical probe technique (based on the measurement of polarisation resistance) and other electrochemical techniques were also used. The latter involve monitoring of potential as a function of time, measurement of corrosion rates from polarization resistance and by drawing Tafel polarization curves and impedance diagrammes.

Measurement of corrosion rates using coupons and probes.

For these investigations on carbon steel, metal specimens or probes were placed either in a test pilot connected in parallel with an industrial plant exploiting geothermal reservoir in the Dogger (at Fresnes : see § 3.1.2.5 and report by Ignatiadis I. et al., 1991a and 1991e ; at Melun l'Amont : see § 3.2.3.3 and reports by Ignatiadis I. and Le Dinh Bao B., 1992), or placed directly in pipes that were in use (at Villeneuve la Garenne, la Courneuve Nord, Meaux Hôpital, Meaux Collinet, Cachan : see report by Ignatiadis I. et al., 1992a ; Melun l'Almont: see report by Ignatiadis I. and Le Dinh Bao B., 1992, Le Dinh Bao B., 1993 and § 3.3.3 ; at Chelles : § 2.1.1.2).

The results supported observations made about carbon steel in actual working conditions, i.e. a high tendency towards generalised corrosion of this material. A more detailed study was made of the action of fluids on unused (new) or precorroded carbon steel, in absence and in presence of a corrosion inhibitor (Solamine 129®, SEPPIC, Paris). The essential results of all these tests were :

- . Rates of corrosion on all test sites without treatment were approximatively the same (0,3 to 0,9 mm/y).
- . The rate of generalised corrosion on carbon steel (API K55) is stabilised with time, but is not stopped.
- . Large decreases in corrosion rate of unused carbon steel (coupons or probes) occurred in presence of a corrosion inhibitor: between 10 and 20 time less.
- . Large decreases in corrosion rate of a precorroded carbon steel (coupons or probes) during various times occurred in presence of a corrosion inhibitor: between 5 and 10 time less.

Measurements of corrosion rates by electrochemical methods.

More in-depth electrochemical experiments were carried out:

- a) in the laboratory with synthetic solutions, treated or non-treated with mineral inhibitors (Le Dinh Bao B., 1993 and paragraph 3.2.3.3),
- b) at the Melun geothermal site on a corrosion pilot using a natural geothermal fluid, within the framework of a study of mineral inhibitors (Ignatiadis I. and Le Dinh Bao B., 1992 ; Le Dinh Bao B., 1993 and paragraph 3.2.3.3).

The main conclusions are given below:

- In spite of the fact that it was difficult to reproduce geothermal conditions, the use of synthetic solutions allowed the authors to verify that corrosion rates obtained on carbon steel are similar to those measured in situ.
- Iron sulphide deposits on samples are not protective.

- The average corrosion rate is around 0.2 to 1 mm/y.
- The study of impedance diagrams proves the existence of a highly localised corrosion. It is not always possible, therefore, to establish a quantitative relationship between polarisation resistance and the corrosion rate as can be done when scaling is relatively homogeneous.

In addition to the numerous results obtained from the samples tested, a general conclusion could be drawn from the laboratory measurement programme that the range of electrochemical equilibrium potentials of the carbon steel immersed in the fluid is highly negative. As regards electrochemical measurements made on-site, the main results obtained were the electrochemical equilibrium potentials of the various samples (between - 400 and - 600 mV/Ag-AgCl), highly negative values, confirming those obtained in the laboratory (Le Dinh Bao B. 1993).

Corrosion rate measurements based on the iron and hydrogen sulphide analyses

This approach uses measurements of corrosion, incorporating its effects on the steels and fluids during exploitation.

The analysis of fluids collected at the surface, in particular dissolved iron content, can give information on corrosion of the production casing. The dissolved iron content at wellheads originates from the initial concentration in the reservoir, from corrosion a large contribution and from a consumption by precipitation of iron sulphides.

In wells where there is a low quantity of scale, a linear relation has been established, by Ouzounian (Ouzounian et al, 1987), between the concentration of iron in the fluid at wellhead and the reciprocal value of the flowrate. The authors used a preliminary model, based on simple assumptions (uniform corrosion of casing, concentrations of iron identical in the various production levels) to give results on corrosion rates very similar to those measured at the surface (for example 0.4 mm/y at Creteil) and iron concentrations in the reservoir compatible with thermodynamic equilibrium between fluid and pyrite ($[\text{Fe}] < 0.1 \text{ mg/l}$). This technique, based on the inverse correlation of dissolved iron concentration in the fluid and the production flowrate, is active in wells with little scaling and used for indirect measurement of casing corrosion.

In addition, assessment of the initial properties of the fluid, particularly redox potential, by Criaud et al., (1989), enabled the nature of the corrosion products to be forecast.

A technique similar to those of Ouzounian et al., (1987) based on the exploitation of dissolved iron and sulphide concentrations in the geothermal fluid at production wellheads and at wellbottoms is studied.

When it is possible to simultaneously sample geothermal fluid directly from the Dogger aquifer (using an inhibitor injection tube or a bottom sampler) and at the production wellhead, analytical results can be used to indicate corrosion/ deposition phenomena in the wells.

Two operations of this type have been carried out (Ignatiadis I. et al., 1992b; Ignatiadis I. and Abou Akar A., 1992) and have demonstrated the value of this method which is briefly described below.

When the sulphide content at the bottom of the well is greater than that measured at the wellhead, this indicates that sulphides are consumed by precipitation of iron sulphide. Therefore, by using the dissolved sulphide and iron contents of the fluids sampled simultaneously at the production wellhead and at the bottom of the well, when the quantity of hydrogen sulphide produced by bacteria is very low, it is possible to calculate the approximate corrosion rate in the well by establishing the iron flux (Φ) balance as follows:

$$Q_T \cdot [\text{Fe}^{2+}]_T = \Phi_{\text{aquifer iron}} + \Phi_{\text{corrosion iron}} - \Phi_{\text{deposited iron}}$$

This equation allows us to estimate the amount of iron produced by corrosion of the casing ($\Phi_{\text{corrosion iron}}$) knowing the iron content at the production wellhead ($[\text{Fe}^{2+}]_T$), the exploitation flowrate, the iron flux coming out of the aquifer ($\Phi_{\text{aquifer iron}}$, calculated from the iron content measured at the bottom of the well or $[\text{Fe}^{2+}]_{\text{bottom}}$) and the iron flux deposited as iron sulphide ($\Phi_{\text{deposited iron}}$). The latter may be estimated from the difference between the sulphide contents measured in the bottom and wellhead samples, if we assume that the deposits are made up only of iron sulphide. Therefore, rates of the corrosion of casing in the ORLY production well (untreated) were estimated at between 0.25 and 0.40 mm/y (see § 2.2.4).

Corrosion rate values can also be tested by modelling the fluid upwelling in the well using the MODEP computer code which is an extension of TPDEGAZ since it allows us to quantify the iron sulphide deposited on the casing walls of a geothermal well (see § 2.1.2). The use of this computer code for the processing of physico-chemical fluid data sampled at the production wellhead and at the bottom of the well allows us to validate the predicted corrosion rates by entering this rate into the code and comparing analysed values for dissolved iron and sulphide concentrations with those calculated using the computer code at the wellhead.

The results of these studies (presented in § 2.2) have improved our knowledge of the behaviour of carbon steel thanks to :

- a) the qualification and quantification of the various types of corrosion, in order to define necessary treatment by corrosion inhibitors
- b) development of various electrochemical measurement techniques (on site and in the laboratory)
- c) a technique for indirect measurement of casing corrosion, based on the analyses of dissolved iron and hydrogen sulphide in the fluids.

2.1.1.2 The diphasic zone case

In most of geothermal plants of Paris basin, an immersed pump is used to increase the flowrate of the geothermal fluid and to avoid its degassing. However, some plants use artesian flow and degassing effect on casing corrosion and scaling must be studied. The aim of this study is to improve our knowledge of these phenomena. After a bibliographical study concerning corrosion and scaling phenomena in aqueous media (with or without NaCl) under

CO₂ and/or H₂S pressure, experiments in progress are discussed in an artesian production well in the Paris Basin.

Bibliographical study

This study is now in progress, but it seems after data base questioning that there are no studies specific to corrosion in diphasic zone in geothermal production wells.

However, it will be important to specify that corrosion in aqueous media (even in diphasic zone), must be considered as **the consequence of the chemistry and the pH of the aqueous phase**.

Thus Crolet J.-L. (1980) specify: "we often hear talk about corrosion by CO₂, H₂S, O₂, bacteria and chloride",..." All these corrosions constitute in reality different manifestations of the same event : the metal corrosion in aqueous media..."

In the same paper, when discussing the electrochemical monitoring of corrosion, the author insists on the oxidation power of the given medium defined as "the efficiency of the cathodic reactions present in this medium". The chosen example was the case of wash tank water (salt water, pH = 6-7) at 50°C more or less aerated.

Such water contains two oxidizing species: the dissolved oxygen and the H⁺ ions produced either by water dissociation or by acid dissociation (HCl or CO₂). Thus the total cathodic current would be the sum of both oxygen and H⁺ reduction. In aerated medium, metal corrosion is especially due to O₂ reduction, but in deaerated medium this metal corrosion is related to H⁺ reduction (case of geothermal water of Paris Basin).

Numerous papers were published by Crolet J.-L. (1983), Crolet J.-L. and Bonis M.R., (1983, 1986, 1988, 1990), Bonis M. and Crolet J.-L. (1981, 1982, 1984, 1984, 1985, 1990) relating to corrosion and pH measurement in aqueous solutions under high pressure of CO₂ and/or H₂S. Although these papers touched on corrosion in oil or gas wells, the authors used, in each time, the metal/water interface to explain the localized corrosion encountered in both cases.

In all cases, the chemistry of water was taken into account to explain reactions and corrosion phenomena occurring on the metal surface :

- . when considering oil wells, the authors considered the effect of reservoir water saturated or not in CaCO₃,
- . when considering gas wells, they considered the effect of reservoir water film saturated in FeCO₃ and carried by gas (in the well bottom) or the effect of condensed and acid water because of dissolved CO₂ (in the well head).

Ikeda A. et al., (1985) studied the CO₂ corrosion behaviour of carbon and chromium steel in aqueous media (5% of NaCl), experiments were carried out with an autoclave tester. The effects of temperature, H₂S or O₂ contamination and Cl⁻ concentrations were also studied. Results of this study are mentioned and discussed by Amalhay M. and Ignatiadis I. (1992), we only resume here the effect of CO₂ pressure and H₂S contamination at different temperatures.

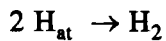
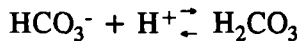
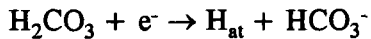
Three temperature regions can be defined : 40°C (1), 100°C (2) and 150°C (3). The good protection of iron and carbon steel was observed only in the type 3 region where a thin and uniform siderite (FeCO_3) film protects the metal surface even in H_2S contamination of less than 330 ppm (in this case FeS was also present in the protecting film). In type 1 and 2 regions, corrosion rate increases with increasing CO_2 pressure up to 30 bars. In the type 2 region corrosion is a ring-worm one. In the type 3 region, corrosion rate is somewhat higher in the lower $\text{P}(\text{CO}_2)$, i.e., 1 bar (Fe_3O_4 could codeposit in the FeCO_3 film at 1 bar and would disturb the formation of this protective film). A small amount of H_2S contamination accelerates the corrosion rate in type 1 and 2 regions through the cathodic reaction, and it decelerates corrosion rate through the deposition of FeS . Over 33 ppm, the ring-worm corrosion becomes general and corrosion rate decreases in the 2 type region.

A solution loop tester and a gas loop tester (Ikeda A. et al. 1983, 1984) were also used to study the flow velocity of fluids. The authors established, for the type 1 region, that corrosion rate increases with increases in the flow velocity up to 0.32 m/s and saturates at higher ones up to 10 m/s and conclude that the effect of flow velocity on corrosion rate could be described as the thickness of the diffusion layer for CO_2 decreasing with the increase of flow velocity up to 0.32 m/s and attaining a plateau level at flow rates of more than 10 m/s. In the type 2 region, the corrosion remains a ring-worm one and the corrosion rate increases with increasing flow velocity from 7 to 15 m/s in the solution loop tester.

The authors established also that in the gas solution two phase flow with high flowrate of 26 m/s, corrosion rates at 100°C and 150°C was much higher than in the solution phase with flow rate of 2.5 m/s. However, they specify that the apparent activity of CO_2 was not the same in both cases and that corrosion mechanism in the former could be essentially different that in the latter. At this date, we have not received these two papers to give more details on this study.

It will also be interesting to mention the work of Ramanarayanan T.A. and Smith S.N. (1990) concerning corrosion of iron at 220°C in gaseous environments and in gas-saturated aqueous environments. We can note that gaseous corrosion occurs only in gaseous environments whereas in gas-saturated aqueous environments, gases (H_2S , $\text{H}_2\text{S}+\text{CO}_2$) act only by their dissociated forms: H^+ , HS^- , S^{2-} , HCO_3^- and CO_3^{2-} . The authors concluded that in gas-saturated aqueous environments, initially, corrosion control by the growth of an iron sulphide scale by outward migration of ferrous ions through the scale is dominant. At a larger stage a steady-state situation is attained where the growth of the scale is balanced by the dissolution of the scale into the aqueous medium so that the scale thickness reaches a constant value. This conclusion is in a good agreement with the theoretical study proposed by Crolet J.-L. (1988, 1990) where corrosion could lead to "soluble scale" after reaching steady-state. Experiments conducted in aqueous environments saturated with $\text{H}_2\text{S}-\text{CO}_2$ mixtures indicate that as long as the H_2S concentration is high enough to effect the formation of iron sulphide surface scale, CO_2 has little influence on the corrosion process.

De Waard C. and Milliams D.E. (1975) proposed for the carbonic acid corrosion of steel under CO₂ pressure (T° < 80°C, pH = 2-5) the following mechanism implying direct participation of undissociated acid molecules instead of a reduction of protons at the metal surface :



At the corrosion potentiel, therefore, the corrosion rate is not limited by H⁺ ions diffusion. This mechanism explains why carbonic acid can be more corrosive than an completely dissociated acid (HCl) at the same concentration. On the one hand, the higher pH associated with carbonic acid increases the rate of iron dissolution reaction, while on the other hand, undissociated carbonic acid catalyzes the hydrogen evolution reaction. The authors also specify that work carried out by Neumann F.K. and Carius W. (1959) indicates that a similar mechanism may be operative with H₂S.

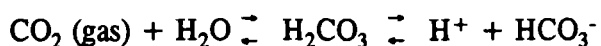
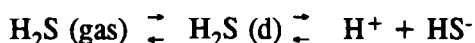
Tewari P.H. et al., (1979) studied the erosion-corrosion of carbon steel in aqueous H₂S solution at 120°C and 16 bars pressure. They concluded that :

"Loss of iron from the carbon steel disc increases with the speed of rotation. However, the amount of iron sulphide adhering to the carbon steel remains the same at different speeds of rotation, as a fresh layer of iron sulphide (mackinawite) replaces the dissolved one almost instantaneously. A preconditioned carbon steel disc with a pyrite surface, however, suffers no measurable metal loss or erosion-corrosion.

Fluid velocity affects the nature of the film of iron sulphide formed on carbon steel surfaces exposed to H₂S solutions. Mackinawite is the predominant phase of the surface film formed at high fluid velocities but it transforms into pyrrhotite and pyrite at low velocities or in stagnant solution. **Transformation of mackinawite to pyrrhotite and pyrite is accelerated in films under gazeous H₂S bubbles.** The thin film of liquid between the bubble and the carbon steel-FeS interface acts as a relatively stagnant layer of Fe²⁺ ions, thereby maintaining a saturated condition with respect to iron ions which induces a rapid sequence of reactions leading to the formation of pyrrhotite and pyrite phases".

To conclude this bibliographical study, it seems that free gas didn't act directly on the metal surface corrosion. They act by their dissociated species and corrosion is only electrochemically controlled.

However, we can expect that differences between saturated and non saturated aqueous environments exist after considering the following equilibria :



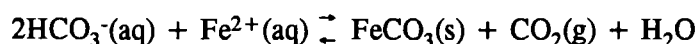
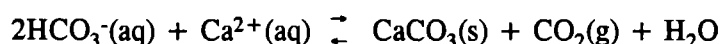
In the case of saturated solutions, the gas phase supplies more reacting species as they are consumed by the corrosion reaction according to the "Le Châtelier principle". The effect of anion concentration was discussed by Crolet J.-L. in his theoretical study (1988, 1990) : a weak concentration gave the "anionic insoluble scale" (non protector, anion diffusion to the metal surface is the decisive step) while a high concentration gave the "cationic insoluble scale" (protector, scaling reaction is not limited by anion diffusion to the metal surface). Free gas molecules could also disturb the diffusion layer, modify the concentration gradients of species in this layer and then modify the corrosion and the scale formation since those reaction can be controlled by diffusion phenomena of reacting species (Fe^{2+} , HS^- , H^+ , ...). In the case of an artesian production well (of a geothermal plant), degassing of fluid near the surface involves :

* an increase in the pH of this fluid which decreases, in general the corrosion rate. The effect of pH on corrosion in geothermal media was discussed by Amalhay M. and Ignatiadis I. (1992). On the other hand, an increase of pH increases the saturation indexes of the fluid in respect to iron sulphides; this increase is more important for pyrite than for mackinawite and pyrrhotite as it can be expected from the H^+ coefficient in the following equilibria (and confirmed by MODEP):



The effect of fluid degassing on pH and mackinawite precipitation was taken into account to model the scaling phenomena (cf: 2.1.2) in geothermal production well.

Fluid degassing is also favourable to calcite and siderite precipitation:



CaCO_3 and FeCO_3 scaling (mainly FeCO_3) constitute in general a protective layer on metal surfaces. However, siderite precipitation is disadvantaged in sulphide media and Honneger J.L. et al.(1986) noted that calcite was encountered in only punctual quantity in the well head.

* a turbulence in the fluid which acts directly on the metal surface and the diffusion layer as we mentionned above. Turbulence could also remove corrosion products from the metal surface and favour pitting corrosion.

It will be of great interest if similar phenomena to those established by Tewari P.H. et al. , (1979) occur in the diphasic zone. Experiments carried out in the Chelles geothermal plant could help us to answer this question. Let us specify that in practice corrosion and boring are more often encountered in the diphasic zone than in the monophasic one. This would not be the case if a pyrite-pyrrhotite protective film was formed on the metal surface. However,

geothermal fluids contain NaCl and CO₂ which was not the case of the aqueous medium prepared by Tewari P.H. et al., (1979).

Experimental study

The "Chelles" geothermal plant, in the east of the Paris basin is a good example for studying the corrosion in diphasic zone. The production well is artesian and geothermal water is not treated with a corrosion inhibitor. Corrosion has been measured for several years using corrosion coupons set on surface both near the production and injection wellheads.

In 1991, IMRG and Geoproduction Consultants (G.P.C.) established a common project to study the corrosion beside the artesian production well. In April 1992, an additif injection tube (TAI®) was lowered into the production well to 150 m. Corrosion coupons were fixed at three different depths: 150 m (monophasic zone); 60 m (depth of the bubble point at winter flowrate) and 4 m (diphasic zone). Some of these coupons were set up in July 1992 and others in October 1992.

The main problem encountered in this study is the crevice corrosion which concerns nearly all the coupons fixed to the tube. The system is now undergoing some modifications to resolve this problem.

At the surface, coupons are fixed in a manner which allows good water circulation around them. There is only a uniform corrosion and coupons used indicate a corrosion rate of 0.12 mm/year in the production well and 0.21 mm/year in the injection well.

It is difficult to explain the difference observed in corrosion rates between the production and the injection wells. Gas was evacuated from the fluid and corrosion rate increases in general with the temperature. This increase in corrosion could be attributed to the formation of a FeCO₃ film which protects the coupons in the production well. Polished cross section observation could produce interesting results concerning the nature of corrosion products.

Table 1 summarizes some results obtained on immersed coupons. Despite the crevice corrosion, they gave some indications on the corrosion in the production well. Let us specify that there is no good circulation of water all around the coupons, however all the coupon surface was taken into account to calculate the corrosion rate.

Depth (m)	150		60		4	
Corrosion rate mm/year	0,18	0,20	0,11	0,26	0,05	0,04
Nature of corrosion	c.c	c.c	c.c	c.c	u.c	u.c

Table 1 : Corrosion rates of coupons immersed for 3 months in the production well.
c.c : crevice corrosion, u.c : uniform corrosion.

A comparison can be made between surface coupons (in production well) and coupons set at 4 m (and then near the surface). In all cases, corrosion was uniform. The difference is probably due to the mode of circulation of geothermal water around the coupons as we mentioned earlier.

Coupons set at 150 and 60 meter present high amount of crevice corrosion. We could expect uniform corrosion rate values less than 0.1 mm/year (and may be less than 0.05 mm/year). Polished cross sections of coupons will be observed by optical and scanning electron microscope to identify in each case the nature of corrosion products.

2.1.1.3 Evaluation of the solubility of the mackinawite (CEA)

The aim of this study, carried out by the Commissariat à l'Energie Atomique of Fontenay aux Roses and detailed in appendix 1, is the determination of the solubility constants useful for the modelling of the mackinawite scaling phenomena.

Solubility measurements were performed on mackinawite from 25°C to 200°C. The results at 25°C were in good agreement with bibliography data in acidic medium. In neutral and slightly basic media, the solubility becomes very low and the concentration measured corresponds to the presence of colloids. The mackinawite was found unstable at higher temperatures. The rate of transformation into greigite was probably enhanced by the storage in air before use. The stability appears higher when the pH increases.

2.1.2 Modelling of scaling phenomena

2.1.2.1 Introduction

There are two good reasons why mathematical models are necessary in the field of geothermal energy:

- Laboratory and in situ experiments are costly.
- Computer tools can take a number of reactions into account simultaneously and simulate the effects of variations in the parameters of the geothermal fluid.

BRGM possesses geochemical computer codes that can simulate the behaviour of a fluid according to variations in temperature and pressure. These simulations extend to the gaseous phase, but do not, or only partly treat precipitation phenomena that may accompany these variations. Whence the necessity to deal with this subject.

The modelling of corrosion and scaling phenomena is very useful since those phenomena constitute the main problem encountered in geothermal plant. Casing could be perforated by localized corrosion, scaling increases the pressure losses in the well and reduces the flow rate. Modelling of these phenomena allow the user in geothermal plant to foresee corrosion and scaling evolution and choose optimal exploitation parameters.

2.1.2.2 State of progress

Mechanism of corrosion under scale

A theoretical study of corrosion under scale has been done by Crolet J.L.,(1988, 1990). This study was based on some simplifying hypotheses (needed to establish a basic model) that we can resume as follow :

- only three species are present in the solution : H^+ , Fe^{2+} and A^- .
- corrosion is supposed to be uniform in all the metal.
- there is no interaction between H^+ and A^- .
- only one phase is present in the medium : the liquid phase.
- only thermodynamic consideration of the concerned reaction was taken into account.

Based upon these hypotheses, the author considers the species concentration near the metal (i.e. in the diffusion layer or DL) as varying with the distance from the metal : concentrations are uniform in the convex layer but a gradient exists in the diffusion layer as shown in figure 1.

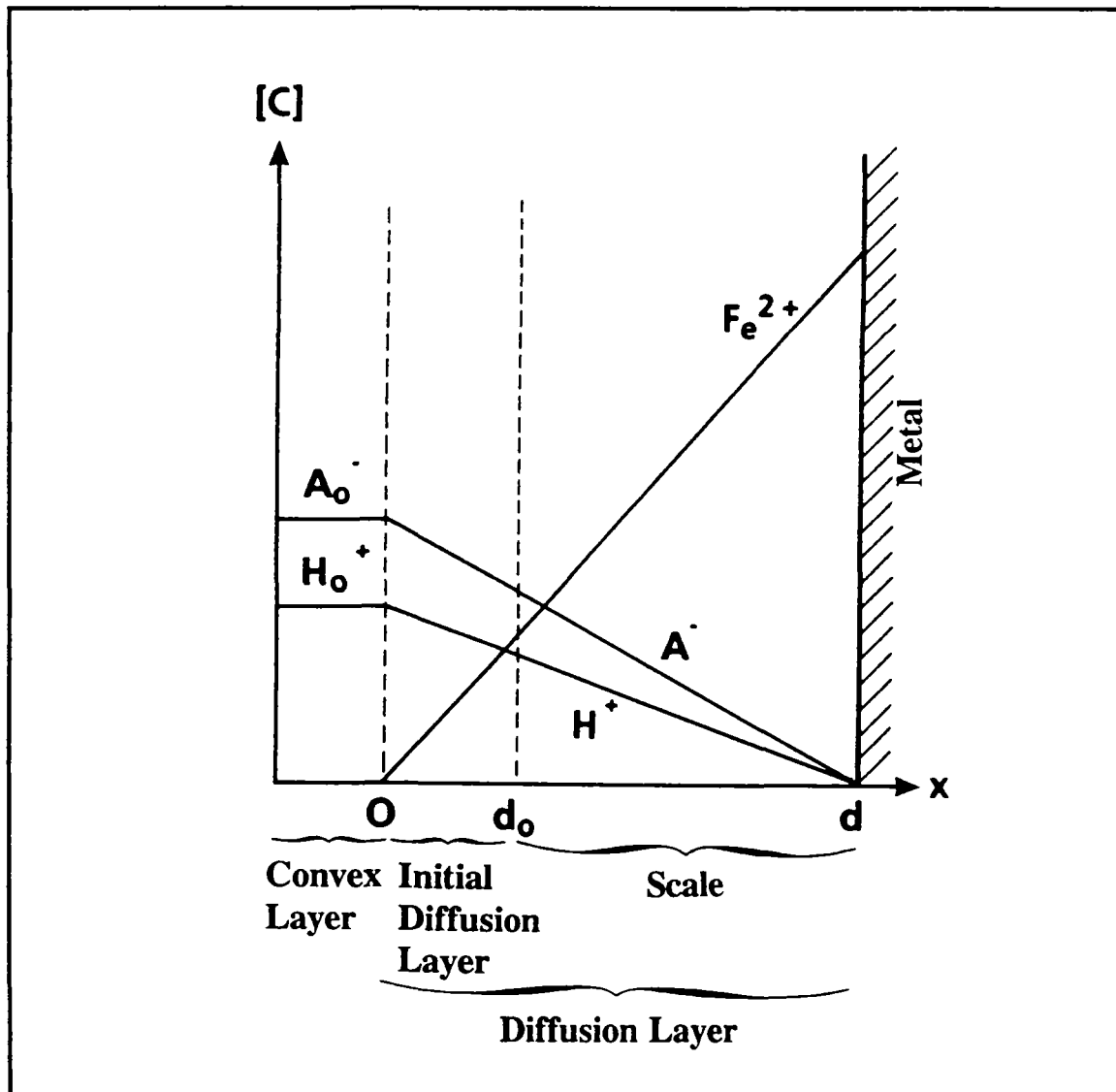


Figure 1: Concentration profiles of Fe^{2+} , H^+ and A^- in the diffusion layer (Crolet J.L, 1988).

Concentrations can then be expressed versus their distance from the metal : $\text{Fe}^{2+}(x)$, $\text{H}^+(x)$ and $\text{A}^-(x)$ which allow the calculation of a solubility product $K_s(x)$.

The author proposed three regulation mechanisms of the encountered scale (which is the same in all cases). These three mechanisms were differentiated by the anion concentration in the convex layer.

- a low A^- concentration gave the anionic insoluble scale (non protective). This is the case of abundant scales.
- a high A^- concentration gave the soluble or cationic insoluble scale (the latter is protective).

The starting point

The starting point was the computer code TPDEGAZ, developed at the IMRG, which models the evolution of geothermal fluids according to variations in their temperature (T) and pressure (P). Thus for each P-T couple, the distribution of dissolved species and the saturation indexes with respect to the various minerals that may precipitate are known, and if degassing occurs, the bubble point pressure and the composition of the gaseous phase are also known.

By calculating the saturation indexes with respect to the various minerals, the model enables an assessment of the risk of scaling in the well, but does not calculate the amount of solid that will precipitate.

These calculations are made according to the flow chart in figure 2 (Czernichowski-Lauriol I., 1989). Note that the equilibrium constants are calculated for each increment of T and P; on the one hand from thermodynamic tables, and on the other according to the activities of the species concerned (see appendix 3 for the thermodynamic data). Comparison of the two values gives an idea of the accuracy of the computations. The modules "Variation in temperature" and "Variation in pressure" operate according to the flow chart in figure 3. The same flow chart is used by the module "Iron input from corrosion".

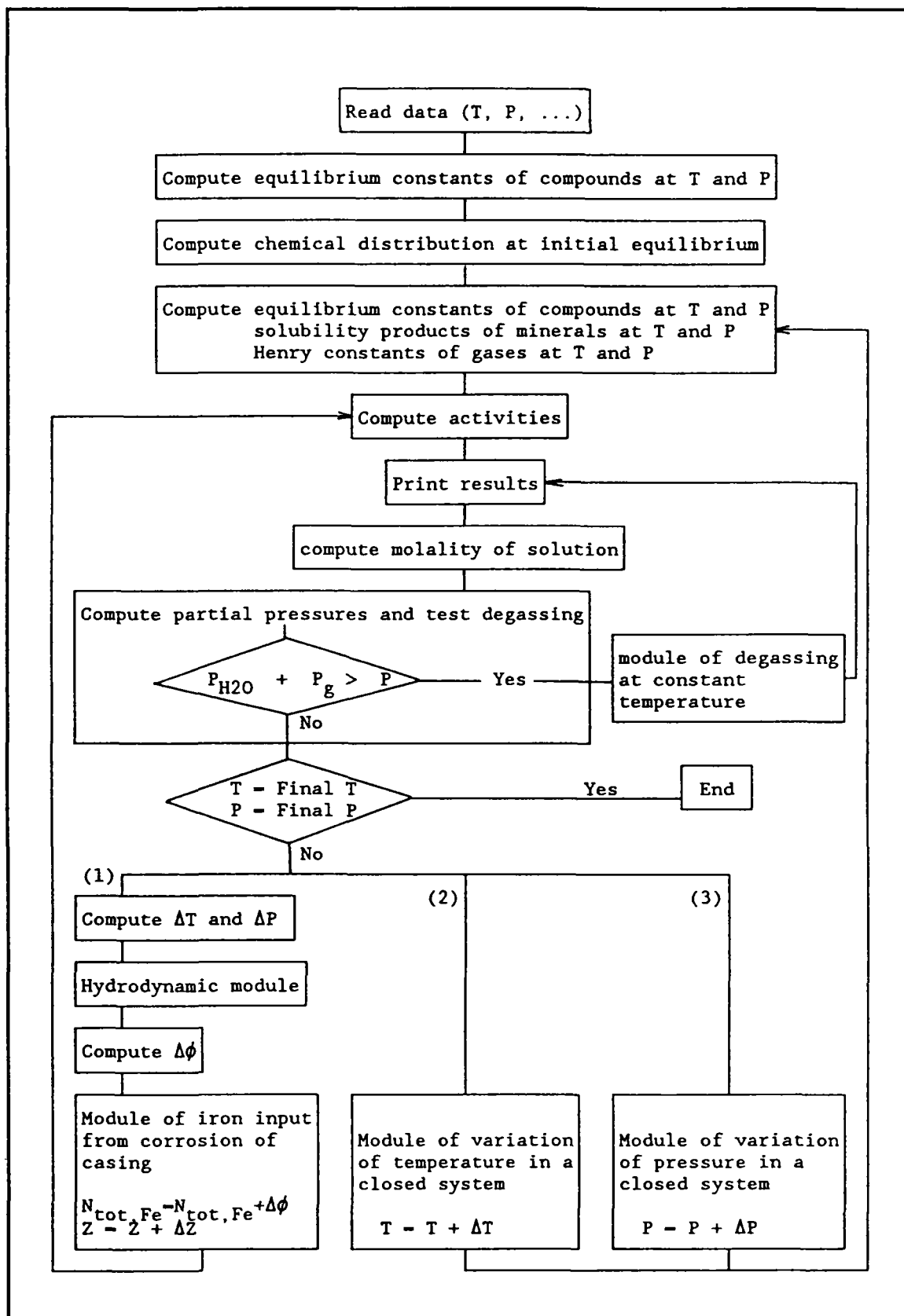


Figure 2: Flow chart 1 - TPDEGAZ model

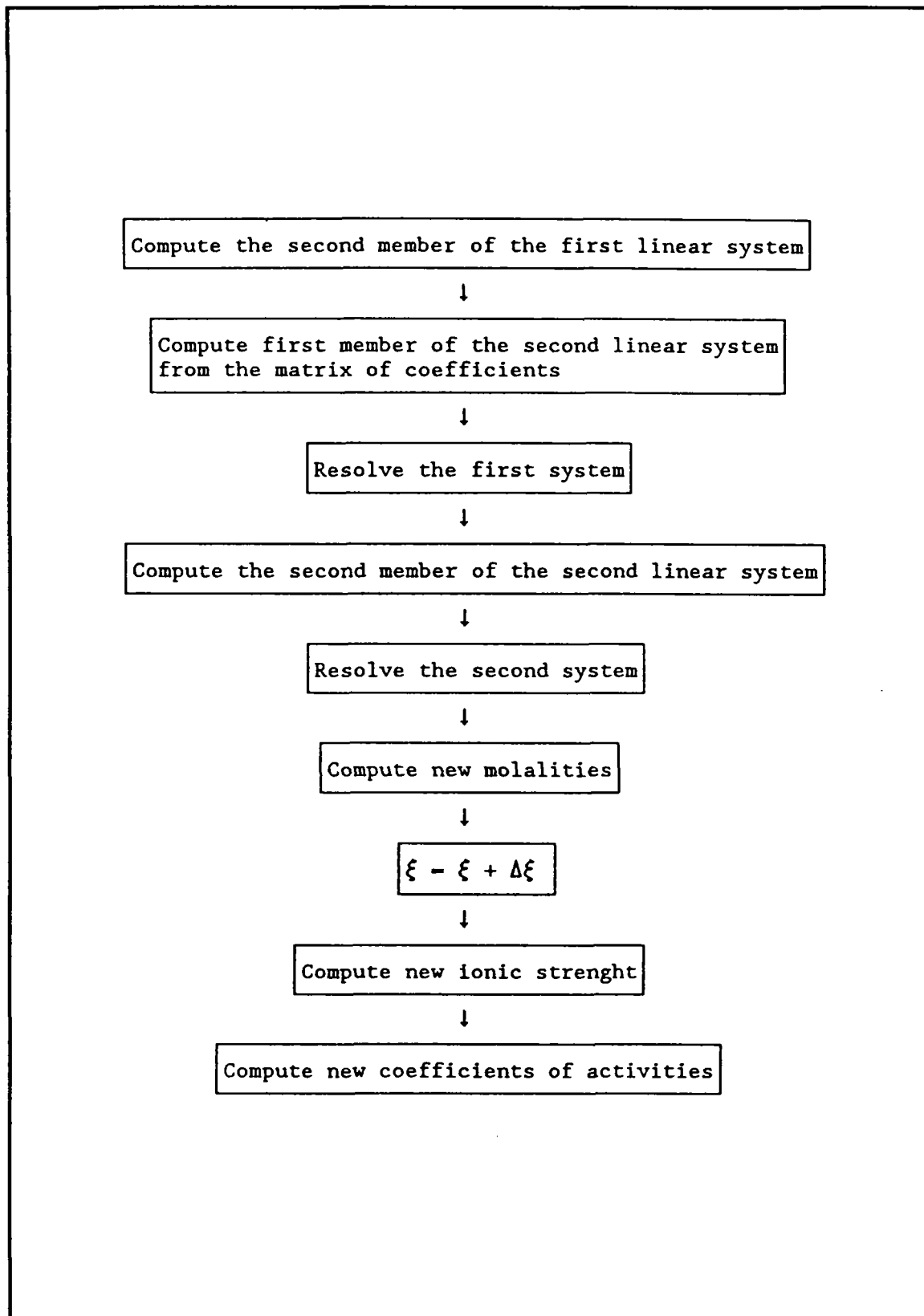


Figure 3: Flow Chart 2 - Module of variation of temperature or pressure in a closed system

The problem

Before embarking upon a study for modelling the phenomena of corrosion and scaling, the complexity of the project must be realised, and it must be understood that it is difficult to achieve an ideal model. Factors that must be taken into consideration are:

- a) The different types of corrosion - uniform, crevice and pitting.
- b) Knowledge of the diffusion layer (the thickness of which depends on the Reynolds number : diameter of casing, flow rate, density and viscosity of the fluid), is very important, for it is in this layer, next to the well wall, that the reactions between the species take place, the concentrations of which vary within the layer along concentration gradients.
- c) A large number of reactions of precipitation and dissolution take place, between which there is competition, so that reaction kinetics must be taken into account.
- d) The model must be validated by comparing the results of the computation, in both type and quantity, with the real facts observed on site by logs, coupon tests and SEM examination of the scale.

Initial objectives

A simplified simulation is proposed here, as a function of time and the depth of scaling in the casing, along the following lines:

1. Uniform input of iron into the solution, limited to the diffusion layer (fig. 4)

This takes place according to the reaction:



which is equilibrated by the reduction of H^+ ions:



2. Uniform total concentration of the other species through the diffusion and convex layers (i.e. no concentration gradient).

3. Computation, on the basis of the Ionic Activity Product (IAP) and the solubility product, of the saturation index of the fluid with respect to mackinawite (the major constituent of scale), and of the precipitation and deposition of the excess iron as FeS on the casing walls.

4. Computation of the new diameter of the casing, i.e. taking into account the thickness of iron dissolved and of scale deposited.
5. Computation of the new distribution of dissolved species after elimination of the iron that will have precipitated.

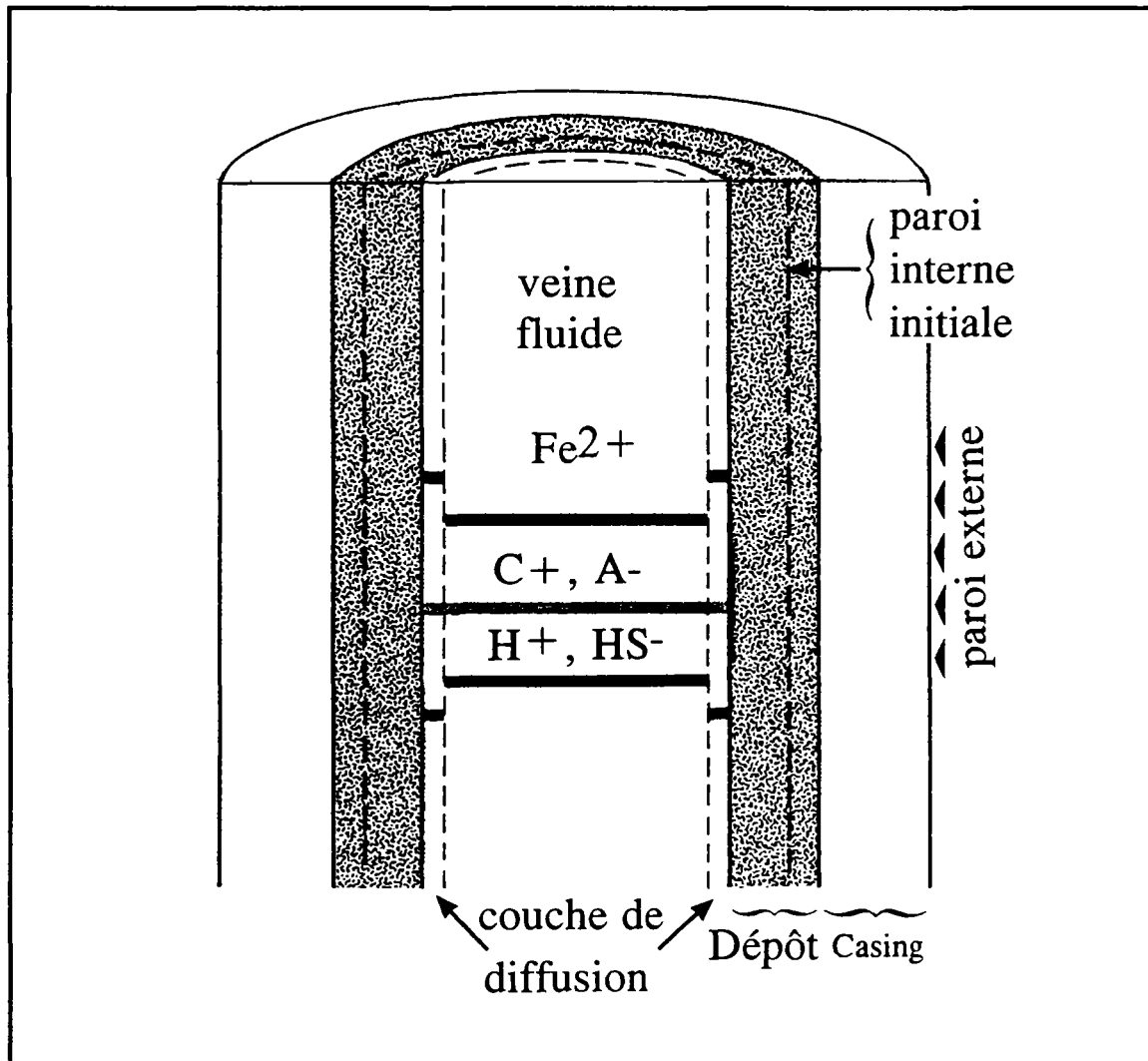


Figure 4: Concentration profiles of Fe^{2+} , H^+ and A^- in the proposed model

2.1.2.3 MODEP organization chart

We present here the supplementary sequences added to TPDEGAZ

Correction of "Iron input from corrosion" (fig 5)

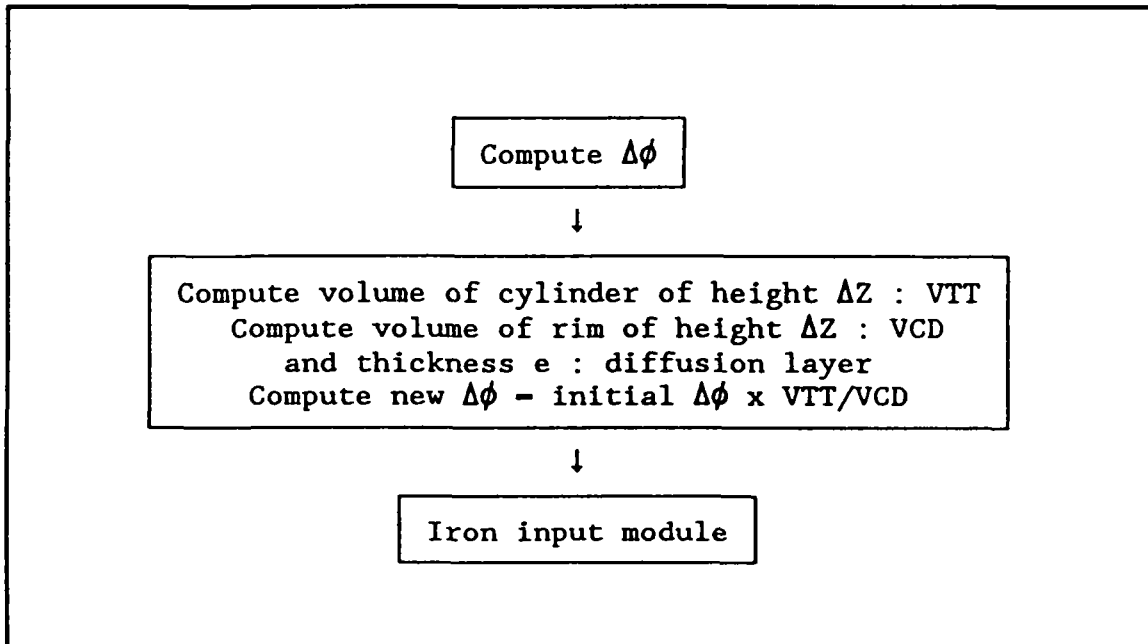


Figure 5 : Flow chart of the iron input from corrosion

Test of the Ionic Activity Product (IAP) of mackinawite

This test is made after computation of activities by the module "Variation of pressure in a closed system" and after degassing when the bubble point is reached. It takes place according to flow chart 3 in the figure 6.

If the saturation index of solution with respect to mackinawite is less than one, the model computes the new diameter by taking into consideration the dissolved iron. If this saturation index is greater than one, it will compute the excess of iron, eliminate it from solution, compute the new distribution of dissolved species and the new diameter of the casing by also taking into account the iron sulphide precipitated and deposited on the wall.

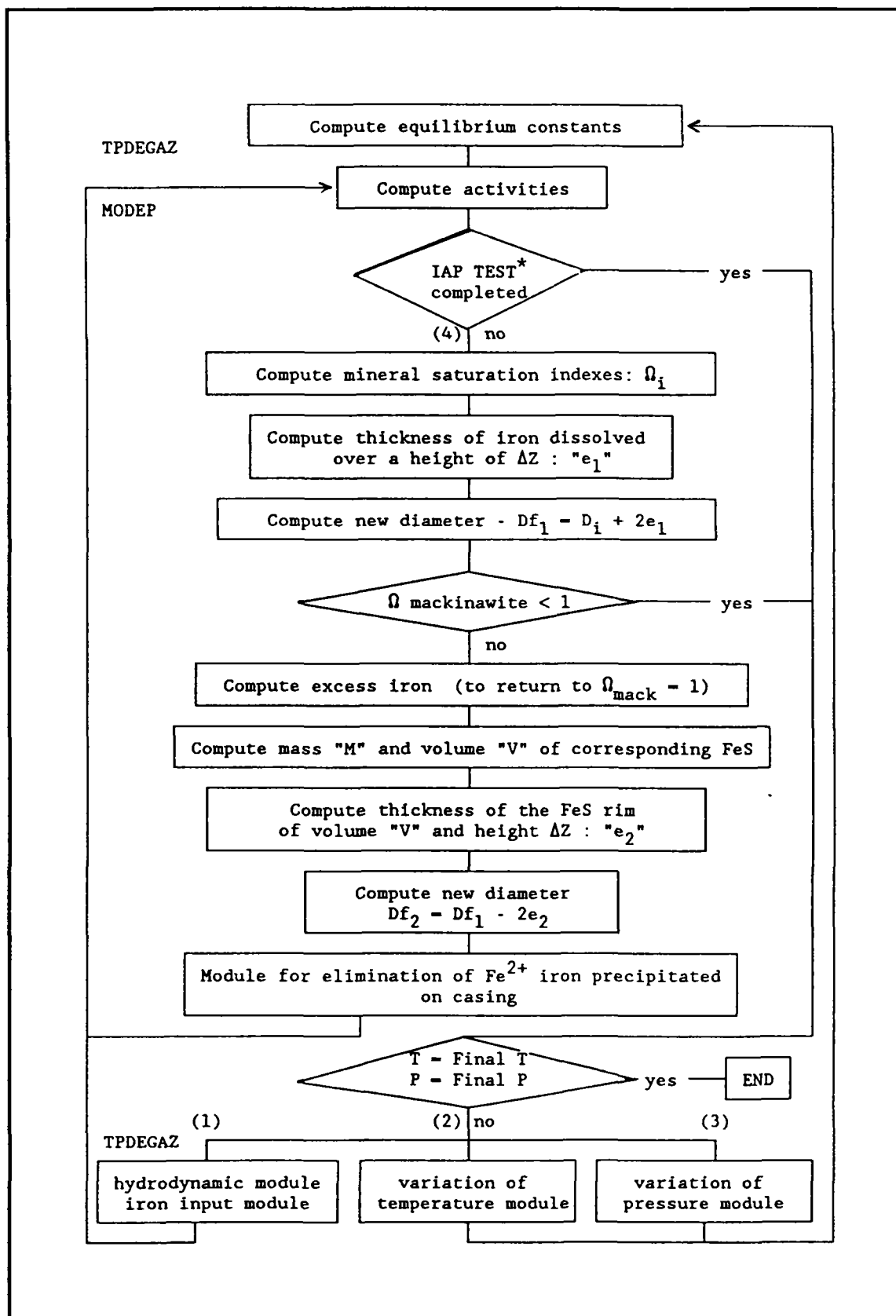


Figure 6: Flow Chart 3 - MODEP coupled to TPDEGAZ ("* ":Only after (3) and (4))

Computation of time passed

The computer code TPDEGAZ simulates the rise of a fluid segment, rising in steps of VZ, each of which corresponds to a head loss of VP. The present code simulates the rise of "n" segments (n being introduced by the user), with the particular feature that the "i"th segment will pass through a casing the diameter of which has been modified:

$$d_i = d_{i-1} + 2 \cdot (\text{thickness of iron dissolved})_{i-1} - 2 \cdot (\text{thickness of scale})_{i-1}$$

After the arrival of the "n"th segment, MODEP computes the time taken for the first segment to traverse the casing from the well bottom to the surface, and adds to this the successive times corresponding to the arrival of the following segments.

2.1.2.4. Results and discussion

The selected example is that of the "La Courneuve" geothermal project, in Seine-St-Denis, where the fluid has a high sulphide content, 33 ppm, and the following parameters:

Flow rate of geothermal fluid	200 m ³ /h
Well head temperature	58.4°C
Well bottom temperature	58.4°C
Well head pressure	1.013 bar
Well bottom pressure	160.8 bar
Depth	1980 m
Casing diameter	15.94 cm
Depth of deviation	843.40 m
Angle of deviation	45° 45'
Depth of pump	120 m
Increase in pressure at pump level	7.8 bar
Estimated corrosion rate	600 µm/year
pH of fluid in reservoir	6.19 (computed by TPDEGAZ)

The effect of the thickness of the diffusion layer "e" on the pH and the saturation index of the fluid with respect to mackinawite has been studied for the four following cases:

1. No diffusion layer (i.e. "e" = radius of casing = 7.97 cm)
2. Thickness of diffusion layer 1 cm
3. Thickness of diffusion layer 0.1 cm
4. Thickness of diffusion layer 0.01 cm

This obviously means that the iron concentration increases as the thickness decreases, and thus that saturation with respect to mackinawite is achieved for progressively deeper zones.

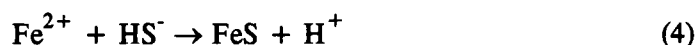
Another consequence of the increase in iron concentration is a decrease in the concentration of H⁺ ions, i.e. an increase of the pH in the diffusion layer.

Variation of pH

Figure 7 shows the variation of pH against fluid pressure and the thickness of the layer "e". Examination of the four curves shows that for a given pressure, the variation in pH becomes exponential as "e" decreases.

The layer corresponding to $e = 0.01$ cm shows that the pH may reach very high values in the diffusion layer, thus promoting precipitation and the deposition of iron sulphides.

Note that the elimination of precipitated iron is done in flow chart 2 (fig.4): variation of equilibria according to Le Chatelier's principle following a perturbation of VD which corresponds to the elimination of Fe^{2+} according to the following reaction:



This reaction, like reactions (2) and (3), has had to be added to the 67 already included in the TPDEGAZ code.

Note: The addition of the reaction of precipitation of mackinawite brings into question the validity of using thermodynamics alone for simulating precipitation reactions. This provisional choice can be justified on the one hand by the predominance of mackinawite among the scales encountered (owing to a sufficiently rapid precipitation kinetic), and on the other hand by the lack of kinetic data concerning these reactions. Experiments are in progress to improve our knowledge in this domain.

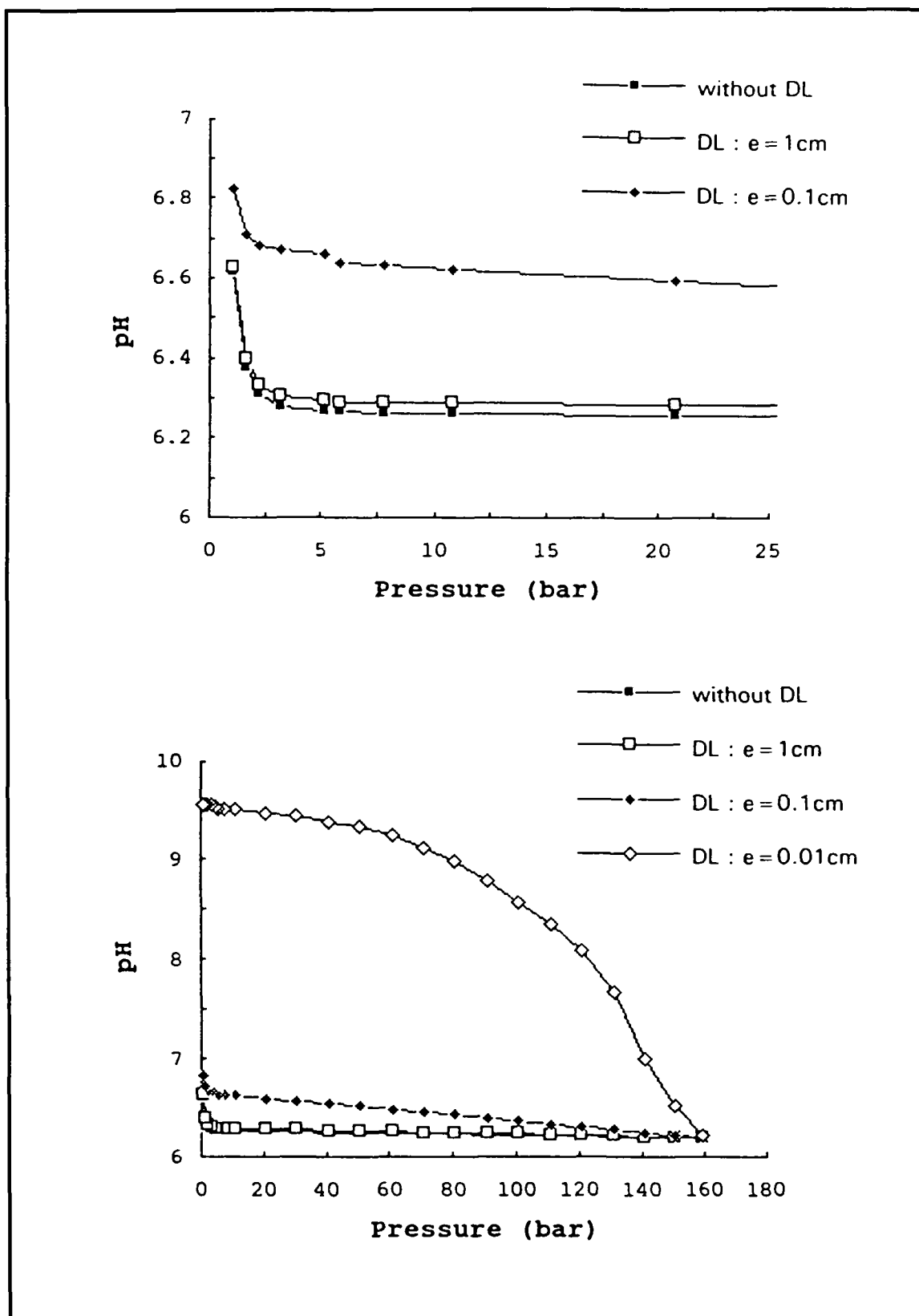


Figure 7: pH versus fluid pressure

These equilibria bring about a change of pH. Figure 8 enables comparison of the pH computed by MODEP with that computed by TPDEGAZ in the absence of a diffusion layer.

A similar pH is obtained at each step, enabling validation of the calculation done by MODEP. It is logical that the pH computed by MODEP should be slightly higher, because at each increment two H⁺ ions are consumed by reaction (2) for the production of only one by reaction (4).

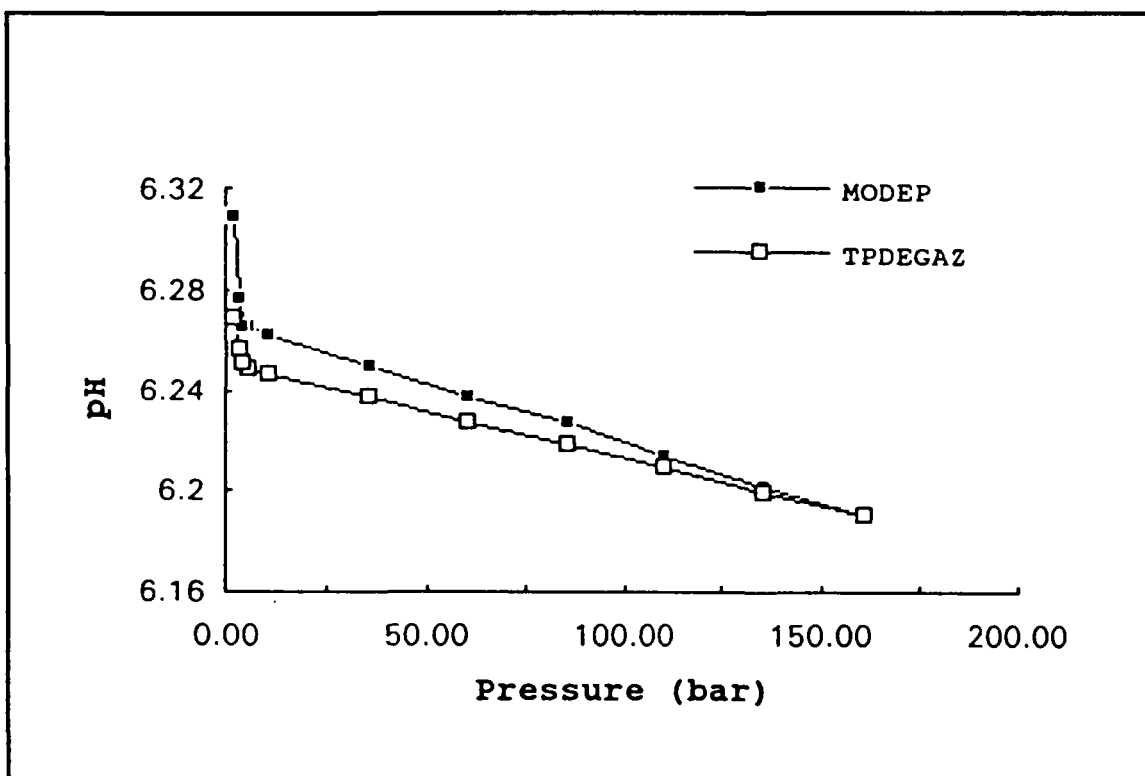


Figure 8: Comparison of pH computed by MODEP and TPDEGAZ

Variation of the saturation index with respect to mackinawite: $\log \Omega$ (mack)

Figure 9 represents $\log \Omega$ (mackinawite) as a function of the depth of the well for the four cases cited in the beginning of paragraph 2.1.2.4 ($\log \Omega = 0$ corresponds to equilibrium). A quasi-stationary regime is achieved in each case owing to the precipitation of the excess iron, in contrast to the product of TPDEGAZ, where n increases up to the surface. The slight fall in Ω at 120 m corresponds to the compression of the fluid at the pump, and the increase at the end of its passage is due to the degassing of the fluid.

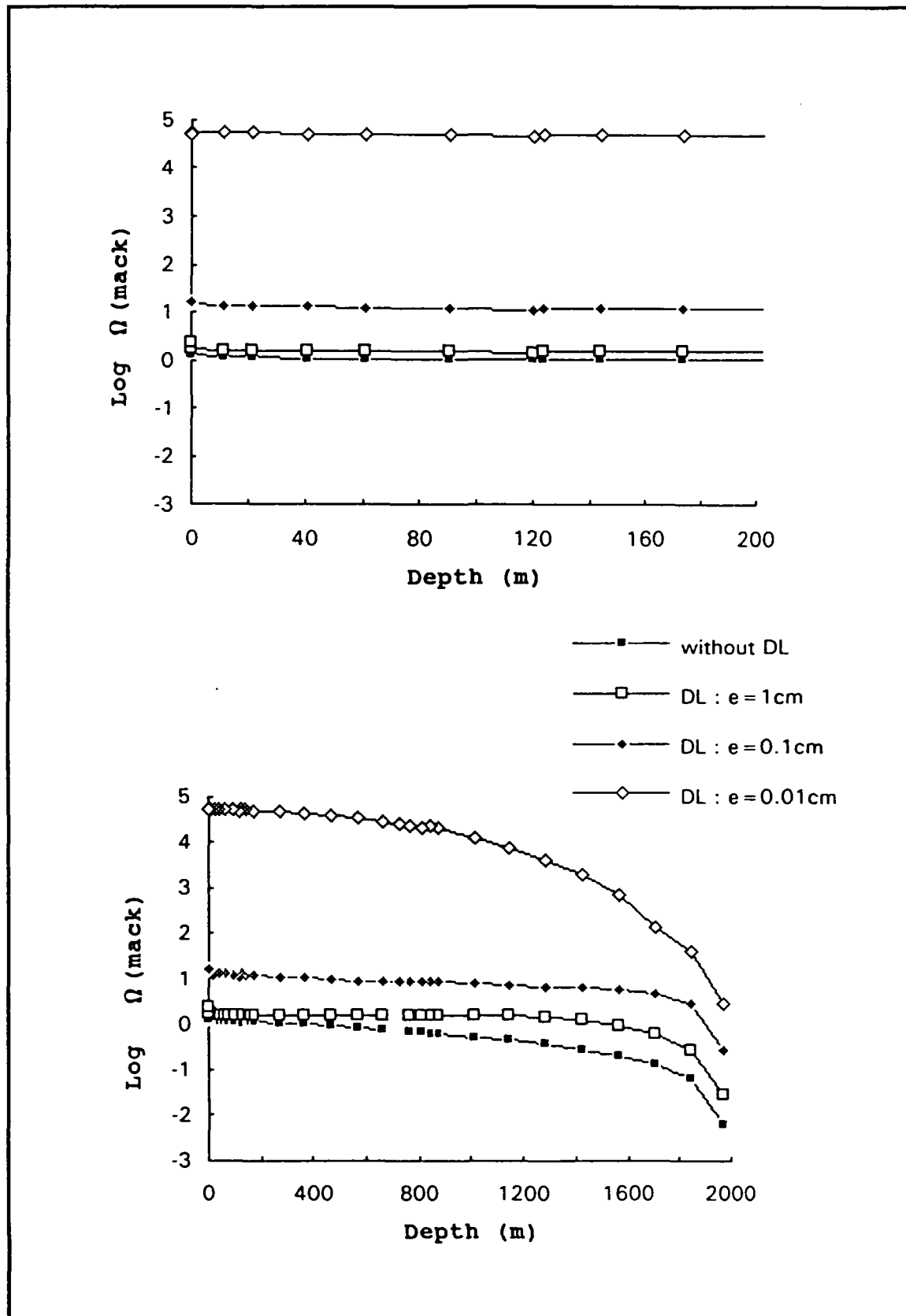


Figure 9: $\text{Log } \Omega$ (mackinawite) versus well depth

Improvements and new routines added to MODEP :

This code, as presented in May 1992 (Fourth biannual meeting in Thessaloniki), was not able to simulate the variation of casing diameter over a long exploitation time. Indeed, it could not even simulate the evolution of one water segment (§ 2.1.2.3) before the last one reached the surface (all casing contains a large number of water segments, 150 in general). Since the diameter varies slightly over a short period (a few days for example), it will be possible to attribute the water circulating in this period to only one water segment. Tests must therefore be done to select the optimal period and the user will define the duration of this period as an input. The new model can thus calculate the variation of diameter up to the end of the selected period. It can also modify the input diameter when the casing diameter changes (for example 7" $\rightarrow$ 9"^{3/8}).

In the previous version of this code, temperature and pressure increments (DP and DT) were the same for the entire casing. In case of casing deviation, this fixed DP gave a different depth variation (DZ) leading to a different supply of iron from corrosion since this is related to DZ. Since we follow the evolution of an initial segment "S" of geothermal water determined by the initial pressure increment DP and the corresponding depth variation DZ (also represented by 1kg of pure water having the average temperature and pressure of this segment), the new MODEP maintains the volume of this segment unchanged, by increasing the pressure increment after the casing deviation (to maintain the initial DZ) and by reducing DZ after reaching a casing of different diameter (to maintain the initial segment volume). The new MODEP can also modify the initial corrosion rate with depth and exploitation time.

Figure10 shows the variation in casing radius versus well depth for different exploitation times (in the absence of a diffusion layer and without corrosion in the riser pipe above the pump). Before reaching saturation in mackinawite, only corrosion takes place and casing diameter increases. After saturation, mackinawite precipitates and forms scale on the casing wall, reducing the diameter. In the riser pipe ("HAGUSTA" rubber coating), corrosion is stopped but mackinawite continues to precipitate to eliminate the excess of iron (produced by soluble iron complexes according to Le Châtelier's principle). Iron concentration and consequently scale thickness decrease, leading to an increase in the casing diameter up to bubble point. Fluid degassing significantly increases the pH and the saturation index with respect to mackinawite (and thus its precipitation) which reduces the diameter.

Figure11 shows the variation in casing radius versus well depth after 2.9 years of exploitation (in the absence of a diffusion layer, with two different fixed Diffusion Layer Thicknesses DLT 0.1 cm and 1 cm, and also with no corrosion in the riser pipe above the pump). As can be expected from figure 9, scale is encountered at greater depth when the DLT decreases but the difference between diameters is reduced after the beginning of scaling in the first case (with no diffusion layer). In the riser pipe above the pump, the geothermal water is more saturated in iron in the two cases with a diffusion layer and excess iron is then precipitated and eliminated more quickly than with no diffusion layer at the bottom of the riser pipe, which decreases deposition at the well-head.

For computing the chemical distribution at each depth, the total sulphide concentration is assumed to be the same in the diffusion and convex layers. This assumption will be eliminated in the future, in which case other species will precipitate when medium becomes poor in sulphide. Also, the DLT was assumed to be respected in the riser pipe.

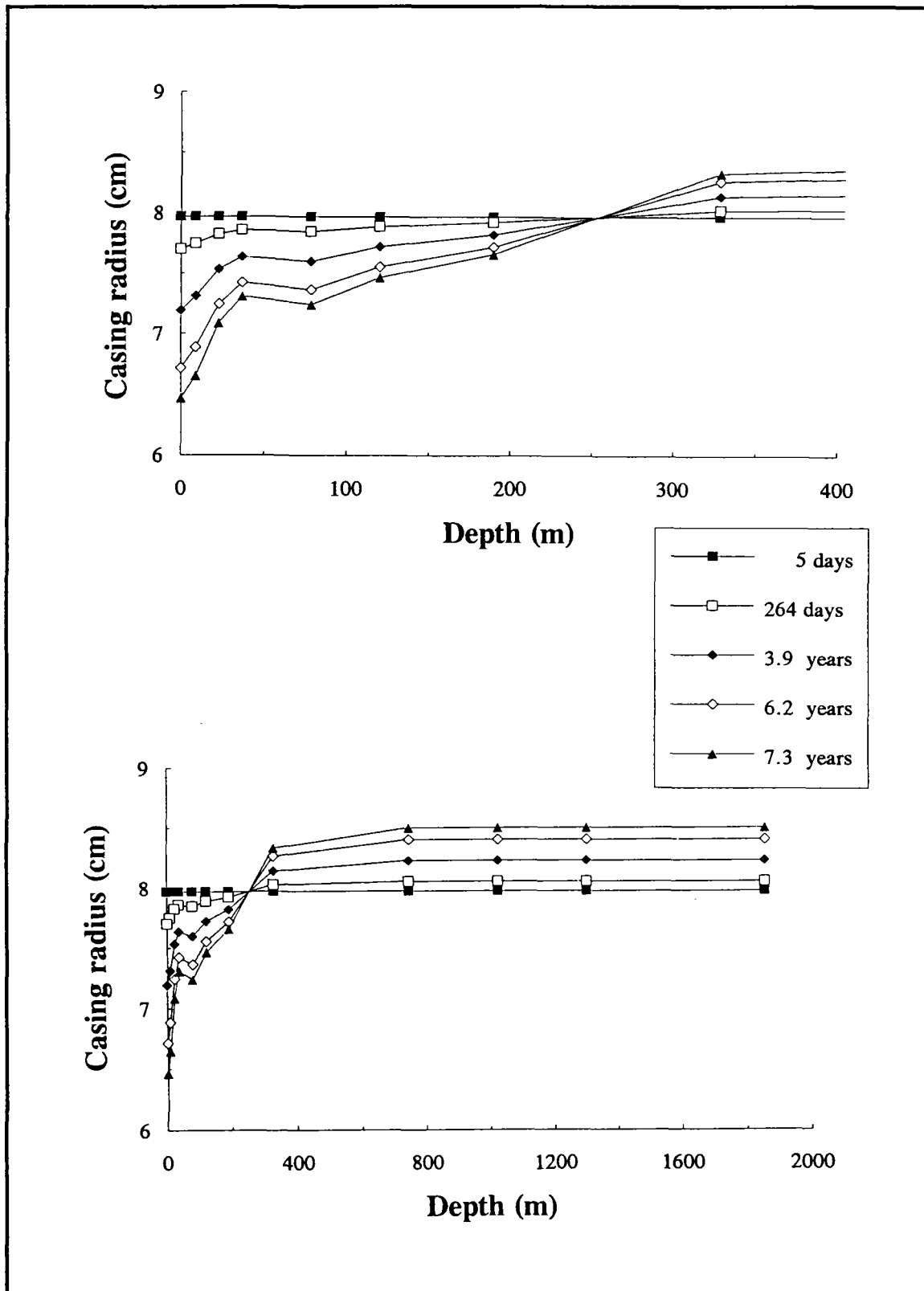


Figure 10: Casing radius versus well depth at different exploitation times and without diffusion layer - from 0 to 2000 m and "zoom" from 0 to 400 m.

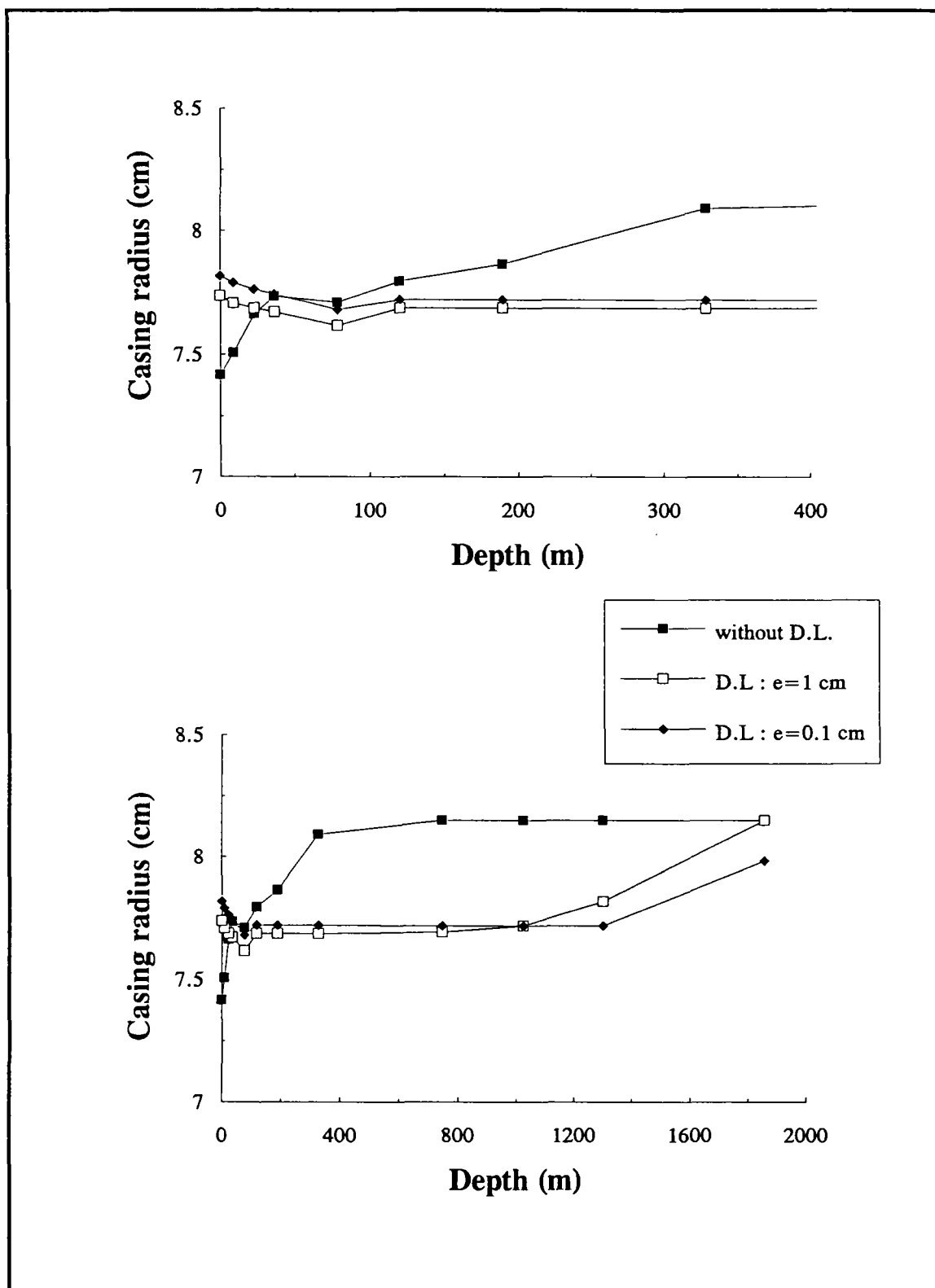


Figure 11: Casing radius after 2.9 years versus well depth of exploitation time. The different curves account for 3 thickness for the diffusion layer (DL) - from 0 to 2000 m and "zoom" from 0 to 400 m.

2.1.2.5. Conclusion and future objectives

The new MODEP code can simulate the variation in casing diameter versus well depth and exploitation time. Exploitation parameters (head pressure and flow rate) and fixed data such as corrosion rate, can now be modified to study their effect on the variation of the diameter. This code was tested and results are reported in paragraphs 2.2.3 and 2.2.4. Computed iron and sulphide concentrations were in good agreement with those determined by well-head analyses.

Let us specify that only thermodynamic considerations are taken into account to precipitate the mackinawite, indeed the first precipitate, amorphous iron sulphide, changes to mackinawite in a few hours (Morse J.W et al., 1987 ; Rickard D., 1989). Precipitation of other iron sulphides (pyrite, pyrrhotite, etc...), of iron and calcium carbonates must take into account the kinetic of precipitation and transformation, since some of these minerals need a long time to be precipitated. Their precipitation is function of temperature, flowrate and presence or absence of H₂S bubbles as was shown by Tewari P.H. and al. (1979).

2.2. RESEARCHS ABOUT IRON AND SULPHIDES CONCENTRATIONS OF THE DOGGER GEOTHERMAL FLUID

2.2.1. Introduction

The characteristics of the geothermal water from the reservoir were already known at the start of the program, from samples taken at the production wellheads or, less frequently, at well bottoms using instruments developed by specialist service firms.

The major disadvantage of these sampling methods was that the fluid they brought up was not fully representative of the reservoir:

- the steels used to construct the classic samplers can pollute the sample with the iron they contain (to the extent of a few tenths of a mg of iron per litre of geothermal water);
- wellhead samples are "polluted" by corrosion in the 2000-odd metres of casing; there can be reactions with substances in the fluid (production of iron sulphide scale, for example);
- the fluid can be degassed as it comes up the well, thus modifying the equilibria of the original fluid.

Two ideas were put forward to make up for these shortcomings: (a) a well-bottom sampler that would be inert with respect to such reactive species as iron and sulphides and (b) well bottom sampling experiments using a special tube made entirely of a composite material, to extract a fluid that has not been in contact with the steel casing.

After several years in operation, significant variations in sulphide concentrations had been observed in the geothermal fluids of the Paris basin geothermal systems.

With a view to gaining an understanding of these phenomena, a sampling programme was carried out on the fluids of about ten such sites to the East and South of the Paris basin.

As a part of this programme, isotopic analyses (sulphur isotopes of sulphates and sulphides) were used to determine with certainty the origin of these variations. These sampling operations also enabled us to improve analytical methods for sulphides in these geothermal fluids and make them more accurate – improvements that were immediately applicable by the firms responsible for monitoring the operation of the doublets.

2.2.2. Construction of the "PRNPIMO" down hole fluid sampler

2.2.2.1 The specifications

The aim was to construct a down hole fluid sampler that would make it possible to bring a sample of monophasic fluid to the surface with its original pressure conditions and chemical

composition. The sampler had also to be usable for measuring bubble point and gas/liquid ratio, and allow transfer of the fluid under controlled conditions.

The characteristics of the fluids to be sampled were as follows:

- . Maximum temperature 200°C,
- . Pressure at the moment samples taken: 250 bars,
- . Highly saline (up to 35 g/l) and containing H₂S (up to 150 mg/l),
- . Dissolved gases with high bubble point (max. 20 bars)
- . GLR (gas:liquid ratio) 20% or less.

Additional limitations were defined:

- . Sample volume was to be at least one litre,
- . External diameter had to allow the implement to pass through a 2"1/2 tube,
- . Length less than 3 metres,
- . Mechanical and electrical connection by 4- or 7-strand Gerhart Owen cable head,
- . Use of materials that will not pollute the fluid to be sampled,
- . Strainer allowing the passage of particles of at least 25 microns.

2.2.2.2. The chosen solutions

To meet these specifications, a certain number of technological choices were made:

- A variable-volume sampling chamber (zero volume at start of sampling), using a "free" piston to vary the volume;
- Use of a double non-return valve at the inlet, to isolate the fluid sample from the external medium;
- Control of the speed of movement of the piston, from start to end of filling operation, by means of controlled reduction of pressure in a transit gas;
- A solenoid valve, isolated from the fluid to be sampled, operating in the transit gas at a temperature of less than 200°C;
- For those parts in contact with the fluid sample, use of inert materials such as titanium and Hastelloy C-22 (Hastelloy and C-22 are registered trade marks of Haynes International Inc.);
- A system involving a calibrated constriction, to limit the flow of transit gas;
- For those parts in contact with the fluid to be sampled, joints to be sealed with inert materials such as PTFE.

Figure 12 shows the different parts of the instrument. A patent application was filed on March 19th, 1992 (Application N° 92.03308).

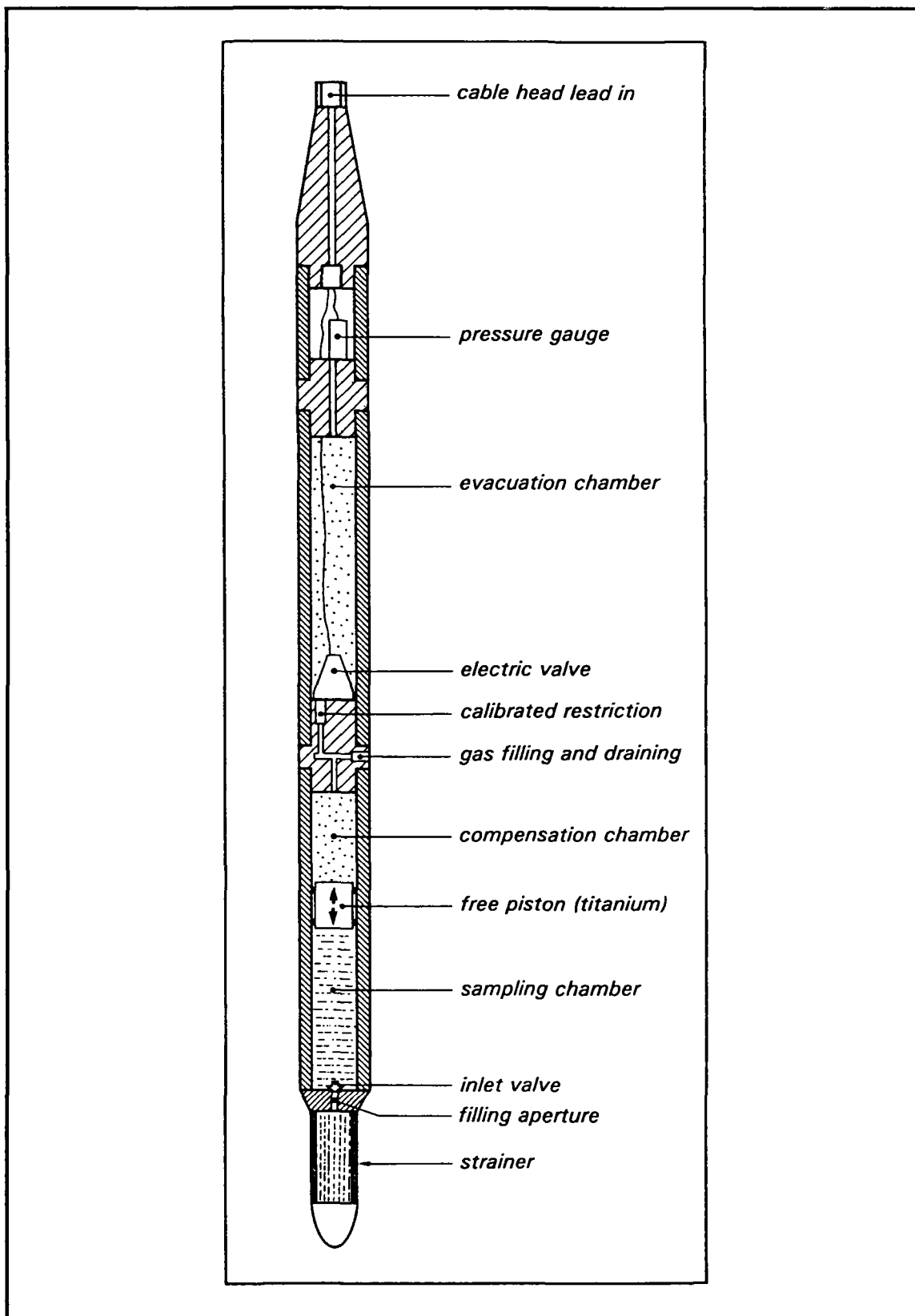


Figure 12: Plan of the down hole fluid sampler "PRINPIMO"

2.2.2.3. Operating principle

Preparation

Before the sampler is sent down the well, the piston is positioned at the bottom of the sampling chamber, reducing the volume of the chamber to virtually nil. The piston is held in place by pressure exerted by the transit gas (nitrogen) which fills the space between piston and solenoid valve, which we shall call the compensation chamber. This pressure must be higher than that of the fluid to be sampled. The evacuation chamber, above the solenoid valve, is at a lower pressure (e.g. atmospheric pressure), regulated according to the amount of fluid required. The solenoid valve is closed.

Sampling

Once the instrument is in position for sampling in the well, sampling is triggered by charging the coil of the solenoid valve: the transit gas passes into the evacuation chamber through a calibrated constriction (to restrict its flowrate). The pressure this gas exerts on the piston is reduced, allowing the piston to rise and letting fluid into the space so created in the sampling chamber. The pressure in the evacuation chamber, and hence the filling of the sampling chamber, are monitored by means of a pressure sensor connected to the surface.

The end of the sampling operation, identified at ground level by the stabilization of the pressure measured in the evacuation chamber, occurs either when the piston meets the end of the chamber on the solenoid valve side, or at the point when there is equal pressure in the sampling chamber, evacuation chamber and compensation chamber.

The sampler is then raised; the double non-return valve closes as a result of the drop in external pressure. The solenoid valve can be kept open while the sampler is brought up, to keep the fluid sample under pressure (the pressure would otherwise tend to fall rapidly as the temperature dropped on the way up).

Recovery

At the surface, the sample is recovered by opening the double non-return valve with a special tool. If the piston has not abutted at the end of the sampling process, the gas and liquid phases can be separated in the sampling chamber. The sampler is placed vertically, end up: the gas pressure drops in the compensation chamber (solenoid valve open), the piston drops and the fluid pressure drops in a controlled manner until atmospheric pressure is reached, so separating the two phases. The gaseous part is transferred by re-expanding the evacuation chamber; the liquid part is then evacuated in the same way.

2.2.2.4. Capacities of the implement at the present development stage

Different tests were carried out under field conditions: in the GPF well in Couy, Cher, in February 1991, and in Soultz (GPK1) and Clermont-Ferrand (la Croix de Nérat) in December 1991. These tests served to validate the use of this sampler (christened PRINPIMO, for PRéleveur INerte à Piston MObile) for sampling fluids under the following conditions:

- temperatures below 160°C,
- pressure less than 210 bars.

It was first used in a production well on the Paris Region Dogger in June 1992, bringing up a fluid sample taken at the shoe of the well casing of the Ris Orangis production well, Essonne.

A procedure for operation and maintenance has been worked out.

This prototype (only one of which has been made) is currently operational for sampling from wells in the Paris Region Dogger, or other wells within the above pressure and temperature limits.

2.2.3. Sampling of fluid at the well bottom with the "PRINPIMO" down hole sampler

Results of this study are given in a BRGM report (Ignatiadis I. and Abou Akar A., 1992).

In June 1992 the opportunity arose to collect samples using the IMRG's inert bottom sampler in the Ris-Orangis production well (GRO-2) after its cleaning and before the insertion of a tube for production well anti-corrosion treatment and the reinstallation of the pumping unit. In this case, as for sampling with the W.B.T.T. (see paragraph 2.2.4.), the samples collected are never in contact with any metallic surface and preserve their original (reservoir) iron and sulphide contents. The objectives of this operation were to:

- 1) Sample the well bottom using the sampler (PRINPIMO) before the installation of the immersed pump from which the inhibitor injection tube is suspended.
- 2) Measure the iron and sulphide contents in the Dogger aquifer directly below Ris-Orangis (before they come into contact with the casing), compare them with those measured simultaneously at the wellhead and calculate the dissolved iron input caused by corrosion of the casing by comparing the iron concentrations measured at the production wellhead with those measured in the bottom sampler.
- 3) Calibrate a model of the behaviour of the fluid (MODEP, § 2.1.2.) during its rise.

Before lowering the sampler, we monitored the evolution of the physical parameters and fluid concentrations of chemical species produced by the well. This ensured that the fluid produced was indeed representative (e.g. in ion chloride content) of the aquifer fluid. The bottom of the well and the production wellhead were sampled simultaneously. The geothermal water was collected under an artesian flowrate of 74 m³/h.

Sulphide and iron concentrations measured in the fluid obtained from the sampler are assumed to represent those of the aquifer: $[\text{Fe}^{2+}]_{\text{bottom}} = 0.60 \text{ mg/l}$; $[\text{S}^{2-}]_{\text{bottom}} = 0.57 \text{ mg/l}$. The concentrations measured at the production wellhead are assumed to be representative of those resulting from corrosion/deposit phenomena in the casing: $[\text{Fe}^{2+}]_{\text{well}} = 1.55 \text{ mg/l}$; $[\text{S}^{2-}]_{\text{well}} = 0.57 \text{ mg/l}$.

The comparison of the composition of fluids obtained with the bottom sampler and those sampled at the wellhead showed that only the iron content varies significantly with the origin of the sample. It should be noted that the iron content in the well bottom is not zero but rather around 0.6 mg/l. The sulphide content at the bottom of the well is identical to that measured at the wellhead. This demonstrates that there is no loss of sulphides by precipitation of iron sulphide nor any production of sulphides by bacterial reduction of sulphates.

The approximate corrosion rate in the well at the time of the sampling was calculated from iron mass balances as described in § 2.2.4. The amount of iron produced by corrosion of the casing was estimated from the iron content at the production wellhead ($[\text{Fe}^{2+}]_T$), the iron in the aquifer (measured in the fluid collected by the bottom sampler, $[\text{Fe}^{2+}]_{\text{bottom}}$) and the iron deposited as sulphide (none). The amount of iron produced by corrosion is, therefore, approximately 0.95 mg/l which corresponds to a generalized corrosion rate of 60 $\mu\text{m}/\text{year}$.

Sulphide and iron concentrations reported above and computed corrosion rate were used to calibrate the MODEP code according to the same scheme proposed in § 2.2.4. Results of calculations are given in table 2 (*).

Samples (16/06/92)	$[\text{Fe}^{2+}]$ (mg/l)	$[\text{S}^{2-}]$ (mg/l)
by the PRINPIMO bottom sampler (analysis)	0.60	0.57
by the head of the production well (analysis)	1.55	0.57
by the head of the production well (with the computer code MODEP)	1.53	0.56

Table 2: Iron and dissolved sulphides concentrations from Ris Orangis sampling: comparison between the analysis and the modelling by MODEP

Calculated concentrations are in a good agreement with the analyses at the production well head. They confirm that geothermal fluid remains unsaturated in mackinawite (the saturation index with respect to mackinawite was less than 1). All iron produced by corrosion reaches the well head.

The decrease in sulphide concentration is caused by fluid degassing at the surface (the bubble point pressure is 8.5 bar). This loss of sulphides is too small to be determined by analysis.

(*) *Calculations by MODEP were done without using a diffusion layer for two reasons : a) in the well head we are not able to analyse iron and sulphide in the diffusion layer. Only the average value of the whole casing can be analysed; b) the MODEP code don't treat yet the species migration between the diffusion and the convex layer .*

2.2.4. Sampling of fluid at the well bottom with a special composite tubing

Results of this study are reported in a BRGM report (Ignatiadis I. and al., 1992b).

In 1989, when the Blanc-Mesnil geothermal doublet was rehabilitated and a tube installed to inject additives at the well bottom (Well Bottom Treatment Tube (WBTT) CFG-Forplex), the IMRG used this tube to carry out physico-chemical monitoring and sampling (Ignatiadis I.

and Brach M., 1989; Boisdet A. et al., 1989). Despite the difficulties encountered in the course of this preliminary operation, two samples of geothermal water were brought up using this tube. A comparison between the analytic results from the fluid sampled with the tube and those of the fluid sampled in the well casing did not provide a basis for any definite conclusions as to the iron and sulphide concentrations in the reservoir, particularly in view of the contribution of the 250 m of semi-flexible new steel tubing (internal diameter 7 mm) which formed the link with the CFG-Forplex tube (the CFG-Forplex tube began at the well shoe and stopped at the immersed pump, where it was suspended).

It seemed necessary to use a tube made entirely of composite for this kind of sampling operation. The opportunity presented itself in July 1991 at the Orly 1 production well (GOR-2), an artesian well. There being no immersed pump, a tube made entirely of composite (CFG-Forplex WBTT) was specially installed, running from the shoe right to the surface. With this setup, the samples are never in contact with a metal surface and will retain their original iron and sulphide contents, although one cannot exclude the possibility of deposits on the tube wall. One can thus estimate the amount of iron in solution contributed by the casing by comparing the concentrations of iron produced at ground level by the two pipes, the WBTT and the production well casing.

This sampling operation was carried out on July 19th-20th, 1991, prior to treatment with a corrosion inhibitor by means of the injection tube. The operation consisted of taking samples at ground level from the injection tube and the well casing, at two different flowrates and on two consecutive days. The aim of the operation was to:

- 1) Take samples at ground level using the CFG-Forplex WBTT composite tube (glass fibre + epoxy resin), before this tube was used to inject a corrosion inhibitor;
- 2) Evaluate the iron and sulphide concentrations and the number of sulphate-reducing bacteria in the Dogger aquifer below Orly 1.
- 3) Work out a correct model of the fluid's behaviour on its way up (model currently being developed by IMRG) (see § 2.1.2).

Prior to sampling with the WBTT, trends in some physical parameters and concentration of certain chemicals in the fluid produced by the well and the WBTT were monitored, so as to be sure that the fluid produced was representative of the reservoir fluid (mean composition of the fluid produced by Orly 1 over the past several years). Four sampling operations were run, involving simultaneous sampling at ground level from the CFG-Forplex WBTT and from the well casing, at two different flowrates (100 m³/h and 60 m³/h) on two consecutive days (19/7/91 from 5 pm to 8 pm and 20/7/92 from 11 am to 1 pm).

The sulphide, iron and manganese concentrations identified in the fluids from the WBTT are assumed to be those of the reservoir. For the first sampling (flowrate=100 m³/h), these were (in mg/l): $[\text{Fe}^{2+}]_{\text{WBTT}}=1.1$; $[\text{S}^{2-}]_{\text{WBTT}}=4.082$; $[\text{Mn}^{2+}]_{\text{WBTT}}=0.024$. For the second sampling (flowrate=60 m³/h), they were: $[\text{Fe}^{2+}]_{\text{WBTT}}=0.73$; $[\text{S}^{2-}]_{\text{WBTT}}=2.841$; $[\text{Mn}^{2+}]_{\text{WBTT}}=0.021$.

Those measured in the production well fluid are assumed to be those resulting from the corrosion-scaling phenomena in the casing. For the first sampling (flowrate= 100 m³/h),

these were (in mg/l): $[\text{Fe}^{2+}]_{\text{well}}=3.0$; $[\text{S}^{2-}]_{\text{well}}=3.016$; $[\text{Mn}^{2+}]_{\text{well}}=0.054$. For the second sampling (flowrate= 60 m³/h), they were: $[\text{Fe}^{2+}]_{\text{well}}=3.2$; $[\text{S}^{2-}]_{\text{well}}=2.128$; $[\text{Mn}^{2+}]_{\text{well}}=0.045$.

Comparison of the compositions of the fluids sampled in the production well and by the WBTT showed that only the iron, sulphide, manganese and SRB cells varied significantly according to the production flowrate and the origin of the sample. It should be noted that iron content at the well bottom is not zero, being about 1 mg/l. Sulphide concentrations are higher at the well bottom than in the wellhead water, proving that sulphides are consumed through precipitation of iron sulphide (scaling on well casing walls).

It was possible to calculate the approximate rate of corrosion in the well during the two sampling operations by establishing the iron balance, as follows:

$$Q_T \cdot [\text{Fe}^{2+}]_T = \Phi_{\text{iron reservoir}} + \Phi_{\text{iron corr.}} - \Phi_{\text{iron scale}}$$

From this equation one can estimate the amount of iron produced by corrosion of the tubing ($\Phi_{\text{corrosion iron}}$), given (a) the iron content measured in the production wellhead fluid ($[\text{Fe}^{2+}]_{\text{well}}$), (b) the reservoir iron ($\Phi_{\text{reservoir iron}}$) (as measured in the WBTT fluid, i.e. $[\text{Fe}^{2+}]_{\text{WBTT}}$) and (c) the iron deposited as sulphide scale. The latter can be roughly estimated as the difference in sulphide concentrations identified by analysis of the WBTT and wellhead fluids. Thus the estimated corrosion rates are V_{corr} (well at 100 m³/h) = 0.41 mm/yr and V_{corr} (well at 60 m³/h) = 0.24 mm/yr.

The same approach applied to manganese concentrations gives rates of corrosion of the same order of magnitude: V_{corr} (well at 100 m³/h) = 0.35 mm/yr and V_{corr} (well at 60 m³/h) = 0.15 mm/yr.

We were able to test these corrosion rate values, as estimated from measurements of the dissolved iron and sulphides from the two sampling operations, using two computer codes, TPDEGAZ and MODEP (MODélisation des phénomènes de DEPôts) which model the rise of the fluid in the production well. MODEP is an extension of TPDEGAZ, since it allows quantification of the iron sulphides deposited on the casing walls of a geothermal well. Using this programme to process the physico-chemical data gathered at the production wellhead and at the top of the WBTT, one can (a) test the programme and (b) verify the rates of corrosion estimated from these data.

The composition of the well bottom fluid is calculated from the WBTT analyses. To carry out the validation tests, the MODEP code simulates the behaviour of the fluid rising up the production well. It performs the validation by comparing the wellhead fluid compositions (a) as sampled at the production wellhead and analysed, and (b) as simulated by MODEP.

Examination of the results shows that, using the MODEP computer code, one obtains values for iron and sulphides that are closer to those analysed from the 20/7/91 samples than to those from the 19/7/91 samples. Further, the 20/7/91 operation gives results closer to the initial state of the fluid, even if the iron concentrations analysed from the WBTT sample seem to be

rather high. The deviations can partly be attributed to the simplificatory hypotheses on which the MODEP code is based.

There is a good correlation between the MODEP code results and the analysis results (cf. Table 3).

Samples (20/07/91)	[Fe ²⁺] (mg/l)	[S ²⁻] (mg/l)
by the head of the WBTT (analysis)	0,73	2,84
by the head of the production well (analysis)	3,20	2,13
by the head of the production well (with the computer code MODEP)	2,75	1,88

Table 3: Iron and dissolved sulphides concentrations from Orly 1 sampling: comparison between the analysis and the modelling by MODEP

It should be noted that at the present time, the treated wells (inhibitor injected at the well bottom) in the northern zone, where the fluid is rich in sulphides, do not show significant levels of iron at the wellhead. On the other hand, the wells in the southern and eastern zones, where the fluid is less sulphide-rich, show iron levels above a certain threshold, specific to each well, even though these wells too are treated. Knowing that the production of iron by corrosion is reduced, this would seem to mean that the iron produced in the southern zones largely comes from the reservoir, whereas in the northern zone it is probably precipitated and deposited on the casing walls by the strong sulphides present in the reservoir fluids of the zone.

Where a treatment system using a CFG-Forplex WBTT made of a composite material is introduced, therefore, the tube can be used not only for its original purpose in injecting additives at the well bottom, but also to take fluid samples without the fluid coming into contact with the steel well casing, so enabling more accurate determination of iron and sulphide concentrations.

It will be a good thing to continue sampling operations of this kind where possible; it is necessary to know the iron concentrations in the reservoir below each production well, for better anticipation of scaling phenomena in the wells. This is equally useful for geochemical work and for the purposes of operating geothermal systems. The physico-chemical fluid data gathered at production wellheads and from the WBTTs enable calculation of corrosion rates, while processing of the data by means of the MODEP code makes it possible to validate these calculated rates.

2.2.5. Mapping of sulphide concentrations

The geothermal fluids in the Paris Basin Dogger aquifer form an anaerobic medium characterized by the presence of hydrogen sulphides. These compounds have been present since the aquifer was first exploited. Sulphur is mainly present in the form of hydrogen sulphides H_2S/HS^- (between 0 and 100 mg/l), mercaptans (organic sulphides) RSH/RS^- (between 0 and 10 mg/l) and sulphates SO_4^{2-} (between 300 and 1200 mg/l).

Systematic analytical studies showed that one zone, to the North and West of Paris, was particularly rich in sulphides (several tens of mg/l) while values in the remainder of the aquifer were considerably lower. There is a clear difference in sulphide concentrations between the North and West compared to the South and East. This distribution corresponds to the stable sulphur isotope ^{34}S distribution in sulphates (Fouillac C. et al., 1986; 1990). It was also found that dissolved sulphide concentrations were always high in areas where significant well clogging occurred (Fouillac C. et al., 1989).

As early as 1987, analyses carried out by IMRG and the companies who operate the geothermal plants, showed that the sulphide content was increasing in certain geothermal wells (Boisdet A. et al., 1989, 1990; Cheradame J.M. and Ignatiadis I., 1990; Ignatiadis I. et al., 1990a, 1990b, 1991b and 1991c).

It was decided, in 1989, that IMRG would carry out a comprehensive study on the concentration and development of sulphide contents in the fluids at production wellheads in the Paris Basin Dogger aquifer. The aim of this study, which continued through 1990 and 1991, was to:

- 1) map the distribution and classify zones by their sulphide contents.
- 2) highlight variations in sulphide concentrations caused by variations in the well flowrate, interpret and quantify sulphide production phenomena and, finally, determine the origin of the increases in sulphide concentrations found.

2.2.5.1. Description of a method for sulphide analysis

Rapid and sensitive methods of analysing the sulphide species, such as hydrogen sulphide and mercaptans, were developed in our laboratory at this time and can be employed with the same accuracy both in the laboratory and on site. This study has already been published in a BRGM report (Ignatiadis I. et al., 1991b).

The dissolved sulphides and mercaptans must be regularly measured at the geothermal sites by a potentiometric titration method using a +II mercury salt, mercuric nitrate $Hg(NO_3)_2$ or mercuric chloride $HgCl_2$. Given the poor conservation capacity of sulphides and mercaptans, which oxidize when exposed to air, they must be measured on site.

This is done manually, necessitating the permanent presence of an operator and careful attention at all stages of the manipulation. Moreover, it is difficult to process the data on site, and this results in a delay in interpreting the results.

The aim of this study was to examine this manual method and possibly replace it with a computer-aided method. In particular, it was of prime importance to try to develop a method based on the same principle, but faster and more reliable, giving immediate results enabling processing of the data on site.

The manual analysis method was examined with precision, on a statistical basis, using previous and present monitoring studies. On statistical examination, the results prove to be uniform and the relative error small (variation coefficients of about 1% for measurement of sulphides, and around 39% for the mercaptans). Computer-aided titration equipment was then used to measure the dissolved sulphides and mercaptans. For dissolved sulphides, this method is as accurate as the manual method (variation coefficient of 3%), while for mercaptans it is much more accurate (variation coefficient of 16%). The larger systematic errors are due to the independence of the different measurements in the sequence, which in turn is a result of the use of different instruments to measure the different variables such as temperature, potential difference, electrode calibration, data processing. It therefore seems clear that computer-aided titration is preferable to the manual method, which is not at all practical on site, takes ten times longer, and gives less accurate results.

The development of this analytical technique for the determination of sulphide concentration made the end of the present study easy (mapping the sulphide concentration, mapping highlighting variations in sulphide concentrations and interpreting and quantifying sulphide production phenomena).

2.2.5.2. Mapping of sulphide concentrations

The map of dissolved sulphide concentrations throughout the Dogger aquifer, prepared in 1990-1991, revealed two distinct zones and two type of variation (Ignatiadis I. et al., 1991c):

A zone of high sulphide concentration (30 to 100 mg/l) lying to the North and West of Paris (Departements 93 and 95) and in the Melun-Fontainebleau sector to the South. In this zone, where the initial sulphide content was already high, it was found that the concentration did not vary significantly over time nor with the flowrate.

A zone with lower initial sulphide concentrations, lying to the South and East of Paris (Departements 91, 94 and 77 except the Melun-Fontainebleau sector) where sulphide concentrations at the wellhead do vary in time and with the flowrate.

The two types of variation are:

Regional variations: the dissolved sulphide concentrations vary by several orders of magnitude between certain wells to the South and East of Paris and a few sites in Seine-Saint-Denis or Beauvais (up to 100 mg/l), even though the total salinity (TDS) only varies by a factor of 5 to 6 (5.8 to 35 g/l) over all geothermal wells. There is no general correlation between sulphide concentration and fluid temperature and/or total dissolved salt.

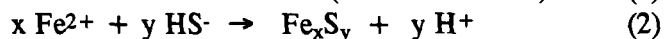
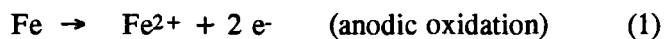
Local variations: hydrogen sulphide concentrations do not remain stable over time, particularly in the "low sulphide" zones in the Val de Marne and Seine et Marne.

2.2.6. Analysis of the present bacterial contribution to the increase of sulphide concentration in the geothermal fluid

2.2.6.1. By a flowrate variation method

The first important step was to closely consider all potential sources which could cause variations in sulphide and iron concentrations at the production wellhead, to allow experimental methods of triggering variations to be determined so that these variations could be studied.

Dissolved sulphides and iron arise directly from corrosion-scale deposit phenomena occurring in the well casings. The reactions that occur are:



The half reaction (1) explains how iron is produced by corrosion of the casings while the reaction (2) indicates how both iron and sulphide are consumed by precipitation of iron sulphides. It is possible that, under certain conditions (reduced pH), this second reaction reverses, i.e. iron sulphides on the casing could be redissolved, releasing dissolved sulphides and iron.

To this first iron and sulphide production-consumption mechanism must be added sulphides produced by bacterial reduction of sulphates, schematically represented by $\text{SO}_4^{2-} \rightarrow \text{HS}^-$. In fact, sulphate-reducing bacteria are known to be capable of producing sulphides by reduction of sulphates in anaerobic water in a medium more or less in equilibrium (Rozanova E.P. and Khudyakova A.I. 1974 ; Daumas S. et al., 1985a, 1985b, 1986) . This reduction may or may not cause sudden changes in the physico-chemical properties of the medium.

Consequently, we must consider two systems: S_1 = the aquifer and S_2 = the production well.

Theoretical description of S_1 :

S_1 is an aquifer which may consist of several productive levels designated $n_1, n_2, n_3 \dots n_n$. Each productive level contributes a flowrate $q_1, q_2, q_3 \dots q_n$ respectively to the total flow Q_T measured at the surface: $Q_T = \sum q_i$. The temperature difference between the upper productive level and the lower productive level is small (from 1 to 3°C). The chemical and biological composition of the water produced may vary between the various levels (for example, different concentrations of a certain types of bacteria).

The amplitude of any variations between different productive levels could not be determined from earlier studies.

The dissolved sulphide and iron concentrations in the deep fluid, i.e. the fluid before any contact with the casing steel, on a given site at a given time are unknown.

Theoretical description of S₂:

S₂ is the well itself, i.e. the casing and any scale attached to it. In fact, S₂ could be extended to include the nearby aquifer, i.e. the part of the aquifer very close to the production well which could be affected by intense operation of the well. There are sulphate-reducing bacteria (and other types) in the fluid flow but also on or under the scale. These bacteria reduce sulphates to sulphides released into the fluid at a rate which is constant at time *t* and at a given flowrate. The rate at which sulphides are released into the fluid can vary if the flow varies. However, on contact with iron originating from the aquifer or corrosion of the tubes, these sulphides can also precipitate as Fe_xS_y. The iron sulphides may then either bond to the tubes or be entrained in the fluid flow.

In any event, all measurements and analyses are carried out at the wellhead, where the fluid composition results from both systems S₁ and S₂.

To fully understand trends when the well flowrate varies, we must select the concentrations as parameters (considering both systems S₁ and S₂) and introduce the concept of ion flux.

The general case for an ion at the wellhead:

The total flux of a given ion reaching the wellhead at any given instant can be written:

$$Q_T \cdot [\text{ion}]_T = \sum_{i=1}^n q_i \cdot [\text{ion}]_i$$

where

Q_T = flowrate measured at the wellhead (in m³/h)

$[\text{ion}]_T$ = the ion concentration measured at the production wellhead

$\sum_{i=1}^n q_i [\text{ion}]_i$ is the part of the ion flux generated by the deep aquifer which consists of different productive levels each providing a flow q_i (where $1 \leq i \leq n$). If the concentration is expressed in mg/l and the flowrate in m³/h, the ion flux is in g/h.

q_i = the flow from each productive level *i* in the deep aquifer (in m³/h).

$[\text{ion}]_i$ = the ion concentration produced by each level *i* in the deep aquifer.

In the special case where the ion concentration at the wellhead does not vary with flowrate, the ion concentration produced by the deep aquifer must be the same as at the wellhead and the above equation becomes:

$$[\text{ion}]_T = [\text{ion}]_{\text{aquifer}} \quad \text{since } Q_T = \sum q_i$$

Dissolved sulphides and iron at the wellhead:

The total fluxes of sulphide and iron ions at the wellhead, at any given time, can be written:

$$Q_t \cdot [S^{2-}]_T = \sum_{i=1}^n q_i \cdot [S^{2-}]_i + \Phi_{bact.sulph.} - \Phi_{deposit.sulph.}$$

$$Q_t \cdot [Fe^{2+}]_T = \sum_{i=1}^n q_i \cdot [Fe^{2+}]_i + \Phi_{bact.iron} - \Phi_{deposit.iron}$$

where

$[S^{2-}]_T$ and $[Fe^{2+}]_T$ = dissolved sulphide and dissolved iron concentrations measured at the production wellhead

$[S^{2-}]_i$ and $[Fe^{2+}]_i$ = dissolved sulphide and dissolved iron concentrations produced by each level i in the deep aquifer.

and $\sum_{i=1}^n q_i \cdot [S^{2-}]_i$ and $\sum_{i=1}^n q_i \cdot [Fe^{2+}]_i$ are the part of the dissolved sulphide and iron fluxes respectively produced by the deep aquifer which consists of various productive levels, each of which produces a flow q_i (where $1 \leq i \leq n$). If the concentration is in mg/l and the flowrate in m³/h, the ion flux is in g/h.

$\Phi_{bact.sulph.}$ = the part of the sulphide flux currently produced at time t by bacteria in the casing and the close aquifer (in g/h).

$\Phi_{deposit.sulph.}$ = the part of the sulphide flux deposited, in the form Fe_xS_y , on the casing walls (in g/h).

$\Phi_{corr.iron}$ = the part of the iron flux currently produced at time t by corrosion of the casing (g/h).

$\Phi_{deposit.iron}$ = part of the iron flux deposited in the form Fe_xS_y on the casing walls (in g/h).

If it is assumed that the fluid produced by the deep aquifer has the same dissolved sulphide and iron concentrations, $Q_T = \sum q_i$ and the above equations become:

$$[S^{2-}]_T = [S^{2-}]_{aquifer} + \frac{\Phi_{bact.sulph.}}{Q_T} - \frac{\Phi_{deposit.sulph.}}{Q_T}$$

$$[Fe^{2+}]_T = [Fe^{2+}]_{aquifer} + \frac{\Phi_{corr.iron.}}{Q_T} - \frac{\Phi_{deposit.iron}}{Q_T}$$

In this case, the part of the dissolved sulphide concentration currently produced by bacteria and the part deposited as iron sulphides would be inversely proportional to the flowrate and the part of the dissolved iron concentration due to corrosion and the part deposited in the form of iron sulphides would also be inversely proportional to the flowrate.

Physico-chemical monitoring of an artesian well in the southern zone, before and after bactericidal treatment.

A decisive experiment was carried out in the Southern zone, known to have a low initial sulphide concentration. The internal walls of the ORLY 1 geothermal doublet were treated with a bactericide. The results demonstrated that sulphate-reducing bacteria contribute to increasing the dissolved sulphide content at the wellhead: the bactericidal treatment reduced the wellhead dissolved sulphide concentration by 60% from its previous value. No significant variations in the major anion and cation concentrations were found. The results of this study have already been published in a report (Cheradame J.M. and Ignatiadis I., 1990) and an international paper (Ignatiadis I. et al., 1990b).

Physico-chemical monitoring of composition as a function of well flowrate in high sulphide concentration zone.

The physico-chemical parameters and concentrations of various chemical types were monitored daily in the Northern zone, known to have a high sulphide concentration. The results of the measurements, taken both during the summer and winter, showed that there is no significant change in the sulphide concentration between the winter and summer flowrates. Moreover, the dissolved sulphide concentrations have remained constant for several years in this zone. Further, these investigations showed that there is no chemical heterogeneity either horizontally or vertically in the aquifer. A comprehensive result on the report of the study were published in a BRGM report (Ignatiadis I. et al., 1990a).

Physico-chemical monitoring of composition against flowrate in the low-sulphide zone.

The composition of the fluid was monitored at various flowrates on two wells to the East of Paris (Meaux Beauval 1 (GMX-5) and Meaux Beauval 2 (GMX-7)) and on two other wells to the South-East of Paris (Creteil (GCRT-1) and Fresnes (GFR-2)). The fluid was monitored between 9th and 12th July 1990 and again between 6th and 12th September 1990. These experiments consisted in taking on-site measurements of the dissolved sulphide, dissolved iron and total iron concentrations at several stabilized (for 24 hours) flowrates (for example, 100%, 50%, 33% and 25% of the nominal flow). Samples were also taken, under the same conditions, for laboratory analysis of anions-cations, sulphur isotopes (in sulphides and sulphates) and oxygen isotopes (in sulphates). The results of this study were published in a BRGM report No. R 33518 IRG SGN 91 (Ignatiadis I. et al., 1991c).

The total dissolved salt did not vary significantly regardless of the flowrate. This is illustrated by figure 13, which shows total dissolved salt (TDS) plotted against flowrate and the reciprocal of the operational flowrate. This stability of the fluid composition, regardless of the flowrate in the various wells, suggests that the chemical composition of the fluids from the various productive levels (if such levels really exist) is uniform, i.e. either the fluid from each level has the same chemical composition $[\text{ion}]_i = [\text{ion}]_T$ or the relative contribution of the various productive levels remains stable at different flowrates.

The dissolved iron and total iron concentrations do not clearly follow a function of the flowrate (nor its reciprocal). The dissolved and total iron concentrations were either stable or increased only very slightly with flow (figures 14 and 15). This is also shown on figures 16 and 17 which are plots of the iron and total iron flux at the outlet against the flowrate or reciprocal of the flowrate.

Earlier experiments show that the corrosion rate is higher at lower flowrates (CFG, 1990 ; Plante G., 1990). At first sight, therefore, it would seem that iron sulphide precipitation would inevitably be higher at low flowrates (the dissolved sulphides and iron are in contact longer).

The only logical explanation for the stability, or very slight increase, in iron and free iron concentration at high flowrates is that the reduction in the production of corrosion iron at high flows is accompanied by lower consumption of iron precipitated as iron sulphides. It would seem that the iron concentration at the wellhead self-compensates in such a way that it becomes independent of flowrate. Consequently, we may consider that $[Fe^{2+}]_T \approx \text{Constant}$.

The dissolved sulphide concentrations vary considerably as a function of the flowrate (figure 18). At the same time, the dissolved sulphide flux remains relatively constant (figure 19), suggesting that the flowrate only affects the degree of dilution of the sulphides present (and produced) per unit time.

It can be seen that plotting $[S^{2-}]_T$ against the reciprocal of flowrate always gives a straight line (figure 18). If it is assumed that the sulphide concentration in the fluid from the deep aquifer depends solely on flowrate, the ordinate at the origin of straight line $[S^{2-}]_T = f(1/Q_T)$ would be $[S^{2-}]_{\text{aquifer}}$. The slopes of these lines would represent the difference:

$$\Phi_{\text{bact. sulph.}} - \Phi_{\text{deposited sulph.}}$$

Ignoring analytical problems, three apparently possible hypotheses were considered and explored to explain the variations in sulphide concentration with flowrate. They are described above:

- 1) A reduction in iron sulphide (Fe_xS_y) precipitation in the production well (reduction in the $\Phi_{\text{deposited sulph.}}$ term): either due to a reduction in casing corrosion or to a reduction in the fluid pH.
- 2) A decrease in pH leading to iron sulphides (Fe_xS_y) already precipitated being redissolved.
- 3) A sulphide production, constant at a given instant t , due to current bacterial activity in system S_2 (extended to include the near aquifer).

The first hypothesis depends on how corrosion and iron sulphide deposition rates vary with the wellhead flowrate. If corrosion decreases when the flowrate decreases, the water would contain less iron and precipitate and correspondingly smaller quantities of sulphide. However, experiments have shown that corrosion increases at low flowrates (CFG, 1990 ; Plante G., 1990). A reduction in pH at low flowrates would increase the iron concentration in the fluid. However, the pH does not decrease nor vary with the flowrate and, moreover, no increase in iron concentration is found at low flowrates. Obviously, it is not possible to directly correlate the increased sulphide concentrations with this hypothesis since the sulphide concentrations increase at low flowrates to an extent which cannot be explained solely by corrosion and/or less precipitation.

The second hypothesis assumes a variation in the fluid pH. However, the fluid pH does not vary significantly with flowrate. Moreover, this would be incompatible with observed results since a reduction in the pH should increase corrosion and the redissolution of iron sulphates. Consequently, in both cases, the dissolved iron (and sulphide) concentration would increase. However, no significant increase in iron concentration was found at low flowrates (see figures 14 and 15).

These two hypotheses are not satisfactory. They contradict each other on the iron, sulphide and pH variations. In fact, it would seem highly unlikely that such high sulphide concentrations could be caused solely by a reduction in corrosion at low flowrates, redissolving iron sulphides already precipitated in the well or by differences in the chemical composition of the aquifer. Moreover, these hypotheses would contradict observations since neither variations in the fluid pH nor in the iron concentration have been found when the flowrate varies.

The third hypothesis relates to the current production of sulphides by sulphate-reducing bacteria. In this case, the hypotheses we are attempting to consolidate is more reasonable since sulphate-reducing bacteria are the only strains known to be capable of reducing sulphates to sulphides in anaerobic water and in a medium which is more or less at equilibrium. This reduction may or may not be accompanied by a sudden change in the physico-chemical properties of the medium. If we assume that the rate at which sulphate-reducing bacteria produce sulphides remains constant over a relatively short period (i.e. the sulphide flux would be constant at the given instant in time t), the sulphide concentration would decrease as the flowrate increased (or vice-versa) simply because the quantity of sulphides produced in a given period would be more or less diluted, depending on the current water flowrate.

In other words, the sulphide flux would be constant at the given instant in time t and the sulphides produced are desorbed into the fluids at a release rate which remains constant at a given flowrate. If the flowrate varies, the rate at which sulphides are desorbed into the fluid also varies and there is a dilution effect.

This seems the most plausible hypothesis since a plot of the sulphide concentration $[S^{2-}]_T$ against the reciprocal of the flowrate is always a straight line (figure 7). The ordinate at the origin of this straight line is $[S^{2-}]_{\text{aquifer}}$ while the slope of the lines represent the difference:

$$\Phi_{\text{bact. sulph.}} - \Phi_{\text{deposited sulph.}}$$

From the reasoning in hypotheses 1 and 2, we cannot eliminate the term $\Phi_{\text{deposit sulph.}}$ but we can be reasonably sure that it is very little dependent on flow.

This supports the hypotheses that current and increasing bacterial activity is the reason for the increased sulphide concentration at certain wellheads which use the Dogger aquifer. This is also supported by the fact that the dissolved sulphide concentration increases over time and this could be related to the increased proliferation and activity of bacteria.

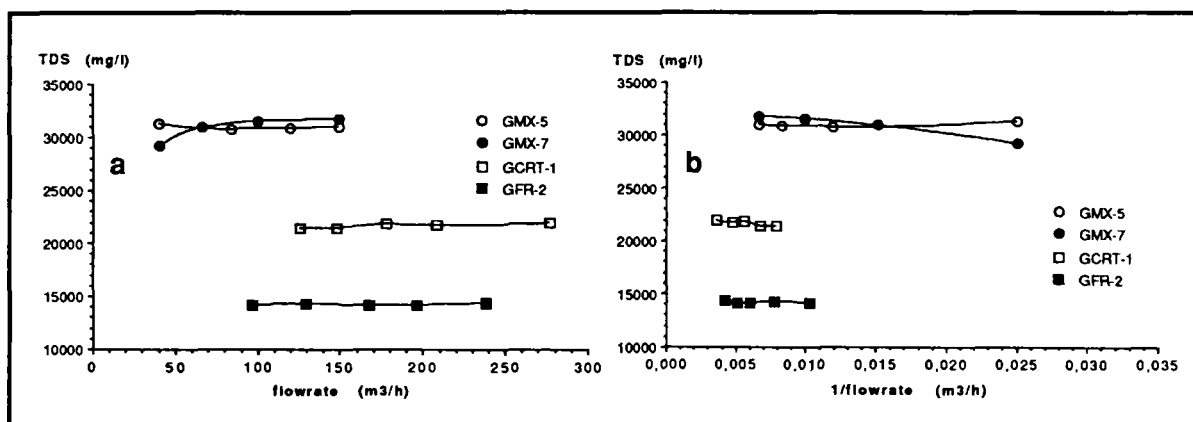


Figure 13: Total dissolved salt (TDS) in geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

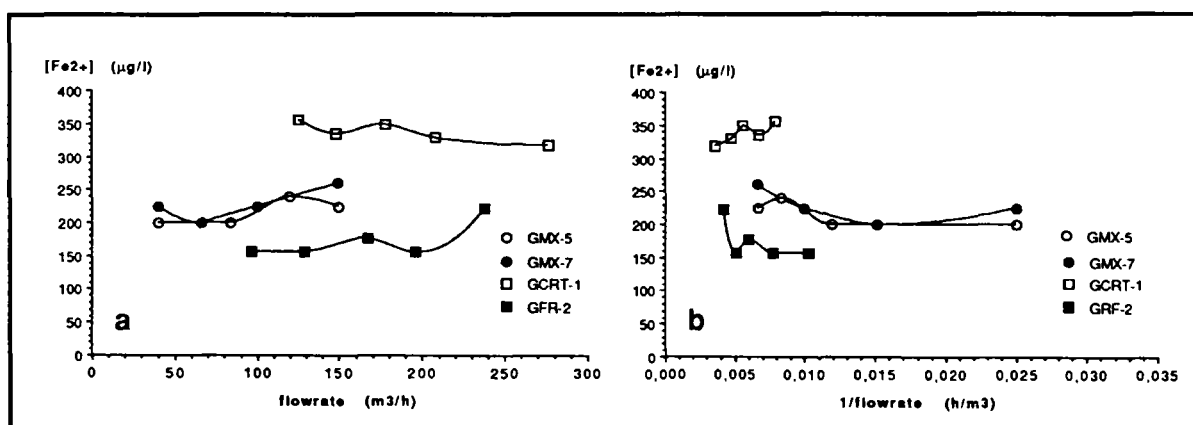


Figure 14: Dissolved iron concentration in the geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

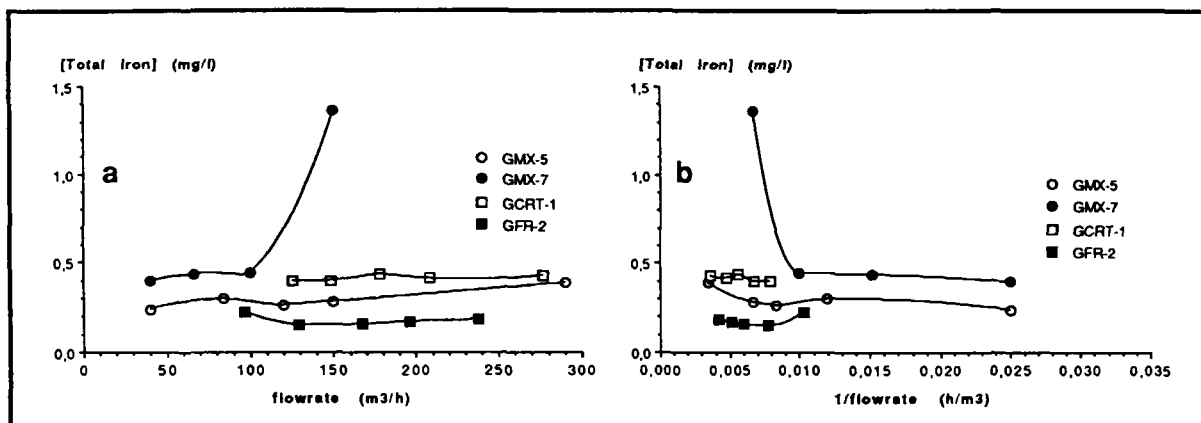


Figure 15: Total iron concentration in geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

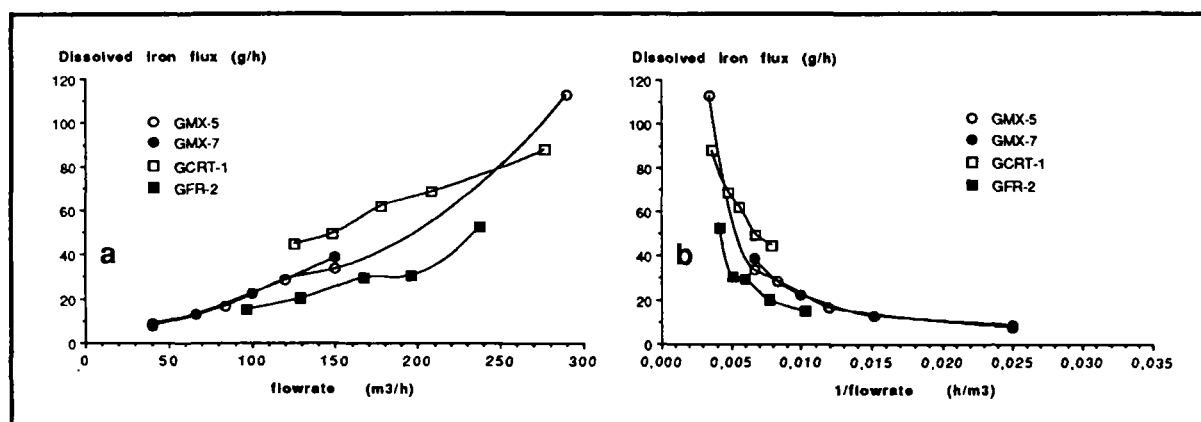


Figure 16: Dissolved iron flux in the geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

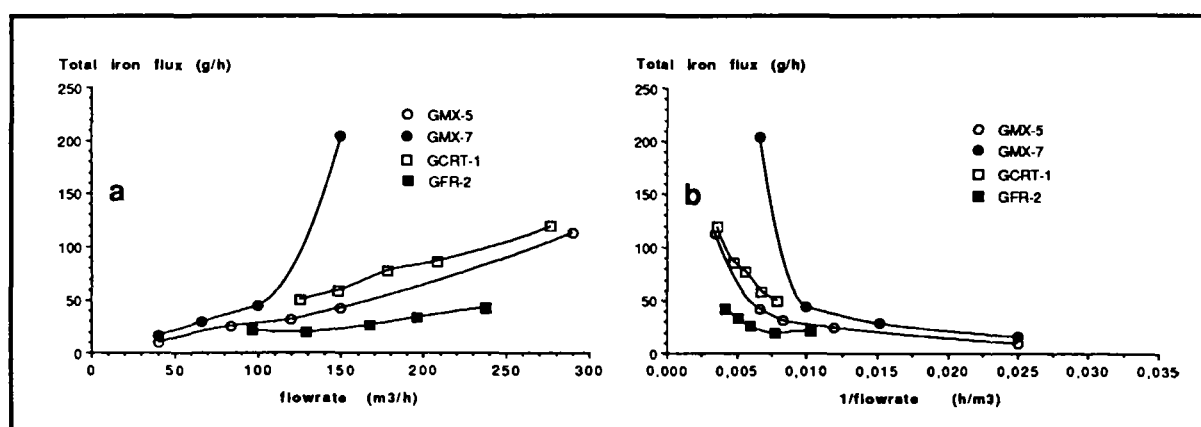


Figure 17: Total iron flux in the geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

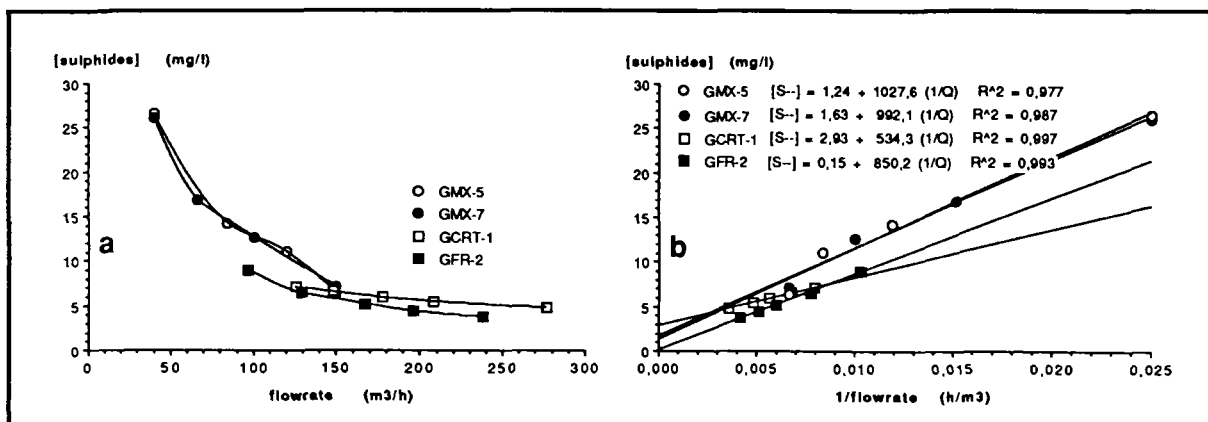


Figure 18: Dissolved sulphide concentration in geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

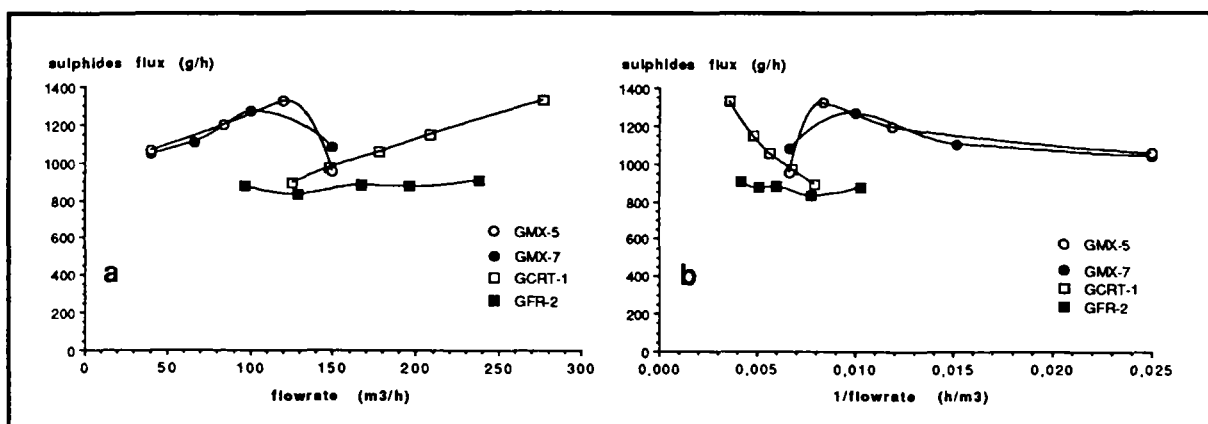


Figure 19: Dissolved sulphide flux in geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

2.2.6.2 By isotopic analysis

Although previous experiments, the bactericidal treatment of the Orly well (para 2.2.6.1) and the above reasoning concerning variations in iron or sulphide concentrations with flowrate in certain geothermal wells (para 2.2.6.1) are alone sufficient to indicate the presence of current bacterial activity, an innovative tool is now available to obtain additional information on variations in sulphide concentration with flow and to provide absolute confirmation of this hypothesis. This tool is based on the measurement of the $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{34}\text{S}(\text{HS}^-)$ isotopes and variations in the ratio between the sulphur ^{34}S and ^{32}S isotopes in sulphides and sulphates as the flowrate varies.

A systematic study of the proportion of sulphur isotopes in various natural compounds reveals a number of systematic variations and typical compositions. Sulphur has two stable isotopes: ^{34}S and ^{32}S .

Since it is difficult to accurately measure absolute values, the ratio between the two isotopes is measured. The "isotope ratio" of a sample is, therefore, the ratio between the rare heavy isotope present and the common lighter isotope. For sulphur, we obtain the following ratio:

$$R_{sample} = \left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{sample}$$

Because the variations in composition are extremely small, they are expressed by a special unit known as " δ ". The relative abundances in the samples are generally compared with those measured in an international standard known as the Canion Diablo Troilite (CDT) for sulphur. The heavy isotope concentrations can then be expressed as $\delta \text{ ‰}$:

$$\delta {}^{34}\text{S}_{sample} \text{ ‰} = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \cdot 1000 \quad \text{relative to the CDT}$$

" δ " is therefore a unit of relative deviation from the standard (these are chosen so that the variations occur about the value $\delta = 0$ which, by definition, is that of the standard).

In anaerobic water, such as that in the Paris Basin Dogger aquifer, sulphate-reducing bacteria can reduce sulphates into sulphides, this reaction being simply represented as $\text{SO}_4^{2-} \rightarrow \text{HS}^-$. This reaction increases the ${}^{34}\text{S}$ in residual sulphates (meaning that their $\delta {}^{34}\text{S}(\text{SO}_4^{2-})$ increases) and reduces the ${}^{34}\text{S}$ in the sulphides produced (i.e. $\delta {}^{34}\text{S}(\text{HS}^-)$ decreases). Consequently, the ${}^{34}\text{S}$ in the residual sulphates increases as the fluid is reduced (Harrison A.G. and Thode H.G., 1958; Kaplan I.R. and Rittenberg J.C., 1964; Kemp A.L.W. and Thode H.G., 1960; Kaplan I.R., 1975; Krouse H.R., 1980; Fouillac C. et al., 1990).

To study the physico-chemical properties as a function of flowrate in a low-sulphide zone (para 2.2.6.1), samples were taken under identical conditions (at all flowrates and from all three sites) to measure the ratio between the sulphur ${}^{34}\text{S}/{}^{32}\text{S}$ isotopes in the sulphides and sulphates and the ${}^{18}\text{O}/{}^{16}\text{O}$ in sulphates.

Table 4 gives the results, expressed in the form $\delta {}^{34}\text{S}(\text{SO}_4^{2-})\text{ ‰}$ and $\delta {}^{34}\text{S}(\text{HS}^-)\text{ ‰}$ measured at different flowrates in three wells. This table also shows the sulphide and sulphate concentrations measured at different flowrates in these three wells.

It can be seen that the $\delta {}^{34}\text{S}(\text{HS}^-)\text{ ‰}$ (and the sulphide concentration) varies very considerably with the flowrate (figure 20). The $\delta {}^{34}\text{S}(\text{SO}_4^{2-})\text{ ‰}$ and the sulphate concentration are not so sensitive to flowrate (figure 21) but nonetheless, appreciable variations still occur.

These variations are significant and must be understood to prove the current bacterial activity in the well.

Let us consider a simplified diagram of a production well whose casing and near aquifer are contaminated by sulphate-reducing bacteria. This situation can be considered as comprising two systems S₁ (the aquifer) and S₂ (the casing and the contaminated part of the near aquifer) (figure 22).

System S₁ can produce fluid at different flowrates, measured at the surface. If we assume that the chemical composition of the fluid from the aquifer is the same at all flowrates, the sulphate and sulphide concentrations $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{34}\text{S}(\text{HS}^-)$ are constant:

$$[\text{SO}_4^{2-}]_{\text{aquifer}} = \text{Constant} ; \quad [\text{HS}^-]_{\text{aquifer}} = \text{Constant}$$

$$\delta^{34}\text{S}(\text{SO}_4^{2-})_{\text{‰ aquifer}} = \text{Constant}, \quad \delta^{34}\text{S}(\text{HS}^-)_{\text{‰ aquifer}} = \text{Constant}$$

System S₂ comprises the casing (with a surface area of 1000 to 5000 m²), the scale attached to the casing and the near aquifer (the surface area of a 1 m³ core from the Dogger is approx a million m²). There are sulphate-reducing bacteria on or under the casing scale and in the near aquifer. These bacteria produce sulphides by reducing sulphates. The quantities of sulphide produced remain constant over a short period of time (the production flow is constant). The samples for analyses are taken at the surface (at the production wellhead) where the fluid composition results from the combined effects of both systems S₁ and S₂.

As the geothermal fluid flows through the contaminated zone in the near aquifer and then through the casing, it picks up sulphides produced at a constant flux by the bacteria (the production rate remains constant over a relatively short period of time). The concentration measured at the wellhead is therefore sensitive to changes in flowrate. It increases as the flowrate decreases. However, the sulphides the bacteria produce are depleted in ³⁴S and their $\delta^{34}\text{S}(\text{HS}^-)_{\text{‰}}$ is less than that of the fluid in the deep aquifer. Consequently, because these two types of sulphide - aquifer sulphides and bacterial sulphides - are mixed, the $\delta^{34}\text{S}(\text{HS}^-)_{\text{‰}}$ in sulphides measured at the wellhead, i.e. the $\delta^{34}\text{S}(\text{HS}^-)_{\text{‰T}}$, decreases as the flowrate decreases. If we assume that the sulphides at the surface originate from the two sources, i.e. from both systems S₁ and S₂, we can write:

$$\delta^{34}\text{S}(\text{HS}^-)_{\text{‰T}} = x \cdot \delta^{34}\text{S}(\text{HS}^-)_{\text{‰ aquifer}} + (1-x) \delta^{34}\text{S}(\text{HS}^-)_{\text{‰ bacteria}}$$

where x is a non-dimensional number which indicates the mixing proportion. In other words, the sulphide concentration measured at the wellhead decreases with flowrate while the $\delta^{34}\text{S}(\text{HS}^-)_{\text{‰}}$ increases.

The effect of flowrate on $\delta^{34}\text{S}(\text{SO}_4^{2-})_{\text{‰T}}$ is the reverse of that on $\delta^{34}\text{S}(\text{HS}^-)_{\text{‰T}}$ but is far weaker, due to the high initial sulphate concentration in the deep aquifer. We can then write

$$\delta^{34}\text{S}(\text{SO}_4^{2-})_{\text{‰T}} = x \cdot \delta^{34}\text{S}(\text{SO}_4^{2-})_{\text{‰ aquifer}} + (1-x) \delta^{34}\text{S}(\text{SO}_4^{2-})_{\text{‰ bacteria}}$$

but we also know $\delta^{34}\text{S}(\text{SO}_4^{2-})_{\text{‰T}} - \delta^{34}\text{S}(\text{SO}_4^{2-})_{\text{‰ aquifer}}$

Figures 20 and 21 illustrate these variations. Figure 23 shows that $\delta^{34}\text{S}(\text{HS}^-)_{\text{‰T}}$, $\delta^{34}\text{S}(\text{SO}_4^{2-})_{\text{‰T}}$ and the sulphate concentration vary significantly with the sulphide concentration.

In all three cases, the isotope results indicate that the quantity of dissolved sulphide which reaches the production wellhead largely results from current bacterial activity.

These isotope results will be more thoroughly analysed in an article to be published shortly (Ignatiadis I. et al., submitted to Journal of Isotope Geosciences, 1992).

We used a new, original isotope tool, based on measuring how the ratio between the sulphur ^{34}S and ^{32}S isotopes varies in sulphides and sulphates as the wellhead flowrate varies, to confirm the hypothesis that wells in which the sulphide concentration varies with flowrate were the seat of current bacterial activity.

This is the first time the sulphur isotopes in sulphides and sulphates have been used to demonstrate current bacterial activity in wells when the sulphide concentration varies with the flowrate. In certain cases, it was also used to estimate the quantities of sulphides which originate from current bacterial activity and the aquifer respectively. This new method could be used, in certain cases, to measure current bacterial activity to the same ends as conventional bacteriological analysis of the fluid.

	Flow rate (m ³ /h)	[sulphides] (mg/l)	[sulphates] (mg/l)	$\delta^{34}\text{S}(\text{sulphates})$ (‰)	$\delta^{34}\text{S}(\text{sulphides})$ (‰)
GMX-5 Meaux Beauval 1	40	26,59	1000	25,8	6,6
	84	14,28	1040	25,3	7,0
	120	11,05	1050	24,5	7,1
	150	6,39	1050	24,8	7,6
GMX-7 Meaux Beauval 2	40	26,15	1040	25,1	3,9
	66	16,83	1040	24,1	5,8
	100	12,72	1065	23,8	7,6
	150	7,21	1065	24,2	7,5
GFR-2 Fresnes	97	9,06	765	25,7	0,3
	129	6,46	780	26,1	1,0
	167	5,28	785	25,8	1,4
	196	4,46	780	27,0	2,4
	238	3,82	780	26,0	1,9

Table 4: Sulphide and sulphate concentrations and $\delta^{34}\text{S}(\text{HS}^-)\text{‰}_T$ and $\delta^{34}\text{S}(\text{SO}_4^{2-})\text{‰}_T$ in the geothermal water at 3 wellheads in the East and South of the Paris Basin, at the flowrates indicated.

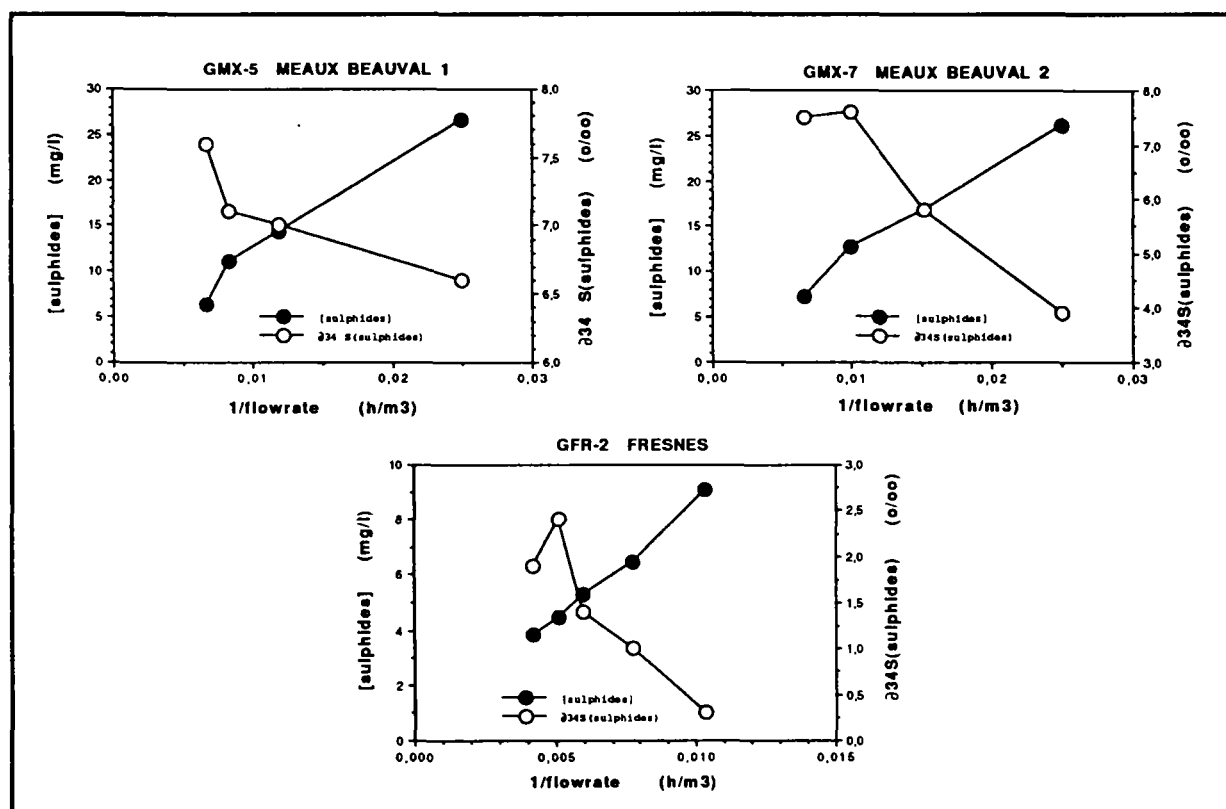


Figure 20: Dissolved sulphide and $\delta^{34}\text{S}(\text{HS}^-)\text{‰}_T$ in the geothermal water at 3 wellheads, in the East and South of the Paris Basin, plotted against the reciprocal of the flowrate.

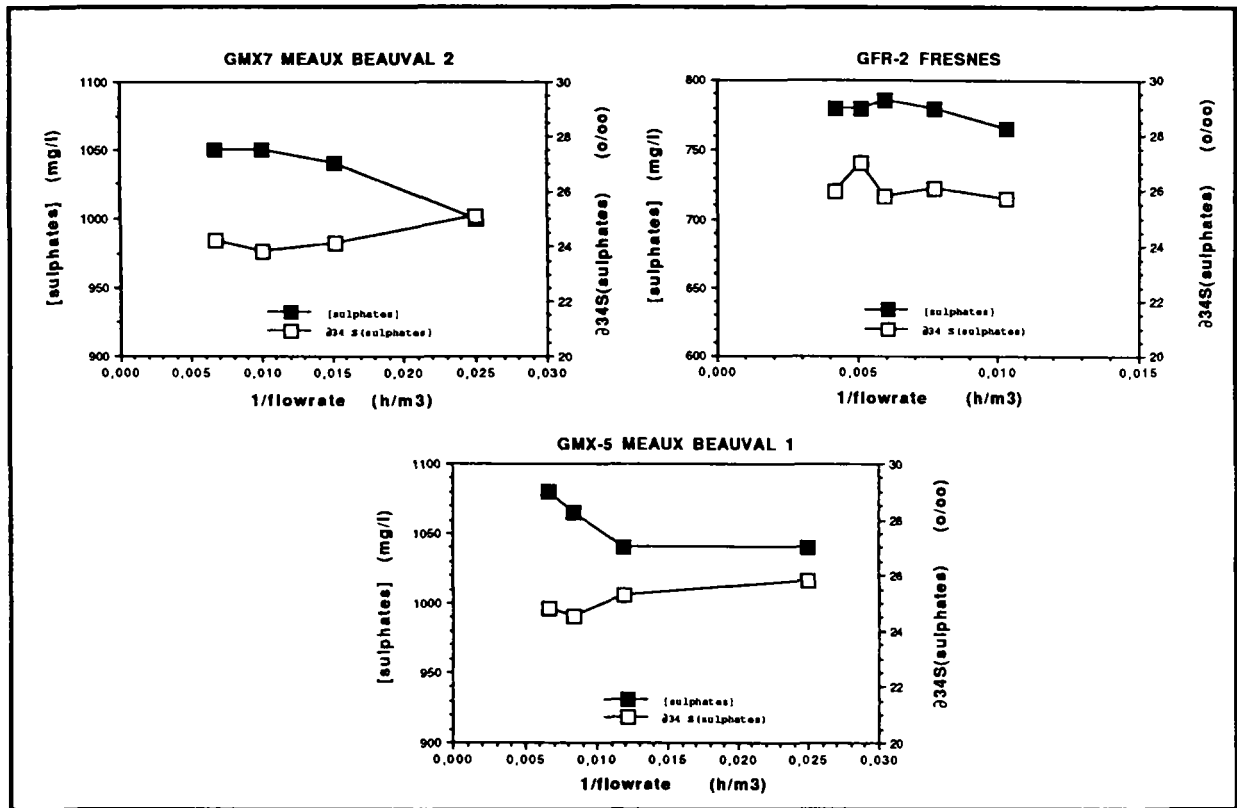


Figure 21: Dissolved sulphate and $\delta^{34}\text{S}(\text{SO}_4^{2-})\text{‰}_T$ concentrations in the geothermal water at 3 wellheads in the East and South of the Paris Basin, plotted against the reciprocal of the flowrate.

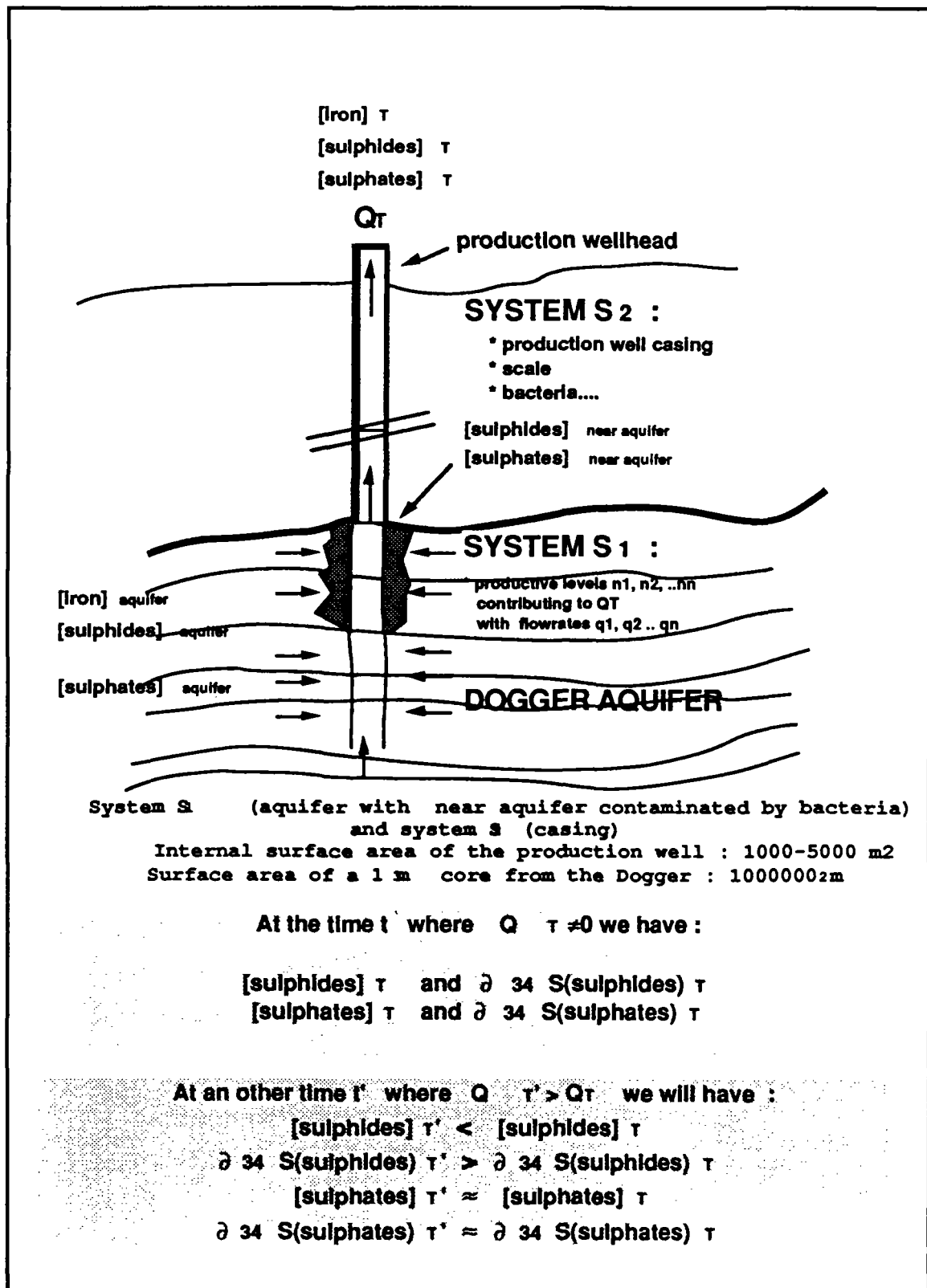


Figure 22: Description of systems S₁ (aquifer) and S₂ (production well and near aquifer).

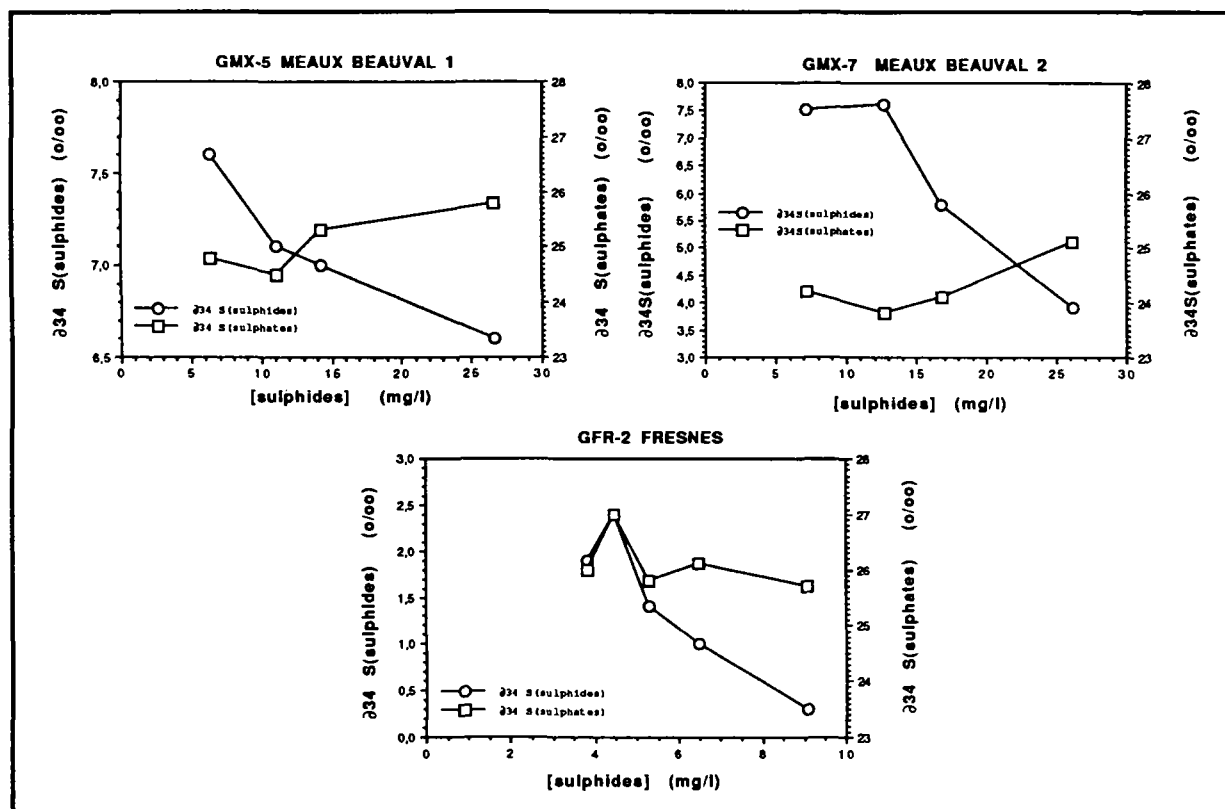


Figure 23: $\delta^{34}\text{S}(\text{HS}^-)\text{‰}_\text{T}$ and $\delta^{34}\text{S}(\text{SO}_4^{2-})\text{‰}_\text{T}$ at different flowrates in the geothermal water at 3 wellheads, in the East and South of the Paris Basin, plotted against the dissolved sulphide concentrations.

3. PROCESSES FOR A RELIABLE EXPLOITATION OF GEOTHERMAL DOUBLETS

The geothermal plants in the Paris region are subject to corrosion problems because of the aggressive nature of the geothermal fluids, which are particularly rich in Cl, CO₂ and H₂S. The corrosion is due to complex interactions that finally result in depolarization of the electrochemical system involved (metal/fluid). The corrosion problem is conditioned by the particularly aggressive chemical nature of the geothermal fluids in the Dogger aquifer. On the one hand they are rich in chloride ions, which reduce the protective power of the surface layers and lead to localized attacks (pitting). On the other hand, they contain dissolved species of CO₂ and H₂S which attack the metal and form corrosion products.

The dissolved sulphides and iron are the two entities at the root of well scaling phenomena. The search for solutions to the problems of well operation must therefore focus on mechanisms involving these species.

It is impracticable to use an acid to act on the pH of the fluid: if the pH is low enough, the product of ionic activity will be greatly reduced and will be less than the product of FeS solubility, so preventing precipitation. One could therefore consider either acting on the sulphides (by oxidizing them to produce sulphur) or acting on the iron with a corrosion inhibitor (stopping the transfer of Fe²⁺ ions in the fluid) and using a crystal growth inhibitor.

3.1. ORGANIC INHIBITORS USE OPTIMIZATION IN GEOTHERMAL SYSTEMS

Most geothermal wells are currently treated by injecting a corrosion inhibitor at the bottom of the production well. The corrosion inhibitors used were initially developed for use in oil wells. They are cationic surfactants of the quaternary ammonium salts type. They persist for a few hours, forming a protective film at the interface between the fluid and the casing wall.

Generally speaking, they work by forming a film on the surface of the metal, preventing metal and water from coming into contact and so blocking the corrosion process and reducing the production of ferrous iron in solution. They are generally adsorbed onto the surface of the metal, but the fluid flow tends to desorb them.

They must:

- . be compatible with the fluid to be treated (pH, presence of H₂S, CO₂, etc),
- . be sufficiently apt to form a film,
- . not clog the reservoir on reinjection,
- . be fairly persistent, so as to provide protection for as long as possible,
- . be compatible with the various materials used,
- . be reasonably priced.

The reports (Ignatiadis I. et al., 1991a, 1991e; Ignatiadis I. et Police O., 1991; Amalhay M. et Ignatiadis I., 1992) provide a non-exhaustive bibliography on corrosion inhibitors, their classification and how they work, bactericidal and bacteriostatic products, scaling inhibitors, and currently-used methods of treatment with these additives.

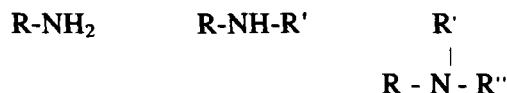
Nonetheless, injection of these products does involve some technical problems.

3.1.1. Organic inhibitors description and use

The nature of the products used

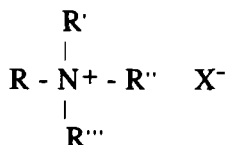
These are organic products, mainly nitrogen derivatives: fatty amines, polyamines, quaternary ammoniums etc. They are called cationic inhibitors, even though some are molecular and not ionic (see paragraph on "Mode of action"). These surface active agents ionize in an aqueous solution. The commercial inhibitors (Solamine 129® of SEPPIC Company, Aquaprox MDC 1300 of Protex Company) partly consist of a mixture of the following compounds:

- Primary, secondary and tertiary amines:



where R, R' and R'' are alkyl radicals

- Quaternary ammonium salts:



where R, R', R'' and R''' are alkyl radicals, possibly linked to benzyl groups, and X⁻ is a small anion: Cl⁻, Br⁻

- A solvent, generally alcohol-based

Mode of action

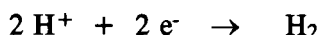
These corrosion inhibitors settle on the surface of the metal in a layer one molecule thick, blocking the corrosion process (Amalhay M. et Ignatiadis I., 1992). They are adsorbed onto the surface of the metal (or the surface of a deposit of corrosion products on the metal), either directly or after reacting with the aggressive medium.

There is a double action:

- . Chemical blocking of at least one of the reactions involved in the corrosion process,

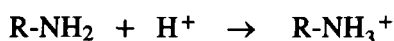
. Physical isolation of the metal.

If no inhibitor is present, the metal corrodes, reducing the H^+ ions present in the water through the following reaction:



The metal becomes coated with chemisorbed HS^- ions which give the surface a negative charge. The presence of these ions speeds up and accentuates the adsorption and reduction of H^+ ions and hence the rate of corrosion.

The cationic inhibitor, which is generally a mixture of compounds with complex structures, can be very roughly represented by a primary amine of the formula $R-NH_2$ (R represents a carbon chain long enough to be hydrophobic). In the presence of an aqueous phase, it is ionized according to the equilibrium reaction:



The proportion of amines ionized is a function of their acidity constant and the pH of the water, but it is usually high. Part of the inhibitor introduced therefore passes into the aqueous phase in cationic form, whatever the method used to introduce it.

The $R-NH_3^+$ ions are adsorbed onto the surface of the metal in the same way as the H^+ ions, and their adsorption is generally enhanced by the presence of chemisorbed HS^- ions. Unlike the H^+ ions, however, the $R-NH_3^+$ ions do not react, so they block the sites where they are adsorbed. A high proportion of the reactional sites (over 99% in some cases) are blocked in this way.

The R type hydrocarbon chains of the inhibitor molecules give the surface of the metal a hydrophobic tendency, helping to isolate it from the corrosive medium and further strengthening the inhibition effect.

Properties of the quaternary ammoniums used in the formulation

These are powerful surface active agents. The salts of alkyldimethyl benzyl ammonium in particular have a very high adhesion tension with respect to most solid surfaces. They are called inverted soaps, the usual soaps (detergents, shampoos, lyes etc.) being generally anionic. They lower the surface tension of their aqueous solutions, giving them wetting, foaming and detergent properties.

Because of their chemical structure, they react with certain heavy anions to form insoluble compounds. This is the case with soaps, anionic surfactants, anionic coloring agents, etc.

They have a strong germicidal potential, so reducing corrosion of bacterial origin, especially where it involves bacteria connected with the sulphur cycle. The bactericidal action of quaternary ammonium salts, for example, has been attributed to a blockage of cell enzymes owing to their powerful adsorption ability and their bulkiness.

They are soluble in alcohol and acetone.

The IMRG is currently studying the dispersing properties of these surfactants with regard to corrosion deposits (I. Ignatiadis et al., 1991b).

3.1.2. Practical use of inhibitors

3.1.2.1. Choice of the inhibitors

As the inhibitor, mixed with the geothermal fluid, must circulate in the casing (production well, surface installation, injection well) and also, in some cases, in the injection tube, one must take into account of the various characteristics of these mixtures (concentrations, temperature, pressure) when choosing an inhibitor :

There are certain risks involved:

- . Coagulation of one of the inhibitor ingredients could lead to clogging of the treatment tube or even the reservoir;
- . The active principles of the inhibitor may lose their efficacy under certain medium conditions (temperature, pressure, pH etc.);
- . Pollution may be significant in the event of a leak.

At this level, therefore, the composition of the inhibitor and its physico-chemical properties (pH, density, viscosity etc.) have to be known under different temperature and pressure conditions, etc.

We must find a reliable way of measuring concentrations of the inhibitor in a geothermal fluid of the Dogger type.

The following steps should therefore be taken:

a) Measuring inhibition efficacy (filming)

This type of test can be carried out with a diversion from a production pipe, measuring the protection provided at different dosages (using a corrosion probe or an electrochemical measurement system). The geothermal fluid should also be analysed before and after the inhibitor is introduced. A probe will measure the pH of the fluid before and after introduction of the inhibitor.

The curves for corrosion rate = $f(\text{time})$ and $\text{pH} = f(\text{time})$ are drawn up for each dosage of inhibitor (eg. 0.5 mg/l, 1 mg/l, 1.5 mg/l etc.), during injection of the product and after injection has been stopped, in order to assess the persistence of the film-forming effect.

Fluid is sampled to measure the bactericidal capacity of the product (pure geothermal fluid, fluid with different concentrations of inhibitor).

b) Use of geochemical computer codes TPDEGAZ, SOLMINEQ, EQ3/6

The inhibitor can be regarded as a foreign body which changes the equilibrium characteristics of the geothermal fluid. The question of the likelihood of precipitation of certain chemicals can be tackled by simulation software such as EQ3-6 or SOLMINEQ. For these simulations, the characteristics of the geothermal fluid and the inhibitor need to be known.

c) Inhibition tests on a surface covered in iron sulphide scale and inhibitor action on such scale

The apparatus used for the test described above can also be used for this test, replacing the "new" corrosion probe with one whose measuring element has previously been in contact with untreated geothermal fluid and on which a deposit of iron sulphide has formed. The rate of corrosion is measured with several different dosages of inhibitor. Metal samples bearing previously deposited iron sulphide scale are put in contact with the mixture to be tested; they will be used for a cell count of sulphate-reducing bacteria.

It is also possible to carry out laboratory tests of the inhibitor's aptitude to help dissolve and/or destroy the coherence of iron sulphide scale, at two or three different dosages in a reconstituted geothermal fluid. Metal samples covered with iron sulphide scale are set in a cell in which a mixture of geothermal fluid and inhibitor is circulated. The weight loss is measured after 1 day, 3 days, one week and one month. The same experiment is run, under the same conditions, with a fluid containing no inhibitor, in order to measure the effect due to treatment with the inhibitor.

d) Measuring the bactericidal effect of the inhibitor

Three types of test can be run in parallel:

In a microbiology laboratory, mixtures of reconstituted geothermal water (salinity, temperature etc.) and inhibitor at different dosages (0 to x ppm) are put into contact with SRB's. Bacteria counts are made after one hour, one day and one week.

To complete the above trials, a bacteria count must be carried out on the metal samples that have been in contact with the treated fluid in the diversion.

The inhibitor trials described in a) above, carried out in a diversion from a geothermal loop, will provide samples of treated geothermal water on which bacteria levels can be measured.

e) Inhibitor action on non-metallic materials

In the laboratory, the material to be tested is put in contact with the mixture of inhibitor + reconstituted geothermal water. Depending on the characteristics required of the material, the corresponding analyses (surface state, solidity, hardness, composition etc.) are carried out after one week, two weeks, one month, two months, six months and one year in contact.

We suggest testing the following materials with the corresponding analyses:

- . exchanger seal: surface state, crushing resistance;
- . Hagusta lining: surface state, porosity, shock resistance;
- . composite materials: surface state, porosity, solidity;
- . plastic sleeves of electrical cables: porosity, surface state, crush resistance.

f) Effects of the inhibitors on the reservoir

The IMRG carried out the first tests of percolation of inhibitor-treated fluid in 1990, using representative cores of the Dogger aquifer (cf. para. 3.1.2.4). These tests showed a significant reduction in the permeability of the medium. It is therefore important to be able to classify the different inhibitors liable to be used in terms of their propensity to clog the medium. Previous trials (of inhibition efficiency) will have defined the dosage or dosages at which to run clogging trials on a percolation pilot.

Permeability should be measured at temperatures close to those of the fluid when it is reinjected.

g) Long term degradability

The supplier of the product must indicate the degradation products obtained and the rate of degradation under the conditions of the geothermal system in question.

h) Full scale tests

Once the best products have been identified, it is necessary to run full-scale tests on the doublet for a minimum period of three months with the help of a specific instrument array:

- . electrochemical measurement equipment,
- . a flowmeter on the treatment tube (monitoring the amount of inhibitor),
- . geoprobes with corrosion samples mounted on them,
- . geoprobes for testing non-metallic materials.

The measurements to be made concern:

- . rate of corrosion (on new metal sample and scale-covered metal sample),
- . analyses of geothermal fluid (inhibitor, iron, sulphides, bacteria etc.),
- . bacteria count on corrosion samples,
- . testing of non-metallic materials.

3.1.2.2. Injection processes

Two types of tubes for the injection of additives were installed: CFG Forplex resin/glass fibre tubing (internal diameter = 25 mm), and GPC Scoflex polymer/steel tubing (int. diam. = 8 mm).

The CFG Forplex tubing (TTFP®), composed of glass fibre/epoxy resin sections 3 m long, with conical-threaded ends, was installed in 15 production wells. Tubing of this type at La Courneuve-Nord, Blanc-Mesnil (after two years of operation) and Clichy-sous-Bois (after three years of operation) has been raised and lowered some 200 m, during maintenance of the immersed pumps with no problems.

The GPC Scoflex tubing (TAI®) consists of a continued tubular stainless steel core encased in protective and reinforcing polypropylene in which four stranded cables are embedded. It is installed in the well by unrolling from a drum operated by a coil-tubing unit similar to that used for well-cleaning operations by Otis. About 10 production wells have been equipped with this tubing.

At first, corrosion inhibitors were injected into geothermal systems at the production pump level. The drawback with this technique was that it only protected the reinjection well and the surface loop, the production well remaining unprotected.

The present tendency is to inject inhibitors by means of a well bottom additive injection tube (WBAIT), thus protecting the whole installation.

These corrosion inhibitors were initially developed for use in oil wells, where the following application methods are used:

Continuous treatment:

By way of pre-treatment, a large quantity of the product is injected to form an initial film. This film is then maintained by continuous injection of a small amount of the inhibitor (a few ppm to a few dozen ppm).

Semi-continuous treatment:

With this method, after the pre-treatment phase, periods of injection (eg. 10 minutes at 10 ppm) are alternated with periods of non-injection (30 minutes), taking full advantage of the persistence of the product. This saves on the amount of inhibitor used without significantly increasing the rate of corrosion compared to continuous treatment.

Flood treatment:

The dose injected to control electrochemical corrosion is often not high enough to kill the bacteria present. For this reason, and also to replace the surface film, a large quantity of the product is periodically injected.

The most common technique is semi-continuous treatment using a well bottom additive injection tube (WBAIT).

3.1.2.3. Measuring concentrations of organic surfactants

A way of measuring the concentration of corrosion inhibitor in the geothermal fluid is needed, as this could help to optimize this treatment method. This raises some analytical problems, however.

Research has been done on the question, and in 1991 a BRGM report was published (Ignatiadis I. and Police O., 1991).

We wished to find a way of measuring the organic corrosion inhibitors currently in use in geothermal systems. The inhibitor we chose for the tests was SEPPIC's Solamine 129®. We had to define an analytical method that would be applicable on site and reliable for concentrations varying between 0.1 and 100 mg/l of inhibitor.

We therefore described, experimented, tested and compared several methods for measuring concentrations of amines and cationic and non-ionic surfactants: four colorimetric methods, one volumetric method and high-performance liquid chromatography (HPLC). These methods of measuring inhibitor concentration (amines and ammoniums) were tested (a) on synthetic solutions of fresh and salt water in the laboratory and (b) on geothermal fluids taken from sites in the Paris region.

By evaluating and comparing these methods, we were able to choose the most reliable ones and those that could most readily be used under site conditions with inhibitor concentrations ranging between 0.1 and 100 mg per litre of water.

We found that some methods could only detect concentrations higher than those found in geothermal mediums (the volumetric method and HPLC). These are not applicable without previously concentrating the compounds to be measured, a technique which is too complex to be used in field conditions. HPLC also requires an unreasonably long time for analysis.

Some other methods are not applicable when the product to be measured is in a matrix consisting of water from the Paris Basin Dogger aquifer, either because of the sodium chloride in this medium, which interferes with the process (colorimetric method N° 3), or because of the calcium carbonate (colorimetric method N° 2).

Two of the methods tested meet the initial specifications (colorimetric methods N°s 1 and 4). Both are based on the same measuring principle: spectrophotometry in the visible wavelengths (colorimetry) of a coloured IB complex formed according to the reaction $I^+ + B^- \rightleftharpoons IB$ (liquid-liquid extraction of a pair of I^+B^- ions, where I^+ is the cation of the inhibitor to be measured in the sample solution and B^- is an anionic coloured indicator). The first method is more sensitive, and is the one we preferred. Its main drawback is that it involves manually agitating a separating funnel for six minutes, which is a tedious and burdensome task when one has a large number of samples to analyse. Use of a magnetic agitator for this purpose did not affect the quality of the measurement.

With these methods, cationic surfactant concentrations can be measured in one extraction step, from any aqueous fluid, at concentrations between 0.15 and 15 mg/l without dilution (more if diluted).

Use of these methods on treated sites has already provided us with some very interesting data on the degradation of the organic corrosion inhibitors and on variations in concentrations of this product at the wellhead, in two installations treated semi-continuously (at well bottom and at production pump). Based on all of these experiments, we can now propose a sampling protocol for measuring inhibitor concentrations in geothermal water. Other applications of these methods may be found in the future. The analytical support they provide will help in further work aimed at optimizing treatment with organic corrosion inhibitors.

3.1.2.4. Long term effects of reinjection of inhibitor on the reservoir

The geothermal fluid into which a certain amount of organic inhibitor has been injected at the well bottom, at pump unit level or at ground level, is reinjected into the aquifer after giving up a part of its heat energy through the exchangers at ground level.

The temperature on reinjection can be as low as 35°C, or even 25-30°C where the geothermal station at the surface is equipped with heat pumps with evaporators that absorb the calorific energy of the geothermal water at lower temperatures before it is reinjected.

Broadly speaking, the reinjection temperature depends on the method used for heating the buildings (radiators or low-temperature under-floor heating) and the type of heat distribution system.

Despite the small dosages used in inhibitor treatments, it is important to find out what impact the reinjection of treated water may have on the characteristics of the reservoir: is there a risk of reservoir clogging in the long term, leading to an increase in injection pressures and consequently higher electricity costs for the reinjection pump? What changes are there, if any, in the permeability of the reservoir near the injection well?

In order to simulate the long-term effects of the injection of organic corrosion inhibitors, two series of experiments were carried out with the IMRG percolator. This percolator was connected to the production wells at Fontainebleau which was not treated by inhibitor, and then at Cachan, where inhibitor was injected, twice a day, at the pump level.

The cores used were from the Dogger in the Melun l'Almont geothermal well, drilled in 1989.

Behaviour of samples in contact with an untreated fluid

In order to determine the effect of the inhibitor, the first trials were carried out on the Fontainebleau doublet where the geothermal water received no treatment.

Five core samples were used (diameter 40 mm, lengths 36.5 to 45 mm).

Upstream pressure was 135-165 bars; the geothermal water flowrate was regulated in steps between 6 and 50 kg/h; the geothermal water was filtered at 25 microns at the percolator inlet and 10 microns at the outlet.

The results are presented in table 5.

During the last three trials, carried out with cores 9-0, 10-1 and 10-2, the fluid was sampled at the percolator outlet, in order to determine out the fluid's capacity to dissolve the calcite that holds the core together. The Ca was analysed and these results correlated with the measured weight loss of the core.

Dissolution of calcite was observed resulting from the undersaturation of the fluid (reservoir temperature 74.2°C) in this mineral: at 50°C, 2.8 mg of calcite were dissolved per litre of water, while at 25°C, dissolution reached 15 mg/l.

The result was improved permeability of the samples at both test temperatures.

The consequence regarding reinjection and the cooled zone is the creation of "holes" which significantly improve the permeability of the medium and the skin index on reinjection.

N° sample	duration of the trial	Coring type	Flow rate (kg/h)	Temperature (°C)	Permeability (milli-Darcy)	Ca dissolved (mg/l)	Observations
9-2	30 mn	longitudinal	6	27,6	180		
	"		13,2	28,2	159		
	"		25,2	40,1	150		
	"		50,1	45,2	121		
	"		25	46,6	182		
	"		13,6	44,1	203		
9-1	25 mn	transversal	26	36,4	711		
	25 mn		52,7	42,9	535		
	25 mn		25,5	49,6	701		
	13 days		13	20	infinite		core disintegrate
9-0	30 mn	transversal	11,1	24,6	366		
	30 mn		26,3	25,9	348		
	30 mn		53,8	27	294		
	30 mn		26,5	32,2	396		
	30 mn		11,4	32,9	504		
	24 hours		12	20 to 25	> 2020		
	8 days		12	20 to 25	infinite	+5 to +7	core disintegrated
10-1	45 mn	transversal	1,5	24	152		
	68 mn		6,3	25,7	144		
	18 mn		12,3	28,6	146		
	36 mn		6,8	26,9	160	+12	dissolving calcite
	5 days		6	25	infinite	+10 then +3 at the end	core disintegrated
10-2	143 hours	vertical	9,9 to 10	50 à 55	287 to 340	+0 à +3	
	24 hours		10,2	31,2	569	+6	
	24 hours		10	22,5	1997	+5	
	48 hours		10,1	21,3	4800		dissolving calcite
	48 hours		10,1	21,4	10000	+3	

Table 5: Résultats of the percolation trials in Fontainebleau (1990).

Behaviour of samples in the presence of a fluid treated with an inhibitor

The second trials, at Cachan, were carried out with inhibitor-treated water.

The treatment usually consists of two injections (pure Norust 486 inhibitor from CECA), each of five litres in the space of half an hour, at the level of the immersed pump, one at around 9 am and the other around 5 pm.

Four cores were used for these long-duration trials (35 days).

The results are given in Table 6.

Appreciable losses of permeability were recorded at 45°, the temperature normally observed on reinjection into the Dogger. This effect was most marked for the least permeable samples. At high circulation rates a decrease in permeability was recorded despite large material losses; weight measurement showed a loss of 8 mg per litre of water percolated through the samples. Analyses of the fluids showed a corresponding increase in their calcium content. All samples tested at 45°C suffered a decrease in permeability from the first hours of the experiments. This was not observed at 25°C.

Some reservations must be expressed, however, as to extrapolation of these results to real situations. The geothermal water used by the percolator came from the production well, whereas the treatment was carried out at pump level, 120 metres down. Given the type of injection, it is to be feared that at the time of the percolation trials, the inhibitor was not evenly distributed over time (about 55 mg/l during the injection itself, almost 0 a few minutes later).

By contrast, at the injection well bottom, when the fluid has been in contact with 2000 metres of casing which the inhibitor is supposed to protect by forming a film, it is likely that the inhibitor content of the fluid is lower but more uniform.

Clogging, if it occurs, will therefore not be as clearcut as the clogging observed with the percolation experiments.

Conclusion

The behaviour of the Dogger reservoir near the injection well when cooled fluid treated with corrosion inhibitor is reinjected, is the combined result of two antagonistic phenomena: improved permeability due to dissolution of the calcite, and clogging by the amines in the inhibitor.

The experiments show (a) the value of ensuring a more uniform flow when injecting the inhibitor into the geothermal water, to reduce the risk of clogging of the near reservoir on reinjection, and (b) the importance of carrying out percolation trials prior to introducing a new inhibitor in a geothermal system.

N° sample	duration of the trial	Coring type	Flow rate (kg/h)	Temperature (°C)	Permeability (milli-Darcy)	Ca dissolved (mg/l)	Observations
15	10 mn	transversal	2,6	30	190		
	16 mn		5	30	170		
	15 mn		9,5	30	150		
	40 mn		5	30	170	+6	
	5 days		5	25 to 30	400	+1	weight loss = 4%
10	14 mn	transversal	5	28	50		
	12 mn		10	28	55		
	12 mn		5	30 to 36	60		
	2 days		5	46	22		weight loss = 0,2 %
20	11 mn	transversal	6	29	1300		
	5 mn		12	32	750		
	2 hours		5,75	40	700		
	4 h 40 mn		5,75	45	500		
	14h 10 mn		5,75	44	580		
	24h 30 mn		5,75	43 to 47	500		
	10 mn		5,75	22	700		percolator stopped
	6 h 20 mn		5,75	45	400		
	12 days		5,75	45	300 to 400		increased weight = +1,8 g
19	15 mn	transversal	2,5	41	120		
	15 mn		5	42	270		
	10 mn		10,5	42	330		
	10 mn		5	42	260		
	10 mn		2,5	42	170		
	10 mn		20	42	350	+3	
	16 hours		20	45	670		
	28 hours		20	45	810	+6	
	24 hours		20	47	670		
	3 days		20	45	240	+2	
	21 hours		20	45	240		weight loss = 19 % or 8 mg/l of percolated water

Table 6 : Résultats of percolation trials in Cachan (1990).

3.1.2.5. Assessing the action of an inhibitor on scale

Because it was not treated against corrosion from the beginning, the casing of the geothermal systems has been corroded and there is scale on the inner walls.

Cleaning operations cannot completely eliminate these deposits on all parts of the casing inner walls. At present it is generally recognized that scaling by iron sulphide on carbon steel does not provide complete protection from corrosion, as the scale may be more or less porous. It is certain that corrosion is slower where there are scale deposits, but it is not stopped completely.

In view of this, the essential questions are:

- . Do the inhibitors have a particular effect on the scale? Can they, for example, restore the scale to the state of matter in solution or suspension?
- . How effective are organic corrosion inhibitors on a casing where there is scaling? In particular, does the inhibitor provide real protection against corrosion that may be continuing underneath the scale?

To answer these questions, it was necessary to define a procedure to evaluate the action of a product on the scale and so make an experimental demonstration in two complementary stages:

- . In the laboratory, study the behaviour of the scale in powder form, exposing it, in a controlled atmosphere, to a partly reconstituted geothermal fluid, with or without inhibitor;
- . On site, study the behaviour of a corrosion probe by exposing it to a corrosive fluid with and without inhibitor.

The results of this study have been presented in a report (Ignatiadis I. et al., 1991e).

Having chosen the materials and methods (in particular the scale, the inhibitor, the measuring instruments and the analysis methods), experiments were carried out in the laboratory and on site. The results of these experiments enabled us to partly answer the questions raised above.

It was found that the organic corrosion inhibitor used in the laboratory experiments does not seem to be capable of degrading the scale. It has no chemical action on the scale, therefore. However, these laboratory studies were not entirely representative of real conditions. In the geothermal wells where, because of their particular operating conditions, hydrodynamic conditions are particularly severe (the rate of circulation of the fluid in particular, at up to 3 m/s), there might be a considerable physical impact on the scale. One can imagine large cationic molecules of the inhibitor first of all attaching themselves to the scale by adsorption, and then being detached, taking with them small particles of the scale. The inhibitor cation-scale particle pair would then rise up the well to the surface, to be reinjected via the injection well.

The on-site experiments carried out with a corrosion probe (a simplified electrochemical probe, Corroprobe, made by CEA-CFG) show that the inhibitor may act physically on the scale. First of all, it was observed that, from the first instants of the experiment and even if the fluid is not treated, the rate of corrosion measured by the probe slows down in proportion to the time of exposure to the fluid (cf. Figure 24). Taking all cases together (bare metal or after previous scaling due to exposure to fluid), one can see that, the longer the previous time of exposure to untreated fluid, the less sharply the rate of corrosion is slowed when the inhibitor is injected (cf. Figure 24). But where iron sulphides have had time to form scale deposits, the rate of corrosion falls far less quickly when the inhibitor is added. The fact that the rate of corrosion does slow down when inhibitor is injected, in spite of scale deposits, might be proof that the inhibitor has a physical action: it may either form a film over the scale, or reach the metal, giving it some protection and slowing down corrosion. At this stage, the experiments carried out do not provide a basis for concluding one way or the other.

This work has shown that the inhibitor can pass through a young, very thin deposit (30 to 150 nm). Indeed, thickness seems to play a very important part in the action of the inhibitor. Scale texture may also be important: the scale may present more or less of an obstacle to effective action by the inhibitor, depending on its texture. No direct extrapolation can be made from these results to the real situation of the steel casing of the geothermal wells, where the deposits are probably several millimetres thick and, having aged, have stabilized thermodynamically (mackinawite → pyrite → pyrrhotite) and mechanically (structure, texture and porosity).

Further studies must be undertaken. Now that all the wells exploiting the Paris Basin Dogger aquifer are being, or are going to be, treated by injecting inhibitor at the production well bottoms, it is very important to know the role played by the scale, with and without treatment, and to evaluate the efficacy of the inhibitors with regard to continuing corrosion underneath the scale.

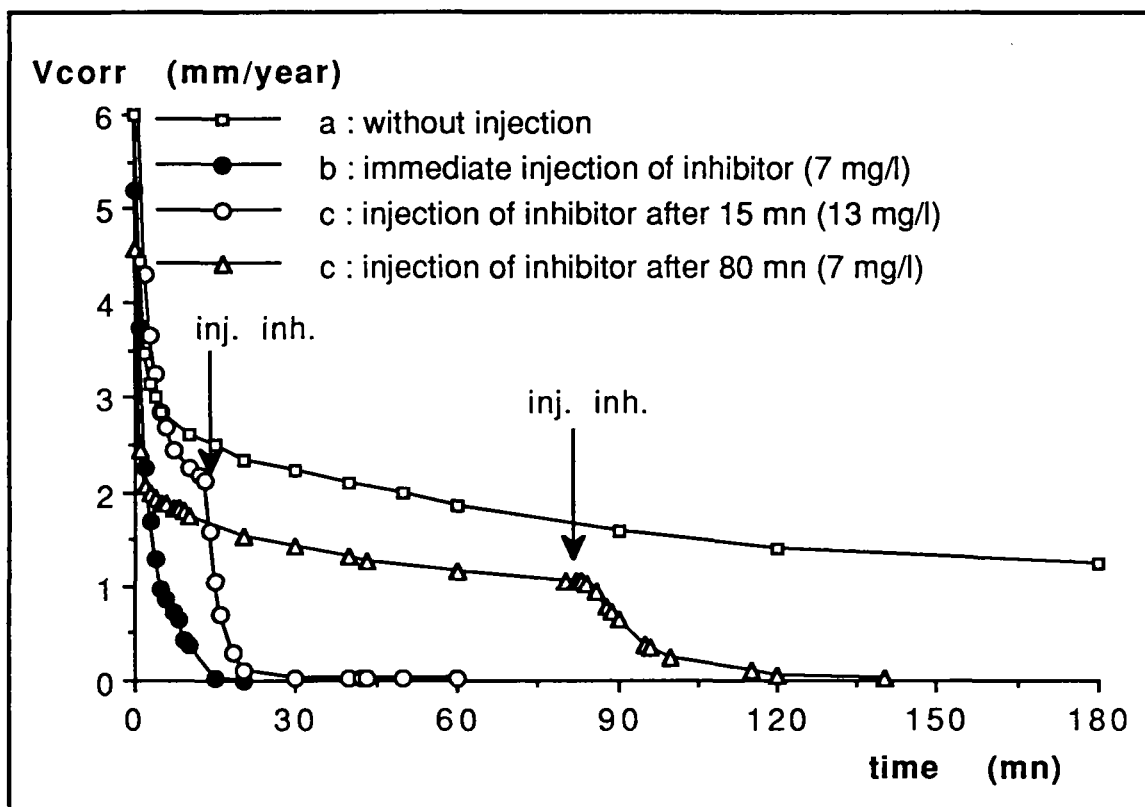


Figure 24 - Rate of corrosion - Vcor - (recorded with a corrosion probe using the polarization resistance method) as a function of length of time exposed to the geothermal fluid in Fresnes:

a - untreated (no inhibitor injected)

b - treated (inhibitor concentration 7 mg/l)

c - treated (concentration 7 or 13 mg/l) after 15 or 80 minutes prior exposure to untreated fluid.

3.2. New processes for the geothermal doublets protection

3.2.1. Chemical cleaning of geothermal wells

Because there has been no protective treatment against corrosion since the initiation of exploitation of the wells, the casings have been corroded, and scale remains on the internal surfaces.

In the framework of maintenance of the geothermal installations, the internal walls of the casings are cleaned of scale once every few years. The purpose of this is to expose the clean metal, before continuing normal operation, with or without treatment of the geothermal fluid by introducing a commercial cationic surfactant at the bottom of the production well in order to avoid renewed harmful scaling. The surface active agents used are composed mainly of nitrogen derivatives of quaternary ammonium salt type, and are supposed to have anti-corrosive, anti-scaling and bactericidal effects.

The first rehabilitation operations, carried out in 1986, were done with mechanical cleaning methods using drilling equipment. The 1990 and 1991 operations used the same techniques and sometimes mixed techniques such as hydraulic/mechanical techniques, using a reverse-circulation device attached to standard drill rods, or hydraulic techniques, using a jetting tool attached either to standard drill rods or to a continuous flexible tube. Total elimination of scale from the entire internal surface of the casing cannot, however, be guaranteed.

It is now generally accepted that sulphide scale coating carbon steel does not completely protect it from corrosion, as the scale may be porous to varying degrees. Corrosion is undoubtedly decreased when scale is present, but it is not halted. In addition, corrosion can take place beneath scale, in particular when bacteria develop on and beneath the scale, producing hydrogen sulphide by reduction of the sulphates contained in the geothermal water. It is also certain that corrosion inhibitors in sufficient quantity produce an effective film on clean, non-scaled metal, and may do the same on new, thin scale (Ignatiadis et al., 1991a), but the efficacy of organic corrosion inhibitors on casing where scale persists, and in particular whether or not they can protect against corrosion beneath old, thick scale, is unknown.

The essential aim of the IMRG in this sphere was to develop reliable procedures for rehabilitation and treatment and, more particularly, to study a new procedure: chemical cleaning.

3.2.1.1. Introduction

The persistence of scale in rehabilitated geothermal wells is a nuisance and has conditioned this study. As it is not known what takes place beneath scale, it is preferable to eliminate it by chemical treatment, either directly or as a complement to mechanical, hydraulic, or mixed mechanical/hydraulic cleaning.

The main objective of this study was to develop a process for the chemical cleaning of the walls of geothermal doublets. This involved attempting to dissolve the scale, composed mainly of iron sulphides, on the casing by chemical treatment. The advantage of such a process lies in the fact that it could be used directly, on a slightly fouled well, or additionally to mechanical treatment to improve the efficacy of the cleaning. The basic question to be answered at present is: can scale, remaining after mechanical, hydraulic or even mixed cleaning, be removed directly in a well by a chemical cleaning that puts the scale into solution or suspension, without producing problematic side-effects?

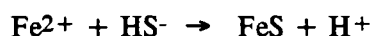
In order to answer this question, an experimental demonstration needs to be made in two stages, in the laboratory, and on a pilot and on site. The laboratory study would deal with the behaviour of scale exposed, under a controlled atmosphere, to a partly reconstituted geothermal solution, in the presence or not of certain chemicals. On the pilot and on site, the behaviour of the scale would be studied under exposure to different chemicals in an actual geothermal environment.

The present study dealt only with the first stage, the principal aim of which was to find a scientifically possible solution. The study has been fully reported in a BRGM report (Ignatiadis et al. ,1991a) and in a publication (Ignatiadis I. and Teton S., 1992). After selection and testing of various chemicals for their reactivity to scale, those which, alone or in combination, are able to give an acceptable kinetic of attack on the scale, are completely non-aggressive towards clean metal, and produce no or very little aggressive or toxic products of reaction will be proposed for the second stage. This can begin only when the results of the first stage are known, and will enable the proposal of a process for the breakdown and dissolution of scale on well walls.

3.2.1.2. Preliminary studies

A bibliographic search was made on the nature and structure of the scale encountered in the geothermal wells exploiting the Dogger of the Paris Basin (Ignatiadis et al. 1991b). The results are summarised below.

The formation of scale can be represented by:



The Ionic Activity Product (IAP) of the reaction can be written:

$$I.A.P. = \frac{(\text{HS}^-) \cdot (\text{Fe}^{2+})}{(\text{H}^+)}$$

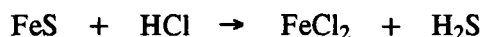
where (Fe^{2+}) is the activity of ferrous iron in the solution, (HS^-) is the activity of dissolved sulphide HS^- in the solution, (H^+) is the activity of H^+ ions, which represents the pH of the solution $(-\log (\text{H}^+))$

Iron sulphide can be precipitated if the IAP of the reaction becomes greater than the solubility product $K_s(P,T)$ of the mineral FeS. K_s is a thermodynamic value that is dependent only upon temperature and pressure.

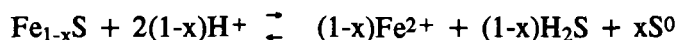
It is obvious that by "treatment of iron sulphide scaling" is meant the various types of attack such as breakdown, dissolution or oxidation of the scale. Bibliography in this field is scarce. A non-exhaustive bibliographic review resulted in the selection of certain attack processes for testing on scale (Ignatiadis et al., 1991a), they are: redissolution of iron sulphides by the action of a strong acid and the oxidation of sulphides by a strong oxidant.

Redissolution of iron sulphides by a strong acid

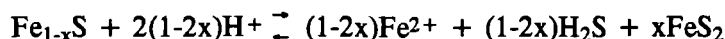
The addition of acid enables reduction of the IAP, thus favouring the dissolution of iron sulphides. The best known reaction for the laboratory preparation of hydrogen sulphide is cold HCl attack on iron sulphide in a Deville's or Kipp's type apparatus, according to the reaction:



The process for a sulphide of the type Fe_{1-x}S can be described by the following reactions:



and



Experiments by Luganov and Shabalin (1985) gave results that could only be explained by the first equation. Their results also enabled a more precise identification of the mechanism, showing that the attack in fact takes place in two stages. Initial formation of an iron sulphide deficient in iron is in the next stage accompanied by the formation of elementary sulfur according to the reactions:

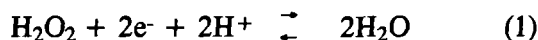


where y is greater than x , and of the order of 0.13 to 0.145.

Oxidation of iron sulphides by an oxidant

The corrosion of iron exposed to geothermal fluids is very strongly influenced by temperature and by the content of the fluid in sulphide compounds. The potential-pH electrochemical diagram of the system Fe-S-H₂O makes it possible to represent the limits of thermodynamic stability of the metal and to identify the products of its corrosion. On the basis of the Pourbaix Fe/H₂O diagram, Pound B.G. et al. (1985) were able to establish diagrams taking into account both temperature and the sulfur species. The different reactions considered, and

the values of the coefficients of activity and of potential are given in the report of Ignatiadis et al. (1991b). It is thus possible to draw the diagram of the system Fe-S-H₂O at 373°K, which is the temperature closest to that of the Dogger fluids, and to superpose on this diagram the system corresponding to the selected oxidant, which in our case was hydrogen peroxide, H₂O₂ (Detoc-Karimi S., 1990, 1991), which is a non-linear chain of polyoxides, the oxidizing power of which increases with acidity (Doré M., 1989):



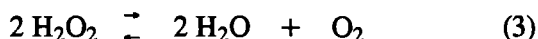
where $E^0_{\text{H1}} = 1.776 \text{ V}$

H₂O₂ can also be a reducer:



where $E^0_{\text{H2}} = 0.700 \text{ V}$

When the redox potential of E^0_{H1} is greater than E^0_{H2} , the H₂O₂ dismutation reaction can take place. This is the reaction:



which is none other than the spontaneous decomposition reaction of hydrogen peroxide. H₂O₂ is thus thermodynamically unstable.

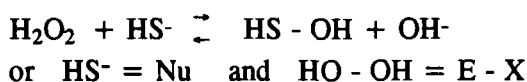
The equilibrium conditions (at 25°C, i.e. at 373°K) corresponding to reactions (1) and (2) are:

$$E^0_{\text{H1}} = 1.776 - 0.074 \text{ pH} + 0.038 \log(\text{H}_2\text{O}_2)$$

$$E^0_{\text{H2}} = 0.700 - 0.074 \text{ pH} - 0.038 \log(\text{H}_2\text{O}_2)$$

The action of H₂O₂ on inorganic substrates takes different forms (Weres and Tsao, 1983; Doré, 1989):

- a) If the substrate is nucleophile, H₂O₂ behaves like an electrophile; for example:

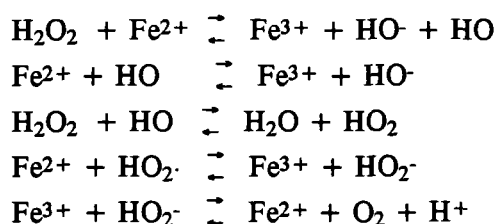


- b) Substitution by HOO⁻ may take place

- c) H₂O₂ may form the radical ion HO[•], a powerful oxidant which reacts with the substrate, initiating a series of reactions (Duke F.R., 1959).

The dismutation of H₂O₂ to give water and oxygen according to the reaction

$2 \text{H}_2\text{O}_2 \rightleftharpoons 2 \text{H}_2\text{O} + \text{O}_2$ is catalysed by many different metals. The couple H₂O₂-Fe is of particular importance (Fenton's reaction), (Doré M., 1989). The principal reactions taking part are:



In order that the reaction of oxidation of iron sulphides take place and be quantitative, it is necessary that the normal conditional potential of the hydrogen peroxide be greater than the normal conditional potentials of the sulfur species considered. By superposing the pH/Eh diagram for H_2O_2 upon that for the sulfur species, it can be deduced that the field of oxidation of H_2O_2 is substantially above the curves for the sulfur system being considered. The oxidation reactions given will therefore be thermodynamically possible.

3.2.1.3. Experimental results and discussion

The selected chemicals were hydrochloric acid with or without glyoxal or a commercial surfactant, Solamine 129® (Seppic Co., Paris, France) and hydrogen peroxide alone. Samples of two types of scale were used. The major element composition of sample 1 is given in table 7 below. Sample 2 consisted essentially of arborescent pyrite.

Element	Fe	S	Na	Cl	SiO ₂	Ca
Weight %	49.3	21.55	1.07	0.27	1.17	0.87

Table 7: Composition, in weight %, of scale sample No.1, from the Cergy Pontoise (Paris Basin, France) geothermal production well.

Dissolution of scale by hydrochloric acid with and without glyoxal

The scale used was sample No.1, in the form of a powder of 100 μm particle size. The experiments were carried out in the laboratory, in a glass cell under a controlled, oxygen-free atmosphere, at a thermostatically controlled temperature of 70°C, and at atmospheric pressure. The solution was agitated, the contact time was 24 hours and the ratio of sample weight to volume of solution was 1 g to 300 ml. The hydrochloric acid used was 37.5 wt %, and the oxidant used with it was glyoxal (glycol aldehyde - $\text{C}_2\text{H}_2\text{O}_2$).

The experimental conditions and results are given in Table 8. The acid and oxidant were used at various concentrations in order to determine the minimum concentrations necessary and to see whether or not any secondary reactions took place. The role of the glyoxal in the breakdown was also studied. In view of the chloride ions provided by the acid, no salts were added. One litre each of solutions E200, E50, E20, E20 without glyoxal, and E10 were

prepared. The analytical procedure used is simple, consisting in weighing the dry scale before and after, and analysing for the chemical species in solution. The effects of the concentrations of acid and of glyoxal in the attack on the scale can be compared. The acid concentration varied from 0.0206 to 0.4114 mol/l (i.e. pH 0.38-1.69). The effect of duration of contact cannot be determined as the time was fixed at 24 hours. When breakdown of the scale occurs, hydrogen sulphide and iron in solution should be produced. It can be seen in Table 8 that in fact the quantity of iron in solution after reaction is substantial and represents 82-98% (according to the conditions) of the amount of iron initially present in the scale. The breakdown with respect to iron proceeded to 89, 93, 82, 90 and 98% respectively in the five solutions. There were thus apparently no side reactions as the excess acid took no part. Elemental sulfur is not present in the scale, and neither is S° found as fine particles in the filtrate; only very small amounts of S° were found, i.e. 1.9%, 0.06% and 0.01% with respect to the sulfur initially present in the scale. The S° is undoubtedly oxidized in soluble form, such as sulphates, in the water. The glyoxal appears to have no effect on the decomposition reaction; the percentage breakdown with respect to iron, for solutions E20 and E20 without glyoxal are comparable - 82 and 89%.

Conditions	SAMPLES						
	E200	E50	E20	E20 without glyoxal	E10	E0,2 H2O2	E0,3 H2O2
[HCl] (mol/l)	0,4114	0,1028	0,0411	0,0411	0,0206	-	-
[HCl]/[FeS] ratio *	20	5	2	2	1	-	-
Glyoxal volume (ml) for 1 l of solution	200,00	50,00	20,00	0,00	10,00	-	-
[H2O2] (mol/l)	-	-	-	-	-	0,200	0,300
[H2O2]/[FeS] ratio **	-	-	-	-	-	6,66	10,00
contact time (h)	24	24	24	24	24	24	24
[Cl-] (mol/l)	0,4114	0,1028	0,0411	0,0411	0,0206	-	-
weight loss (%)	76	79	76	79	75	9	13
breakdown/iron (%)	88,7	93,3	82,4	90,3	97,6	9,3	11,3
breakdown/sulfur (%)	1,9	0,1	0,1	0,1	-	14,9	18,4

Table 8: Dissolution and/or oxidation of scale by hydrochloric acid (with or without glyoxal) and by hydrogen peroxide alone.

Figure 25 below shows the results of the experiments in graphic form.

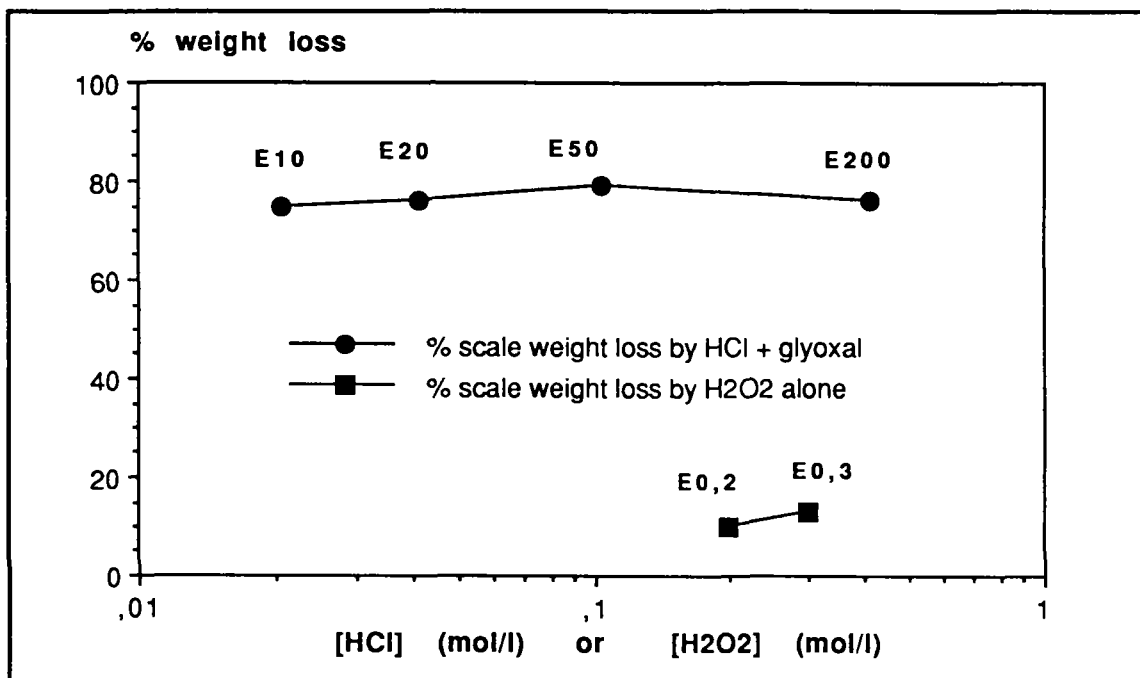
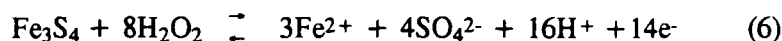
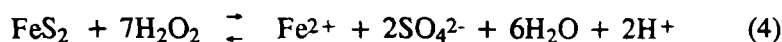


Figure 25: Percentage of weight loss with respect to the initial weight of scale against concentration of hydrochloric acid and hydrogen peroxide.

Oxidation of scale by hydrogen peroxide

The experiments were carried out in the same apparatus as before and the conditions were identical. Experimental conditions and results are given in Table 8. The hydrogen peroxide used was a 30 wt % aqueous solution.

Where the oxidation reaction of S^{2-} sulfides is total (the oxidation state of sulfur changing from -II to +VI) the reactions considered are the following:



According to the analyses of the powder, it contains about 80% iron sulfide equivalent of FeS type, i.e. for the test amount of 1 g, 0.01 mol of equivalent FeS. If H_2O_2 is taken in slight excess (10 times more than the iron sulfides as against 7, 4 and 8 respectively), the volume of hydrogen peroxide (30% solution) to be used is 38 ml. This is made up to 1000 ml with milli-Q water. The concentration of oxidizing agent is thus 0.3 mol/l, whence:

$$E^0_{H1} = 1.756 - 0.074 \text{ pH} \quad \text{and} \quad E^0_{H2} = 0.720 - 0.074 \text{ pH}$$

Two experiments were carried out, at concentrations of 0.2 mol/l and 0.3 mol/l, corresponding respectively to H_2O_2 /FeS ratios of 6.66 and 10. The reacting medium had a much yellower appearance than that of the previous experiments (acid plus glyoxal), and bubbles were given off for about 30 minutes in the flask of 0.5N NaOH. The colour of the liquid indicates the presence of elemental sulfur during the reaction, and indeed 14.9% and 18.4% of the sulfur initially present was transformed into elemental sulfur (Table 10). In addition, the pH increased. If reaction (5) was dominant, the pH should not change, and furthermore reactions (4) and (6) should induce a lowering of pH. It is probable that in these cases the acid reaction, seen in the preceding paragraph, takes over from oxidation, whence a consumption of the H^+ ions produced and the formation of S^0 in the scale. Nevertheless, the oxidation reaction appears to be very complex. The reaction rate, based on dissolved iron, was only 9 and 11%, indicating that other reactions took place. Figure 25 gives the results of this experiment and enables comparison with the results of the hydrochloric acid plus glyoxal experiments.

Breakdown of scale and carbon steel by hydrochloric acid and a surface active agent

The breakdown of iron sulphide by the use of hydrochloric acid appears quite conclusive. Its action, however, is not only strong but also corrosive to metal, so it would undoubtedly also attack the carbon steel casings of geothermal wells. It therefore seemed a good idea to combine the use of acid with a second proposed treatment, that of a surfactant corrosion inhibitor, which would penetrate down to the metal and protect it, while not affecting the action of the acid in breaking down the scale. In order to verify this hypothesis, two types of laboratory experiment were carried out:

- a) The first was to investigate the behaviour of a carbon steel in the presence of both Solamine 129®, a cationic surfactant and hydrochloric acid, in order to determine if the inhibitor prevented the acid from attacking the steel by creating a film on the metal.
- b) The second was to investigate the behaviour of a scale in the presence of the two components in order to determine whether the acid attack or the filming was predominant.

The concentrations of acid and Solamine 129® were chosen according to the behaviour of the Solamine 129 in an acid medium. Solamine 129® still acts as an inhibitor at a concentration of 1-2 g/l in a solution of pH 1. It should create a film on bare metal protecting it from corrosion. Its action on scale, however, is relatively poorly known. It is known to be a softening agent (i.e. it promotes the spreading of the liquid over the surface of scale, or increases the rate of penetration into porous scale) and to be a detergent-dispersant (i.e. facilitates the dispersion of particles in water).

Effect of hydrochloric acid and surfactant on a carbon steel

The experiments were carried out in the same laboratory equipment. The experimental conditions and results are reported in Table 10. The temperature was thermostatically controlled at 70°C and the pressure was atmospheric pressure. The solution was agitated by a magnetic agitator, contact time was 2 hours, and the ratio of steel to volume of solution was

fixed at about 16.4 g steel to 300 ml of solution. The steel samples used were Anticor Co. (Thonon, France) type XC38 (0.38% C), in the form of coupons 44 x 24 x 3 mm with no middle orifice, rectified on both sides, grease-free, marked, dried, weighed and packed according to NACE standard RP 07-75. The total surface area of each coupon is 25.2 cm². The average composition of this steel is given in Table 9 below:

Element	Mn	Si	P	S	Ni	Cr	Cu	Al
Weight %	0.65	0.10	0.017	0.016	0.05	0.03	0.062	0.022

Table 9 : Composition in weight % of steel XC38 (0.38 % C and 98.673% Fe).

The acid used was 37.5 wt % hydrochloric acid; a single concentration was used - 0.02 mol/l (pH 1.69). The concentration of Solamine 129® was varied from 0 to 2000 mg/l.

The coupon of XC38 was placed in the bottom of the cell and plunged into a solution of 300 ml 0.02 mol/l acid and variable concentrations of Solamine 129®, brought to 70°C and deoxygenated by nitrogen bubbling for about three quarters of an hour. The Solamine 129® was injected first in order to coat the sample, and the acid was introduced half an hour later. The reaction time was fixed at a total of two hours. In order to test the efficacy of the Solamine 129®, an experiment was first carried out without inhibitor.

The analytical procedure consisted in weighing the dry steel before and after, and analysing the species in solution. The corrosion of the steel was expressed by its weight loss after exposure.

When the steel coupon comes into contact with the acid alone, it is attacked, and a slight "effervescence" can be distinguished on its surface. In contrast, in the presence of Solamine 129® (at 2000 mg/l) this effect is not observed. The results (Table 10) show that the steel is attacked by the acid, but that the rate of corrosion is slowed by the inhibitor when present in sufficient quantity. The Solamine 129® resists the HCl and prevents steel XC38 from being attacked by the acid. The rate of breakdown with respect to iron is 40 times less when the inhibitor is present in concentrations greater than 50 mg/l.

Conditions	SAMPLES XC38 carbon steel coupon N° or scale coupon N°								
	coupon 1	coupon 2	coupon 3	coupon 4	coupon 5	coupon 6	coupon 7	scale 1	scale 2
(Solamine 129®) (mg/l)	0	2,5	10	50	100	500	2000	50	2000
(HCl) (mol/l)	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02
reaction time (h)	1,50	2	2	2	2	2	2	2	2
weight before reaction (g)	16,4776	16,4212	16,4244	16,4111	16,4322	16,4348	16,4895	6,3105	6,0679
weight before reaction (g)	16,1939	16,1662	16,3374	16,3982	16,4268	16,4341	16,4888	6,1829	5,9555
weight loss (g)	0,2837	0,255	0,087	0,0129	0,0054	0,0007	0,0007	0,1276	0,1124
weight loss (%)	1,722	1,553	0,530	0,079	0,033	0,004	0,004	2,022	1,852
corrosion rate (mm/day)	0,23393	0,15770	0,05380	0,00798	0,00334	0,00043	0,00043	0,54530	0,48034
corrosion rate (mm/year)	85,38487	57,56030	19,63822	2,91187	1,21892	0,15801	0,15801	199,03419	175,32479
iron initially present (mg/l)*	54196,47	54010,97	54021,49	53977,75	54047,15	54055,70	54235,61	8812,99	8474,18
[Fe2+] in solution (mg/l)	892,00	764,00	261,00	48,00	16,00	15,00	21,00	27,00	31,00
breakdown/iron (%)	1,65	1,41	0,48	0,09	0,03	0,03	0,04	0,31	0,37

Table 10: Action of hydrochloric acid on a carbon steel and a scale in the presence of a surfactant (Solamine 129®).

Figure 26 shows the rate of corrosion of the carbon steel, in mm/day, against the concentration of Solamine 129®.

As the results have been fairly conclusive at the experimental values, it would be interesting now to determine the minimum concentration of Solamine 129® that can be used effectively. Its practical use at a concentration of 2000 mg/l cannot be envisaged, in particular from an economic point of view. A value of 50 mg/l seems a reasonable compromise, as this is a low concentration and the loss of steel remains acceptable.

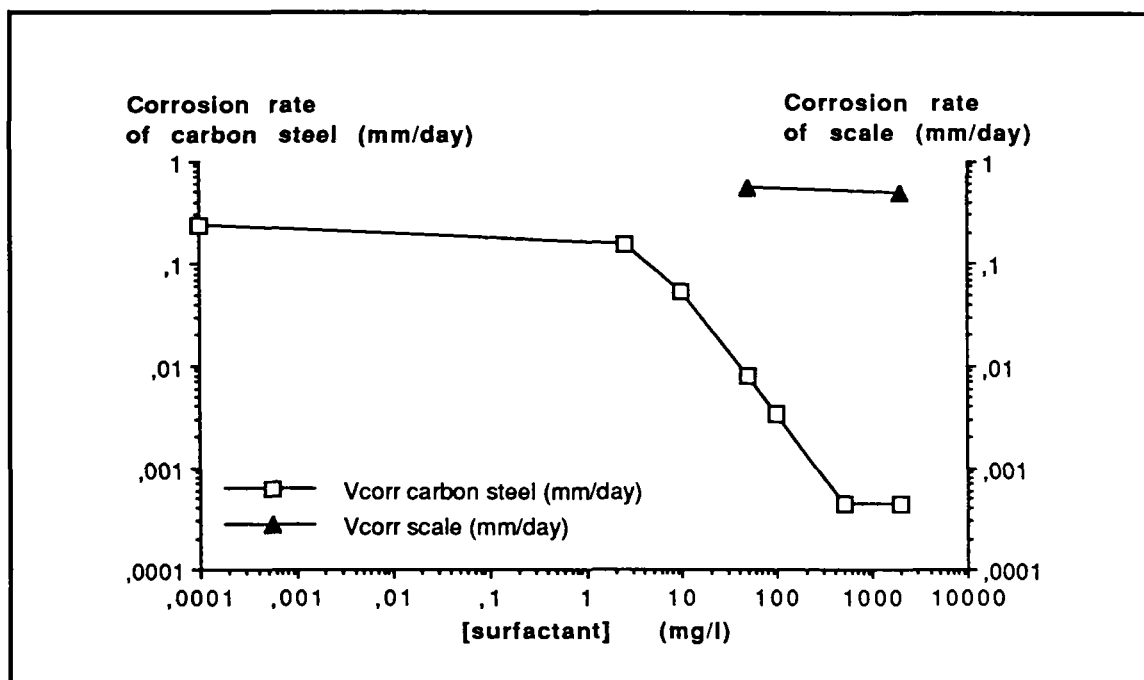


Figure 26: Corrosion rate of carbon steel and raw scale in the presence of 0.02 M HCl and various concentrations of Solamine 129® at 70°C and one atmosphere.

Effect of hydrochloric acid and a surfactant on iron sulfide scale

The experiments were carried out in the same laboratory apparatus and under the same conditions as above, except that the ratio weight of scale to volume of solution is 6.2 g to 300 ml of solution. The experimental conditions and results are given in Table 10. The scale used was extracted from the extraction column of the production well at La Courneuve Nord (GCLN-2). The samples were in the form of plates 20 x 20 x 3 mm, giving a total surface area of 10.4 cm². A metallographic study showed that the scale consists of more than 90% arborescent pyrite (Ignatiadis et al., 1991b). Only two experiments were done. The acid used was 37.5 wt % HCl. A single acid concentration was used (0.02 mol/l) with two concentrations of Solamine129® (50 and 2000 mg/l). The coupon of scale was placed in the bottom of the cell and plunged into a solution of 300 ml of 0.02 mol/l acid and Solamine 129®, brought to 70°C and deoxygenated by bubbling nitrogen for about three quarters of an hour. The Solamine 129® was injected first in order to film the sample, and the acid was added half an hour later. The reaction time was fixed at a total of two hours. No experiment was done without inhibitor, so the attack on scale without Solamine 129® cannot be studied. The analytical procedure consisted in weighing the dry scale before and after, and analysing for the species in solution. The corrosion was expressed as weight loss after exposure. When the acid is introduced, half an hour after the Solamine, a slight "effervescence" appears on the surface of the scale and fine particles of scale are also present in suspension in the solution. Acid attack has thus taken place. The predominant reaction is usually written:



If reaction is complete, the amount of acid present in the solution would enable the breakdown of about 1.3 g of iron sulphide, i.e. 20-22% breakdown with respect to the quantity of scale used. If the theoretical and actual percentages are comparable, acid attack predominates, but if the actual percentage is appreciably lower than the theoretical one, this indicates that the Solamine® has filmed the scale and prevented acid attack. In fact, according to the above, no secondary reaction seems to have intervened, so that only the inhibitor can have an effect. The loss of mass of the pyritic scale, which is very stable in air, is of the order of 2% for 2 hours of exposure. This would correspond to a loss of thickness of about 0.5 mm/day, or 180 mm/y. Thus, even at 2000 mg/l the Solamine 129® does not totally film the scale. Figure 26 shows the rate of corrosion of the scale, in mm/day, against the concentration of Solamine.

It has been shown that the carbon steel and the scale can be protected by the surfactant despite the presence of acid. The action of HCl on a carbon steel in the presence of a surfactant has shown an acceptable degree of corrosion of the steel above a certain concentration of the surfactant (fig.26). The scale in the presence of surfactant is attacked by the acid, but the rate of corrosion is sufficiently slowed down by the inhibitor when the latter is present in large amounts. Nevertheless, in the same reactive solution and exposed for the same length of time, the scale is broken down much more rapidly than the steel. A range of concentration of the surfactant from 50 to 2000 mg/l has been determined, within which the steel resists acid attack whereas the scale is attacked. Within this range there exists a clear difference in the rates of corrosion of the steel and the scale that can be exploited in order to treat selectively the scale without corroding the steel.

3.1.2.4. Conclusion

The results of our experiments could open up a line of research that would lead to a process of chemical cleaning of geothermal wells by acid attack of scale accompanied by injection of an organic inhibitor to prevent the acid from attacking the steel. Nevertheless, these results cannot be extrapolated directly and be expected to immediately achieve a cleaning process under real conditions. They are, above all, laboratory results, certainly very promising, but dealing only with certain aspects of the problem. Further laboratory studies need to be undertaken before a valid extrapolation can be made. It would then be possible to pass to the stage of pilot and on-site testing to quantify the reactions, pay attention to the correct neutralization of the liquid and/or gaseous discharges (pH, inhibitor, H₂S), and assess the technical and economic feasibility of the process. The logical extension of work at present is the continuation of laboratory experimentation, followed by pilot testing.

3.2.2. New geothermal fluid treatments

3.2.2.1. Treatment by chemical oxidation of dissolved sulphides and cross-flow microfiltration

Oxidation of sulphides in the aqueous phase is currently being investigated in our laboratory as a means of treating geothermal fluids. This technique aims to reduce the formation of iron sulphide scale by chemical oxidation (by hydrogen peroxide) of dissolved sulphides in the aqueous phase (Detoc-Karimi S.,1990) followed by cross-flow microfiltration (CFM) through a mineral membrane (Detoc-Karimi S.,1990; Ignatiadis I. et al, 1992c; 1992d).

The work carried out was aimed at determining the feasibility of continuous treatment of the geothermal fluid by oxidation by hydrogen peroxide (H_2O_2). The separation of an oxidation product, elemental sulphur, by cross-flow microfiltration was then studied and tested on a geothermal site in the Paris region.

All these studies were carried out as part of a doctorate thesis for the Université des Sciences et Techniques du Languedoc, Montpellier, France, process engineering option (Detoc-Karimi S.,1990). On the same topic, one undergraduate practical training report (Falguerie P.,1990) have been written, two articles published (Detoc-Karimi S. et al.,1991a; Ignatiadis I. et al.,1992c), and three international papers have been presented (Detoc-Karimi S. et al,1991b; Ignatiadis I. et al., 1991f; 1992d).

Chemical oxidation of dissolved sulphides

A study of the bibliography and a certain amount of experimentation a few years ago made it possible to assess the various methods for eliminating dissolved sulphides in geothermal fluids. The performances of various oxidizing agents (air, O_2 , $NaOCl$, H_2O_2) with and without catalysts were compared, and hydrogen peroxide was selected. At the same time, in order to analyse possible problems related to by-products of the oxidation, it was decided that the process of cross-flow microfiltration on a mineral membrane would be assessed.

On-site oxidation experiments were carried out on the fluids at Tremblay-en-France and Fontainebleau. This involved several stages in the laboratory, on site, and in pilot setups.

NB: Geothermal fluid from Fontainebleau

The Fontainebleau geothermal fluid comes from the Dogger limestone reservoir of the Paris Basin at depths between 1680 and 1780 m. The production temperature is 74.2°C and the production flow rate varies during the year between 40 and 120 m³/h. The pH at the surface is 6.73 and the salinity is 5.8 g/l (concentration, in mmol.kg⁻¹, of Na⁺ : 8.30, Cl⁻ : 72.30, HCO₃⁻ : 7.88, SO₄⁻ : 7.12). The fluid contains dissolved gases, principally CH₄ : 54%, CO₂ : 11% and N₂ : 24% by volume. The concentration in total sulphides is 7.10⁻⁴ mol/l (1). Bubble point pressure is about 6 bar.

Rapid and sensitive methods for analysing the sulphur and its compounds present in the fluid, in particular $\text{H}_2\text{S}/\text{HS}^-$, SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} and S, that were developed at this time can be used with the same accuracy both in the laboratory and on site.

The development of these analytical techniques for the determination of sulphur species made it possible to study the oxidation of sulphides by hydrogen peroxide (Detoc-Karimi S., 1990). The results of this study were in turn used to carry out kinetic studies on a Dogger reservoir geothermal fluid, from Fontainebleau, France.

Aspects that were studied included the concentration of the oxidant, the influence of the initial concentration of the sulphides to be oxidized, the oxidant/reducer ratio, the role of catalysts, the influence of pH, and the effect of any products of reaction. The basis of assessment was the rates of disappearance of sulphides and appearance of reaction products, which provided data on the oxidation kinetics of the sulphides.

The relative efficiencies and yields of the catalysts used for oxidation were also assessed. The results show that, in almost every case, the use of hydrogen peroxide, in excess relative to the sulphides to be oxidized, gave sulphates as the end products of oxidation. Under certain conditions of oxidant/reducer ratio, pH and catalyst, however, elementary sulphur was produced (Fig. 27). The results give the relative amounts of the reaction products, and enable modelling of the oxidation reaction and definition of the rate law (order of reaction and rate constant). The studies showed that no simple rate law, describing all the observed phenomena, can be derived. Variations in reaction rate depend upon the ratio of concentration of oxidant to dissolved sulphide, on pH and on catalysts. Identification of the products of reaction enabled stages to be recognised that could take place during oxidation in neutral or acidic and in alkaline solutions (Detoc-Karimi S., 1990).

Two equations for the rate law have been proposed for the pH interval 6-9; neither, however, perfectly reflects the system in its entirety:

$$\text{Eq. 1. : } -d[\text{H}_2\text{S}]/dt = 5.7 [\text{H}_2\text{S}][\text{H}_2\text{O}_2]$$

$$\text{Eq. 2. : } -d[\text{H}_2\text{S}]/dt = 1.86 \cdot 10^5 [\text{H}_2\text{S}]^2[\text{H}_2\text{O}_2]^{4/3}$$

Equation 2 appears better to represent the variation in the oxidation of the sulphides when the oxidant is in excess relative to the sulphides initially present in the solution.

Kinetic cell studies provided further information on the phenomena and on the choice of conditions for optimal pilot treatment. These were followed by on-site dynamic tests using test loops, which enabled determination of the optimum conditions for treatment in actual operating conditions.

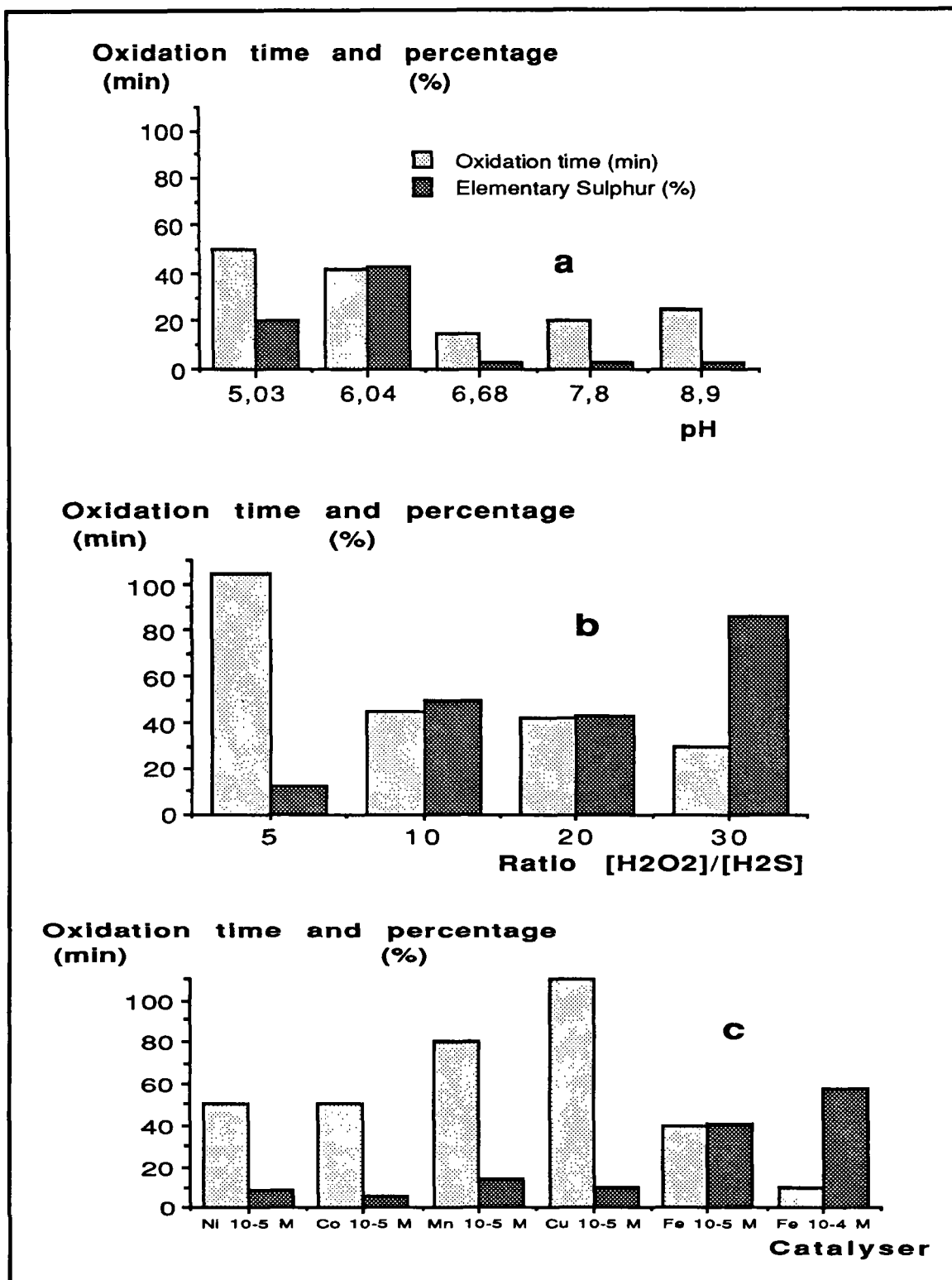


Figure 27: Oxidation time and percentage plotted against: a) pH; b) the ratio [H₂O₂]/[H₂S]; c) the catalyst used.

Use of cross-flow microfiltration for the determination of solid suspended matter concentration and for the elimination of sulphur produced by oxidation of dissolved sulphides in geothermal brines

The second phase of the treatment, cross-flow microfiltration, has been applied here for the first time to a low-temperature geothermal fluid (Detoc-Karimi S., 1990, Falguere P., 1990).

Optimizing the exploitation of the geothermal fluids in the Dogger of the Paris Basin by physicochemical treatment, requires an accurate knowledge of the solid suspended matter (SSM) content of the fluids before treatment in order to estimate the magnitude of the problems caused by scaling on well casing and in heat exchangers. It is also essential to know the effect of a treatment (by a surfactant dispersing agent, for example) on the SSM. The SSM concentration in geothermal fluids is not well or not at all known on any geothermal brine. The methods used up to now (staged filtration, laser granulometry, particle counting) have not given conclusive results, though they have often shown that the value is very low, less than 1 mg/l.

It was decided first to test the feasibility of CFM, on an α -alumina mineral membrane of 0.2 μm pore size, with a geothermal brine.

We report here the use of CFM on a geothermal brine from the Dogger aquifer of the Paris Basin (Fontainebleau geothermal site) and we determine the efficiency of this method first for estimating the quantities of suspended solids in the raw geothermal fluid and second for removing the by-products of oxidation of sulphides, in particular colloidal sulphur.

Selection of technique and membrane

A number of preliminary tests of cross-flow microfiltration were carried out to select appropriate mineral membranes and to establish the optimum treatment conditions (Falguere P., 1990).

The geothermal fluid must be treated under conditions as close as possible to those of production, i.e., at a temperature not less than 74°C and, in order to avoid degasing the fluid, at a pressure above that of bubble point, which at times reaches 12 bar. These constraints determined the choice of membrane and governed the design of the pilot setup. The configuration of the CFM pilot was selected for the advantages it presented, which are that it can be used at pressures up to 17 bar, temperatures of over 100°C, is resistant to corrosion and adaptable to the variations in flow rate of the fluid. The CFM process was thus tested in this pilot, installed on the production site. The CFM technique was first applied to the raw fluid and second to the fluid oxidized by hydrogen peroxide. The pilot treatment system possesses a mineral membrane, enables work to be carried out in a closed loop and includes a system of automatic declogging by flow reversal. The inorganic membrane is the SCT multichannel membrane type P19/40 (SCT, Tarbes France). The main characteristics of this membrane are: nature: α -alumina; length: 850 mm, filtration area: 0.2 m², pore size 0.2 μm . This inorganic membrane possesses a high degree of mechanical, thermal and chemical resistance (to corrosion) and it can operate in these extreme conditions (Aulas F.,

1983; Galaj S., 1984). Figure 28 shows a simplified flow scheme of the experimental CFM pilot which was used for these studies.

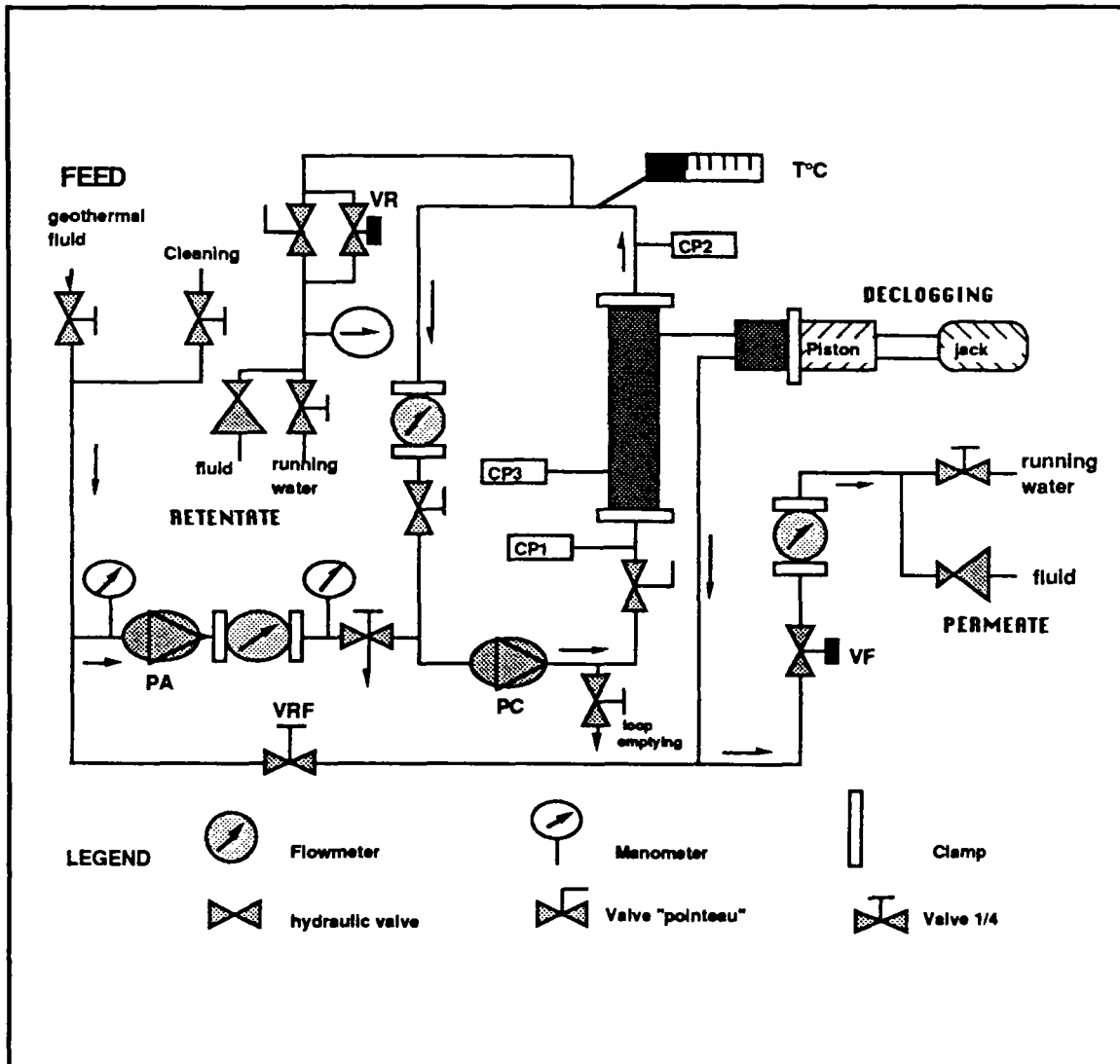


Figure 28: Simplified scheme of the experimental CFM pilot

Microfiltration of the raw fluid

Cross-flow microfiltration (CFM) on a mineral membrane of α -alumina of $0.2 \mu\text{m}$ pore size was applied to a raw brine, which contains 22 mg/l dissolved sulphides. The tests were carried out on the CFM pilot in a closed loop with a system of automatic declogging by flow reversal. The total load of suspended solids was evaluated at this time using a system of concentration in the closed loop, showing that the load was small, less than 0.5 mg/l (Ignatiadis I. et al., 1991, 1992). The variation in flow rate of the filtrate shows that clogging occurred from the first hour of the experiment, reducing the flow rate by about 15% (Fig. 29). The fall in filtrate flow rate remained small even after several days (20% after 4.5 days)

(Fig. 29). Clogging of the membrane, both on and beneath its surface, was slight. Flow reversal is ineffective for declogging the membrane and filtrate flow rate does not improve. It only reduces concentration in the filtration loop and momentarily destroys the polarization layer. In contrast, chemical cleaning of the membrane using 2% in volume sodium hydroxide and 100 mg/l chlorine as NaOCl, followed by 1% in volume nitric acid returned flow rate and transmembrane pressure difference to their initial values (Fig. 30). Raw fluid can be filtered for no more than 4-5 days without clogging. During this period, if filtration is done at a transmembrane pressure of about 1 bar, and a cross-flow rate reduced to only 3 m/s, the filtrate flow rate remains in the interval 800 - 1000 l/(h.m²). The turbidity of the fluid is reduced by 55% after microfiltration.

Determination of the solid suspended matter

A large quantity (several m³) of geothermal fluid is microfiltered, and the water from the filtration loop, which remains closed and clogging-free during the test, is recovered. Retention on the membrane is assumed to be total for particles larger than 0.2 μ m, while the total weight of particles smaller than 0.2 μ m is considered to be negligible. The water charged with the particles retained on the mineral membrane is evaporated in an oven at 70°C. The residue, which consists of crystallized salts and solids formerly in suspension, is weighed. Since the precise dissolved salts fluid composition is known, the weight of suspended matter in the quantity of fluid evaporated can be determined by subtraction. The method is accurate provided that the total volume of filtered geothermal fluid and its composition in dissolved salts are known. Repeated tests gave results that differed appreciably from each other in absolute terms (0.22 - 0.42 mg/l), but were of the same order of magnitude (see Table 11). From the point of view of procedure, these tests show the desirability of long-duration filtering, as this decreases the proportion of dissolved salts in the final residue and the SSM becomes predominant. After filtration for 90 hours the SSM represented 15% of the total weight of the residual deposit.

	Run n° 1	Run n° 2
Microfiltration time (h)	3	92
Volume microfiltered (l)	939.2	16812.0
Vol. of the water recovered from the filtration closed loop (l)	5.091	5.105
Total dissolved salts in water (g)	5.712 $\pm$ 0.050	5.712 $\pm$ 0.050
Weight of total dissolved salts in the recovered volume (g)	29.080	29.160
Weight of dry vessel (g)	292.241	479.152
Weight of scale + vessel (g)	321.713	512.020
Weight of recovered SSM (g)	0.392	3.708
Concentration of SSM (mg/l)	0.42	0.22

Table 11 : Conditions of the procedure and determination of SSM concentration in a geothermal brine by Cross-Flow Microfiltration

Microfiltration of the oxidized fluid

The CFM technique was applied to the fluid oxidized by excess H_2O_2 (3.6 to 18 times more than the dissolved sulphide content of the fluid). Oxidation conditions vary as a function of flow rate load: $[H_2O_2]/[H_2S]$ ratio vary between 3.6 and 18. According to the $[H_2O_2]/[H_2S]$ ratio, the concentration in different by-products of oxidation (sulphur, polysulphides, thiosulphates, sulphites, sulphates) varies. If the reaction goes to completion the H_2O_2 converts the sulphides into sulphates. In the present case an intermediate product, sulphur (Detoc-Karimi S.,1990; Falguere P.,1990; Gourmelon C.,1977), was detected by nephelometry and UV absorption spectrophotometry at 276 nm (Detoc-Karimi S.,1990; Friedman H.L.,1953; Maurice M.J. 1957).

CMF tests on the oxidized fluid gave a loss in filtrate flow rate much greater than that recorded with unoxidized fluid, the rate falling from 1165 to 700 l/(h.m²) (i.e., a decrease of 40%) in one hour and from 1165 to 425 l/(h.m²) (i.e. a decrease of 64%) in 3.5 days, without declogging by flow reversal. Declogging every 30 minutes brings about a 10% increase in flow rate (Fig. 31). Declogging reduced the rate of decrease in flow rate, but chemical cleaning is required in the short term to recover a filtrate flow rate near the initial rate. In order not to foul the membrane irremediably, it appears necessary to do this every day or two. After daily cleaning and declogging every 30 minutes, the filtrate flow rate can be maintained at close to 600 l/(h.m²), at a transmembrane pressure of 1 bar and a circulation rate of 4 m/s.

Concerning the performances in the retention of particles, we note that turbidity is virtually eliminated, and colloidal sulphur by about 80%. That part of the sulphur remaining in the fluid will correspond to newly formed particles that have not yet reached a size sufficient for them to be retained on the membrane (Zaiser E.M., 1948).

The difference in flow rate measured for the two types of fluid, raw and oxidized, demonstrates the clogging role of the colloidal sulphur in the CFM process. The process of clogging with the oxidized fluid is different from that with the raw fluid - a film is adsorbed onto the surface of the membrane and can be slightly detached by flow reversal.

The cause of the large decrease in flow rate during filtration is the colloidal sulphur (produced by the incomplete oxidation of the sulphides), which seems to provokes two types of distinct phenomena: first the formation of a layer easily detachable on the surface of the membrane (that has been shown by the efficiency of declogging by flow reversal) and second a deeper type of clogging which hinders filtration and reduces flow rate.

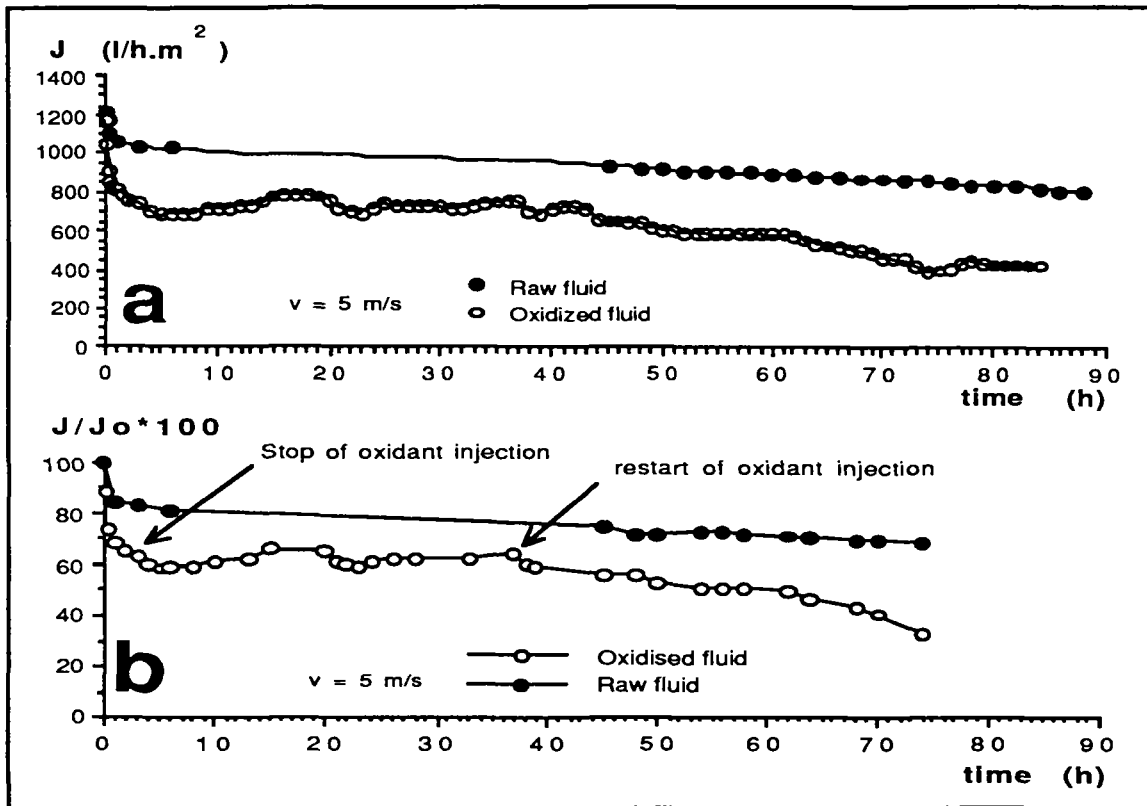


Figure 29: Comparison of the variation in the flow density of the permeate. Raw and oxidized fluid; v = cross flow rate (m/s),
 a: Flow density of the permeate J (l/(h.m²))
 b: Normalized flow density of the permeate $100 \cdot J/J_0$ (l/(h.m²))

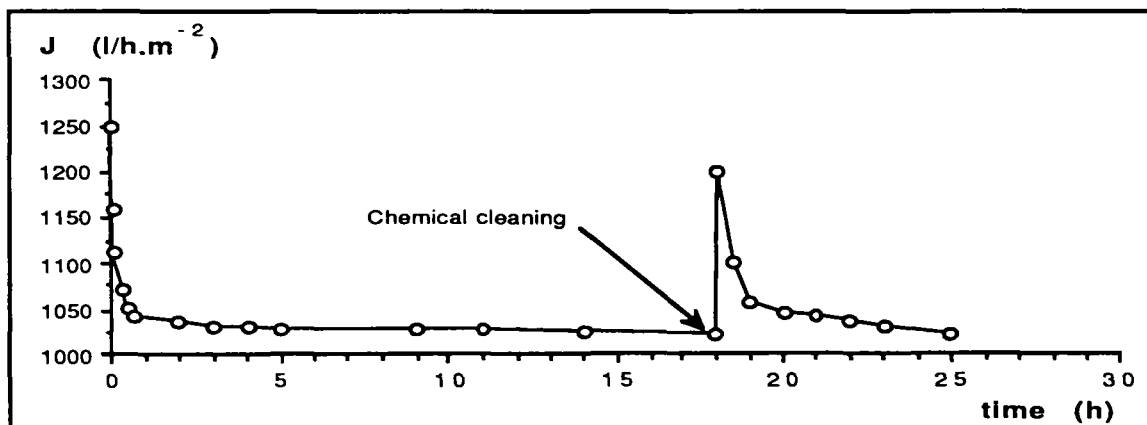


Figure 30: Efficiency of the chemical cleaning of the membrane. Raw Fluid.

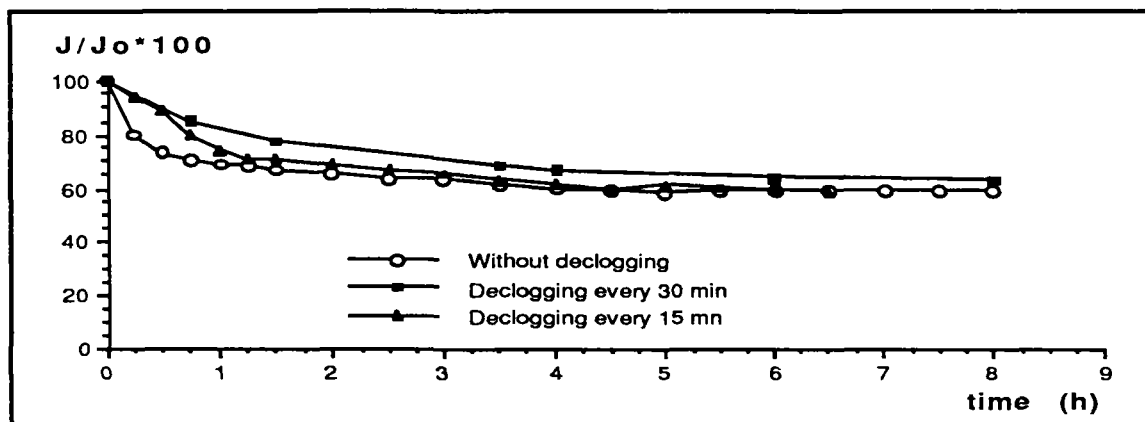


Figure 31: Influence of the frequency of declogging. Oxidized fluid.

J = flow density of the permeate ($l/(h.m^2)$),

$100 \cdot J/J_0$ = normalized flow density of the permeate ($l/(h.m^2)$)

Applications in present or future geothermal projects

To protect the greater part of a geothermal system, oxidation must be initiated at the bottom of the production well, using an injection tube. The oxidation produces sulphur, which can be removed by cross-flow microfiltration.

This study made it possible to quantify the performances of this type of filtration of a raw fluid or the fluid oxidized by hydrogen peroxide. The results, both in flow rate and in retention of particles, clearly demonstrates the technical feasibility of using the CFM process on a geothermal fluid. Cross flow microfiltration renders the fluids (the raw fluid or the fluid oxidized by hydrogen peroxide) clear and totally free of colloids. These results, and the advantages in using this process on a geothermal fluid (maintenance of pressure and temperature, resistance to corrosion, adaptability to variations in fluid flow rate) should encourage and enable more detailed investigation of the geothermal applications of CFM. The CFM pilot has been shown to be of considerable interest as a tool for estimating the quantities of suspended solids in the raw geothermal fluid, a parameter little or unknown for any of the wells on the Dogger (Ignatiadis I. et al, 1992).

An overall economic assessment (tableau 12), however, shows that this type of treatment cannot at present be considered for the low-temperature fluids of the Dogger. With techniques in their current state, this particularly costly process could only be used to a limited extent. Nevertheless, this study could be the starting point for the application of these processes to high-temperature geothermal fluids or, for example, to treat fluids on surface before releasing them into the sanitation system (only for small quantities of geothermal water). A market study must be realized before to decide the continuation of this kind of research.

	Investment (10^3 ECU)	Operating costs (10^3 ECU)
Chemical oxydation with H_2O_2	1.5	360
CFM with inorganic membrane	360	46

Table 12: Chemical oxydation process costs for a conventional geothermal plant (Dogger of Paris basin)

3.2.2.2. Study of solid inhibitors for the treatment of the geothermal wells (by ARMINES-FR)

The study concerns the treatment using corrosion inhibitors at the bottom of the production wells of geothermal loops in the Dogger aquifer. It is detailed in appendix 2.

In this field, at the time of the call for proposals of the Joule 1 program, tests were conducted using small diameter tubings introduced into the production wells to the production zone level.

The experiments gave uneven results:

- a steel tube was installed on a site in the Seine-Saint-Denis area; it was rapidly corroded.
- a tube made of synthetic material broke,...

Now, after an experimentation phase, this technique seems to be more reliable.

In 1989, it seemed useful to recommend the study of other methods as the specialists were not sure they would be able to correctly, under the present economical conditions, install and maintain small diameter tubes, under the Dogger geothermal conditions.

A sample study was carried out to determine the possibility of using the SQUEEZE method of injection of inhibitors directly into the formation.

Clogging of the samples and the difficulties encountered when experimenting at a real scale led us to stop further studies.

Under this conditions, we proposed to study the treatment of production wells using solid inhibitors. This method was used in the petroleum field, especially in Sahara in the early 60's.

The main task was to simplify the equipments installed in the production well and to avoid the need to install small diameter tubes in the wells.

The idea was to package the amines into balls or sticks using a suitable binding agent. These solids elements were to be filled with ballast made of an inert component and dropped down to the well bottom. After having reached the bottom of the production well in the dead zone of the well, a change of phase and a progressive diffusion of these elements toward the upper productive horizons induced by chemical diffusion and natural convection related to the geothermal gradient would occur.

Such a system is easy to implement; the conditioning under solid form also increases the security of transport and of handling on the site, and particularly would reduce the equipment in the wells.

Consequently, and in a schematical way, this is the type of process we proposed to study. As a matter of fact, if the concept is easy in its principle, its use needs a feasibility study to answer the following main questions:

- . what should be the geometrical and physical properties of the elements, ... ?

- . what should be their chemical composition (which chemical agents to increase the density, and to avoid their fusion during the gravitational fall) ?
- . how will spread the product from the bottom well toward the producing layers ?

Before answering to the call for proposals, we got in touch with an important chemical company in order to determine roughly the following principles.

According to them, it was possible to imagine the solid sticks made of amine mixed with a soluble binding agent raised to a high temperature (more than 70°C) made of polyethylene glycool and ballasted with anhydrous baryte.

Under these conditions, elements made of 60% of amines, 10% of polyethylene glycool and 30% of baryte should have a density near to allowing their natural fall into the wells.

According to the completion of the Dogger wells, it seemed possible to consider such a system. However, its feasibility, under reasonable economical and technical conditions was to be studied.

This work should have been done by the Centre d'Informatique Géologique, in connection with the CECA company for the realization of inhibitors.

Unfortunately, a major problem occurred: as a matter of fact, in opposite to what had been assessed at the time of the proposal, we could not conceive, under realistic conditions, solid elements adapted to the geothermal conditions: the manufacturer encountered two problems: it was impossible to find a chemical agent able to avoid the dissolution of the product during its fall into the well. The classically considered products such as the polyethylene glycool have a melting point which, in fact, does not raise over 70°C. Tests in laboratory at this temperature showed that solid elements dissolved.

Besides, it was also found difficult to implement a high density ballast in the elements. This made necessary to complete the elements with a too high percentage of ballast.

Complementary studies bearing on the composition of the elements should have been possible, but it appeared obvious that the results would have been quite unrealistic both on technical and economical points of view.

A point which appeared initially as easily controlled was, in fact, a significant obstacle preventing, particularly, to work out the tests.

Under these conditions, taking into account the fact that it was almost impossible to obtain valuable results, it was proposed to the Commission to stop the study before its end. The main initial goal which was to prepare the realization of an in situ test became obsolete, taking into account the impossibility to obtain correct solid sticks.

The main results concern the hydrodynamical conditions of the falling down of the elements into the wells according to their physical properties. A first analysis concerning the diffusion of the amines from the bottom of the wells has also been undertaken.

3.2.3. Mineral corrosion inhibitors

Various physicochemical treatments, in particular the injection of organic inhibitors, are currently being investigated in our laboratory as means of treating geothermal fluids. The use of organic corrosion-inhibitors in geothermal wells necessitates the use of well-bottom additive injection tubes (WBAIT), and continuous or semi-continuous injection of the inhibiting agent. Although effective, this technique is expensive, complex and its application difficult.

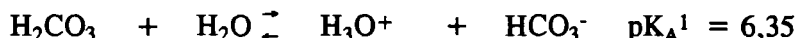
In our search for a simpler, less expensive method, using less risk-prone equipment, we investigated mineral inhibitors, in order to find one capable of creating a permanent protective film thus avoiding the need to lower an injection device to the well bottom.

3.2.3.1. Investigations of different mineral inhibitors

By the end of 1989, an extensive bibliographic search had been made, inhibitors for investigation selected and a work programme for 1990 and 1991 drawn up. These studies serve as the basis for a thesis entitled "Assessment of the performances of mineral corrosion-inhibitors, control of efficacy and conditions of utilization", by Mlle B. Le Dinh Bao. The work deals with the investigation of the composition of protective films, formation conditions and kinetics of their formation and disappearance. It was decided to pay particular attention to zinc phosphate, sodium molybdate and silicate, and iron sulphide scale formed rapidly in situ.

The first phase of the investigations was carried out in the laboratory. This work was done in close collaboration with the Atomic Energy Commission laboratory at Fontenay-aux-Roses, in the Corrosion, Electrochemistry and Chemistry of Fluids Service.

Laboratory experiments carried out in a thermostated reactor (electrochemical type water-jacketed cell bottom), under controlled oxygen-free atmosphere, consisted in studying the creation of films on soft-steel samples under different conditions (reconstituted or natural geothermal fluids, with or without addition of mineral inhibitor). Preliminary tests of the stability of the artificial aqueous solutions were carried out in order to simulate as closely as possible actual geothermal conditions. The solution used for the tests had a pH of 6.5, contained 35 g/l NaCl (0.6 M), 100 mg/l (3.10^{-3} M) of dissolved sulphides and was saturated in CO₂. Its composition is accurately calculated on the basis of the following equilibria (at 25°C):



and considering mass and electroneutrality balances. Precise quantities of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, NaCl , NaHCO_3 , HCl (which fixes the pH at 6.5) and of demineralized-deoxygenated water are thus used to reconstitute the geothermal fluid. In addition, the reconstituted solution must be free of O_2 , which necessitates working in a glove box and a deoxygenated water circuit. The H_2S content is maintained constant, and continuous ventilation is effected using a precisely calculated gaseous mixture of H_2S , CO_2 and N_2 .

Comparative tests of fixation, anti-corrosion protection (i.e. decrease in rate of corrosion), and of film quality, thickness and composition were made on the film obtained in the different experiments by the four compounds. The parameters set at the onset were the time of fixation of the film (48 hours), temperature (70°C), pressure (1 atm) and the stirring rate.

The average weight per cent composition of the steel samples is as follows: C:0,42% ($\pm 0,04$); Mn:1,08% ($\pm 0,001$), Mo:0,014% ($\pm 0,01$); Si:0,34% ($\pm 0,04$), Ni:0,092% ($\pm 0,005$); Cr:0,100% ($\pm 0,005$). The samples are either cylindrical, with a surface area of 5 cm^2 , or flat, with a surface area of 4 cm^2 , and are rectified, de-greased, dried, weighed and conditioned according to NACE standard RP 07-75 (NACE, 1975).

The films obtained were also investigated by the laboratory procedure for comparing the films in the artificial sulphide medium including both weight loss and electrochemical methods, the latter involving monitoring of potential as a function of time, measurement of corrosion rates from polarization resistance, drawing of Tafel polarization curves and electrochemical impedance methods. The films obtained were also investigated using physical methods of surface analysis such as:

- X-ray diffractometry (to identify phases),
- optical microscopy (for macroscopic description),
- electronic scanning microscopy (for observing morphology, spectrum microanalysis and element distribution images),
- ESCA, a type of photo-electron spectroscopy (for determining the thickness and chemical composition of the film).

Chemical methods for analysis of solids and liquids were also used.

The results are very encouraging for sodium silicate, whose films provided outstanding anti-corrosion protection (Figure 32).

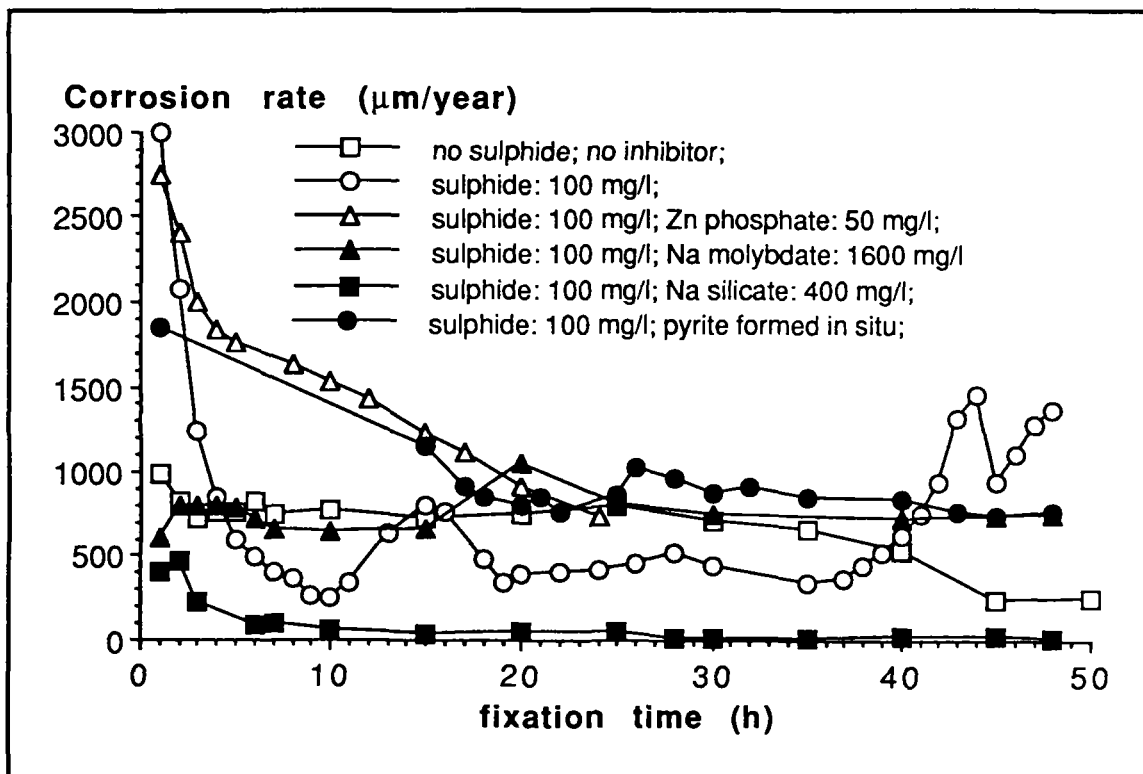


Figure 32: Corrosion rates in $\mu\text{m/y}$ of carbon steel for 6 electrochemical cell tests in aqueous solution containing 35 g/l NaCl and 0 or 100 ppm sulphides and an inhibiting agent; at pH 6.5, temperature 70°C and pressure 1 bar.

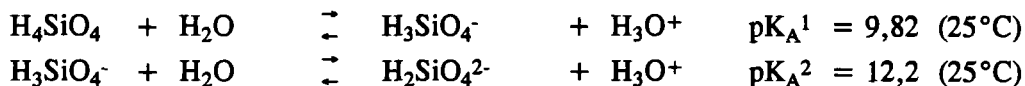
3.2.3.2. Anti-corrosion treatment of a carbon steel using sodium silicate to deposit a silica film. Analysis of films by photon-electron spectroscopy (ESCA).

The laboratory work on mineral corrosion-inhibitors is being restricted to sodium silicate [Lerhman L. and Shuldener H.L.,1952; Shuldener H.L. and Sussman S.,1960; Lane R.W. and al.,1973; Rozenfield I.L.,1981] also because of the presence of dissolved silica in the natural Dogger water, which suggests the possibility of maintaining the protective film. Furthermore, silica satisfies the requirements for a mineral inhibitor, i.e. low cost, non-toxicity, and compatibility with the environment. The ultimate objective is to obtain a silicate film that, once deposited on the well walls, will be able to utilize the dissolved silica in the Dogger fluid to be self-sustaining.

The work deals with the investigation of the composition of protective films, and of the conditions and kinetics of their formation.

Sodium silicates of the type $\text{Na}_2\text{O} \cdot x(\text{SiO}_2)$, with $x = 3.5$ (it may be between 2 and 5) were used.

The deposition of silica is based on the property of silicates to precipitate amorphous silica in aqueous media at pH values greater than 9.82:



the mass balance equation being: $\Sigma[\text{Si}] = [\text{H}_4\text{SiO}_4] + [\text{H}_3\text{SiO}_4^-] + [\text{H}_2\text{SiO}_4^{2-}]$ and the solubility being limited by the equilibrium:



The first films obtained in a reconstituted geothermal fluid in the presence of sodium silicates showed good fixation and very good protection, but the deposit (film) was not uniform, as shown by the presence of pits on the surfaces of the samples. The chemical composition of the film, and in certain cases its thickness remain to be precisely determined, and the mechanism of adhesion of the film to the metal surface is poorly understood. In order to resolve these problems, the methods of forming, i.e. depositing the films, were improved. Samples were systematically sectioned in order to estimate the thickness of the protective layer in each case and to see if it had a well-defined stratification. The surfaces of the samples were also analysed using ESCA (Electron Spectroscopy for Chemical Analysis, in the CEA Laboratory of Analysis and Characterization of Surfaces and Interfaces, Saclay-FR) photoelectron spectroscopy, to determine the chemical composition of the layer and its mineralogical form, and tests were continued on the durability of the film in solutions with and without silicates.

It was observed that the temperature and pH of the solution (modified by the addition of HCl after the injection of sodium silicate) play an important role in the fixation and quality of the film. It was thus evident that it was necessary to optimize the mode of deposition of silica in a reconstituted geothermal medium. The necessary quantity to prepare a solution of sodium silicates at concentrations of 100-5000 mg/l is injected into the reconstituted geothermal fluid and pH is adjusted to 10.5-11 by addition of NaOH. The solution is brought to a temperature between 25° and 95°C (optimum 70-75°C) at atmospheric pressure and stirred. The pH is next brought to 6.5 by rapid injection of HCl. Under these conditions the films in certain cases reached thicknesses of 3-5 µm. The inhibition could be cathodic, although the silicate ions, if they existed in solution, would act as anodic inhibitors.

The film was tested in a silicate-free solution for ten days, at the end of which a slight decrease in resistance to corrosion was observed, but this property nevertheless remained much higher than without the film.

The films obtained by sodium silicate were also investigated using ESCA photoelectron spectroscopy, to determine the composition and thickness of the film (Sastri V.S. and Packwood R.H., 1987). The ESCA analyses were made on a VG Instruments Escalab S MkII apparatus equipped with a VG Instruments electrostatic-dispersive analyser, on which angular measurements can be made (150° in this case). The photon source was AlK α with a kinetic energy of 1486.6 eV. Detection was by a Channeltron electron multiplier (factor 10⁸) placed after the analyser exit slot. Data acquisition and processing were done on a Compaq 386.20

computer using an AEI Cybernetix software. The eroded surface was a disc of 6 mm diameter. The surface of the samples was subjected to bombardment by photons and the Channeltron received the photoelectrons emitted to give the energy spectra of the core electrons from the atoms, which is characteristic of the surface composition.

Three types of film were deposited on the surfaces of the carbon steel samples and studied: 1) films obtained in the reconstituted geothermal fluid alone (sample 1), 2) films obtained in the reconstituted geothermal fluid containing an additional 400 mg/l of silicates (sample 2), and 3) films obtained in a solution of 400 mg/l silicates in de-ionized water at 25°C (sample 3).

Type 1 films (reconstituted geothermal fluid alone) give protection that is unacceptable even in the short term (Figure 33). Investigation of the film by ESCA shows it to be a thin layer consisting mainly of iron sulphides with a thickness > 120 nm. Traces of carbonates, oxides and hydroxides of iron were also present.

Type 2 films (reconstituted geothermal fluid with added silicates) provide excellent protection of the steel sample (Figure 33). Electron microscopy showed that the film was uniformly distributed over the surface, and ESCA analysis showed it to be a mixture mainly of iron sulphides (Figs. 34a, b, film thickness 240-360 nm), silica (Figure 34c, film thickness 240-360 nm) and ferrous silicate (Figure 34d). At the start of deposition, traces of iron carbonates, oxides and hydroxides were also deposited. The density of iron sulphides in these samples was less than in the type 1 sample.

Type 3 films (silicates in de-ionized water) were shown by ESCA analysis to be very thin (2-20 nm), irregularly distributed and composed of silica with traces of iron oxides and hydroxides. The thickness and composition of this film suggested that the precipitation of silica is favoured by temperature and the presence of hydrogen sulphide.

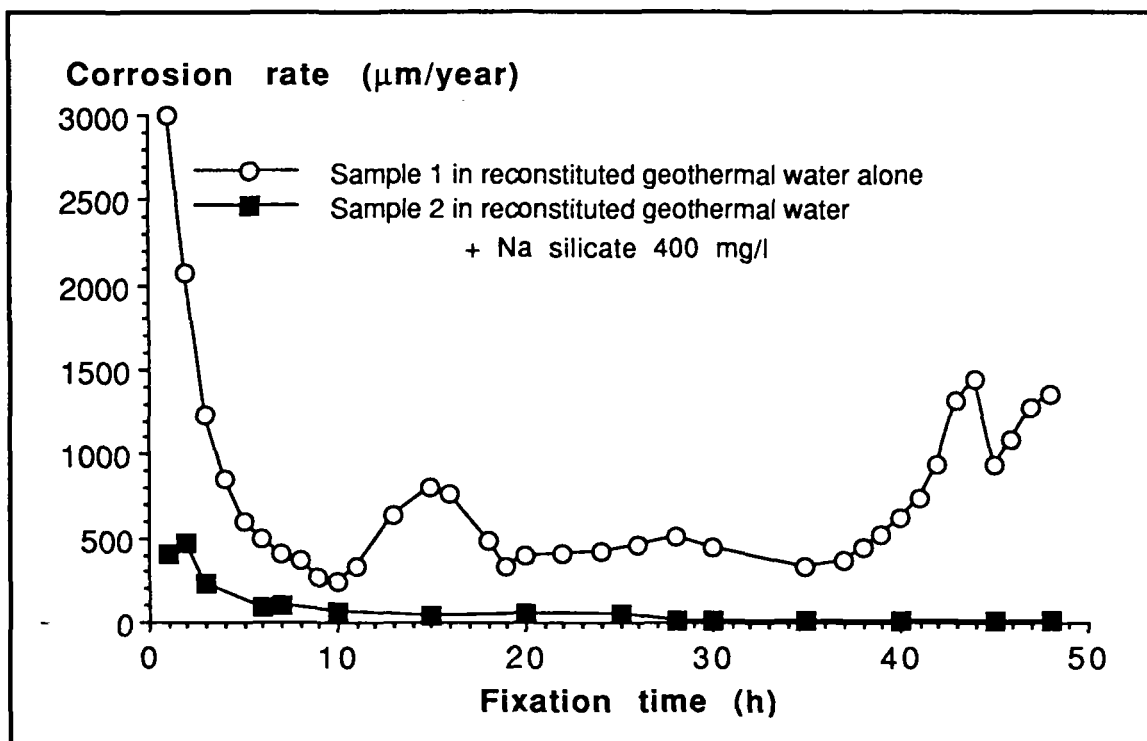


Figure 33: Corrosion rates of carbon steel in aqueous solution containing 35 g/l NaCl and 100 mg/l sulphides in presence and absence of sodium silicates at pH 6.5, temperature 70°C and pressure 1 bar.

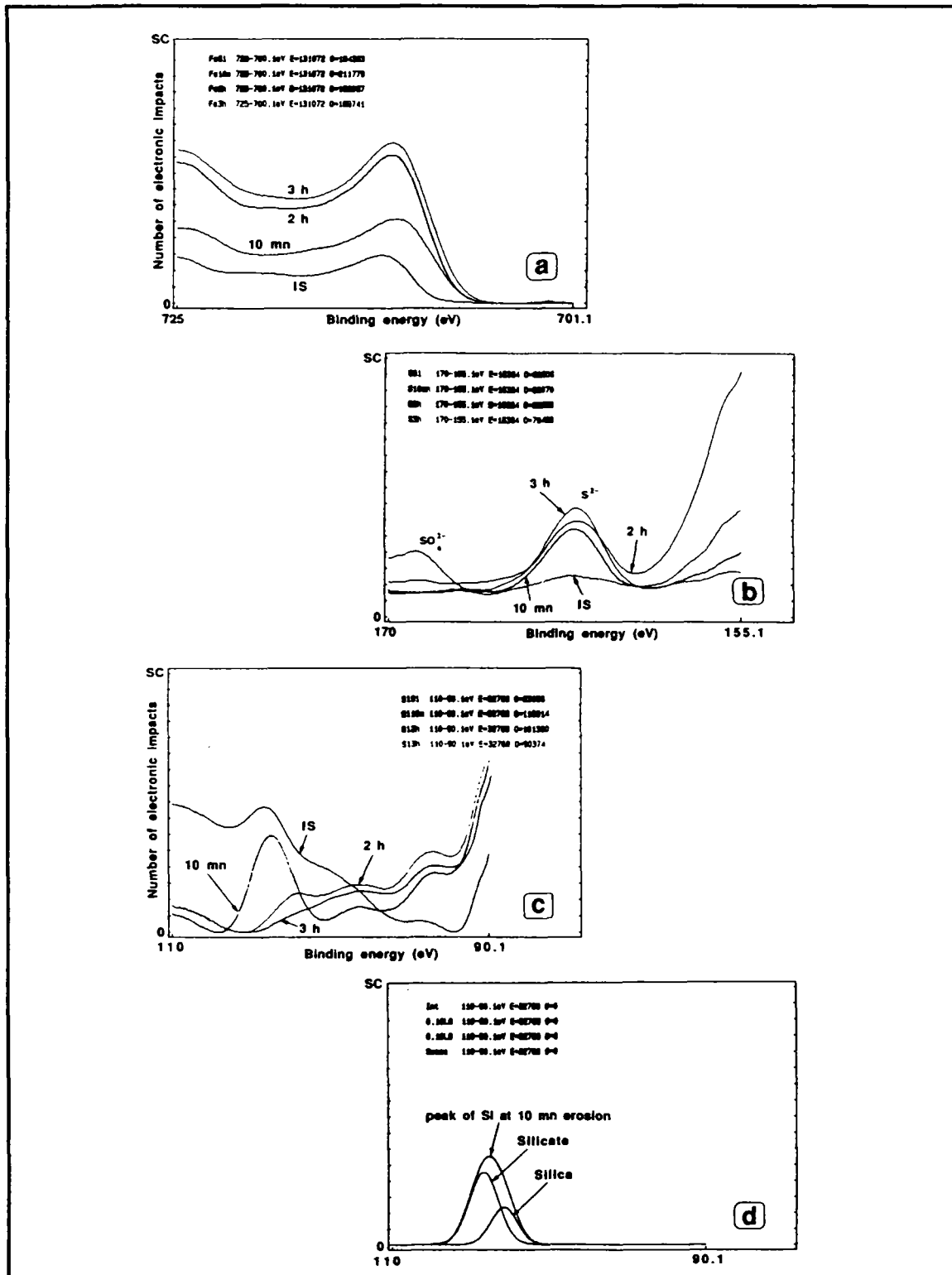


Figure 34: ESCA analysis of a sample treated with sodium silicates. Variation of peaks for Fe (Fig.34a), S (Fig.34b) and Si (Fig.34c) against erosion time (IS - initial surface, 10 mn, 2 h and 3 h; erosion approx. 2 nm/mn). Fig.34d shows the recomposition of the Si peak at 10 mn time of erosion.

The abscissa of the ESCA spectra gives the binding energies in eV corresponding to the energy level of the element concerned, and the ordinate gives the number of photoelectron impacts received by the Channeltron. The erosion time determines approximately the thicknesses examined (the length of erosion corresponds to a thickness eroded). The thickness of the film on a sample can thus be calculated according to the disappearance or appearance of a substance after a known erosion time, e.g., disappearance of iron sulphides or silica and appearance of metallic iron. The state of oxidation of an element can be distinguished.

The tests performed have shown that the best protection against corrosion, over 48 h fixation time periods, is provided by sodium silicates. The formation of a silica film, protecting against corrosion, results from the adsorption of the silica onto the steel.

It was possible to qualitatively evaluate the thicknesses of the films and to study their composition. The variation of the abundance of the elements Fe, Si, S, O and C was monitored as a function of the time of erosion of the films by photoelectron impact. Samples placed in a corrosive sulphide medium that were immediately treated with sodium silicate for 48 h were covered with a film on the order of 360 nm thick, consisting of iron sulphides, silica and ferrous silicate, and were found to be well protected.

This work also demonstrates the use of a local spectroscopic surface analysis technique for determining the optimum conditions for the creation of films providing the best anti-corrosion protection.

3.2.3.3. In situ studies (in actual geothermal media) of anti-corrosion treatment of a carbon steel using sodium silicate to deposit a silica film

Pilot testing of films was planned for 1991, in order to observe the protection provided by the silica in the actual geothermal medium, and confirm the behaviour of the material already tested in the laboratory in an artificial geothermal medium.

We tested the resistance of the silica film over time and the protection it provides on samples of either new metal or previously corroded metal. This was done on an actual geothermal site not previously treated with an inhibitor (Melun l'Almont, summer 1991), with the help of a corrosion pilot.

This work included several preparatory stages in the laboratory (to perfect the corrosion pilot), and the in situ experimental stages.

For this decisive experiment, a diversion from the geothermal loop was set up, consisting of two PVC pipes (or "modules"), placed vertically, one after the other. In these pipes were placed flat samples of metal, treated with silica either before immersion or after about 200 hours of immersion. The silica film was deposited on the samples by injecting silicates into a partially reconstituted geothermal fluid circulation system.

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 representative of the sites to the south of Paris in general (salinity = 12.7 g/l; surface pH = 6.4; production temperature = 72°C;

concentrations (mg/l): $[\text{Na}^+] = 4250$, $[\text{Ca}^{2+}] = 580$, $[\text{Cl}^-] = 7200$, $[\text{SO}_4^{2-}] = 680$, $[\text{SiO}_2] = 42.5$; dissolved gas (GLR=14.9), mainly $\text{CO}_2 = 17.6\%$, $\text{CH}_4 = 53.3\%$, $\text{N}_2 = 19.7\%$. The production flowrate varies over the year between 25 m³/h (in a thermosiphon) and 150 m³/h. The bubble point pressure is in the region of 7 bars. Dissolved sulphur content does not vary with flowrate; it is 16 mg/l in H₂S equivalent.

Description of the measurement apparatus

The flat metal samples (XC38 steel with 0.38% C), with an identical composition to that of the well casing, were prepared in accordance with NACE Standard RP07-75 (NACE, 1975). Before any treatment, an electrical wire was soldered to one side and the sample together with its wire was weighed. The samples were then coated with an epoxy resin and glued to a mount so that only one side was exposed (area exposed: 10.65 cm²); the electrical wire led out of the module by an airtight exit when the sample mount was put in the module. The metal samples were thus fixed to mounts which were themselves placed in pairs, opposite each other, with two generators facing each other, inside the modules. A cylinder, also made of plastic, was placed in the pipe following its axis, so as to reduce the usable diameter of the pipe and increase the linear velocity of the fluid. Each pipe was closed with a metal cap, enabling a silver-sulphide-coated silver electrode to be placed in the liquid along with an electrolytic bridge connected to an external Ag-AgCl reference in a saturated solution of KCl.

Figure 35 shows how the samples were laid out. Those in Module 1 were given a silica-based treatment before being exposed to the geothermal fluid. Those in Module 2 were factory-new at the start of the trial. The polarization resistance (R_p) measurements were made on the working electrodes (identified by the letter W). The other samples were used either as auxiliary electrodes (A), or as so-called reference electrodes (R). The latter, having no current passed through them, could maintain a constant potential throughout measurement-taking if this was brief but, unlike true reference electrodes, did not make it possible to compare several experiments.

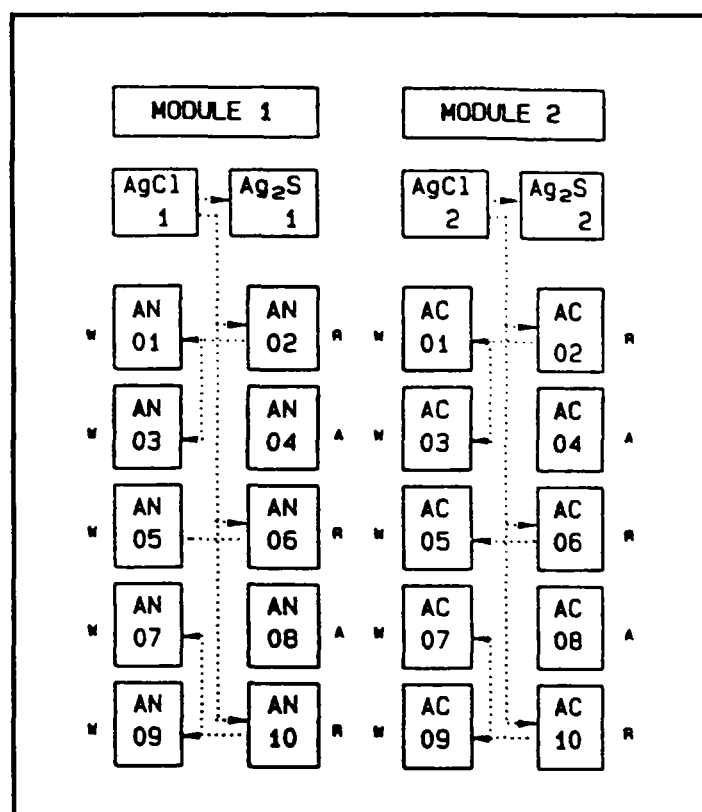


Figure 35 - Layout and functions of the samples: working electrodes (W), "reference" electrodes (R), auxiliary electrodes (A). Measurement of potential: distance from arrow base to tip. Modules: silica-based treatment (1) prior to immersion, (2) during immersion.

The potential of the W samples (cf. Figure 35) was measured in two stages. A direct measurement was taken of the difference in potential between these samples and their respective "reference" electrodes. Secondly, the difference in potential between the "reference" electrodes and a true reference electrode (Ag-AgCl) was measured. It was then easy to process these data with the help of a computer, to find the potential of all the samples compared to a selected reference electrode. This procedure was chosen as a safeguard against failure of the reference electrode.

To determine the polarization resistance of a sample, the apparatus first measured the difference in potential between it and its "reference" electrode. It then varied the sample's potential by an amount v ($V \approx -10\text{mV}$ approx) by passing a current i between the sample surface and the solution (return current was via the auxiliary electrode). The computer received these measured values of v and i , calculated the polarization resistance v/i and multiplied it by the surface area of the sample, to give the value per unit of area. The apparatus displayed the successive values calculated while the current stabilized, and stored the value obtained after five minutes.

To complement the information provided by the above measurements, electrochemical impedance measurements were also taken from all the samples.

The main data acquisition and apparatus management software and the specific software packages (designed by the CEA) enabled:

- . automatic management of the measurement apparatus,
- . recording of the data,
- . expressing of the measurements of potential with respect to the chosen reference electrode,
- . rapid viewing of all the impedance measurements taken on a given sample,
- . point-by-point calculation of the rate of apparent corrosion corresponding to the polarization resistance measured,
- . and, finally, the creation of files compatible with the graphics software used to plot and present the curves.

Procedure and results of trials

These trials were carried out in a mobile laboratory near the Melun l'Almont geothermal station.

The silica film was applied to the new or corroded samples by a precise method involving no use of actual geothermal fluid. The coating method involved a first stage when the sodium silicate solution was prepared, and a second stage when this solution circulated continuously in a closed circuit, in contact with the new or corroded metal samples, for the time it took to deposit a significantly thick film of silica.

At the start of the test, the geothermal fluid was let into the two modules simultaneously. After roughly two hundred hours in operation, circulation was halted and Module 1, containing the previously treated steel samples, was isolated. The corroded samples in Module 2 were now treated. After this halt, which lasted about a hundred hours, the geothermal fluid was again circulated through both modules. The experiment was halted roughly 1,500 hours after the initial immersion.

During the experiment, the temperature varied between 50° and 70°C depending on the operating conditions of the geothermal station.

Measurements of potential (on all the samples) and polarization resistance R_p (on samples 0 to 10) were taken every four hours. Electrochemical impedance was measured between two sequences. A complete cycle therefore lasted 44 hours.

Figure 36 shows the recordings of potential and R_p on the samples in both modules, throughout the duration of the experiment.

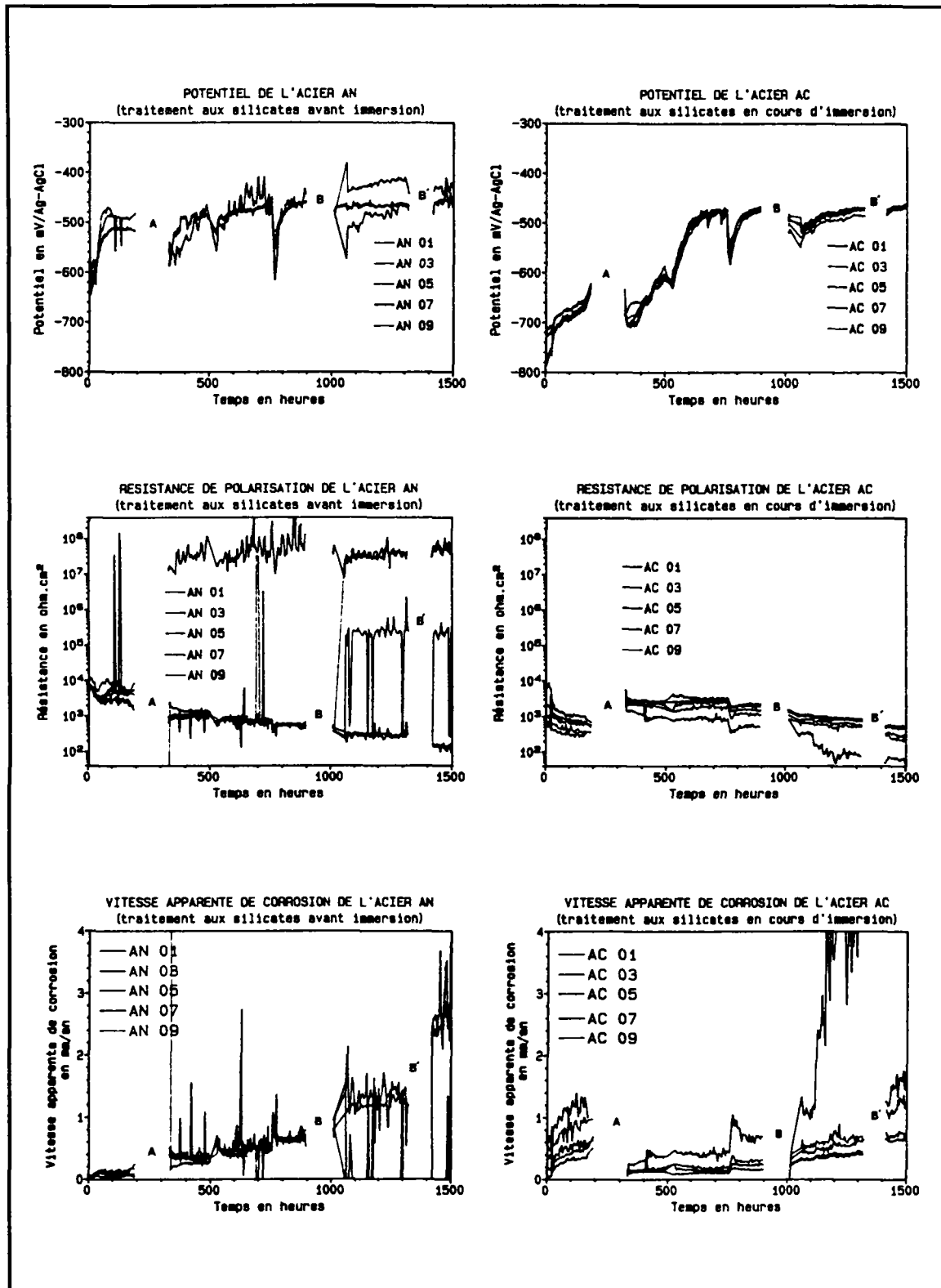


Figure 36 - Trends in potential, polarization resistance and rate of corrosion of the samples - A: interruption for treatment of AC samples; B, B': measurement apparatus halted.

The relation between instantaneous rate of corrosion and polarization resistance can generally be expressed by the formula $de/dt = ke(1/R)$. If de/dt is the loss of thickness per unit of time in mm/yr and R is polarization resistance in ohm.cm², several series of measurements taken in the geothermal stations (Plante G., 1990abc) give a value in the region of 360. Figure 36 shows the evolution of the ratio of de to dt (calculated using this coefficient), for steels AC and AN. We would emphasize that this ratio gives an apparent rate of corrosion which needs to be confirmed by gravimetric measurements, since these are new conditions, of which our experience is not yet sufficient to allow firm conclusions to be drawn.

Between 0 and 200 hours, the potential of the treated samples was about 200 mV higher than that of the untreated samples. Their rate of corrosion, as evaluated from polarization resistance, remained significantly slower than that of the second batch. After about 200 hours of immersion, the same treatment was applied on site to samples that were not treated at the onset, while the other samples were left in the now static fluid. When circulation began again, about a hundred hours later, the initially treated samples seemed to have lost all the benefit of treatment. The freshly treated samples, by contrast, now corroded less quickly than before. The rate of corrosion then increased in most of the samples, of both types. On weighing at the end of the experiment (1,500 hours, i.e. roughly two months), all the samples showed considerable loss of mass, corresponding to an average loss, in terms of thickness, of around 1 mm a year. From Table 13 one can compare the calculated losses of mass by integrating the curves of Figure 36 with the actual, measured loss of mass at the end of the experiment, after desquamation. The correlation between the electrochemical measurements and the gravimetric measurements is poor: the estimate is far below the reality, and the very high polarization resistance observed in some AN steels is not reflected in a slower rate of corrosion. Under these conditions, it is difficult to express the rate of corrosion at each moment of the experiment in quantitative terms. The electrochemical measurements do, however, show that the treatment has a protective effect, which would not be observable from the final weighing alone.

Average of the rate of corrosion (mm/year)		
Sample n°	From weight loss measurement	From measurement of the polarization resistance
MODULE N°1		
AN01	1.46	0.8 ± 0.2
AN03	1.25	0.3 ± 0.1
AN05	1.09	0.8 ± 0.2
AN07	0.87	0.03 ± 0.01
AN09	1.28	0.3 ± 0.1
MODULE 2		
AC01	1.67	1.6 ± 0.5
AC03	1.56	0.5 ± 0.1
AC05	1.28	0.4 ± 0.1
AC07	1.57	0.3 ± 0.1
AC09	1.62	0.3 ± 0.1

Table 13 - Comparison of electrochemical and gravimetric measurements

The fact that the AC samples were more severely corroded cannot be attributed to additional corrosion during the experiment. According to the measurements taken from the samples treated in the laboratory, the loss of metal during the experiment was in the region of a few milligrams for a plate from which the corrosion loss in terms of mass was around 2 grammes.

The random and very sudden way in which the very high values for polarization resistance appeared in samples AN03, AN07 and AN09 prompted us to examine the electrochemical impedance measurements.

There were three types of impedance diagram:

- Type I (impedance lower than 3 Kohm.cm², never inductive, cf. Figure 37). Examples: AN03 62h, 393h, 875h; AN07 146h; AC07 122h, 361h, 493h, 645h, 799h, 887h, 1205h; AC10 745h. This was encountered, alternating with Type II, on all the samples except those showing a very strong polarization resistance.
- Type II (impedance below 3 kohm.cm², apparently inductive for frequencies of more than kHz, cf. Figure 38). Examples: AN03 349h, 545h; AN05 58h, 783h, 1097h; AN07 10h; AC07 113h.
- Type III (impedance above 3 kohm.cm², never inductive, cf. Figure 39). Examples: AN03 1101h, 1149h, 1433h; AN07 581h, 713h, 1069h, 1141h. This type is observed only on steels AN03, 07 and 09, after various periods of immersion (see Figure 36 showing polarization resistance).

It often happens that curves of types I and II are to be seen one after the other on the same sample. In this case, the low frequency loop (right) is common to the two NYQUIST diagrams, which are continued to the left by a loop (type I) or by an almost vertical section (type II). If one compares the various Type I diagrams for one sample, one can see that the real component at 10 kHz does not remain constant but diminishes over time, as does the diagram as a whole.

It will be noted that, to establish BODE diagrams, one can calculate the module of Z using the imaginary component unchanged, whereas one subtracts from the real component its particular value at 10 kHz.

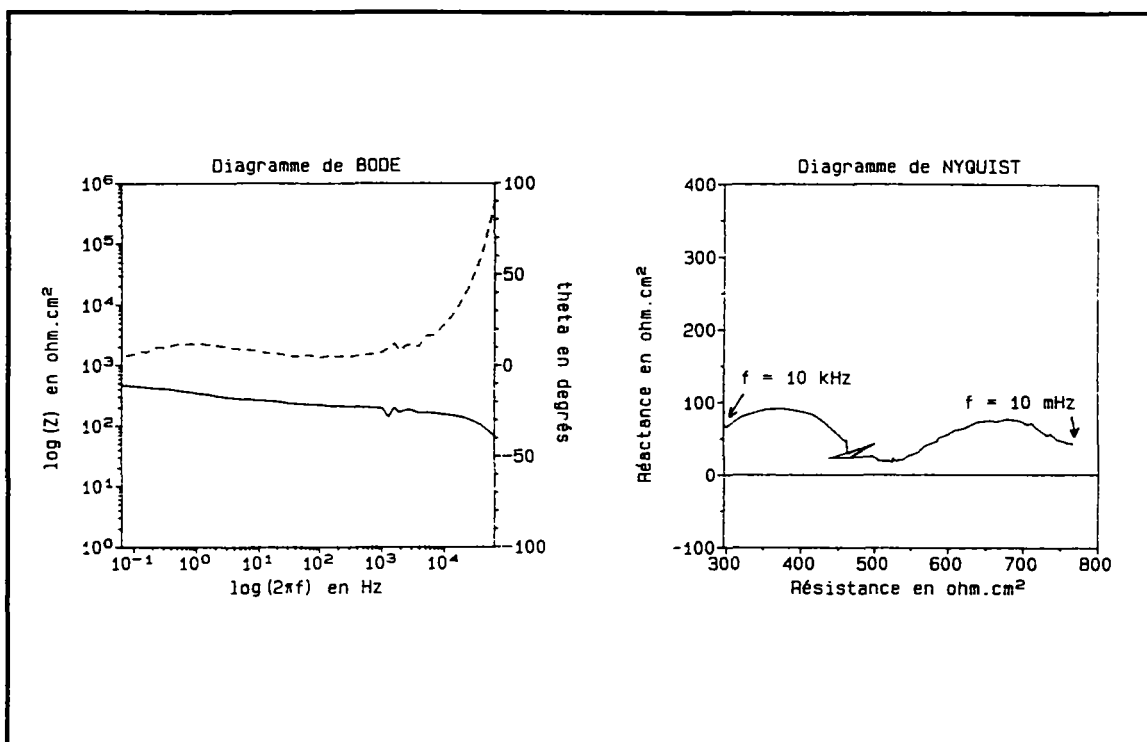


Figure 37 - Type I impedance (AC07 steel, 122h of immersion)

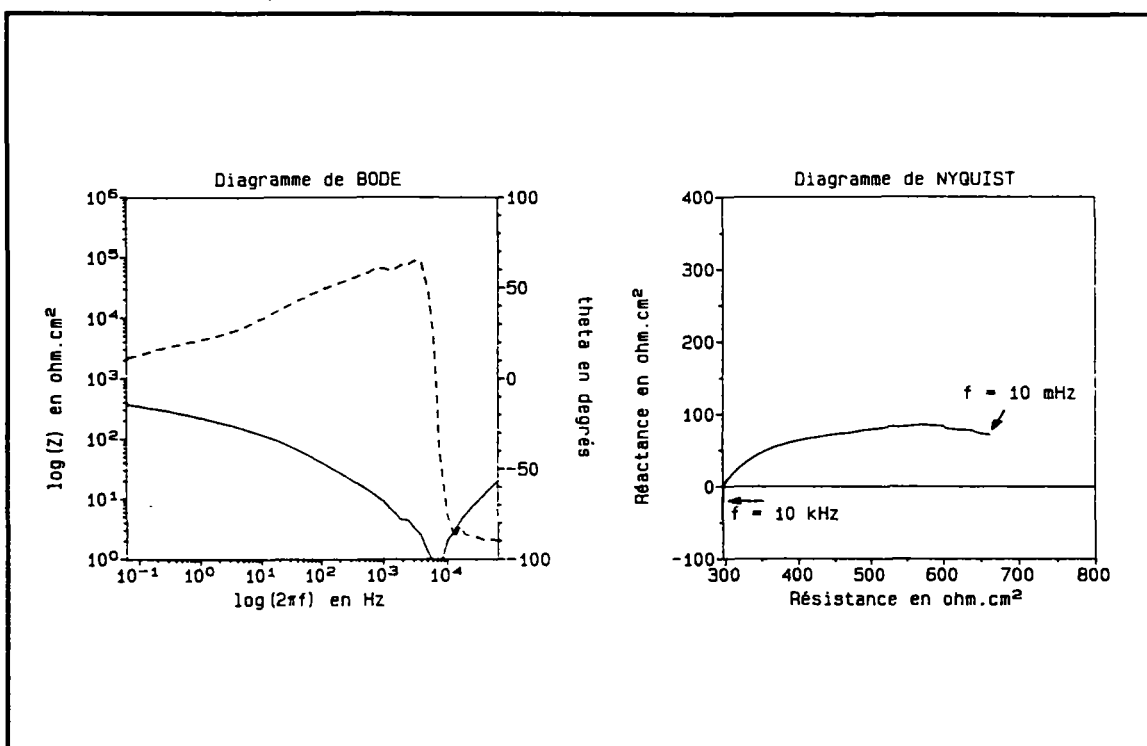


Figure 38 - Type II impedance (AN03 steel, 545h of immersion)

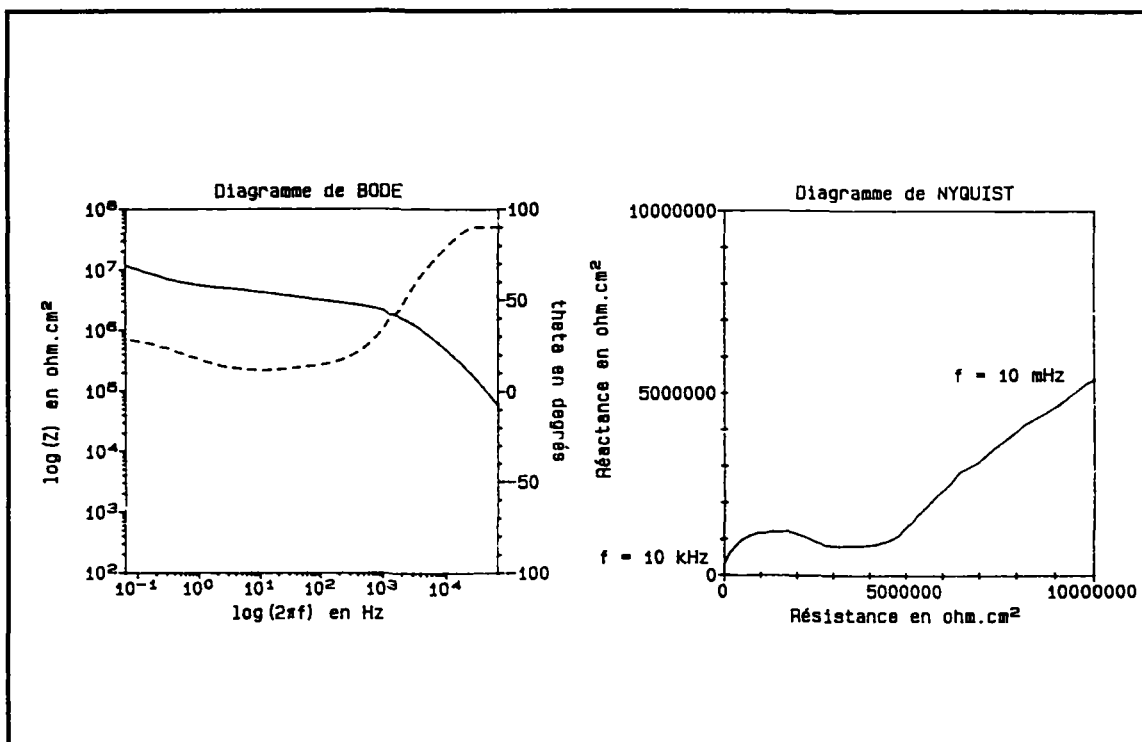


Figure 39 - Type III impedance (AN07 steel, 713h of immersion).

Comparing the NYQUIST diagrams of one type obtained from the same sample in the course of the experiment, one can see that the components of the impedance are quite clearly proportionate for all frequencies. For a relatively uniform corrosion, it is generally considered that the real component at a high frequency is quite close to the resistance of the electrolyte and does not change when the rest of the diagram varies. On the diagrams obtained from Fontainebleau one can see, for example, values of 40 to 60 ohm.cm² (with reference to the geometrical surface area of the sample) whichever diagram one considers. The proportionality observed in the present experiment therefore requires explanation.

The "electrolyte resistance" corresponds to the fall in the ohms which the measuring current produces in the solution between the sample and the reference. Where the corrosion is well distributed and the electrodes are far enough apart, the fall should depend, for a given geometry, on the electrolyte alone. Nor should it be affected by a change of surface area due to a change in surface texture. By contrasts, if the corrosion is very localized, the corresponding current takes a relatively narrow pathway through the neighbouring liquid and the resistance of the electrolyte results, to a large extent, from the resistance of this section. Thus each point of corrosion appears as a tiny electrode with which a portion of the electrolyte is associated. In this situation, the development of a limited number of fresh corrosion points leads to NYQUIST diagrams which are smaller, but are almost proportional to the preceding ones, including in the part corresponding to the electrolyte resistance.

In the case of these samples, therefore, it seems that the accumulation of iron sulphides completely distorted the electrochemical measurements. It must be remembered that these sulphides are conductive and can form a screen between the sample and the electrodes used to take the measurements, just as a metal mesh connected to the sample would do. Thus corrosion of the metal can continue without the electrochemical measurements revealing it. Moreover, an examination of the impedance diagrams proves that the corrosion is very localized on most of the samples, as is otherwise confirmed by examination using optical and scanning microscopes. So no quantitative relationship can be established between the polarization resistance and the rate of corrosion, as can be done in the case of relatively uniform corrosion.

The curves in Figure 36 nonetheless provide some information which, though not quantitative, allows an appreciation of the general trend in the rate of corrosion of the samples (apart from the three exceptions identified above). Weighing indicates that, in its present form, the treatment does not give satisfactory results. However, the apparent rate of corrosion as seen from the curves shows that the treatment does have a positive effect, and that it remains effective for a certain length of time after application. The possibility of using electrochemical methods to monitor the rate of corrosion in real time has enabled us to show the protective effect of a new treatment, even though this effect is not durable under the conditions of this experiment.

These on-site trials using metal samples show that the protection provided by the silica treatment is not as good as under laboratory conditions, that the coating kinetics are acceptable, but that the un-coating kinetics are not acceptable. All of these results will be presented in a thesis by Mme Berthille Le Dinh Bao (Le Dinh Bao B., 1993) and in a BRGM report (Ignatiadis I. and Le Dinh Bao B., 1992) .

4. CONCLUSIONS

The various modules of the contract were carried out over a period of about 30 months (March 1990 to October 1992).

The objective of our study of corrosion and scaling in the geothermal wells was to understand these mechanisms. The corrosion was measured (between 0.4 and 0.9 mm/year) using electrochemical and gravimetric methods and these techniques are now used by plant operators. Further work will deal with the determination of processes involved in under scale corrosion and iron sulphide scale growth.

This work will allow us to develop a model of scaling phenomena more complete than the one presented here. The current code models only the formation of mackinawite (the main iron sulphide in Dogger geothermal doublets) on the well wall. The solubility of the mackinawite, studied by the CEA (the thermodynamic and kinetic constants are necessary for modelling), cannot be determined in all temperature ranges because of its instability under operating conditions. The kinetics and precipitation of other main scale products (FeCl_2 , FeCO_3) must now be integrated into the code.

We originally planned to sample fluid from the well bottom in order to gain a better knowledge of the characteristics of the fluid aquifer and its role in corrosion and scaling in geothermal wells.

We are now finally able to do a well bottom sampling of the fluid of the Dogger aquifer with the new well bottom sampler (PRINPIMO). Its design took longer than expected because of problems with some systems for water- an air-tightness. A patent was registered in March 1992. The use of a composite tube to sample fluid is validated: one geothermal artesian well (of the five in the Paris basin) was equipped with a whole composite tube for injection of inhibitor in the well bottom.

We therefore have a better knowledge of the characteristics of geothermal fluids in the aquifer, in particular, that the dissolved iron concentration in this fluid is higher than expected (iron in equilibrium with the pyrite in the reservoir matrix) and the increase in dissolved sulphide concentrations was determined to be caused by bacterial activity in the well and in the aquifer near the well bottom. These facts allow plant operators to better interpret fluid analysis results. The isotopic methods which we used (sulphide $^{34}\text{S}/^{32}\text{S}$ ratio) allow a more accurate measurement of bacterial activity than bacteria cell counting in the fluid.

Five main studies were carried out to determine the optimal conditions for the elimination of the causes of corrosion and scaling.

a) The first study deals with the optimization of the use of the organic corrosion inhibitors. Criteria for the choice of these inhibitors and methods for determining the quantity required in geothermal fluid were defined. These methods are now used for the supervision of corrosion inhibitor injection systems.

The organic inhibitors currently being used in the Paris basin have no chemical effect on the iron sulphide scales. They were shown to be less efficient on iron recovered by scale than on new iron. Therefore, a thorough cleaning of the wells is a prerequisite for efficient use of the inhibitor when it is injected at the bottom of the production well. Further work must be done to determine the ability of the corrosion inhibitor to protect iron covered by scale and evaluate the risks of pitting corrosion caused by the presence of an organic inhibitor.

We studied the long term effects of inhibitor injection on the aquifer. The behaviour of the Dogger reservoir near the injection well when cooled fluid treated with corrosion inhibitor is reinjected is the combined result of two antagonistic phenomena: improved permeability due to dissolution of calcite and clogging by the amines in the inhibitor. Tests carried out show (a) the value of ensuring a more uniform flow when injecting the inhibitor into the geothermal water in order to reduce the risk of clogging of the near-by reservoir upon reinjection and (b) the value of carrying out percolation tests before introducing a new inhibitory into a geothermal system.

Further work must now determine (by electrochemical methods) the risk of pitting corrosion using these inhibitors and their ability to protect iron covered by scale.

b) The second study deals with the processes for cleaning iron sulphide scale from well walls and especially the chemical cleaning system. The latter gave good results in the laboratory when it is used simultaneously with hydrochloric acid and an organic inhibitor. An article has been published in the G.R.C. proceedings (San Diego, 1992).

c) The third study deal with the chemical elimination of dissolved sulphides in the fluid. We have demonstrated the faisability of the use of hydrogen peroxyde (with catalyst). Economic conditions, however, make this treatment unfeasible in the Paris basin geothermal wells. This study could nevertheless be the starting point for the use of these processes to treat high enthalpy geothermal fluids or fluids at the surface prior to their disposal.

d) A feasibility study for the use of solid organic inhibitors placed at the bottom of the well (by gravity), to be carried out by ARMINES, was not successful. The manufacturer of the inhibitor was not able to produce the product originally planned because of specification restrictions.

e) The fifth study deals with the faisability of using a mineral inhibitor (mainly, sodium silicate). The principal is to create a permanent protective film and thus avoiding the need to lower an injection device to the bottom of the well. First, in the laboratory, we conceived a method to simulate as closely as possible actual geothermal conditions. The anti-corrosion effect of the silica films obtained under these laboratory conditions was sufficient to merit on-site experiments. During the on-site experiment, the possibility of using electrochemical methods to monitor the corrosion rate in real time has enabled us to show the protective effect of the treatment (not as good as under laboratory conditions), even though this effect is not durable enough to justify a development of their use.

These results were presented at the IMRG annual meetings to which geothermal companies are invited. IMRG annual reports and some study reports (appendix 4) have also been sent to them in order to spread the information. Eight publications in international meetings have been made (appendix 5).

5. REFERENCES

- AMALHAY M. et IGNATIADIS I. (1992) - Etude de la corrosion en milieu geothermal du Bassin parisien : Historique, état actuel et perspectives. Rapport BRGM n° R 36054 IRG SGN 92, 120 p.
- AULAS F., RUMEAU M., TYBURGE B. (1983) - Sciences et Techniques de l'Eau, Vol. 16, n° 3, 261-274.
- AVRAHAMI M., GOLDING R.M. (1968) - J. Chem. Soc. (A), 647-651.
- BOISDET A., IGNATIADIS I., LONGIN G., FOUCHER J.C., BRACH M., CZERNICHOWSKI I., LAFFORGUE M., DETOC S., LE DINH BAO B. (1990) - Connaissance et exploitation du Dogger du Bassin parisien - Exploitation du réservoir : Rapport annuel d'activités 1990. Institut Mixte de Recherches Geothermiques, BRGM/ADEME, Orléans, France, pp. 19-36.
- BOISDET A., IGNATIADIS I., FOUILLAC C., BRACH M., FOUCHER J.C., PAUWELS H., DETOC S., LE DINH BAO B. (1989) - Connaissance et exploitation de réservoirs géothermiques : Dogger du Bassin parisien. - Rapport annuel d'activités 1989. Institut Mixte de Recherches Geothermiques, BRGM/AFME, Orléans, France, pp. 13-26.
- BONIS M., CROLET J.L. (1990) - Les bases de la prévision des risques de corrosion par CO₂ dans les puits de pétrole et de gaz. Matér. Tech., 78, n° 7-8, pp. 3-10.
- BONIS M., CROLET J.L. (1985) - La véritable nature de la corrosion des aciers dans les puits de pétrole et de gaz, et les mécanismes correspondants. Matér. Tech., 73, n° 2-3, pp. 55-64.
- BONIS M., CROLET J.L. (1984) - pH measurements under high pressures of CO₂ and H₂S. Mater. Perform., pp. 35-42.
- BONIS M., CROLET J.L. (1984) - Mesures de pH sous hautes pressions de CO₂ et H₂S. Mét. Corr. Ind., 59, n° 701, pp. 16-27.
- BONIS M., CROLET J.L. (1982) - Le rôle des ions acétates dans la corrosion par CO₂. Mét. Corr. Ind., 57, n° 685, pp. 681-694.
- BONIS M., CROLET J.L. (1981) - Mesure du pH des solutions aqueuses de CO₂ sous haute température et haute pression. Mét. Corr. Ind., 57, n° 675-676, pp. 361-374.
- CASTELAS B., RUMEAU M., COT L., GUIZARD C., ALLARDY J.A. (1984) - FILTRA 84, Société Française de Filtration, Paris.

CHERADAME J.-M., IGNATIADIS I. (1990) - Traitement bactéricide des puits géothermiques par mise en place d'un fluide traité durant un arrêt d'exploitation. Rapport 90 CFG 03, Janvier 1990, CFG - IMRG, pp.50.

COMPAGNIE FRANÇAISE POUR LE DEVELOPPEMENT DE LA GEOTHERMIE ET DES ENERGIES NOUVELLES (CFG) (1990) - Démonstration de la fiabilité des méthodes électrochimiques pour le suivi de la corrosion en géothermie. Rapport final projet CCE n° GE-81/87 Fr., 3 Volumes.

CZERNICHOWSKI-LAURIOL I. (1988) - Modélisation de l'évolution des fluides géothermaux lors de leur exploitation par forages, document BRGM n° 159, 196 p.

CRIAUD A., FOUILLAC C., MARTY B. (1989) - Low enthalpy geothermal fluids from the Paris basin : 2 - Oxidation-reduction state and consequences for the prediction of corrosion and sulphide scaling. Geothermics, Vol. 18, n°5.

CROLET J.L., BONIS M. R. (1990) - An optimized procedure for corrosion testing under CO₂ and H₂S gas pressure., Mater. Perform., 90 n° 29, pp. 81-86.

CROLET J.L. (1990) - Electrochimie de la corrosion sous dépôt de corrosion, Mét. Corr. Ind., 64, n° 764, pp. 91-106.

CROLET J.L. (1988) - Mécanismes de la corrosion uniforme sous dépôt de corrosion, Mét. Corr. Ind., 63, n° 757, pp. 279-302.

CROLET J.L., BONIS M.R. (1988) - Optimization de la conduite d'un essai de corrosion sous pression de CO₂ et H₂S., Mem. Etud. Sci. Rev. Metall., 85 n° 7-8, pp. 375-386.

CROLET J.L., BONIS M.R. (1986) - A tentative method for predicting the corrosivity of wells in new CO₂ fields. Materials Performance, 26, n° 3, pp. 41-49.

CROLET J.L., BONIS M.R. (1983) - pH measurements in aqueous CO₂ solutions under high pressure and temperature., Corrosion, 38 n° 2, pp. 39-46.

CROLET J.L. (1983) - Acid corrosion in wells (CO₂, H₂S) : metallurgical aspects. J. Pet. Technol., 35, n° 9, pp. 1553-1558.

CROLET J.L. (1980) - Présentation des phénomènes de corrosion et des différents moyens de lutte disponibles., Bull. Cent. Rech. Explor.-Prod., Elf-Aquitaine, 4 n°1, pp. 179-203.

DAUMAS S., GOYENECHE O. et BIANCHI A. (1985a) - Activités métaboliques des bactéries des eaux géothermales du Dogger et du Trias du Bassin Parisien. C. R. Acad. Sc. Paris, t. 301, Série III, N°6, pp. 295-297.

DAUMAS S., LOMBART R. et BIANCHI A. (1985b) - A Bacteriological study of Geothermal Spring Waters Dating from the Dogger and Trias Period in the Paris Basin. Geomicrobiology Journal, Vol.4, N°4, pp. 423-433.

DAUMAS S. (1986) - Corrosion bactérienne en géothermie à basse température. Mécanismes de corrosion par les bactéries sulfato-réductrices. Thèse, Université de Provence, Aix-Marseille I, 118 p.

DETOC-KARIMI S., FALGUERE P., FOUCHER J.C. PERSIN F. and IGNATIADIS I. (1991) - Use of Cross-Flow microfiltration for the elimination of the sulphur produced by oxydation of dissolved sulphides in a geothermal brine. Communication *in* the Second International Conference on Inorganic Membranes, July 1-4, 1991 à Montpellier, France.

DETOC-KARIMI S., FALGUERE P., FOUCHER J.C. PERSIN F. and IGNATIADIS I. (1991) - Use of Cross-Flow Microfiltration for the elimination of the sulphur produced by oxydation of dissolved sulphides in a geothermal brine. Proceedings of the Second International Conference on Inorganic Membranes, ICIM2'91, July 1-4, 1991, Montpellier, France. ED. Trans Tec Publications, Switzerland, Inorganic Membranes ICIM2'91. Engeneering Materials, Vol. 61-62 1991 pp.561-564.

DETOC-KARIMI S. (1990) - Thèse d'Université de Montpellier II - BRGM/IMRG. Traitement des fluides géothermaux du Dogger (Bassin parisien, France) par oxydation chimique des sulfures dissous et microfiltration tangentielle, 257 pp., December 1990.

DE WAARD C., MILLIAMS D.E. (1975) - Carbonic acid corrosion of steel., Corrosion, 31 n°5, pp. 177-181.

DORE M. (1989) - Chimie des oxydants et traitement des eaux. Editions Lavoisier, Tec et Doc, Paris, 504 p.

DUKE F.R. (1959) - Mechanisms of oxydation - reduction reactions in "Treatise of Analytical Chemistry", Part I, Vol.1, Kolthoff & Elving, Editions Interscience, pp. 629-660.

EL GHOUL G. (1991) - Contribution à l'évaluation des performances des silicates de sodium comme inhibiteurs de la corrosion des aciers doux en milieu géothermal. Conditions de mise en oeuvre des films et contrôle de l'efficacité apportée contre la corrosion. Rapport de stage de fin d'études de la Maîtrise de Chimie de l'Université d'Orléans. Institut Mixte de Recherches Géothermiques - BRGM/AFME, Septembre 1991, 69 p.

ELLIS P.E. (1981) - A geothermal corrosivity classification system. Geothermal Resources Council, TRANSACTIONS, Vol. 5, pp. 463-466.

FALGUERE P. (1990) - Rapport de stage d'ingénieur ISIM, Université de Montpellier II - BRGM/IMRG. Etude de la faisabilité technique en géothermie du procédé de microfiltration tangentielle sur membrane minérale, couplé ou non à l'oxydation des sulfures, pp.80, June 1990.

FOUILLAC C., FOUILLAC A.M., CRIAUD A. (1990) - Sulphur and oxygen isotopes of dissolved sulphur species in formation waters from the Dogger geothermal aquifer, Paris Basin, France. Applied Geochemistry Vol. 5, N° 4 p. 415-427.

FOUILLAC C., CRIAUD A., HONEGGER J.L., CZERNICHOWSKI-LAURIOL I. (1989) - Sulphide deposition and well clogging in the Dogger aquifer of Paris Basin (France). European Geothermal Update, Florence, (Italie), Avril 1989, EEC Contract n° EN3G - 0033-F.

FOUILLAC C., FOUILLAC A.M., CRIAUD A., IUNDT F., ROJAS R. (1986) - Isotopic studies of oxygen hydrogen and sulfur in the Dogger aquifer from Paris Basin. Proceedings of the 5th Inter. Symposium on Water-Rock Interaction, Reykjavik, pp. 201-205.

FRIEDMAN H.L., KERKER M., J. (1953) - Colloid. Sci., Vol. 8, 80-87.

GALAJ S., WICKER A., DUMAS J.P., GILLOT J., GARCERA D. (1984) - Le lait, Vol. 64, 129-140.

GOURMELON C., BOULEGUE J., MICHARD G. (1977) - C.R. Acad. Sc. Paris, Vol. 284, série C, 269-284.

HARISSON A.G., THODE H.G. (1958) - Mechanism of bacterial reduction of sulphate from isotope fractionation studies. Trans. Faraday Soc. Vol. 54, p.84-92.

HONNEGER J.L., TRINEAU H., CRIAUD A., SAINSON S. (1989) - Comportement des matériaux métalliques en environnement géothermal basse enthalpie, Bassin Parisien, France Rapport Final Contrat EN3G-0038F. Rapport BRGM SGN IRG n° 625, pp.138.

HONNEGER J.L. et al (1986) - Expertise dans le domaine de la corrosion et optimisation des matériaux de l'exploitation géothermique. Rapport annuel de l'IMRG 1986.

IGNATIADIS I., AMALHAY M., LAFFORGUE M. (1992a) - Corrosivité du fluide géothermal vis-à-vis de l'acier au carbone neuf ou précorrodé en absence et en présence d'inhibiteur de corrosion. Rapport BRGM n° R 36056 IRG SGN 92, 106 p.

IGNATIADIS I. et TETON S. (1992) - Assessment of the chemical action of different agents on the iron sulphides constituting the scale formed by corrosion of carbon steels in geothermal environments. Geothermal Ressources Council Transactions, Vol.16, pp. 357-363.

IGNATIADIS I., ABOU AKAR A. (1992) - Prélèvement d'échantillons de fluide géothermal en fond de puits de production au moyen du préleveur de fond PRINPIMO 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. (1992b) - 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.

IGNATIADIS I., LE DINH BAO-GOUBERT B. (1992) - Evaluation des performances des silicates de sodium comme inhibiteurs de la corrosion des aciers doux en milieu géothermal. Conditions de mise en oeuvre des films et contrôle de l'efficacité apportée contre la corrosion. Rapport BRGM n°34512 IRG SGN 92, à paraître.

IGNATIADIS I., DETOC-KARIMI S., FALGUERE P., FOUCHER J.C. (1992c) - The use of Cross-Flow microfiltration for the determination of solid suspended matter concentration and for the elimination of the sulphur produced by oxydation of dissolved sulphides in a geothermal brine. Proceedings of the Euromembranes 92, October 5-8, 1992 à Paris, France, in Récents progrès en Génie des procédés, Membranes Processes, P. AIMAR and P. APTEL Editors (Lavoisier Press), N°21, Vol.6, pp. 141-146.

IGNATIADIS I., DETOC-KARIMI S., FALGUERE P., FOUCHER J.C. (1992d) - The use of Cross-Flow microfiltration for the determination of solid suspended matter concentration and for the elimination of the sulphur produced by oxydation of dissolved sulphides in a geothermal brine. Communication in Euromembranes 92, October 5-8, 1992 à Paris, France.

IGNATIADIS I. (1992) - Use of the ratio ^{34}S and ^{32}S isotopes in sulphides and sulphates at different flowrates to confirm current bacterial activity in the well exploiting the Paris Basin Dogger aquifer. Paper submitted to J of Isot. Geosci., 1992).

IGNATIADIS I. et POLICE O. (1991) - Méthodes de dosage d'agents tensio-actifs organiques utilisés comme inhibiteurs de corrosion en géothermie. Rapport BRGM n° R 35517 SGN 91.

IGNATIADIS I., TETON S., LAFFORGUE M. (1991a) - Evaluation de l'action de différents produits chimiques sur les dépôts des sulfures de fer et sur l'acier au carbone en milieu géothermal partiellement reconstitué. Rapport BRGM n°33946 IRG SGN 91, 103 p.

IGNATIADIS I., TETON S., LAFFORGUE M. (1991e) - Evaluation de l'action d'un inhibiteur organique de corrosion sur les dépôts des sulfures de fer en milieu géothermal reconstitué et réel. Rapport BRGM n°33945 IRG SGN 91, 90 p.

IGNATIADIS I., CHERADAME J.M., LAFFORGUE M., CASTAGNE S. (1991c) - Evolution des teneurs en sulfures dissous dans les fluides géothermaux. Rapport BRGM n° 33518 IRG SGN 91, 160 p.

IGNATIADIS I., AMALHAY M., LAFFORGUE M. et BRACH M. (1991b) - Dosage des sulfures et mercaptans dissous dans les fluides géothermaux du Dogger du bassin parisien. Rapport BRGM n° R 33488 IRG SGN 91, 59 p.

IGNATIADIS I., FOUCHER J.C. and FALGUERE P. (1991f) - Determination of the solid suspended matter concentration in geothermal brine by cross-flow microfiltration using mineral membranes. Communication in the Second International Conference on Inorganic Membranes, July 1-4, 1991 à Montpellier, France

IGNATIADIS I., CHERADAME J.-M., BRACH M., CASTAGNE S., GUEZENNEC J. (1990b) - Reduction by biocide treatment of hydrogen sulphide concentration in a geothermal brine. In "Microbially influenced corrosion and biodeterioration". Ed. N.J. Dowling, M.W. Mittelman, J.C. Danco. Proceedings of the International Congress on "Microbially Influenced Corrosion" Knoxville USA 7-12 october 1990, section 8, pp 33-36.

IGNATIADIS I., BRACH M., LE DINH BAO B., LAFFORGUE M. (1990a) - Suivi journalier physico-chimique d'hiver et d'été de fluides géothermaux du Dogger du Bassin Parisien. Rapport BRGM n° R 31928 IRG SGN 90, 77 pages.

IGNATIADIS I., LAFFORGUE M. (1990) - Suivi physico-chimique de l'eau géothermale produite lors d'une opération de nettoyage d'un puits par la nouvelle méthode hydraulique de "Jetting". Note Technique n° 90/209 IRG SGN, 50 pages.

IGNATIADIS I., BRACH M. (1989) - Prélèvement par le tube de traitement en fond de puits (TTFP) sur le puits de production du boulet géothermique du BLANC MESNIL (GBMN-1). Compte rendu de la mission du 19 au 22 septembre 1989, INSTITUT MIXTE DE RECHERCHES GEOTHERMIQUES, BRGM/AFME, Orléans, France, 13 pages.

IKEDA A., MUKAI S., UEDA M. (1985) - CO₂ corrosion behaviour of carbon and Chromium steels., The Sumitomo Search, 31, pp. 91-102.

IKEDA A., MUKAI S., UEDA M. (1984) - Proc. Intern. Corro. Forum. Corrosion 84., New Orleans, Paper n°289, (NACE).

IKEDA A., MUKAI S., UEDA M. (1983) - Proc. Intern. Corro. Forum. Corrosion 83., Anaheim, Paper n°45, (NACE).

KAPLAN I.R. (1975) - Stable isotopes as a guide to biogeochemical processes. Proc. R. Soc. London, Ser. B, Vol. 189, p.183-211.

KAPLAN I.R., RITTENBERG J.C. (1964) - Microbiological fractionation of sulfur isotopes, J. Gen. Microbiol., Vol. 34, p.195-212.

KEMP A.L.W., THODE H.G. (1968) - The mechanism of the bacterial reduction of sulphate end of sulfite from isotopes fractionation studies. Geochim. Cosmochim. Acta, Vol. 32 p. 71-91

KROUSE H.R. (1980) - Sulfur isotopes in our environment in P. Fritz and J.C. Fontes (Editors) Handbook of environmental isotope geochemistry, Vol. 1, p.445-471.

LANE R.W., LARSON T.E. NEFF C., SCHILSKY S.W. (1973) - Materials Performance, 12, 32.

LE DINH BAO B., IGNATIADIS I. (1992) - Anti-corrosion treatment of a carbon steel using sodium silicate to deposit a silica film. Analysis of films by photo-electron spectroscopy (ESCA). Article soumis pour publication in the Proceedings of the 6th International conference on intergranular and interphase boundaries in materials, June 21-26, 1992, Thessaloniki, Greece. Trans Tech Publications Ltd in Materials Science Forum.

LE DINH BAO B. (1991) - Préparation d'un dépôt de silice par les silicates de sodium sur l'acier au carbone en milieu géothermal synthétique et réel. Etude des conditions de création du film, caractérisation du film et évaluation de la cinétique de fixation et de disparition du film et de la protection apportée contre la corrosion.- Thèse de Doctorat Univ. de Paris VI - BRGM/AFME, mars 1993, 250 p.

LERHMAN L., SHULDENER H.L. (1952) - Ind. Eng. Chem., 1952, 44, 1765.

LUGANOV V.A., SHABALIN V.I. (1985) - 15th Congrès international de minéralurgie, (CR), pp. 31-39.

MAURICE M.J. (1975) - Analytica Chimica Acta, Vol.16, 574-577.

MORSE J.W., MILLERO F.J., CORNWELL J.C., RICKARD D. (1987) - The chemistry of the hydrogen sulphide and iron sulphide systems in natural water, Earth Science Reviews, 24, pp. 1-42.

NACE Standard RP07-75, National Association of Corrosion Engineers, Houston, Texas, 1975.

NEUMANN F.K., CARIUS W. (1959) - Arch. Eisenhüttenw., 30, p. 283.

OUZOUNIAN G., CASTAGNE S., FOUILLAC C. et CRIAUD A. (1987) - L'origine du fer dans les eaux géothermales exploitées au Dogger (Bassin Parisien). Géothermie Actualités, Vol.4, N°3, pp. 31-34.

PLANTE G. (1990c) - Mesure en ligne des vitesses de corrosion dans une centrale géothermique traitée par inhibiteur. Commissariat à l'Energie Atomique, Rapport final de la Convention SAF GEOTHERMIE/CEA n° BC 5883 bd, Rapport technique R.T. SCECF.202 (octobre 1990) 29 p.

PLANTE G. (1990b) - Mise en oeuvre d'un dispositif pour la mesure en ligne de l'efficacité des inhibiteurs de corrosion dans une centrale géothermique. Commissariat à l'Energie Atomique, Rapport final de la Convention AFME 8.07.0018, Rapport technique R.T.SCECF.174 (janvier 1990) 25 p.

PLANTE G. (1990) - Démonstration de la fiabilité des méthodes électrochimiques pour le suivi de la corrosion en géothermie. Commissariat à l'Energie Atomique, Rapport technique SCECF.183 (mars 1990) 68 p.

POUND B.G., WRIGHT G.A., SHARP R.M. (1985) - Electrochemical phases diagrams for the iron/sulfur/water under geothermal conditions. Australian Journal of Chemistry, Vol. 38 (5), pp. 643-657.

RAMANARAYANAN T.A., SMITH S.N. (1990) - Corrosion of iron in gaseous environments and in gas saturated aqueous environments., Corrosion, 46, n°1, pp. 66-74.

RICKARD D. (1989) - Experimental concentration-time curves for the iron (II) sulphide precipitation process in aqueous solutions and their interpretation, Chemical Geology, 78, pp. 315-324.

ROZANOVA E.P. and KHUDYAKOVA A.I. (1974) - A new nonspore-forming thermophilic sulphate-reducing organism, Desulfovibrio thermophilus. Nov. Sp. Microbiology (Eng.Transl.) N°43, pp. 908-912.

ROZENFIELD I.L. (1981) - Corrosion Inhibitors, McGraw-Hill, New York.

SAINSON S. and HONNEGER J.L., (1987) - Interprétation de la diagrhpie électromagnétique ETT.D (An interpretation of ETT.D electromagnetic logging). Rapport BRGM N° 681 SGN IRG.

SASTRI V.S. PACKWOOD R.H. (1987) - Werkstoffe und Korrosion, 38, 77.

SHULDENER H.L., SUSSMAN S. (1960) - Corrosion, 16, 126.

TEWARI P.H., BAILEY M.G., CAMPBELL A.B. (1979) - The erosion-corrosion of carbon steel in aqueous H₂S solutions up to 120°C and 1.6 MPa pressure, Corrosion Science, 19, pp. 573-585.

WERES O., TSAO L. (1983) - Reaction of hydrogen sulphide with oxygen in the presence of sulfite. Report of the Lawrence Berkeley Laboratory L.B.L-11377, 76 p.

ZAISER E.M., LA MER V.K. (1984) - J. Colloid. Sc., Vol. 3, 571-598.

6. LIST OF THE FIGURES

Figure 1: Concentration profiles of Fe^{2+} , H^+ and A^- in the diffusion layer (Crolet J.L, 1988).

Figure 2: Flow chart 1 - TPDEGAZ model
Figure 15: Flow Chart 2 - Module of variation of temperature or pressure in a closed system

Figure 3: Flow Chart 2 - Module of variation of temperature or pressure in a closed system

Figure 4: Concentration profiles of Fe^{2+} , H^+ and A^- in the proposed model

Figure 5 : Flow chart of the iron input from corrosion

Figure 6: Flow Chart 3 - MODEP coupled to TPDEGAZ ("* ":Only after (3) and (4))

Figure 7: pH versus fluid pressure

Figure 8: Comparison of pH computed by MODEP and TPDEGAZ

Figure 9: Log Ω (mackinawite) versus well depth

Figure 10: Casing radius versus well depth at different exploitation times and without diffusion layer - from 0 to 2000 m and "zoom" from 0 to 400 m.

Figure 11: Casing radius after 2.9 years versus well depth of exploitation time. The different curves account for 3 thickness for the diffusion layer (DL) - from 0 to 2000 m and "zoom" from 0 to 400 m.

Figure 12: Plan of the down hole fluid sampler "PRINPIMO"

Figure 13: Total dissolved salt (TDS) in geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

Figure 14: Dissolved iron concentration in the geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

Figure 15: Total iron concentration in geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

Figure 16: Dissolved iron flux in the geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

Figure 17: Total iron flux in the geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

Figure 18: Dissolved sulphide concentration in geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

Figure 19: Dissolved sulphide flux in geothermal water at 4 wellheads in the East and South of the Paris Basin plotted against: a: flowrate; b: the reciprocal of the flowrate.

Figure 20: Dissolved sulphide and $\delta^{34}\text{S}(\text{HS}^-)\text{‰}_\text{T}$ in the geothermal water at 3 wellheads, in the East and South of the Paris Basin, plotted against the reciprocal of the flowrate.

Figure 21: Dissolved sulphate and $\delta^{34}\text{S}(\text{SO}_4^{2-})\text{‰}_\text{T}$ concentrations in the geothermal water at 3 wellheads in the East and South of the Paris Basin, plotted against the reciprocal of the flowrate.

Figure 22: Description of systems S1 (aquifer) and S2 (production well and near aquifer).

Figure 23: $\delta^{34}\text{S}(\text{HS}^-)\text{‰}_\text{T}$ and $\delta^{34}\text{S}(\text{SO}_4^{2-})\text{‰}_\text{T}$ at different flowrates in the geothermal water at 3 wellheads, in the East and South of the Paris Basin, plotted against the dissolved sulphide concentrations.

Figure 24 - Rate of corrosion - V_{cor} - (recorded with a corrosion probe using the polarization resistance method) as a function of length of time exposed to the geothermal fluid in Fresnes:
a - untreated (no inhibitor injected)
b - treated (inhibitor concentration 7 mg/l)
c - treated (concentration 7 or 13 mg/l) after 15 or 80 minutes prior exposure to untreated fluid.

Figure 25: Percentage of weight loss with respect to the initial weight of scale against concentration of hydrochloric acid and hydrogen peroxide.

Figure 26: Corrosion rate of carbon steel and raw scale in the presence of 0.02 M HCl and various concentrations of Solamine 129® at 70°C and one atmosphere.

Figure 27: Oxidation time and percentage plotted against: a) pH; b) the ratio $[H_2O_2]/[H_2S]$; c) the catalyst used.

Figure 28: Simplified scheme of the experimental CFM pilot

Figure 29: Comparison of the variation in the flow density of the permeate. Raw and oxidized fluid; v = cross flow rate (m/s), a: Flow density of the permeate J (l/(h.m²)); b: Normalized flow density of the permeate $100 \cdot J/J_0$ (l/(h.m²))

Figure 30: Efficiency of the chemical cleaning of the membrane. Raw Fluid.

Figure 31: Influence of the frequency of declogging. Oxidized fluid.

J = flow density of the permeate (l/(h.m²)),
 $100 \cdot J/J_0$ = normalized flow density of the permeate (l/(h.m²))

Figure 32: Corrosion rates in $\mu\text{m/y}$ of carbon steel for 6 electrochemical cell tests in aqueous solution containing 35 g/l NaCl and 0 or 100 ppm sulphides and an inhibiting agent; at pH 6.5, temperature 70°C and pressure 1 bar.

Figure 33: Corrosion rates of carbon steel in aqueous solution containing 35 g/l NaCl and 100 mg/l sulphides in presence and absence of sodium silicates at pH 6.5, temperature 70°C and pressure 1 bar.

Figure 34: ESCA analysis of a sample treated with sodium silicates. Variation of peaks for Fe (Fig.34a), S (Fig.34b) and Si (Fig.34c) against erosion time (IS - initial surface, 10 mn, 2 h and 3 h; erosion approx. 2 nm/mn). Fig.34d shows the recomposition of the Si peak at 10 mn time of erosion.

Figure 35: Layout and functions of the samples: working electrodes (W), "reference" electrodes (R), auxiliary electrodes (A). Measurement of potential: distance from arrow base to tip. Modules: silica-based treatment (1) prior to immersion, (2) during immersion.

Figure 36: Trends in potential, polarization resistance and rate of corrosion of the samples - A: interruption for treatment of AC samples; B, B': measurement apparatus halted.

Figure 37: Type I impedance (AC07 steel, 122h of immersion)

Figure 38: Type II impedance (AN03 steel, 545h of immersion)

Figure 39: Type III impedance (AN07 steel, 713h of immersion).

7. LIST OF THE TABLES

Table 1: Corrosion rates of coupons immersed for 3 months in the production well.
c.c : crevice corrosion, u.c : uniform corrosion.

Table 2: Iron and dissolved sulphides concentrations : comparison between the analysis and the modelling by MODEP

Table 3: Iron and dissolved sulphides concentrations : comparison between the analysis and the modelling by MODEP

Table 4: Sulphide and sulphate concentrations and $\delta^{34}\text{S}(\text{HS}^-)\text{‰}_\text{T}$ and $\delta^{34}\text{S}(\text{SO}_4^{2-})\text{‰}_\text{T}$ in the geothermal water at 3 wellheads in the East and South of the Paris Basin, at the flowrates indicated.

Table 5: Résultats of the percolation trials in Fontainebleau (1990).

Table 6 : Résultats of percolation trials in Cachan (1990).

Table 7: Composition, in weight %, of scale sample No.1, from the Cergy Pontoise (Paris Basin, France) geothermal production well.

Table 8: Dissolution and/or oxidation of scale by hydrochloric acid (with or without glyoxal) and by hydrogen peroxide alone.

Table 9: Composition in weight % of steel XC38 (0.38 % C and 98.673 % Fe).

Table 10: Action of hydrochloric acid on a carbon steel and a scale in the presence of a surfactant (Solamine 129 ®).

Table 11: Conditions of the procedure and determination of SSM concentration in a geothermal brine by Cross-Flow Microfiltration

Table 12: Chemical oxydation process costs

Table 13: Comparison of electrochemical and gravimetric measurements

APPENDIX 1

CEA REPORT

SOLUBILITY OF MACKINAWITE

COMMISSARIAT A L'ÉNERGIE ATOMIQUE
DIRECTION DES TECHNOLOGIES AVANCÉES
CENTRE D'ÉTUDES ET DE RECHERCHES
SUR LES MATÉRIAUX
DÉPARTEMENT DE TECHNOLOGIE
DES MATÉRIAUX
Service de la Corrosion, d'Électrochimie
et de Chimie des Fluides
Section d'Étude de la Corrosion Aqueuse

Date : 17 septembre 1992
N° interne : SECA-92/401
Fiche action n° 7741 43000
Client : BRGM
Commande n° JOUG-0005-c(ebd)
Equipe élémentaire : LEPC
Nombre de pages : 26

Rapport technique SCECF.268 (Septembre 1992)

SOLUBILITY OF MACKINAWITE

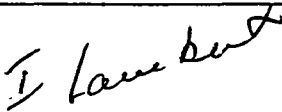
Programme joule PL 0042

Final report

I. LAMBERT

"Les informations contenues dans ce document ne sont pas destinées à la publication. Il ne peut en être fait état sans l'autorisation expresse du contractant".

Ce travail a été effectué avec la participation, pour la partie expérimentale,
de P. L'HENORET, S. LEAL et P. GERLINGER
La réalisation et l'interprétation des diagrammes de diffraction X ont été effectuées
par Ph. OLIVIER et C. MALLET (SCECF/SECNAU)

VISAS	NOMS	SIGNATURES	DATES
Rédacteur	I. LAMBERT		21/9/92
Chef de Section	G. SANTARINI		21/9/92
Chef de Service	G. PINARD LEGRY		21/9/92

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 2

DESTINATAIRES

BRGM

M. BRAY

(2 ex.)

SUMMARY

Solubility measurements were performed on mackinawite from 25°C to 200°C. The results at 25°C were in good agreement with literature data in acidic medium. In neutral and slightly basic medium, the solubility becomes very low and the concentration measured corresponds to the presence of colloids. The mackinawite was found unstable at higher temperatures. The rate of transformation into greigite was probably enhanced by the storage in air before use. The stability appears higher when the pH increases.

KEY WORDS:

- GEOTHERMAL PLANTS
- MACKINAWITE
- SOLUBILITY
- SULPHIDES

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 4

CONTENTS

	<u>Page</u>
1 - INTRODUCTION and BACKGROUND	5
2 - EXPERIMENTAL	6
2.1 - Experimental device	6
2.2 - Materials	6
2.3 - Procedure	6
2.3.1 - <i>Glass device</i>	6
2.3.2 - <i>Autoclave</i>	7
2.3.3 - <i>Iron analysis</i>	7
2.3.4 - <i>Sampling and analysis of the solid phase</i>	7
2.4 - Tests performed	7
2.5 - Evaluation of H ₂ S molality in solution	8
2.6 - Evaluation of pH in autoclave	8
3 - RESULTS	9
3.1 - Nature of the solid phase	9
3.2 - Variation of solubility with pH and H ₂ S concentration	9
3.3 - Variation of measured concentrations with temperature	10
4 - DISCUSSION	14
5 - CONCLUSION	15
REFERENCES	17
FIGURES	19

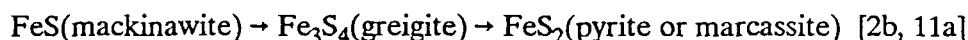
DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 5

1 - INTRODUCTION and BACKGROUND

Mackinawite, $\text{Fe}_{(1+x)}\text{S}$, although not thermodynamically stable, is one of the main corrosion products formed in sulphide-rich geothermal water, especially in the "bassin parisien". In order to predict its deposition, it is necessary to obtain information on its solubility.

Mackinawite is a tetragonal iron sulphide, whose structure can be regarded as consisting of cubic close-packed sulphur lattice with iron in half of the tetrahedral holes, the larger octahedral holes being empty, which enables accommodation of excess cations [1]. Its formula is near from $\text{Fe}_{1.06}\text{S}$.

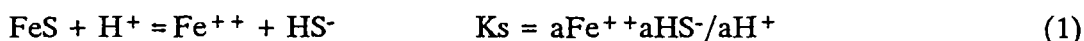
In aqueous H_2S solutions, this compound is unstable with respect to pyrite (FeS_2), which is the thermodynamically stable sulphide, and the evolution towards the stable form takes place through the sequence:



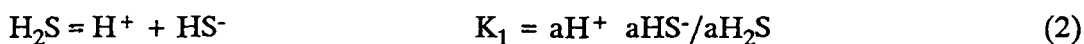
Nucleation of FeS_2 is a very slow process, and either mackinawite or greigite is found in natural sediments, their relative stability being a function of the temperature, H_2S pressure, and redox conditions of the medium [3, 4]. The first corrosion product of iron by H_2S in anaerobic conditions is mackinawite [5].

Several papers are devoted to mackinawite evolution towards stable sulphides, but due to its instability, few data on the solubility are available. The measurements were performed at room temperature, under an H_2S pressure of 1 atm [6, 7], at different pH and ionic strengths. Some data [7] were obtained at 120°C, but were not considered as reliable due to the rapid transformation of mackinawite in these conditions.

The results of these two studies are reported on Fig. 1, in terms of iron concentration as a function of pH. If the solubility equilibrium is written:



this equation combined with:



leads to the relation:

$$K_s = [\text{Fe}^{++}] \gamma_{\text{Fe}^{++}} a_{\text{H}_2\text{S}} K_1 / (a_{\text{H}^+})^2 \quad (3)$$

and $\text{Log}[\text{Fe}^{++}]$ should, if $\gamma_{\text{Fe}^{++}}$ remains approximatively constant, show a linear variation with pH with a slope equal to - 2. It can be seen that Berner's data fit well this relation, but that Tewari's data, although of the same order of magnitude, are more scattered and that the slope is lower (about - 1.4).

We tried to perform measurements in the temperature range 25-200°C with a systematic check of the nature of the solid phase after each experiment.

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 6

2 - EXPERIMENTAL

2.1 - Experimental device

Two devices were used:

- 1) A glass device, suitable for temperatures lower than 100°C.
- 2) A titanium autoclave, convenient to perform experiments at higher temperatures, without any risk of pollution by iron.

The two systems are schematically represented on figure 2.

Both contain:

- a stirring device;
- a gas inlet and outlet;
- a tube equipped with a frit, for liquid sampling;
- a cooling tube on the liquid sampling line in the case of autoclave tests.

A glass electrode for pH measurement is placed in the glass device.

2.2 - Materials

- The preparation of mackinawite was reported previously [8]. It was maintained several months in a desiccator placed in a refrigerator. It was checked, before use, by X-Ray diffraction. The presence of α S was detected beside mackinawite, as well on the samples just prepared as after storing. It was not possible to analyse it quantitatively.
- Hydrogen sulphide, pure or diluted in nitrogen, was provided by the "Air Liquide" company (Alphagaz N27).
- Sodium hydroxide and sulphuric acid were Merck products.

2.3 - Procedure

2.3.1 *Glass device*

The solution was deaerated by nitrogen bubbling during one night, before introducing the mackinawite, under nitrogen atmosphere. H_2S bubbling was then started immediately and, after saturation, maintained at a low flow rate during the test.

The pH was continuously measured by a conventional glass electrode, the reference being a calomel electrode at room temperature. The pH electrode is calibrated before each experiment at the test temperature. When the pH became stable, we waited 5 minutes more before taking successively two samples. The equilibration time varied from 15 to 30 minutes.

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 7

Sampling was performed by closing the valve V and so pushing the liquid through the frit (n° 3) in the flask F. The liquid is then immediately filtered by aspiration through two filters in series (porosity 0.45 and 0.22 μm). Filtration through a filter of porosity 0.1 μm was not possible because of the high pressure drop of the filter.

2.3.2 - Autoclave

The solution, deaerated in the same manner, was pumped into the evacuated autoclave which already contains the dry mackinawite. The autoclave was then connected to the H_2S bottle and the solution saturated at 1 atm at ambient temperature. The autoclave was then heated to the desired temperature.

In this case it was not possible to detect the equilibrium by following the pH, so three samples were taken successively, the first one as soon as the temperature reached its level, the two others half-an-hour and one hour later. The samples were taken through the titanium frit (porosity 1 μm) without further filtration.

2.3.3 - Iron analysis

After acidification of the sample, iron concentration was analysed by colorimetry of the complex formed with tripyridyl-triazine. This method allows the analysis of Fe at concentrations down to 1 $\mu\text{g/kg}$.

2.3.4 - Sampling and analysis of the solid phase

In both experimental devices, at the end of the test, nitrogen was bubbled during about half an hour in order to evacuate H_2S before opening the apparatus, and the solid was quickly filtered and rinsed with water, then with alcohol. It was analyzed by X-Ray diffraction after each experiment.

2.4 - Tests performed

The tests were performed in the following conditions:

1) In glass device

Temperatures: 25 - 30 - 50 - 90°C.

Solutions: Water saturated with:

a) H_2S at total pressure = atmospheric pressure.

b) $\text{H}_2\text{S}/\text{N}_2$ mixture (10% H_2S) at total pressure = atmospheric pressure.

Different pH were obtained by addition of sodium hydroxide or sulphuric acid to the solution. In some cases, buffers were used. Some preliminary experiments, reported previously [9], were not taken into account, the experimental conditions having been improved since then. They will nevertheless be mentioned in the discussion.

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 8

2) In autoclave

Temperatures: 90 - 150 - 200°C.

Solution: NaOH 0.1 N saturated with H₂S at room temperature (21°C) before closing of the autoclave.

2.5 - Evaluation of H₂S molality in solution

We used the relation [9]:

$$\ln x = -24.912 + 3477.1/(T/K) + 0.3993 \ln(T/K) + 0.0157(T/K)$$

with x = molar fraction of H₂S in solution in equilibrium with an H₂S pressure of 1 atm, i.e., as dilute solutions are involved:

$$m_{H_2S}(\text{mol.kg}^{-1}) = 55.55 \times p = S p$$

S being the solubility, expressed as molality and p the partial pressure of H₂S in atmospheres calculated in the following way:

a) In glass device:

p = atmospheric pressure - vapour pressure of water at the experimental temperature.

b) In autoclave:

Pressure is calculated by mass balance

$$N = N(\text{liq}) + N(\text{gas}) = V_L \rho_L p S + V_G p/RT$$

at the filling temperature and at the test temperature, with:

N = moles of H₂S introduced in autoclave;

V_L = liquid volume;

ρ_L = density of the solution (assimilated to pure water);

V_G = gas volume.

2.6 - Evaluation of pH in autoclave

In the case of autoclave experiments, where no direct measurement is possible, it is evaluated by combining the dissociation equation of hydrogen sulphide:

$$a_{HS^-} a_{H^+} / a_{H_2S} = K_1$$

$$pK_1 = -98.08 + 5765.4/(T/K) + 15.0455 \ln(T/K) \quad [11]$$

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 9

with the electroneutrality condition:

$$2[\text{Fe}^{++}] + [\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HS}^-]$$

and the dissociation equilibrium of water :

$$a_{\text{H}^+} a_{\text{OH}^-} = K_w$$

3 - RESULTS

The results, expressed in terms of Fe concentration as a function of pH, H₂S molality, and temperature, are gathered on tables I to VII, and on figures 3 to 5.

3.1 - Nature of the solid phase

At 25°C, we always found mackinawite as solid phase after the experiments, accompanied in all cases by αS, in more or less important amount, as was found in the initial product.

At 30°C, for pH ≥ 5.5, mackinawite was found stable during the time of the experiment. For the lower values of pH, X-ray analysis showed the presence of a mixture of mackinawite and greigite. The behaviour was about the same at 50°C. After one hour at 50°C, pH 3.9, marcassite was observed beside greigite. During the first series of measurements [9], solid analysis were performed after much longer residence time, 4 to 5 hours. In this case the same solid phases were found at 30°C as in the present case, but at 50°C, if mackinawite was always the solid phase at pH 7, at pH 4.5 the transformation into pyrite was complete.

At 90°C traces of mackinawite remained at the highest pH, but the main products are greigite and marcassite. In two special tests, mackinawite was maintained one day in water saturated with H₂S, and the X-ray analysis showed in this case a complete transformation into pyrite.

At 150°C, only greigite and marcassite were found.

At 200°C, no sulphide was present anymore. The X-ray analysis displayed only hematite Fe₂O₃.

In summary, the stability of mackinawite is observed to decrease with decreasing pH and increasing temperature.

3.2 - Variation of solubility with pH and H₂S concentration

♦ Results at 25°C

At this temperature, number of solubility measurements are available, in a rather wide range of pH and for two H₂S concentrations. If we try to reduce the results to the same concentration mH₂S = 0.1 mol.kg⁻¹, by supposing the relation mFe = α/mH₂S, which is expected from the relation (3), we obtain, for pH lower than 5, corrected concentrations m'Fe which vary linearly with pH (except one point, pH = 3.19, which was too low and showed some abnormal experimental behaviour; this point was discarded) (Fig. 7).

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 10

At $\text{pH} > 5.5$, iron concentrations obtained are quasi independent of pH , but seem to be lower at lower H_2S concentration.

♦ *Results at higher temperatures in glass device*

The shape of the variation of solubility with pH is analogous to the one obtained at 25°C . At 30° we observed, in the acidic region, a decrease in solubility with pH increase, but with a slope lower than at 25°C , then a quasi constant value for $\text{pH} > 5$. As the three points obtained in the most acidic conditions are relative to a mixture of greigite and mackinawite the solubility is ill-defined and it is difficult to assess a signification to the value of the slope.

At 50°C , the slope in the acidic region is still lower, for the same reasons as above, amplified by the higher temperature, and we observe even an increase of measured iron concentration at highest pH .

At 90°C no data were obtained in acidic medium, and even in neutral or slightly basic solution, results obtained are relative to greigite. Here again, no trend with pH is observed.

♦ *Results in autoclave (one pH value)*

The concentration obtained at 90°C is much higher than in glass device at the same temperature and pH . $m\text{H}_2\text{S}$ has a higher value, but this must have the opposite effect. This could be due to fine particles of greigite, being formed in greater amount because of the longer residence time allowed. This result is not considered as reliable.

The same remark is valid at 150°C . A point to be noted is the sharp decrease in the iron concentration after 1 hour, which may be related either to a change in solid phase (total disparition of mackinawite?) or to an agglomeration of colloïdal particles making them possible to filter.

3.3 - Variation of measured concentrations with temperature

In the acidic region, the same phase is not obtained at two different temperatures and it is therefore impossible to compare solubilities.

We tried a comparison at $\text{pH} \approx 6.5$, where mackinawite was obtained up to 50°C , the point at 90°C being relative to greigite. The variation is displayed on Fig. 6. A slight, but regular and quite linear decrease in the measured concentrations (which, at this pH , corresponds essentially to colloids) is observed and greigite does not seem to distinguish itself from mackinawite. This may related to an agglomeration of colloïds or a better decantation due to the lower viscosity of water with increasing temperature.

TABLE I

25°C - Pure H₂S

10 ⁴ mFe (mol.kg ⁻¹)	mH ₂ S (mol.kg ⁻¹)	pH	Solid phase (αS always present)
(19) ^(a)	0.101	3.2	Mackinawite
27.5 ± 3.5	0.105	3.59 ^(b)	"
4.75 ± 0.6	0.098	4.16	"
3.5 ± 0,9	0.097	5.27	"
2.97 ± 4x10 ⁻⁶	0.097	6.55	"

^(a)rejected

^(b)pH obtained with a buffer solution.

TABLE II

25°C - Mixture H₂S/N₂

10 ⁴ mFe (mol.kg ⁻¹)	10 ² mH ₂ S (mol.kg ⁻¹)	pH	Solid phase (αS always present)
32.2	0.994	4.09 ^(b)	Mackinawite
18.7 ± 0.2	0.99	4.23	"
2	1.01	5.07	"
1.25 ± 0.05	0.98	6.44	"
2.25 ± 0.35	0.995	7.40	"

^(b) pH obtained with a buffer solution.

TABLE III

30°C - Pure H₂S

10 ⁴ mFe (mol.kg ⁻¹)	10 ² mH ₂ S (mol.kg ⁻¹)	pH	Solid phase (αS always present)
31.1 ± 5	8.81	2.85	Mackinawite + greigite
6.6 ± 0.3	8.92	4.15	
8.8 ± 0.3	8.92	4.17	"
7.7 ± 0.84	8.81	4.26	Mackinawite
2.95 ± 0.04	8.83	5.45	"
3 ± 0.25	8.71	6.00	"
2.9 ± 8x10 ⁻⁶	8.91	6.49	"
3.26 ± 0.24	8.84	6.50	"

TABLE IV

50°C - Pure H₂S

10 ⁴ mFe (mol.kg ⁻¹)	10 ² mH ₂ S (mol.kg ⁻¹)	pH	Solid phase (αS always present)
5.9 ± 0.05	5.57	3.51	Mackinawite + greigite
1.4 ± 0.1	5.65	3.90	Mackinawite + greigite + marcassite ^(c)
2.25 ± 0.05	5.67	5.67	Mackinawite
1.28 ± 0.13	5.57	5.78	Mackinawite
2.15	5.57	6.44	Mackinawite ^(d)
3.22	5.56	6.49	Not analysed
3.1 ± 0.17	5.68	6.49	Mackinawite ^(b)

(c) after 60 minutes in the solution

(d) after 90 minutes in the solution

TABLE V

90°C - Pure H₂S

10 ⁴ mFe (mol.kg ⁻¹)	10 ² mH ₂ S (mol.kg ⁻¹)	pH	Device	Solid phase (αS always present)
1.43 ± 0.03	1.21	5.72	glass	Greigite + εmackinawite + εmarcassite
1.1 ± 0.4	1.22	6.31	glass	Greigite + εmackinawite
1.16 ± 0.04	1.12	6.41	glass	Greigite + εmackinawite
11 ± 0.2	17.6	6.25(e)	autoclave	Greigite

(e)pH evaluated

TABLE VI

Autoclave tests. 150 (± 4)°C (pH evaluated)

Contact time (min)	10 ⁴ mFe (mol.kg ⁻¹)	10 ² mH ₂ S (mol.kg ⁻¹)	pH	Solid Phase
30	11.7	8.5	6.25	Greigite + marcassite? (identification uncertain)
60	11.4			Analysis after 24h in the autoclave
90	5.9			
120	6.2			

TABLE VII

Autoclave tests. 205 (± 4)°C (pH evaluated)

Contact time (min)	10 ⁴ mFe (mol.kg ⁻¹)	10 ² mH ₂ S (mol.kg ⁻¹)	pH	Solid Phase (αS always present)
30	3.4	9.45	6.83	Hematite Fe ₂ O ₃
60	3.4	"	"	Analysis after 24h in the autoclave
90	2.8	"	"	
120	3.2	"	"	

4 - DISCUSSION

Solubility

We consider the experimental points obtained at 25°C, in the acidic region where we observed a linear relationship between Log(mFe) and pH.

On figure 7 are displayed the experimental results, reduced to mH₂S = 0.1 mol.kg⁻¹ by supposing constant the product (mFe⁺⁺ mH₂S), compared to the literature values already cited. We see a good agreement with Tewari's data, the points being a little higher than Berner' data, which fit almost exactly the expected slope - 2.

If we first subtract, from the measured concentration, the value measured at pH > 5.5, i.e. 3 10⁻⁴ mol.kg⁻¹ in pure H₂S solution and 2 10⁻⁴ mol.kg⁻¹ in the dilute H₂S solution, supposed to be an artefact independant of pH, and then reduce the results to mH₂S = 0.1 mol.kg⁻¹, we obtain the solubilities reported on figure 8. It can be seen that the points are, this time, in very good agreement with Berner' data, and both sets together can be fitted by the linear function:

$$\text{Log mFe} = 4.53 - 2 \text{ pH.}$$

This observation confirms that the concentration measured at higher pH is probably due to solid or colloïdal particles, non really participating to the solubility equilibria. Contrary to Berner' data, Tewari's ones present the same artefact. The different behaviour must be related to the preparation method: Berner prepared mackinawite by chemical reaction of H₂S on powdered iron, and transferred it anaerobically to the solubility measurement vessel; we used the same electrochemical preparation method as Tewari, followed by a transfer in air and even, in our case, storage in air (at low temperature) during several months.

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 15

If with our four corrected data at 25°C, we calculate the equilibrium constant K_s by mean or the relation (3):

$$K_s = [\text{Fe}^{++}] \gamma_{\text{Fe}^{++}} a_{\text{H}_2\text{S}} K_1 / (a_{\text{H}^+})^2 \quad (3)$$

$\gamma_{\text{Fe}^{++}}$ being evaluated by the electrostatic term of Pitzer equation [12]:

$$\text{Ln} \gamma = -Z^2 A [I^{0.5} / (1 + I^{0.5}) + (2/1.2) \text{Ln}(1 + I^{0.5})]$$

we find the value:

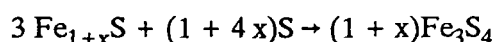
$$\text{p}K_s = 3.45 \pm 0.05$$

The value of $\text{p}K_s$ thus calculated, in agreement with the value 3.6 issued from Berner's data [13], as in agreement with the above hypothesis that the amount substracted, independant of pH, does not take part to the solubility equilibrium. It is probably constituted by fine or colloidal particles of FeS. The reason for an H_2S dependance of their amount is not clear: maybe the colloids are stabilized by a complexation by polysulphide ions (S_4S^{2-}), formed at neutral pH by reaction of S^0 with HS^- [14, 15], which would be a function of H_2S concentration.

Owing to the change in solid phase composition, it is impossible to calculate a solubility constant at higher temperatures.

Stability

Although mackinawite is thermodynamically not stable, it is encountered as metastable species in natural anaerobic conditions, and may be maintained without being decomposed for a longer time as we did. Taylor and al. [2a] observed that contact with air, even for a short time, leads to a superficial oxydation giving rise to S and Fe_3O_4 . Even if Fe_3O_4 is not detectable by X-Ray analysis, mackinawite having been exposed to air reacts easily to form greigite by the reaction:



As we effectively had contact with air and a detectable presence of sulphur, we were in conditions for high transformation rates. The observation that the decomposition rate was higher at lower pH may indicate that the transformation goes through dissolved ions, whose concentration is higher in acidic solution. Another hypothesis compatible with this result would be in neutral solution a complexation of S^0 as polysulphide, which, although being also a possible oxidation agent for greigite formation [16], may lead to a lower transformation rate.

5 - CONCLUSION

We confirmed and precised the results found in the literature on the solubility of mackinawite at 25°C, and its dependance on pH and H_2S concentration. But it was not possible to extend these results to a larger temperature range, because of the unstability of the mackinawite.

Another preparation method, without storage and without any transfer in the air would perhaps have allowed us to obtain results at higher temperature. This would have been a very heavy procedure not

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 16

feasible in the framework of this study. But we have seen that it will be necessary if we want to extend the range of experimental conditions.

We showed the evidence for a relationship between the pH and the transformation rate to greigite but the explanation for that was not proved.

The explanation of other observations (complete oxidation at high temperature) would require a more detailed study.

REFERENCES

- [1] Ward J.C.
Rev.Pure and Appl. Chem. 20, 175, 1970.
- [2] Taylor P., Rummery T.E., Owen D.G.
J. inorg. nucl. Chem., 41, 596, 1979, (a)
J. inorg. nucl. Chem., 41, 1683, 1979 (b).
- [3] Berner R.A.
J. Geology, 72, 826, 1964.
- [4] Berner R.A.
Am. J. Sci, 265, 773, 1967.
- [5] Wikjord A.G., Rummery T.E., Doern F.E., Owen D.G.
Corrosion science, 20, 651, 1980.
- [6] Berner, R.A.(c)
Am. J. Sci., 265, 773, 1967.
- [7] Tewari P.H., Campbell A.B.
Can. J. Chem., 57, 188, 1979.
- [8] Lambert I.
Programme Joule PL 0042
Rapport d'avancement au 1-01-1991.
- [9] Lambert I., Gerlinger P., Leal S.
Programme Joule PL 0042
Progress report on 1-10-1991.
- [10] Fogg P.G.T., Gerrard W.
Solubility of Gases in Liquids
Wiley & Sons, 1990.
- [11] Schoonen M.A.A., Barnes H.L.
Geochim. cosmochem., Acta 55, 1495, 1991 (a),
Geochim. cosmochem., Acta 55, 1505, 1991 (b).
- [12] Silvester L.F., Pitzer, K.S.
J. Phys. Chem., 81, 1822, 1977.
- [13] Davison W.
Solubility Data Series, IUPAC
to be published.

DTA/CEREM/DTM SCECF/SECA	Rapport Technique SCECF.268 (Septembre 1992)	Page 18

- [14] Berner R.A.
Geochim. cosmochem., Acta 27 563, 1963.
- [15] Giggenbach W.
Inorg. Chem., 11, 6, 1201, 1972,
Inorg. Chem., 11, 6, 1724, 1972.
- [16] Wada H.
Bull. chem. Soc. Japan 50 (10), 2614, 1977.

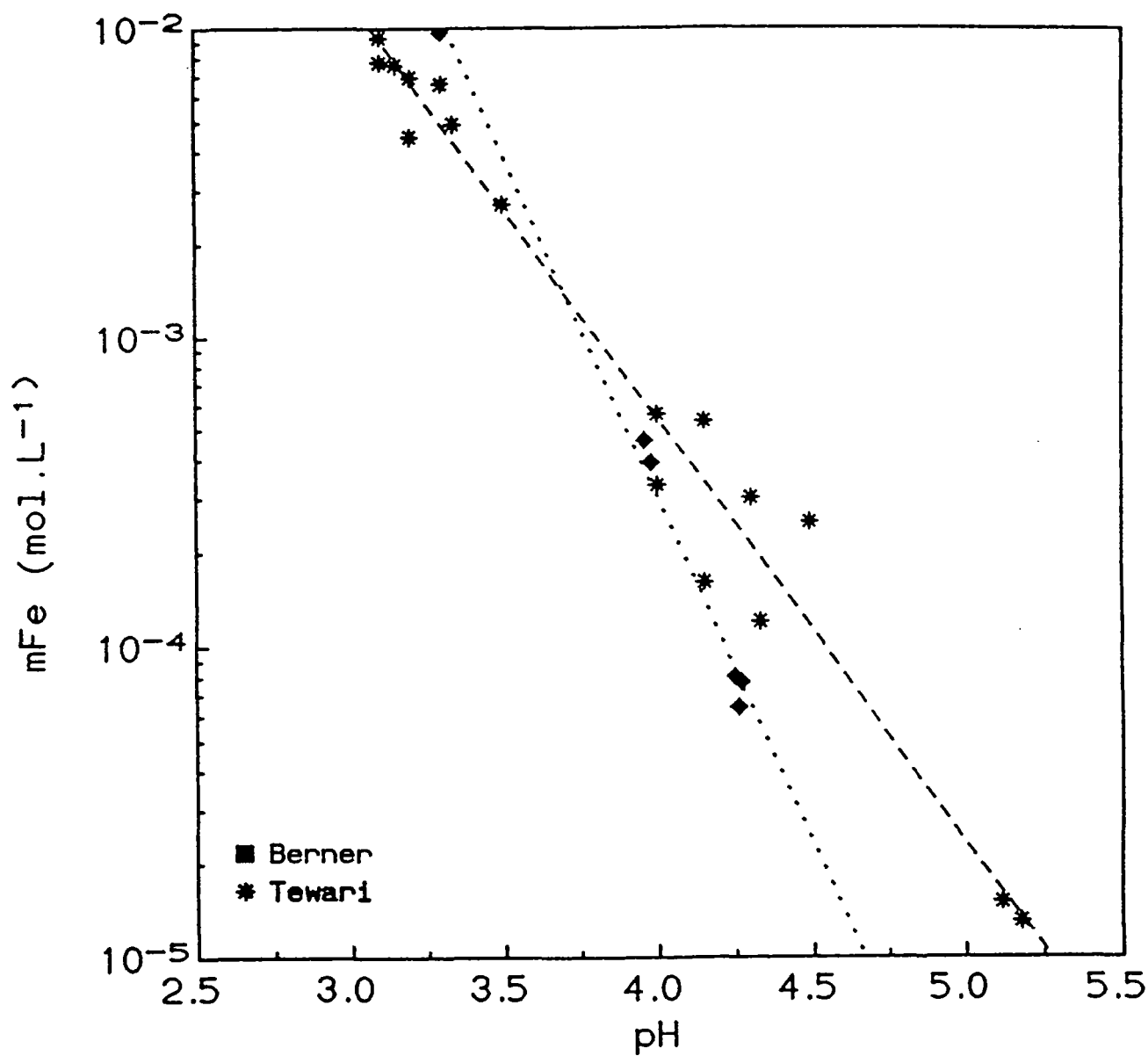
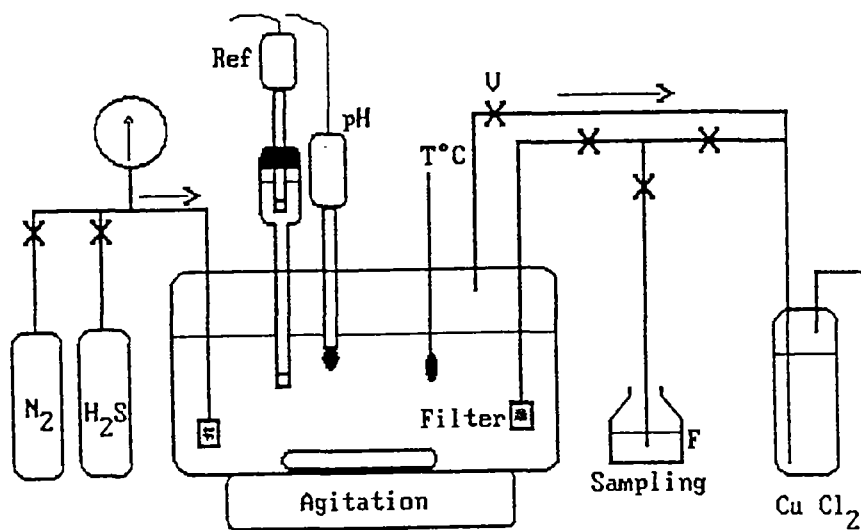
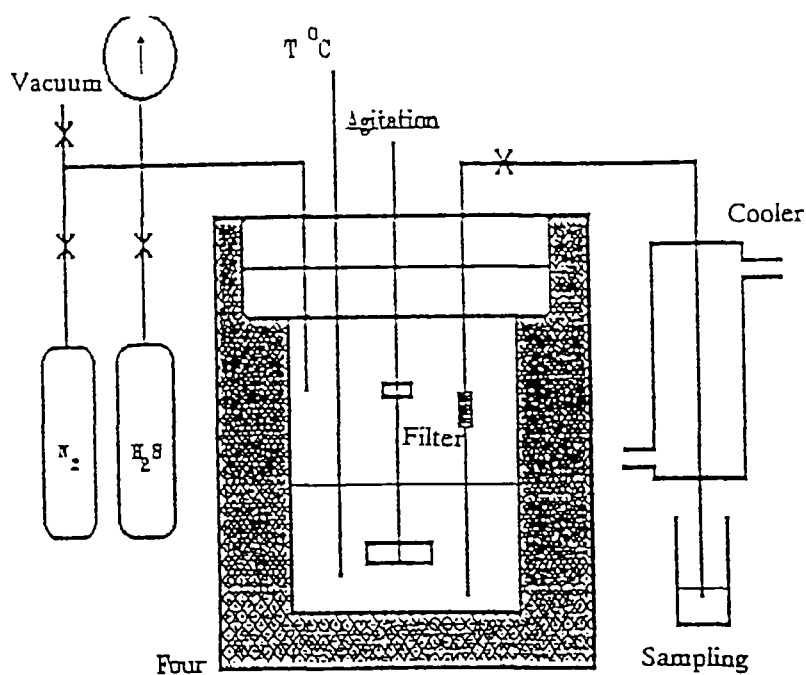


FIGURE 1

Solubility of mackinawite at 25°C
Literature data Berner [6] and Tewari [7]



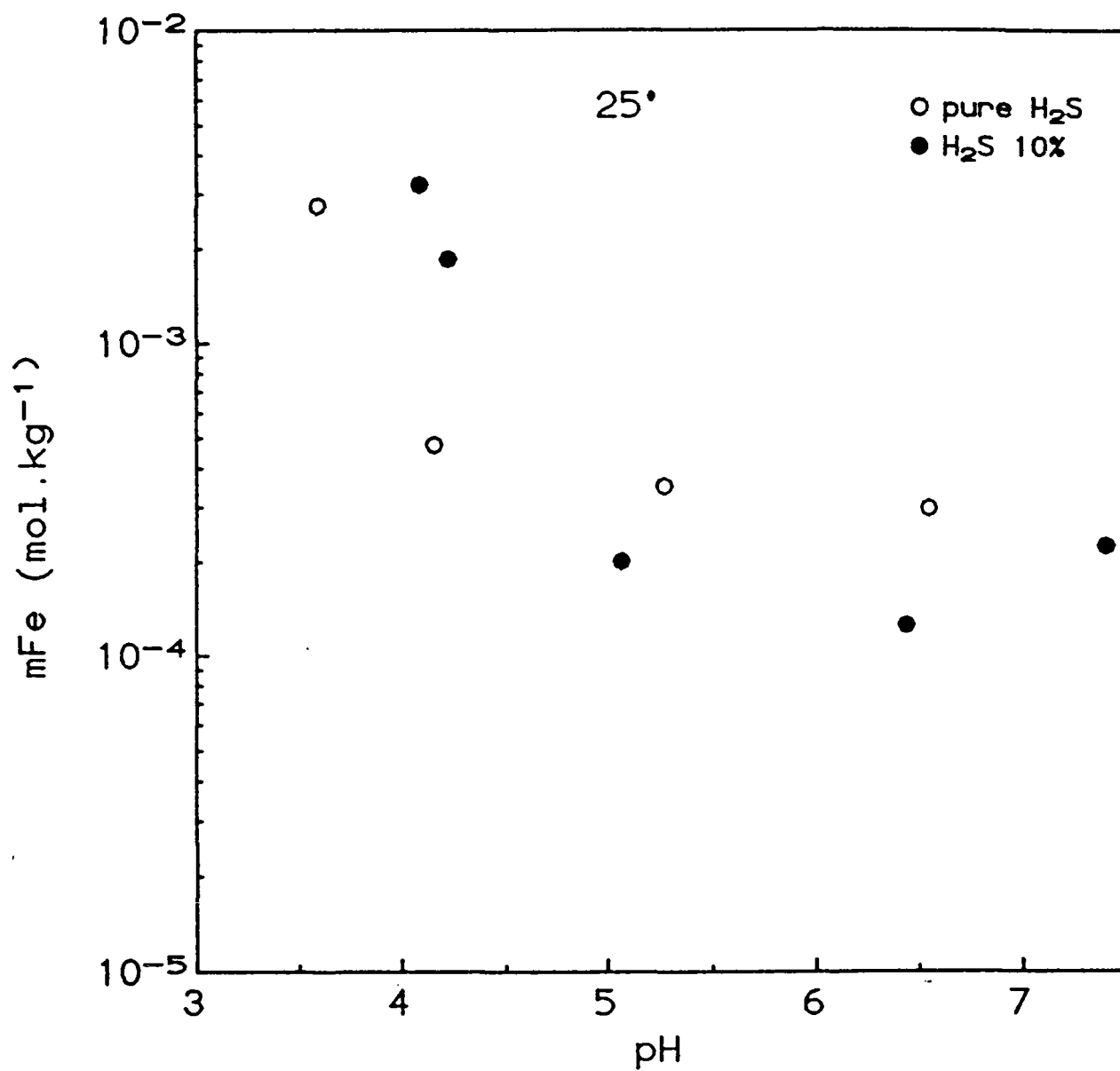
glass device



autoclave

FIGURE 2

Experimental device

FIGURE 3

Experimental results at 25°C

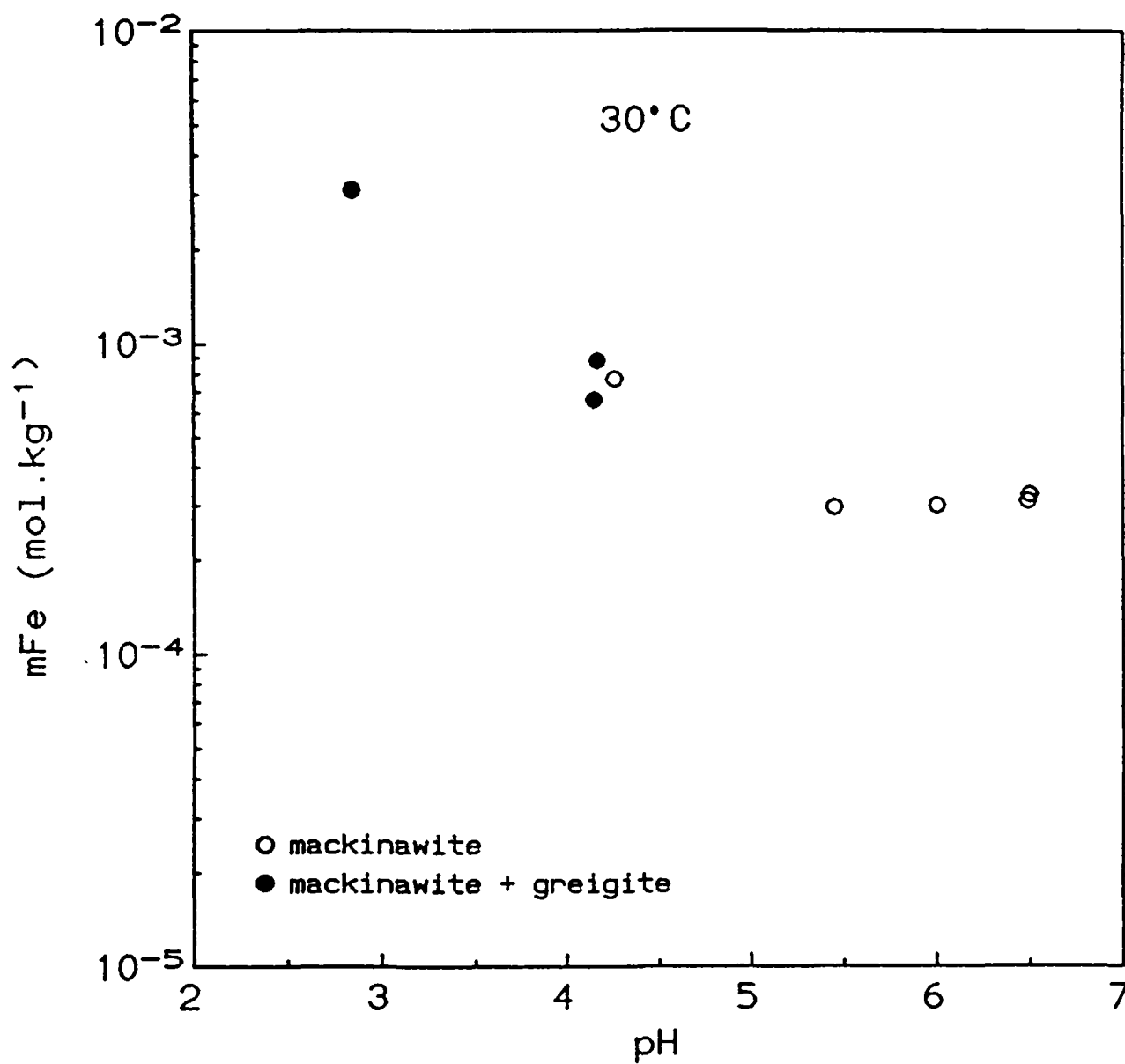


FIGURE 4

Experimental results at 30°C

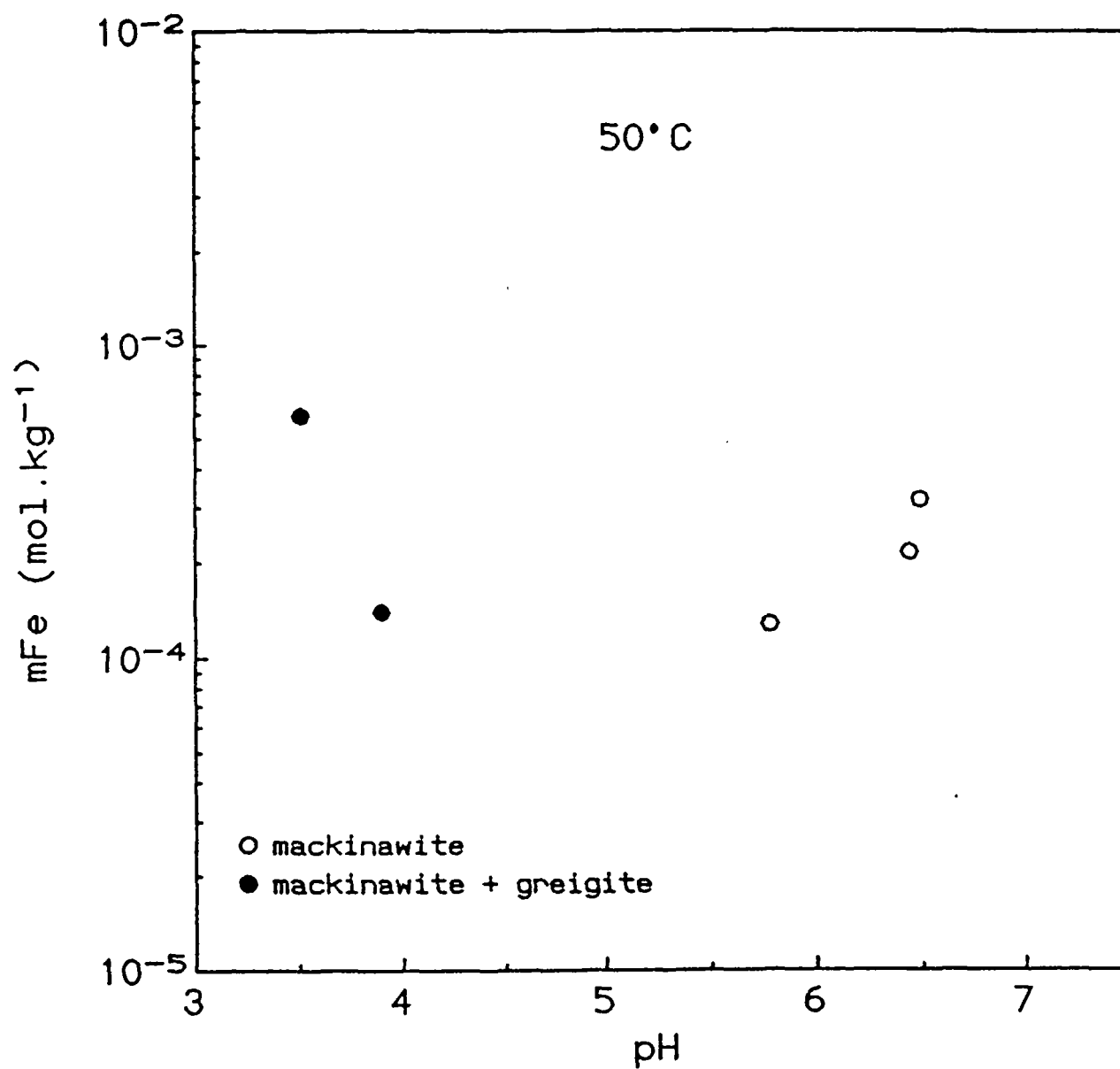


FIGURE 5

Experimental results at 50°C

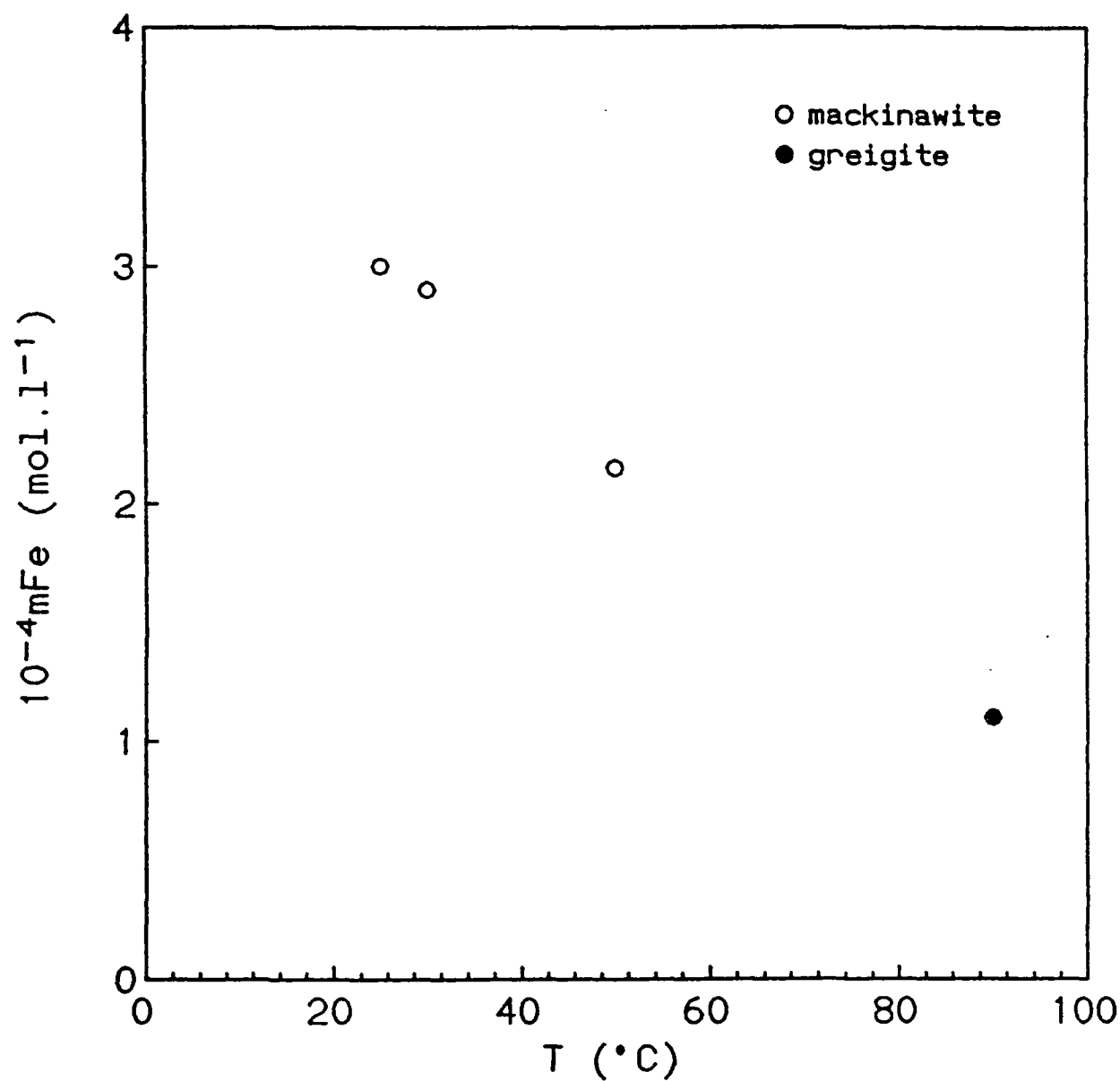


FIGURE 6

Iron concentration as a function
of temperature. $\text{pH} \approx 6.5$

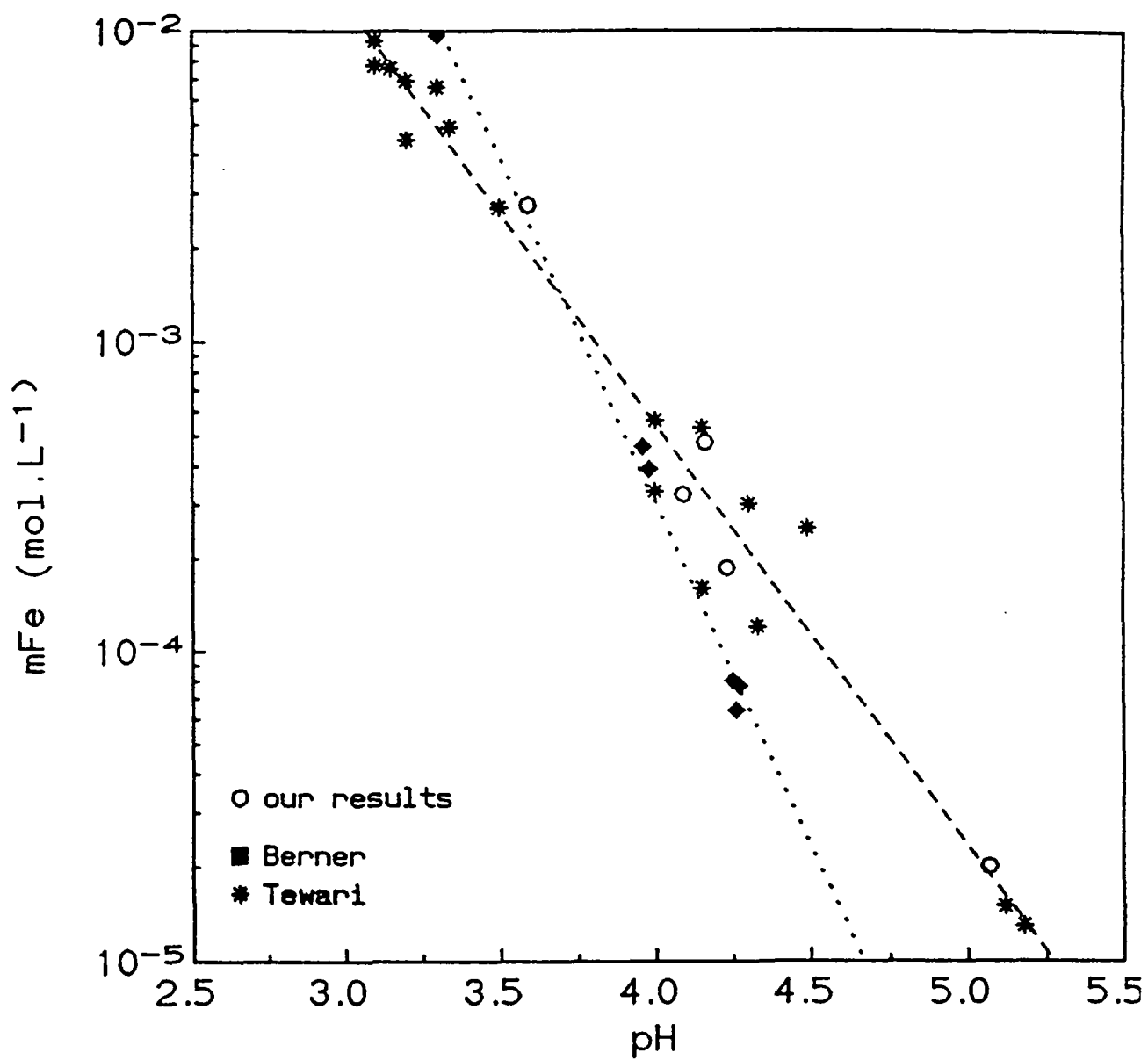


FIGURE 7

Results reduced to $m \text{H}_2\text{S} = 0.1$
compared to literature data

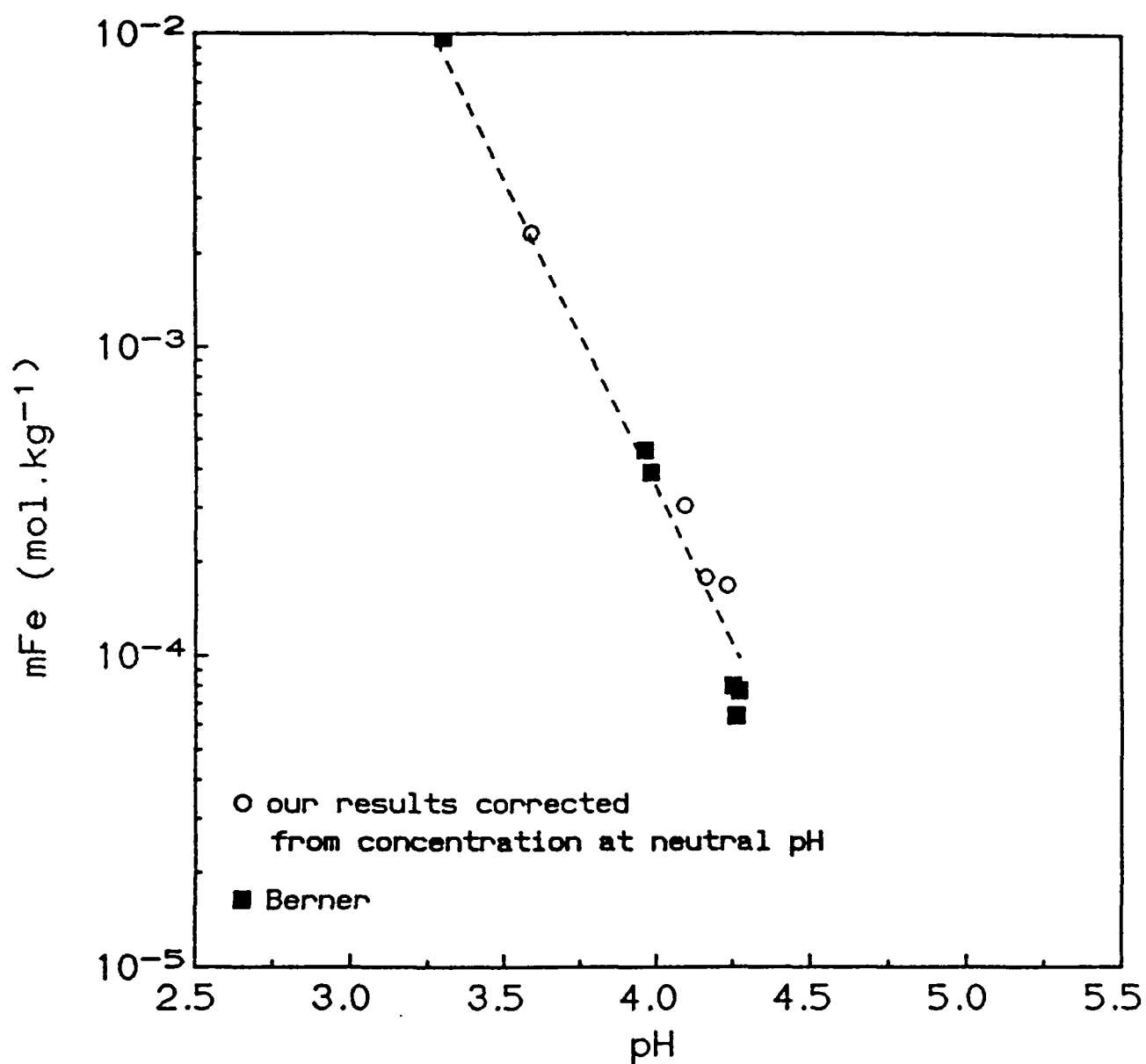


FIGURE 8

Corrected experimental results,
compared to Berner's data

APPENDIX 2

ARMINES REPORT

FAISABILITY OF USING SOLID INHIBITORS IN GEOTHERMAL WELLS

ECOLE NATIONALE SUPERIEURE
DES MINES DE PARIS

ARMINES

CENTRE D'INFORMATIQUE GEOLOGIQUE
LABORATOIRE D'HYDROGEOLOGIE
MATHEMATIQUE

ETUDE D'INHIBITEURS SOLIDES
POUR LE TRAITEMENT DES PUITES
GEOTHERMIQUES DU DOGGER

Compte-Rendu

P. IRIS

15 Octobre 1992

LHM/RD/92/64

SOMMAIRE

RESUME	1
I - ASPECT HYDRODYNAMIQUE : CHUTE DES ELEMENTS EN FORAGE	5
Quelles sont les contraintes liées à la compétion des ouvrages	5
<i>Inclinaison</i>	5
<i>Diamètres</i>	5
<i>Mode de production</i>	6
<i>Conclusion</i>	6
Etude théorique	7
Etude pratique	14
II - DIFFUSION DES PRODUITS	16
III - NATURE DES PRODUITS	19
REFERENCES BIBLIOGRAPHIQUES	21

RESUME

La nappe du Dogger, présente aux environs de 1500 m de profondeur sous l'ensemble de la région Ile de France, est exploitée depuis le début des années 1980 sur le plan thermique.

Une cinquantaine d'opérations géothermiques assurant chacune le chauffage de plusieurs milliers de logements ont été mises en service.

Le dispositif d'accès à la ressource est le doublet géothermique qui permet, à l'aide d'un puits d'injection dont l'impact à la nappe est convenablement calculé, de réinjecter dans le réservoir l'eau dont un échangeur a prélevé la chaleur en surface.

La raison de la mise en œuvre de ce dispositif réside dans la forte salinité de l'eau et sa forte concentration en hydrogène sulfureux qui rend impossible tout rejet important en surface.

Les caractéristiques physico-chimiques du fluide géothermal sont également à l'origine de la principale difficulté rencontrée à l'exploitation de ces installations, à savoir les phénomènes de dépôts corrosion.

Sans rentrer dans le détail, la présence d'hydrogène sulfureux dans l'eau de la nappe produit une attaque des tubages d'où résultent des dépôts de sulfure de fer et une réduction progressive de l'épaisseur de l'acier sain. Ces dépôts ne sont malheureusement aucunement autoprotecteurs compte-tenu des conditions physico-chimiques et thermodynamiques.

Il s'est par conséquent avéré nécessaire de mettre en œuvre des méthodes de traitement. Différents produits ont été testés et on s'accorde, en l'état actuel des connaissances, à considérer que des solutions inhibitrices de corrosion, à base d'amines grasses constituent des agents efficaces. Ces produits, mis en solution dans le fluide géothermal, ont un effet filmant sur les parois métalliques et sont censés assurer ainsi une protection.

Dans un premier temps, les installations de réinjection ont été protégées par ces produits, avec la mise en place de dispositifs d'injection d'amines au niveau des échangeurs, dans les locaux techniques de surface.

L'intérêt de ces produits est la très faible concentration nécessaire puisqu'il apparaît que quelques dizaines de ppm (et sans doute moins) suffiraient à assurer un filmage d'entretien des surfaces métalliques exposées au fluide corrosif.

L'injection de ces produits au niveau des installations de surface a permis d'assurer la protection des équipements de réinjection, mais ne concerne pas les installations de production situées à l'amont.

On s'est donc intéressé, dans un second temps, à la protection des équipements de pompage, colonnes d'exhaure et pompes immergées, en injectant à l'aide d'un tubage de faible diamètre les produits au niveau de la pompe immergée, dans le forage de production.

Les systèmes ont apparemment donné satisfaction, mais n'assurent aucune protection des casines des puits de pompage situés sous la pompe immergée.

Or les puits de production apparaissent également vulnérables. Leur protection rend nécessaire la mise en place de dispositifs d'injection des inhibiteurs à la base des puits de production, ou pour le moins, au sommet du découvert au niveau du sabot de pied de forages.

En continuité avec ce qui s'est fait pour la protection des pompes et des tubages de refoulement, des essais ont été menés, consistant à injecter à la base des ouvrages de production les solutions d'amines grasses à l'aide d'un tubage de très faible diamètre (de l'ordre du pouce) descendu jusqu'à la base des puits.

A l'époque du lancement de l'appel d'offre JOULE 1, les expérimentations dans ce domaine connaissaient des résultats variables :

- un tubing en acier a été mis en place sur un site de Seine-Saint-Denis et a été lui-même corrodé dans des délais très brefs au point qu'il a été impossible de le remonter au jour en totalité ;
- un tube constitué d'éléments en matériel de synthèse a été l'objet d'une rupture, etc...

A l'heure actuelle, après une phase d'expérimentation, il semble que cette technique soit convenablement maîtrisée par les maîtres d'œuvre, contrairement à la situation en 1989.

A cette époque, il paraissait souhaitable de proposer l'étude d'autres méthodes, les spécialistes n'étant pas sûrs de pouvoir maîtriser, dans des conditions économiques viables, l'installation et la maintenance de tubes de faible diamètre, en forages inclinés équipés de pompes immergées et sur des longueurs voisines de 2000 m.

Une étude sur carotte a porté sur la possibilité d'utiliser la technique du SQUEEZE de produits inhibiteurs dans la formation au droit du puits de production.

L'observation de colmatage des carottes et la difficulté d'expérimenter en vraie grandeur a conduit à ne pas poursuivre dans cette voie pour la géothermie du dogger.

La technique du Squeeze est, notons le, largement utilisée dans l'industrie pétrolière.

Dans ce contexte, nous avons proposé d'étudier la possibilité de traiter les puits de production par les inhibiteurs sous forme solide. Cette technique a été utilisée dans le domaine pétrolier, au Sahara en particulier au début des années 60.

Le principal objectif est de simplifier au maximum les équipements mis en place dans le forage de production et de s'affranchir en particulier du tubing jusqu'en fond de puits.

L'idée consiste, pour cela, d'imaginer de conditionner, sous forme de billes ou de bâtonnets solides, les amines grasses au moyen d'un liant convenablement choisi. Ces éléments solides sont supposés lestés à l'aide d'un composant inerte et le dispositif consisterait à faire descendre ces éléments par gravité jusqu'à la base des puits, dans la réserve à sédiments. Ayant ainsi atteint la base du forage de production dans une zone morte, s'opèrerait alors

un changement de phase et une diffusion progressive des produits vers les horizons producteurs supérieurs sous les effets de la diffusion chimique et de la convection naturelle liée au gradient géothermique (ou éventuellement à un gradient thermique renforcé localement artificiellement si besoin était).

Un tel dispositif est caractérisé par sa relative simplicité de mise en œuvre ; le conditionnement sous forme solide renforce également la sécurité du transport et de la manipulation sur le site, et surtout allègerait les dispositifs parasites à installer en forage.

Tel est par conséquent et d'une façon schématique le type de procédé que nous nous proposons d'étudier. En effet, si le concept est simple dans son principe, sa mise en application nécessite une étude de faisabilité qui puisse répondre aux principales questions suivantes :

- Quelles sont les propriétés volumétriques et densitaires des éléments (bâtonnets, billes, quelle taille, quelle masse, etc...) ?
- Quelle doit-être leur composition (quel agent pour le lest, quel lien pour éviter leur fusion au cours de la chute gravitaire) ?
- Comment va se propager le produit de la base du forage vers les horizons producteurs ?

Des contacts ont été pris avec la Société CECA, préalablement à notre réponse à l'appel d'offre, et ont conduit à définir très globalement les principes suivants.

D'après CECA, il était possible d'envisager des bâtonnets solides formés d'amise grasse mêlée à un liant soluble à haute température (plus de 70°C) en polyéthylène glycool et lesté par de la baryte anhydre de densité voisine de 4.

Dans ces conditions, des éléments constitués de 60 % d'amines, 10 % de polyéthylène glycool et 30 % de baryte devaient avoir une densité voisine de deux permettant leur chute densitaire dans les forages.

Une étude menée sur le volume des réserves à sédiments des forages au Dogger de la région parisienne montre qu'en général leur volume est toujours compris entre 1500 l et 2000 l.

Dans l'hypothèse par conséquent d'une réserve à sédiments de 1500 l, d'un débit géothermal moyen sur l'année de 150 m³/h, le remplissage de la réserve à sédiment revient à disposer (en ordre de grandeur) de plusieurs centaines de kilos de produit utilisable, soit de quoi assurer une concentration moyenne de quelques ppm de produits inhibiteurs pour une durée de plusieurs mois. La baryte libérée par le changement de phase des amines se sédimentant à la base de la réserve à sédiments, on pouvait tabler sur la nécessité d'un nettoyage de la réserve à sédiments tous les deux ans environ. La faisabilité d'une telle opération, dans des conditions économiquement et techniquement acceptable, n'étant toutefois pas prouvée.

Ce travail devait être mené au Centre d'Informatique Géologique, en liaison avec la société CECA pour la mise au point des éléments inhibiteurs sur le plan physico-chimique.

C'est malheureusement sur ce dernier point qu'une difficulté majeure est intervenue : en effet, contrairement à ce qui avait été estimé au moment de l'établissement de la proposition, il n'a pas été possible de réaliser dans des conditions réalistes des éléments solides

adaptés aux conditions de la géothermie ; deux difficultés ont été rencontrées par le fabricant : impossibilité de trouver un liant capable d'assurer une non dissolution du produit au cours de sa chute dans le forage. Les produits envisagés classiquement polyéthylène glycool ont un point de fusion qui s'est avéré ne pas dépasser 70°C. Des essais en laboratoire à cette température ont montré que les éléments solides se dissolvaient, devenaient pâteux dans le meilleur des cas aux alentours de cette température, rendant inopérant leur descente jusqu'à la réserve à sédiments.

De plus, il s'est avéré également difficile de mettre en œuvre un produit pouvant servir de lest. La société CECA n'ayant pas pu mettre en œuvre de la baryte anhydre (densité 4) comme prévu mais seulement de la baryte monohydratée (densité 2). Cela a conduit à des concentrations de baryte trop forte dans les éléments solides et par conséquent une inadéquation supplémentaire (remplissage de la réserve à sédiments).

Des études complémentaires sur la composition des éléments auraient sans doute été possibles, mais il est clair qu'elles auraient eu un caractère tout à fait académique en raison des difficultés certaines de mise en œuvre et de coût.

Un point qui apparaissait initialement comme facilement maîtrisable s'est avéré, de fait, un obstacle significatif empêchant en particulier de mener à bien des essais.

Face à cette situation, compte tenu de la quasi certitude de ne pouvoir aboutir raisonnablement, il a été proposé à la commission de ne pas poursuivre l'étude jusqu'à son terme. L'objectif essentiel initial était en fait de préparer la mise en œuvre d'un test in situ s'avérant obsolète compte-tenu de l'impossibilité de réaliser convenablement les bâtonnets solides. Sans cet aspect pragmatique, l'étude perdait sa raison d'être d'autant plus que, parallèlement, les maîtres d'œuvre progressait dans la maîtrise de l'inhibition par tubing en fonds de puits.

Le présent rapport rend compte du principal travail effectué, à savoir essentiellement l'étude des caractéristiques physiques des éléments, une réflexion sur les problèmes de diffusion du produit.

I - ASPECT HYDRODYNAMIQUE : CHUTE DES ELEMENTS EN FORAGE

La première question est de définir les meilleures conditions pour faire parvenir convenablement les éléments solides à la base des forages de production.

Sur ce point, on doit prendre en compte certaines contraintes liées à la configuration des ouvrages existants et prendre en compte les lois de l'hydraulique qui présideront au choix de la volumétrie et de la densité des éléments.

Quelles sont les contraintes liées à la compéition des ouvrages

Trois paramètres principaux doivent être pris en compte dans le cas qui nous intéresse :

- l'inclinaison des ouvrages,
- les diamètres des tubages et des découverts,
- les conditions de passage des pompes immergées.

Inclinaison

En ce qui concerne l'inclinaison, les doublets au Dogger se distribuent en trois classes :

- Doublets à deux puits verticaux, type Melun-Le Mée, Creil I et Creil II, Achères et Cergy Pontoise. Il s'agit d'ouvrages anciens dont la réalisation est antérieure à 1981 et dont certains sont d'ores et déjà arrêtés (Creil I, Creil II et Achères en particulier).
- Doublets à un puits vertical (producteur) et un puits incliné (injecteur) comme la Couronne Sud, Aulnay-sous-bois "Rose des Vents", Clichy-sous-Bois, la Celle-Saint-Cloud, Coulommiers, Beauvais. Ces doublets ont été réalisés au début des années 1980.
- Enfin les doublets à deux puits déviés qui constituent la majorité (une trentaine d'opérations). Les déviations moyennes par rapport à la verticale sont voisine de 30° mais peuvent localement atteindre, voire dépasser 45° (exemples à Villiers-le-Bel/Gonesse, Châtenay-Malabry). Dans tous les ouvrages, la déviation commence à une cote voisine de 400 m.

Diamètres

Deux classes peuvent être distinguées :

- la première génération (jusqu'en 1984) dite des tubages 7" ;
les puits de production sont constitués d'une chambre de pompage en diamètre 13"3/8 jusqu'à une profondeur variant de 200 à 600 m. Au-dessous, un tubage de 7" descendu à 1500 m-2000 m surmonte le réservoir découvert, foré en 6" de 1600 m à 2200 m selon les cas.

A noter que les forages sont équipés à leur base d'une réserve à sédiments, c'est-à-dire qu'il y a une prolongation du forage 6" en découvert au-dessous du plus profond

horizon producteur. Dans les tubages 7", la réserve à sédiments est profonde d'environ 100 m et représente un volume de l'ordre de 1500 à 2000 litres.

- La seconde génération, dite des tubages 9"5/8 a été mise en œuvre après 1984 avec chambre de pompage en 13"3/8, tubage de production 9"5/8 et découvert en 8"1/2. La poubelle à sédiments est profonde d'environ 50 m, soit un volume de l'ordre de 1500 à 2000 litres également.

Mode de production

Deux cas sont à envisager : production artésienne d'une part et assistée par électropompe d'autre part.

Sept doublets sont exploités actuellement en artésien, le reste, soit la grande majorité, étant équipé de dispositif de pompage :

- 25 puits sont équipés de pompes immergées (marques Byron Jackson, Centrilit et Reda TRW) d'un encombrement variable. Sur ce plan, les Byron Jackson sont les plus contraignantes ; on peut considérer qu'il est possible de passer un tube de diamètre externe maximal de 1" entre le corps de la pompe et la chambre de pompage. Ceci limite par conséquent le diamètre des éléments solides susceptibles d'être injectés depuis la surface.
- 8 sites sont équipés de turbo pompes qui *a priori* ne permettent pas le passage d'éléments solides dans des conditions simples.

Conclusion

Nous retiendrons de la nature de la complétion des ouvrages les conséquences suivantes relativement aux caractéristiques physiques des éléments solides :

- Les éléments doivent nécessairement être de volume réduit si l'on veut prétendre à une possibilité de généralisation du procédé. La contrainte majeure dans ce domaine étant l'espace annulaire disponible au passage des pompes immergées, entre les dites pompes et le casing de la chambre de pompage.
A moins de s'en tenir aux opérations exclusivement artésiennes qui représentent une minorité, on s'orientera vers des éléments de dimension maximale extérieure inférieure à 1 pouce.
- De la même façon, il convient de tenir compte de l'inclinaison sur la verticale de la plupart des ouvrages. La chute gravitaire s'en trouvera rendue plus difficile en raison des phénomènes de roulement et de frottement qui auront tendance à freiner les éléments dans leur chute. Ceci conduit à étudier de près la densité des éléments et plus précisément le rapport, poids volume forme qui devra être optimal compte-tenu des contraintes posées.
- La nécessité de tester les écoulements (puisque la densité des amines grasses est voisine de 1) pose le problème de l'évolution de ces produits une fois l'amine dissoute.

Intervient alors le dernier paramètre de la complétion, à savoir la réserve à sédiments : en effet, dans le cas d'un lest peu ou pas soluble (on pense à la baryte par exemple), la

réserve à sédiments se remplira progressivement de ces résidus de lest et une vidange s'avèrera nécessaire une fois la réserve remplie. La fréquence de cette opération de nettoyage aura des conséquences sur l'intérêt économique de la solution que nous étudions, et dépendra de la densité du lest retenu, de sa concentration dans les éléments solides et du volume de la réserve à sédiments.

Etude théorique

Dans un premier temps, nous avons cherché à répondre à la question de savoir si les éléments pouvaient descendre dans le forage par gravité, à contre courant du fluide géothermal, l'installation étant en fonctionnement normal. Si cette manière de faire était possible, cela serait très simple au point de vue de la mise en œuvre.

En cas contraire, il est impératif d'arrêter l'installation le temps de "charger" le puits et la réserve à sédiments, ce qui conduit à une procédure plus complexe et plus coûteuse également selon toute vraisemblance.

Les premiers calculs ont par conséquent porté sur ce point précis, avec les hypothèses suivantes. On suppose le tube vertical, parcouru par le fluide géothermal circulant de bas en haut. On se fixe une vitesse imposée de chute pour l'élément et on estime, dans le cas d'éléments sphériques, la densité nécessaire en fonction du diamètre de l'élément pour remplir cette condition de vitesse de chute. Le calcul est effectué pour différentes valeurs du débit et pour les deux diamètres de tubage 7" et 9".

Le principe est par conséquent d'injecter, dans un forage en production, une bille de densité ρ_b (supérieure à la densité du fluide ρ_e). Il est donc nécessaire que la vitesse de chute de la bille (u) par rapport au fluide, soit supérieure à la vitesse du fluide (v_e) : $u = v_e + v_b$ (où v_b représente la vitesse de la bille par rapport au sol).

Dans nos calculs, nous supposons deux vitesses de chute de la bille par rapport au sol ($v_b = 0,25$ et $0,5$ m/s) ce qui représente, pour un forage géothermique de 2000 mètres, un temps total de chute compris entre un peu plus d'une heure et 2 heures 1/4.

Les débits d'exploitation pris en compte varient de 100 à 300 m³/h et ce pour les deux diamètres de canalisations utilisés (7 et 9"), ce qui correspond à des vitesses moyennes minimales et maximales de 0,67 m/s (100 m³/h dans un tubage de 9") et 3,35 m/s (300 m³/h dans un tubage de 7").

La résistance d'un corps géométriquement simple (bille), immergé dans un fluide en écoulement permanent est donné par la formule :

$$F = C_x \left(\frac{1}{2} \rho_e u^2 \cdot \frac{1}{4} \pi D^2 \right)$$

avec F : trainée
 C_x : coefficient de trainée
 ρ_e : masse volumique de l'eau (kg/m³)
 u : vitesse du fluide/bille (m/s)
 D : diamètre de la bille (m)

En établissant le bilan des forces exercées sur la bille (poids, force de trainée, poussée d'Archimède), on obtient à l'équilibre :

$$4\pi R^3 \rho_e g + C_x \cdot \frac{1}{2} \rho_e (v_e + v_b)^2 \cdot \frac{1}{4} \pi D^2 = 4\pi R^3 \rho_b g$$

avec ρ_b : masse volumique de la bille (kg/m³)
 R : rayon de la bille (m)
 g : accélération de la pesanteur (m/s²)

On obtient la valeur de C_x à partir du nombre de Reynolds :

$R_e = \frac{\rho u D}{\mu} = \frac{V_d}{\nu}$ et d'après la formule de White,

$$C_x = \frac{24}{R_e} + \frac{6}{1 + \sqrt{R_e}} + 0,4$$

avec ν : viscosité dynamique du fluide

La masse volumique nécessaire de la bille pour une vitesse de chute de la bille v_b et une vitesse de fluide dans le tubage v_e est donc :

$$\rho_b = \frac{C_x \frac{1}{8} \rho_e (v_e + v_b)^2 \pi D^2}{4\pi R^3 g} + \rho_e$$

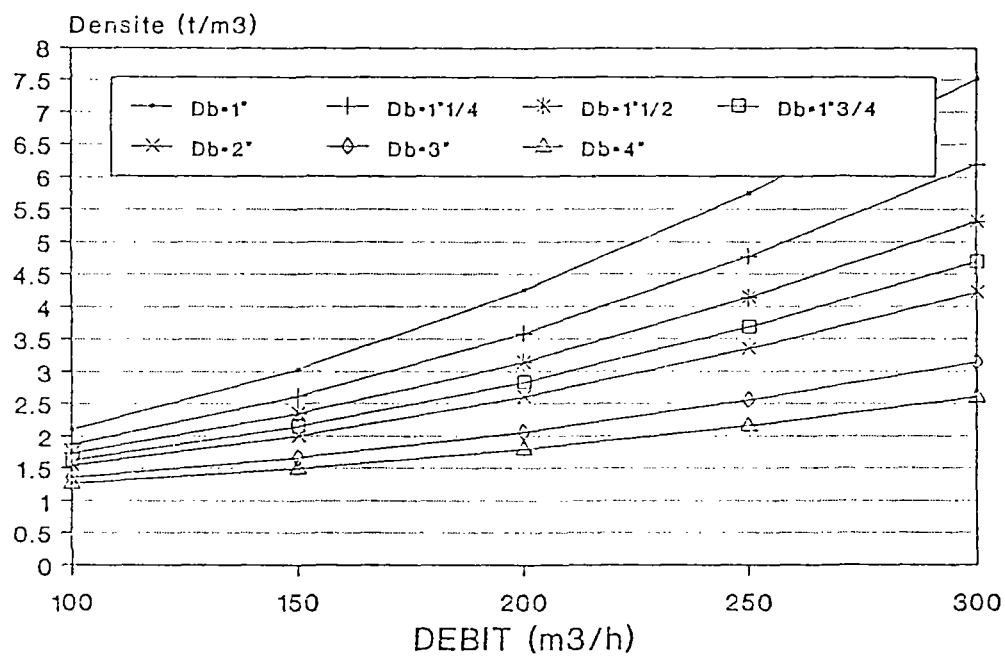
Les deux figures suivantes (figures 1 et 2) présentent la densité moyenne de la bille calculée pour l'obtention d'une vitesse de chute de 0,25 et 0,5 m/s dans des forages en exploitation de 9" et 7", pour des débits d'exploitation de 100 à 300 m³/heure et pour différents diamètres de bille (de 1" à 4").

Ces calculs sont optimistes, dans la mesure où l'effet de l'inclinaison des forages n'est pas pris en compte. On observe malgré cela que, compte-tenu des diamètres qu'il conviendra de ne pas dépasser (en raison de la présence des pompes), on est amené à envisager des densités moyennes des éléments très fortes.

Dans un tube de 9" par exemple (qui est un cas favorable), au débit de 150 m³/h, la densité moyenne nécessaire pour qu'une bille de 1" descende avec une vitesse de 0,25 m/s (soit près de deux heures et demi pour parcourir 2000 m) est de 3. Si le débit est de 200 m³/h, cette densité passe à 4.

Figure 1

DENSITE MOYENNE DE LA BILLE Tubages 9"- Vitesse de chute=0.25m/s



Tubages 7"- Vitesse de chute=0.25m/s

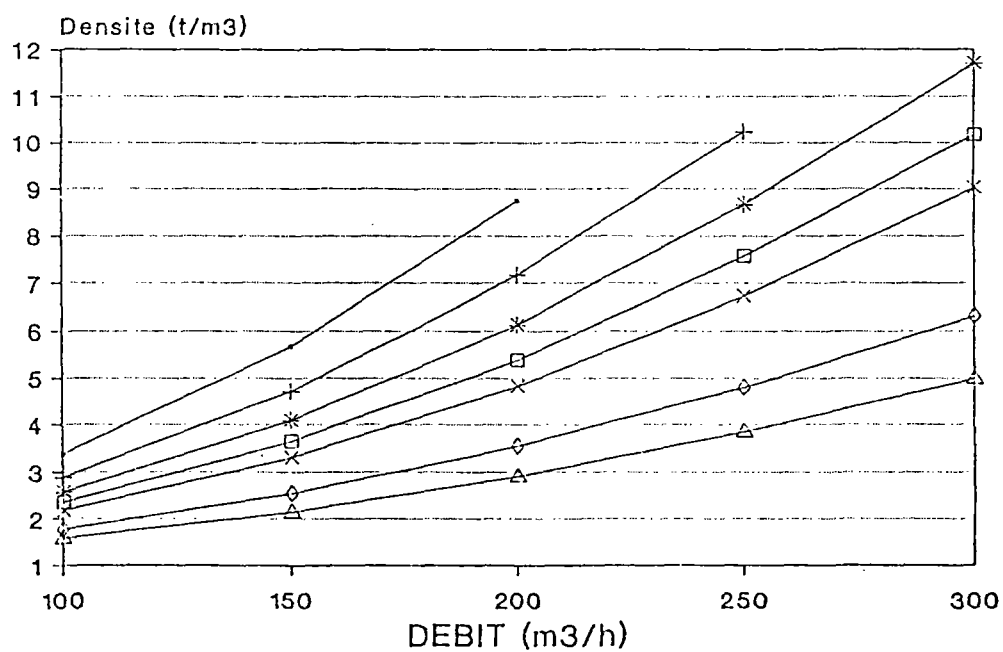
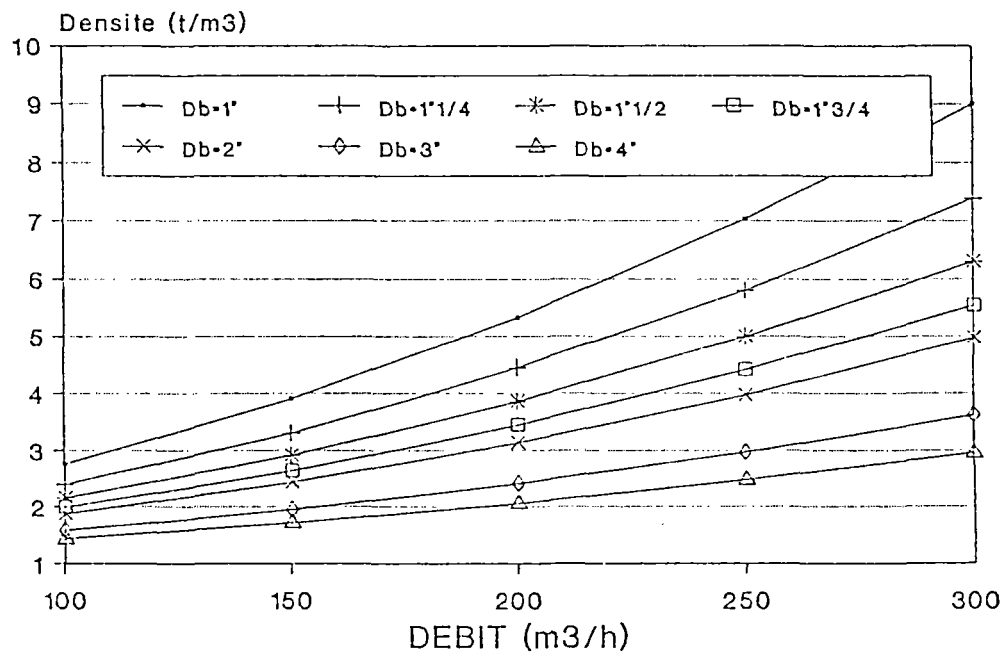


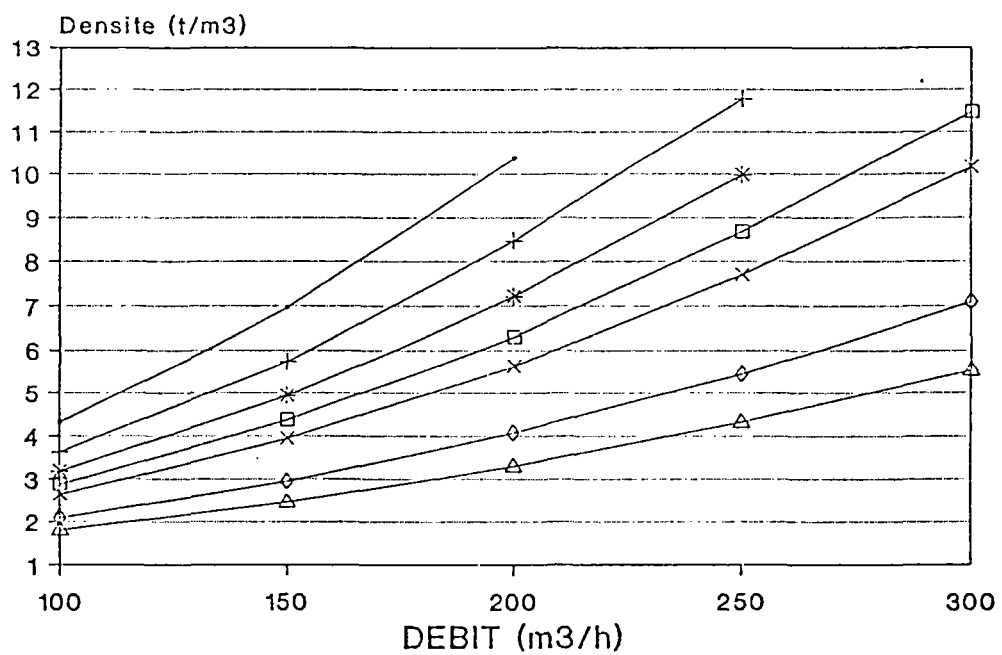
Figure 2

DENSITE MOYENNE DE LA BILLE

Tubages 9" - Vitesse de chute=0.5m/s



Tubages 7" - Vitesse de chute=0.5m/s



Comme nous le verrons par la suite, à moins d'envisager d'adjoindre aux éléments aminés des lests métalliques, il sera difficile de dépasser une densité moyenne de 2. Or, il nous semble irréaliste d'envisager ce type de lest métallique.

Au vu de ces résultats et observations, il paraît à ce stade difficile d'envisager l'injection en fond de puits d'éléments solides sans arrêter les installations sauf à se cantonner aux ouvrages exclusivement artésiens, dont l'absence de pompes permettrait d'utiliser des éléments, de taille relativement importante ($> 1''$). Comme nous l'avons vu, ces forages représentent une minorité.

Dans ces conditions, nous avons étudié dans la suite les conditions d'injection, les installations étant à l'arrêt.

Le fait d'avoir à arrêter les installations pour procéder à l'injection des éléments n'est pas nécessairement très gênant à la condition de remplir deux conditions :

- le temps de chute ne doit pas être trop long de façon à ce que la mise en œuvre ne dépasse pas 1/2 journée par exemple ;
- la fréquence de traitement doit être également assez faible de façon à ne pas réitérer l'opération trop souvent.

En première analyse, il nous paraît qu'un arrêt d'une demi-journée tous les deux à trois mois serait acceptable en terme d'exploitation (le manque à gagner pour le maître d'ouvrage pour une journée moyenne en période de chauffe est de l'ordre de grandeur de 50000 F).

Dans ces conditions, il conviendrait d'avoir des temps de descente des éléments de l'ordre de 1h à 2h maximum, ce qui représente une vitesse de chute de 0,5 m/s à 0,25 m/s pour parcourir les quelques 2000 m des forages (déviés).

Nous avons procédé à des calculs théoriques simplifiés en appliquant les principes élémentaires de la mécanique.

Dans l'hypothèse d'un angle de frottement de 30° et d'un roulement sans glissement (hypothèse *a priori* défavorable), on estime la vitesse limite d'une bille en la supposant sur un plan incliné d'un angle α sur l'horizontale.

En régime permanent, la bille est soumise à un équilibre de forces.

$$(m - \rho_e V)g \sin \alpha - \overline{F} - \overline{T} = 0$$

$(m - \rho_e V)g \sin \alpha$: composants parallèles à la direction de roulement du poids et de la poussée d'Archimède

$\overline{F}$: force de trainée

$\overline{T}$: force de frottement sphère sur surface de contact

V : Volume de la bille

En reprenant pour la trainée les calculs précédents :

$$F = \frac{C_x}{8} \times \pi \rho_e . D^2 . u^2$$

avec ρ : masse volumique de l'élément sphérique
 D : diamètre de l'élément sphérique
 u : vitesse limite de l'élément

$$\overline{T} = -mg \sin \alpha$$

avec m : masse de l'élément

Cette valeur de T correspond à l'hypothèse de non glissement, ce qui contraint α de la façon suivante :

φ : coefficient de frottement $f = tg \varphi$ avec $\varphi = 30^\circ$

$$tg \alpha < \frac{7}{2} f \Rightarrow \alpha \leq 64^\circ$$

Pour un angle de frottement (qui dépend en fait de la texture de l'élément solide et de la rugosité du casing, 30° paraissent une valeur réaliste) de 30° , l'hypothèse de non glissement apparaît dès que la déviation atteint 26° , ce qui est un minimum dans la pratique.

L'équation donne par conséquent une estimation de la vitesse limite de chute de l'élément, dans le cas où ce dernier est de géométrie sphérique.

Les courbes suivantes indiquent les valeurs ainsi calculées.

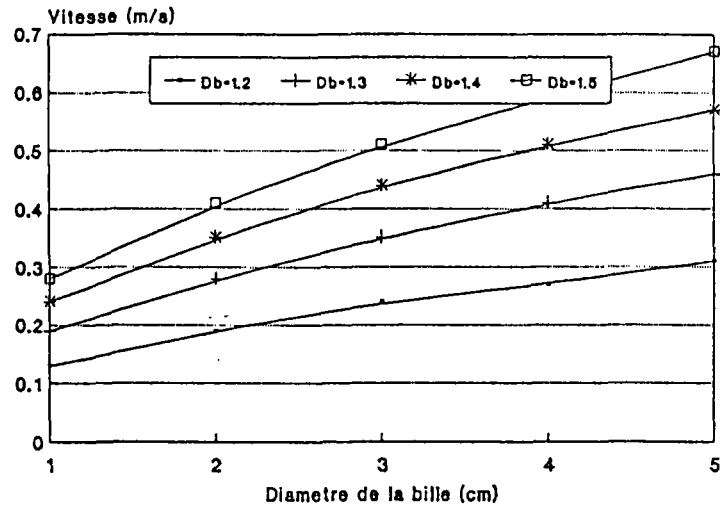
On observe que pour des éléments d'un diamètre de 2 cm, soit légèrement inférieur à un pouce, pour une déviation de 35° , la vitesse de chute estimée est de 0,3 m/s. Si la déviation augmente localement de 10° (il existe ce genre de variation localement dans les forages du Dogger), cette vitesse chute de moitié.

Si on double le diamètre de la bille, la vitesse est augmentée de 40 %.

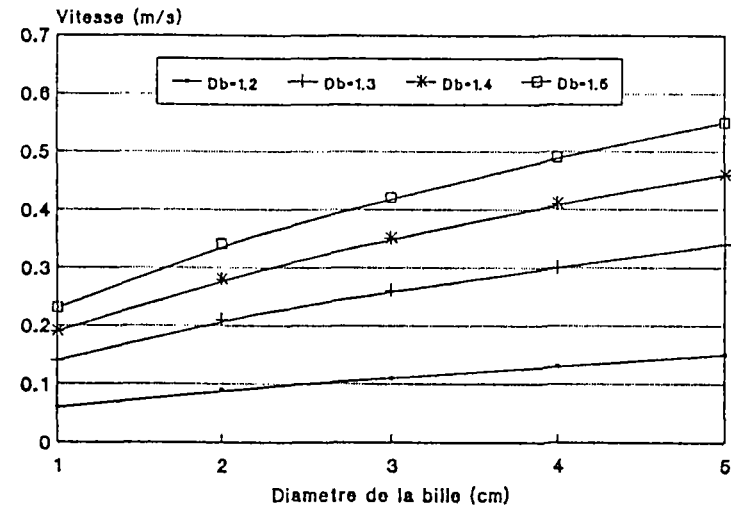
Ces calculs sont bien sûr à prendre en compte avec prudence dans la mesure où ils constituent des estimations schématiques. Ils permettent toutefois de donner des ordres de grandeur.

On en retiendra qu'il ne faut pas utiliser des éléments de densité inférieur à 1,5 et des éléments de diamètre inférieur à 1 pouce. Accroître taille et densité ne peut être que favorable.

Coef. de frottement = 0.15 Deviation=35

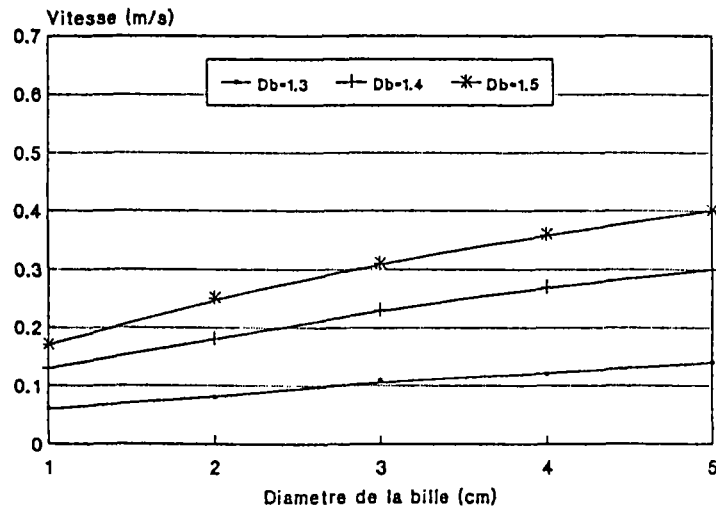


Coef. de frottement = 0.15 Deviation=45



VITESSE DE CHUTE DE LA BILLE - AVEC FROTTEMENT

Coef. de frottement = 0.15 Deviation=55



Coef. de frottement f=0.3

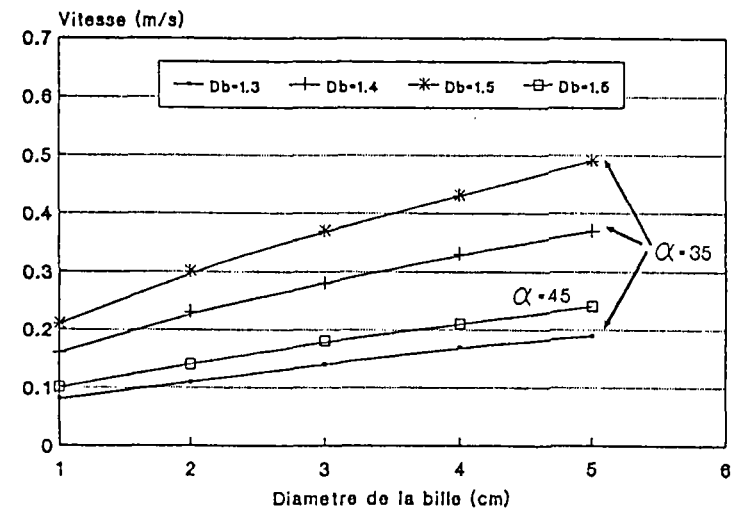
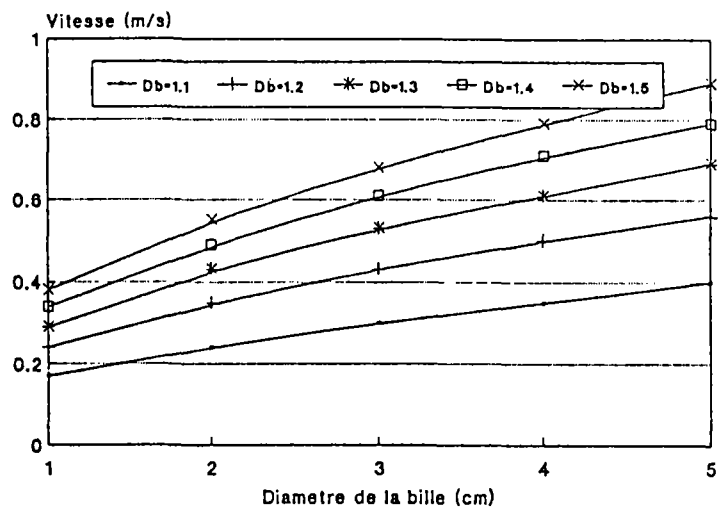
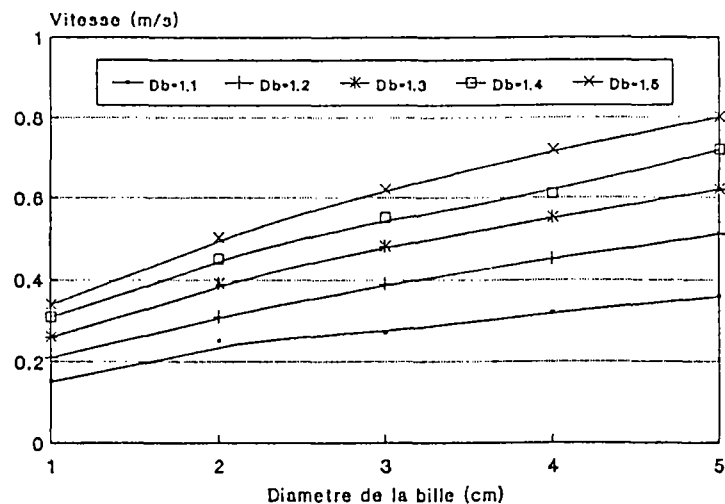


Figure 3

Puits vertical

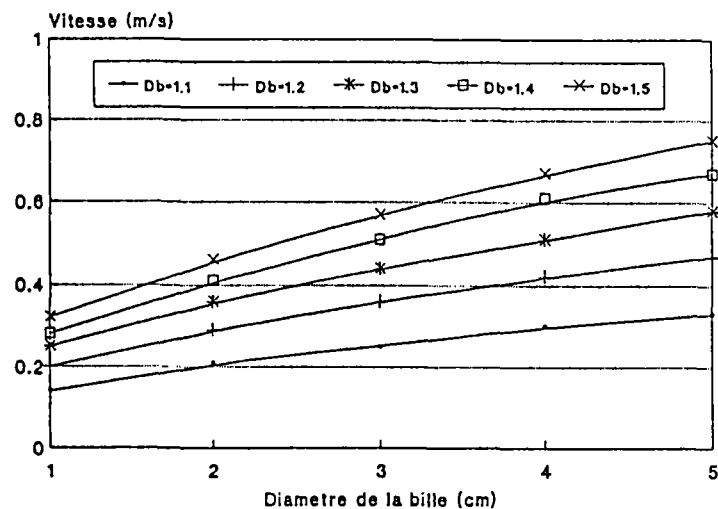


Puits devie Alpha=35



VITESSE DE CHUTE DE LA BILLE - SANS FROTTEMENT

Puits devie Alpha=45



Puits devie Alpha=55

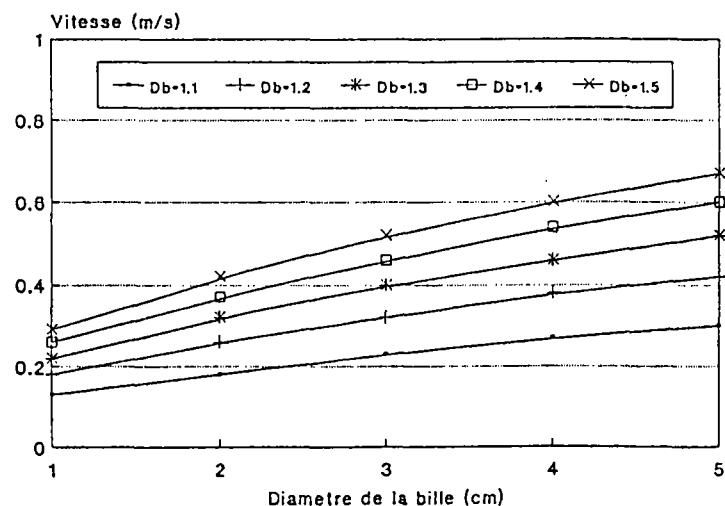


Figure 4

Etude pratique

Pour étayer ces remarques théoriques et issues du calcul, nous avons réalisé un test de laboratoire. Très simplifié également, il a constitué à mettre en œuvre un tube de plexiglass transparent de 100 m de diamètre, équipé d'une "bande de roulement" destinée à simuler la rugosité des casings géothermaux.

Les essais ont été menés à la température ambiante ($\simeq 18^\circ$) avec deux types d'éléments :

- Bâtonnet fourni par CECA contenant de l'inhibiteur mélangé à de la baryte et à un liant polyéthylène glycool :
densité : $1,72 \text{ g/cm}^3$
diamètre : 7 mm
longueur : 32 m
- Bille spérique de sobranite (argile) :
densité : $1,77 \text{ g/cm}^3$
diamètre : 15 mm

Deux dispositions ont été adoptées concernant l'angle du tube par rapport à la verticale :

- déviation 1 : 37°
- déviation 2 : 46°

L'échantillon était lâché à vitesse nulle au sommet du tube, sa vitesse mesurée sur les 1,5 derniers mètres, à la base.

Les vitesses ainsi mesurées ont été les suivantes :

bâtonnet	déviation 46°	$V = 0,08 \text{ m/s}$
sphère	déviation 46°	$V = 0,21 \text{ m/s}$
bâtonnet	déviation 37°	$V = 0,08 \text{ m/s}$
sphère	déviation 37°	$V = 0,21 \text{ m/s}$

On observe que :

- les bâtonnets et les sphères roulent sans glisser ;
- les bâtonnets ont tendance à se bloquer et à former des amas, ce qui n'est le cas des sphères.

Il est vraisemblable toutefois que la moquette utilisée pour simuler la rugosité du tubage présente un coefficient de frottement supérieur. Les résultats sont pour cette raison relativement pessimistes ; ils confirment toutefois les ordres de grandeur calculés ainsi que les conclusions suivantes :

- on s'orientera vers des éléments sphériques ;
- de densité la plus élevée possible, supérieur à 1,5 ;
- de diamètre le plus fort possible, de l'ordre de 1 pouce.

II - DIFFUSION DES PRODUITS

Un problème nous est apparu important, à savoir le mode de diffusion des produits situés dans le poubelle à sédiment, vers les horizons producteurs.

Une fois dissous et à l'état liquide, comment s'assurer, voire contrôler la montée des solutions inhibitrices vers les horizons producteurs, de façon à obtenir une teneur cohérente avec les impératifs de la protection des casings.

Deux phénomènes principaux entrent en jeu :

- la diffusion moléculaire,
- la convection thermique naturelle sous l'effet du gradient géothermique.

Ces mécanismes ont été étudiés par différents auteurs : en particulier SAMMEL (1968), CRESPO et VELARDE (1982), AZOUNI et NORMAND (1983) et BIDAUX (1987).

Il découle de ces travaux, dont les résultats apparaissent parfois contradictoires, que le problème est extrêmement complexe compte tenu en particulier du couplage des phénomènes de transfert convectif lié au gradient de température et aux phénomènes dispersifs liés aux gradients de concentration.

Les auteurs s'accordent toutefois sur le fait qu'en raison du gradient géothermique, il existe d'importants phénomènes convectifs qui jouent un rôle nettement plus important que la diffusion moléculaire seule.

La figure suivante, tirée de SAMMEL (1968) le confirme et montre que même pour des forages de très petit diamètre, pour des températures d'eau (douce) de 70°C, le gradient géothermique ($3.10^{-2}^{\circ}\text{C}/\text{m}$) conduit à une situation d'instabilité dans un forage de 2".

Ceci est confirmé par un essai en forage peu profond de traçage à l'eau distillée (BIDAUX, 1987) dont l'interprétation a conduit à une diffusivité moléculaire équivalente dans le forage de $10^{-5} \text{ m}^2/\text{s}$ alors que la valeur de la diffusivité moléculaire d'un amine dans l'eau (loi de Fick) est de l'ordre de $10^{-9} \text{ m}^2/\text{s}$, soit un rapport de 1 à 10000 qui ne peut s'expliquer que par des mécanismes de convection naturelle dans le forage qui accroissent considérablement les effets de mélange. Si l'on en revient à notre problème, on peut effectuer des calculs simplifiés.

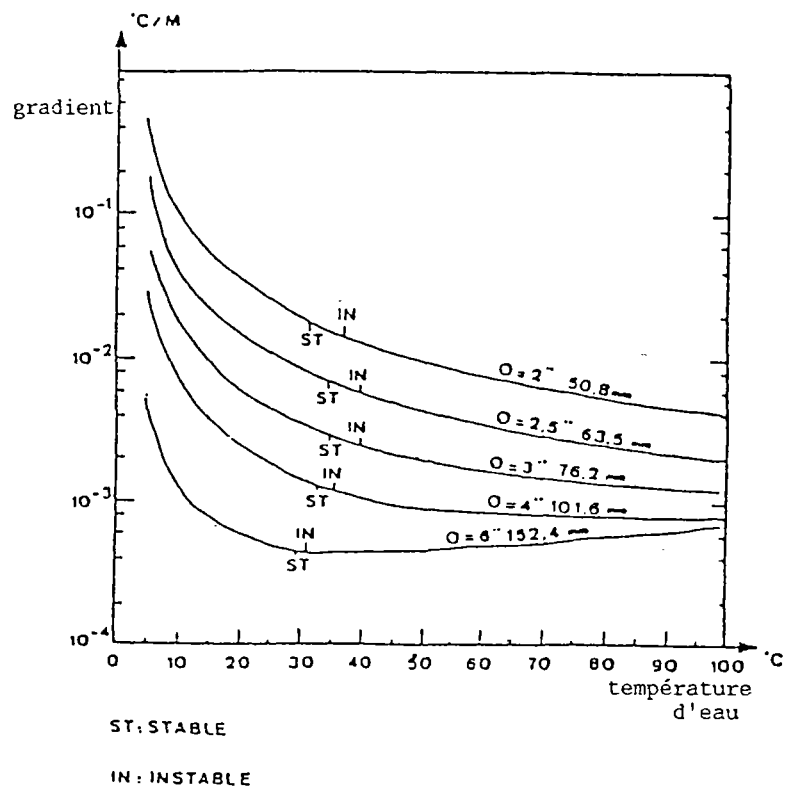
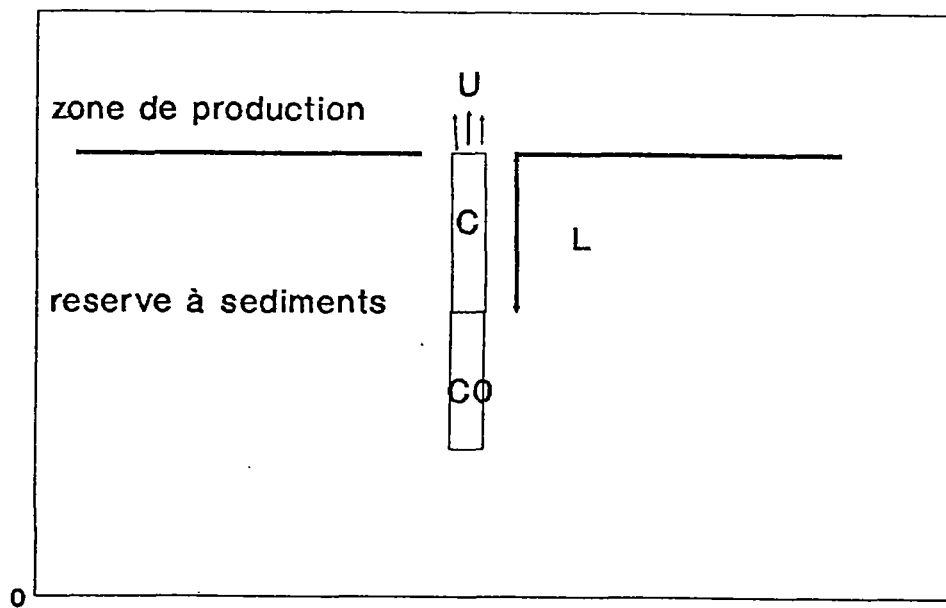


Figure 5. Stabilité d'une colonne d'eau en fonction de son diamètre et de la température (d'après SAMMEL, 1968).

Considérons la réserve à sédiment, supposée étanche et remplie jusqu'à une cote L à compter des horizons producteurs d'amines en solution à une concentration C_0 . Le débit Q prélevé dans la nappe génère une vitesse verticale U dans le forage au toit de la réserve à sédiments.



Soit D la diffusivité moléculaire équivalente et C la concentration en amine au niveau des horizons producteurs. Si l'on considère qu'un régime permanent diffusif s'établit entre le niveau à concentration maximale et la zone productrice, on peut calculer l'évolution dans le temps de la concentration d'amines dans le fluide géothermal ainsi que la cote $L(t)$ du toit de la zone chargée en amine au cours du temps :

$$(1) \quad U.C(t) = D \cdot \frac{C_0 - C}{L(t)}$$

exprime en régime permanent l'égalité du flux diffusif et du flux convectif.

$$(2) \quad C_0 \frac{dL}{dt} = c.U$$

exprime la variation de masse d'amine dans le réservoir à sédiment.

U vitesse du fluide

On tire de (1) $C = \frac{D.C_0}{D+UL} \simeq \frac{D.C_0}{UL}$

Soit $LDL = D.dt$

Soit $L^2 = 2Dt + \text{cte}$ Si l'on suppose à l'instant $t = 0$, la cote $l_0 = 0$

On obtient $L(t) = \sqrt{2Dt}$ et $C(t) = \frac{DC_0}{U\sqrt{2Dt}}$

Soit avec : $Q = 150 \text{ m}^3/\text{h}$ $\Phi = 9''$ $D = 10^{-5} \text{ m}^2/\text{s}$ $C_0 = 700 \text{ g/l}$

$L(1\text{h}) = 0,27 \text{ m}$	$c = 26 \text{ ppm}$
$L(1\text{j}) = 1,3 \text{ m}$	$c = 5,3 \text{ ppm}$
$L(10\text{j}) = 4,15 \text{ m}$	$c = 1,7 \text{ ppm}$
$L(100\text{j}) = 13 \text{ m}$	$c = 0,56 \text{ ppm}$
$L(1\text{an}) = 25 \text{ m}$	$c = 0,28 \text{ ppm}$

Dans le cas d'une diffusivité de $10^{-4} \text{ m}^2/\text{s}$ soit 10 fois supérieure, on obtient les résultats :

$L(1\text{h}) = 0,85 \text{ m}$	$c = 85 \text{ ppm}$
$L(1\text{j}) = 4,1 \text{ m}$	$c = 16,7 \text{ ppm}$
$L(10\text{j}) = 13 \text{ m}$	$c = 5,4 \text{ ppm}$
$L(100\text{j}) = 41 \text{ m}$	$c = 1,8 \text{ ppm}$
$L(1\text{an}) = 79 \text{ m}$	$c = 0,9 \text{ ppm}$

Dans l'hypothèse où la réserve à sédiments est remplie d'amines grasses à haute concentration (700 g/l), on constate que l'évolution de la concentration dans l'eau de forage va dépendre de façon très étroite de la diffusion par convection naturelle dans le forage.

La faisabilité du système est donc fortement dépendante d'un phénomène naturel difficile à contrôler. Si ce phénomène est insuffisant, le taux d'amine dans l'eau le sera également. La réponse à cette interrogation n'est possible à obtenir de façon convaincante que par un essai en vraie grandeur.

III - NATURE DES PRODUITS

Les principales difficultés sont venues de l'impossibilité pour CECA de mettre au point des éléments solides requis.

23 formulations différentes ont été testées à partir de deux types d'amines grasses différents et deux types de liants (polyéthylène glycool et dimethyl).

Deux problèmes techniques n'ont pas été réalisés :

- 1) Le plus important a été l'impossibilité de mettre au point un liant capable d'assurer que les éléments resteraient bien solides jusqu'à leur arrivée à la base du forage. Les produits utilisés avaient un point de fusion ne dépassant pas 70°C, c'est-à-dire que dès que la température du milieu avoisine les 65°C, le produit devient pâteux, puis visqueux et change de phase petit à petit. Des éléments ainsi constitués n'auraient pas manqué d'obturer les forages bien avant leur arrivée dans la réserve à sédiments.
- 2) Une interrogation concernant leur aspect externe et leur capacité à ne pas s'user au cours de leur descente sur environ 2000 m (roulement et frottement) s'est également manifestée au vu de la texture des éléments fournis par CECA.
- 3) Enfin, il n'a pas été possible de trouver sur le marché de la baryte anhydre à forte densité. Il en est ressorti que pour atteindre la densité souhaitée pour les éléments de l'ordre de 1,7 g/cm³, le fabricant a eu recours à de la baryte monohydratée de densité beaucoup plus faible (de l'ordre de 2,3) et par conséquent a été conduit à "charger" en volume les éléments avec des taux incompatibles avec les concepts de départ : à savoir faible valeur de baryte ne nécessitant pas de nettoyage de la réserve à sédiments à une forte fréquence. Les éléments fournis contenaient les proportions de matières suivantes :

baryte monohydratée $\simeq$ 60 %

agent liant $\simeq$ 20 %

agent inhibiteur $\simeq$ 20 %

Soient des proportions quasiment inverses de ce qui était souhaité initialement pour la baryte et l'agent inhibiteur en particulier.

Pour le personnel de CECA, le point n° 1 apparaissait le plus délicat ; deux solutions étaient envisageables :

- Utiliser des cires paraffiniques à haut point de fusion ($\simeq$ 80°C). Ceci pose toutefois le problème du relargage dans l'eau des forages de tels agents liants qui sont insolubles dans l'eau, avec des risques importants de colmatage des équipements de pompage, des échangeurs en surface et de la nappe à la réinjection.
- Envelopper la baryte et l'inhibiteur dans des "sachets" en alcool polyvinylique formulé de façon à avoir un point de fusion élevé et supérieur à 80°C. La mise en œuvre industrielle d'un tel "emballage" et surtout leur comportement au cours de la descente dans le puits producteur apparaissant également très aléatoire.

Il est apparu par conséquent à l'issue des travaux de CECA sur ce sujet que la mise au point des éléments tels que nous les souhaitions était loin d'être acquise et nécessitait en tout état de cause des développements, des recherches manifestement sans commune mesure avec les objectifs initiaux et les moyens consacrés à cette étude et ce sans garantie de résultats techniquement et économiquement acceptables.

REFERENCES BIBLIOGRAPHIQUES

AZOUNI M.A., NORMAND, C. (1983). Thermoconvection instabilities in a vertical cylinder of water with maximum density effect. *Geophy. Astrophys. Fluid Dynamics*, Vol. 23, pp. 209-245.

BIDAUX, D. (1987). Contribution à l'étude des circulations profondes en milieu fissuré peu perméable. Thèse de 3e cycle, Université des Sciences et Techniques du Languedoc.

CRESPO, E., VEARDE, M.G. (1982). Two-component Benard convection in cylinders. *Int. J. Heatmass Transfer*, Vol. 25, n° 4, pp. 1451-1456.

SAMMEL, E.A. (1968). Convective flow and its effects on temperature logging in small diameter wells. *Geophysics*, Vol. 33, n° 6, pp. 1004-1012.

APPENDIX 3

TPDEGAZ CODE

REACTIONS AND THERMODYNAMIC DATA

MODÉLISATION DE L'ÉVOLUTION DE LA CHIMIE DES FLUIDES GÉOTHERMAUX LORS DE LEUR EXPLOITATION PAR FORAGES

par

Isabelle CZERNICHOWSKI-LAURIOL

Documents du B.R.G.M. n° 159



Editions du BRGM
Avenue de Concyr
45060 ORLEANS Cedex 2 - France
Tél. (33) 38.64.30.28

ANNEXE 2

DETAIL DES CALCULS SECONDAIRES UTILISES

- 1 - Constantes d'équilibre (espèces composées) et produits de solubilité (minéraux).
Leurs dérivées premières et secondes par rapport à la température et à la pression.**
- 2 - Pression de vapeur saturante pour une solution saline.**
- 3 - Pressions partielles des gaz incondensables et constantes de Henry.**
 - a) CH₄, Ar et He**
 - b) N₂**
 - c) CO₂**
 - d) H₂S**
- 4 - Produits d'activités ioniques et degrés de saturation.**
- 5 - Coefficients d'activité.**
- 6 - Activité de l'eau.**
- 7 - Recherche de la répartition à l'équilibre initiale.**
 - a) Constantes apparentes.**
 - b) Calcul des molalités des espèces simples.**
 - c) Calcul des molalités des espèces composées.**
- 8 - Appréciation de la précision des calculs.**
- 9 - Volume spécifique de la phase liquide.**
- 10 - Viscosité de la phase liquide.**

1. CONSTANTES D'EQUILIBRE (ESPECES COMPOSEES) ET PRODUITS DE SOLUBILITE (MINERAUX). LEURS DERIVEES PREMIERES ET SECONDES PAR RAPPORT A LA TEMPERATURE ET A LA PRESSION

Les constantes d'équilibre ou les produits de solubilité sont calculés, en fonction de la température et de la pression, par la relation suivante (HELGESON, 1969) :

$$\log K(T, P) = \log K(T, P_r) - \frac{\Delta V_r^\circ(T)(P - P_r)}{2,303 RT}$$

$$\text{et} \quad \log K(T, P_r) = \log K(T_r, P_r) - \frac{\Delta H_r^\circ(T_r)}{2,303 R} \left(\frac{1}{T} - \frac{1}{T_r} \right)$$

$$- \frac{1}{2,303 RT} \int_{T_r}^T \Delta c_{p,r}^\circ(T) dT + \frac{1}{2,303 R} \int_{T_r}^T \Delta c_{p,r}^\circ(T) d \ln T$$

- avec
- K : constante d'équilibre ou produit de solubilité
 - ΔV_r° : volume molaire standard de la réaction (cm^3/mole)
 - ΔH_r° : enthalpie standard de la réaction (cal/mole)
 - $\Delta c_{p,r}^\circ$: chaleur massique standard de la réaction ($\text{cal. K}^{-1} \cdot \text{mole}^{-1}$)
 - R : constante des gaz parfaits ($R = 1,987 \text{ cal. mole}^{-1} \cdot \text{K}^{-1}$
ou $83,142 \text{ cm}^3 \cdot \text{bar. mole}^{-1} \cdot \text{K}^{-1}$)
 - T : température considérée (K)
 - P : pression considérée (bar abs.)
 - T_r : température de référence ($T_r = 298,15 \text{ K}$)
 - P_r : pression de référence ($P_r = 1,013 \text{ bars abs.}$)

- Les valeurs de $\Delta c_{p,r}^\circ(T)$ sont calculées d'après une relation de type :

$$\Delta c_{p,r}^\circ(T) = CA + CB T + CC/T^2 + CD T^2$$

- Les valeurs de $\Delta V_r^\circ(T)$ sont calculées d'après une relation de type :

$$\Delta V_r^\circ(T) = VA + VB T + VC T^2$$

$$\bullet \int_{T_r}^T \Delta c_{p,r}^\circ(T) dT = CA (T - T_r) + \frac{CB}{2} (T^2 - T_r^2) - CC \left(\frac{1}{T} - \frac{1}{T_r} \right) + \frac{CD}{3} (T^3 - T_r^3)$$

$$\bullet \int_{T_r}^T \Delta c_{p,r}^\circ(T) d \ln T = CA \ln \frac{T}{T_r} + CB (T - T_r) - CC \left(\frac{1}{T^2} - \frac{1}{T_r^2} \right) + \frac{CD}{2} (T^2 - T_r^2)$$

La table de données thermodynamiques associée au programme TPDEGAZ contient, pour chaque réaction d'équilibre envisagée, les valeurs de $\log K(T_r, P_r)$ et $\Delta H_r^\circ(T_r)$, ainsi que les valeurs des paramètres CA, CB, CC, CD et VA, VB, VC, VD (cf. Annexe 3).

Les dérivées des constantes d'équilibre ou des produits de solubilité par rapport à la température sont égales à :

$$\begin{aligned} \frac{d \log K(T, P)}{dT} &= \frac{\Delta H_r^\circ(T)}{2,303 R T^2} - \frac{(P - P_r)}{2,303 R T^2} \left[T \frac{d \Delta V_r^\circ(T)}{dT} - \Delta V_r^\circ(T) \right] \\ &= \frac{\Delta H_r^\circ(T_r) + \int_{T_r}^T \Delta C_{p,r}^\circ(T) dT}{2,303 R T^2} - \frac{(P - P_r)}{2,303 R T^2} \left[T \frac{d \Delta V_r^\circ(T)}{dT} - \Delta V_r^\circ(T) \right] \\ \frac{d^2 \log K(T, P)}{dT^2} &= \frac{1}{2,303 R T^2} \frac{d \Delta H_r^\circ(T)}{dT} - \frac{(P - P_r)}{2,303 R T^3} \left[T^2 \frac{d^2 \Delta V_r^\circ(T)}{dT^2} - 2 T \frac{d \Delta V_r^\circ(T)}{dT} + 2 \Delta V_r^\circ(T) \right] \\ &= \frac{\Delta C_{p,r}^\circ(T)}{2,303 R T^2} - \frac{2 \Delta H_r^\circ(T)}{2,303 R T^3} - \frac{(P - P_r)}{2,303 R T^3} \left[T^2 \frac{d^2 \Delta V_r^\circ(T)}{dT^2} - 2 T \frac{d \Delta V_r^\circ(T)}{dT} + 2 \Delta V_r^\circ(T) \right] \\ \text{avec} \quad \frac{d \Delta V_r^\circ(T)}{dT} &= VB + 2 VC T \quad \text{et} \quad \frac{d^2 \Delta V_r^\circ(T)}{dT^2} = 2 VC \end{aligned}$$

Pour le calcul des dérivées par rapport à la pression, on néglige les variations des volumes molaires (l'erreur commise est inférieure à 0,2 ‰ sur le $\log K$ entre 0 et 100 bars). Il vient alors :

$$\begin{aligned} \frac{d \log K(T, P)}{dP} &= - \frac{\Delta V_r^\circ(T)}{2,303 R T} \\ \frac{d^2 \log K(T, P)}{dP^2} &= 0 \end{aligned}$$

2- PRESSION DE VAPEUR SATURANTE POUR UNE SOLUTION SALINE

Elle est donnée par la relation suivante (HAAS, 1976) :

$$\text{Ln } p_{\text{H}_2\text{O}} = e_0 + \frac{e_1}{z} + \frac{e_2 \omega}{z} \left(10^{e_3 \omega^2} - 1,0 \right) + e_4 10^{e_5 y^{1,25}}$$

avec $\omega = z^2 - e_6$

$y = 647,27 - T_0$

$z = T_0 + 0,01$

$\text{Ln } T_0 = m \text{ Ln } T$

$m = (a + b T)^{-1}$

$a = 1,0 + a_1 x + a_2 x^2 + a_3 x^3$

$b = 0,0 + b_1 x + b_2 x^2 + b_3 x^3 + b_4 x^4 + b_5 x^5$

et T : température de la solution (K)

$p_{\text{H}_2\text{O}}$: pression de vapeur saturante (bar)

x : molalité de la solution (moles NaCl/kg H_2O)

Les valeurs des constantes sont les suivantes :

$e_0 = 12,50849$

$e_1 = -4,616913 \times 10^3$

$e_2 = 3,193455 \times 10^{-4}$

$e_3 = 1,1965 \times 10^{-11}$

$e_4 = -1,013137 \times 10^{-2}$

$e_5 = -5,7148 \times 10^{-3}$

$e_6 = 2,9370 \times 10^5$

$a_1 = 5,93582 \times 10^{-6}$

$a_2 = -5,19386 \times 10^{-5}$

$a_3 = 1,23156 \times 10^{-5}$

$b_1 = 1,15420 \times 10^{-6}$

$b_2 = 1,41254 \times 10^{-7}$

$b_3 = -1,92476 \times 10^{-6}$

$b_4 = -1,70717 \times 10^{-9}$

$b_5 = 1,05390 \times 10^{-10}$

Cette formule est applicable jusqu'à 325°C et pour des salinités comprises entre zéro et la saturation.

3- PRESSIONS PARTIELLES DES GAZ INCONDENSABLES ET CONSTANTES DE HENRY

Les pressions partielles sont calculées d'après la loi de Henry ; celle-ci s'exprime de la façon suivante :

$$H = \frac{p}{x}$$

avec H : constante de Henry (bars / fraction molaire)
 p : pression partielle (bars)
 x : fraction molaire du gaz dissous.

Pour des pressions inférieures à 100 bars, telles qu'on les rencontre dans les systèmes géothermaux, les coefficients de fugacité sont voisins de l'unité si bien que les fugacités ont été assimilées aux pressions partielles.

Les constantes de Henry à une température et pression données sont obtenues par la formule suivante :

$$\ln H(T, P) = \ln H(T, P_r) + \frac{\bar{V}^{ol}(T) (P - P_r)}{RT}$$

avec $\bar{V}^{ol}$: volume molaire partiel du gaz considéré dans la phase liquide (cm³/mole)
 T : température (K)
 P : pression (bars)
 P_r : pression de référence ($P_r = 1,013$ bar)
 R : constante des gaz parfaits ($R = 83,142$ cm³.bar.mole⁻¹. K⁻¹).

Faute de données thermodynamiques sur les volumes molaires partiels des gaz en phase liquide en fonction de la température, les valeurs utilisées ont été prises égales, à toute température, aux valeurs suivantes :

Gaz	Température (°C)	$\bar{V}^{ol}$ (cm ³ /mole)	Référence
N ₂	25	33	WILHELM <i>et al.</i> (1977)
CH ₄	25	37.3	WILHELM <i>et al.</i> (1977)
He	25	29.7	WILHELM <i>et al.</i> (1977)
Ar	25	32	WILHELM <i>et al.</i> (1977)
CO ₂	50	35	SEGNIT <i>et al.</i> (1962)
H ₂ S	25	34	CLARKE et GLEW (1971)

Les formules utilisées pour le calcul des constantes de Henry à la pression de référence, $H(T, P_r)$, sont explicitées ci-dessous.

a) CH₄, Ar et He :

La solubilité du méthane, de l'argon et de l'hélium dans l'eau pure et en fonction de la température, a été étudiée par plusieurs auteurs qui sont cités dans le tableau ci-après :

Auteurs	Année	Sources des données	Limite supérieure de température		
			CH ₄	Ar	He
HIMMELBLAU	1960	Compilation de données préexistantes	181°C	- *	320°C
WILHELM <i>et al.</i>	1977	Compilation de données préexistantes	85°C	75°C	72°C
POTTER et CLYNNE	1978	Expériences personnelles	- *	280°C	280°C
CROVETTO <i>et al.</i>	1981	Expériences personnelles	320°C	320°C	- *
SMITH	1985	Expériences personnelles	- *	- *	200°C

* ce gaz n'a pas été étudié

Afin de comparer les différentes corrélations, les valeurs données par chacune d'elles sont reportées en figures 31, 32 et 33. La corrélation donnée par SMITH se référant à la solubilité de l'hélium par rapport à l'argon, il est nécessaire d'y associer une corrélation portant sur la solubilité de l'argon : c'est celle de CROVETTO *et al.* qui a été choisie, étant donnée que SMITH lui-même la trouve en accord avec la sienne.

Les valeurs de POTTER et CLYNNE semblent être remises en cause par celles de CROVETTO *et al.* Pour certaines températures, la différence entre ces deux auteurs peut atteindre 20 % dans le cas de l'argon (et même 40 % pour le néon (cf. CROVETTO *et al.*, 1981)). Les valeurs pour l'hélium, quoique beaucoup plus concordantes, sont tout de même sous-estimées par rapport à celles de SMITH-CROVETTO.

A basse température, les valeurs de POTTER et CLYNNE semblent également être remises en cause par celles de WILHELM *et al.* (cf. Argon et Helium) alors que ces dernières sont très voisines de celles de CROVETTO *et al.* pour les trois gaz considérés. Par contre les valeurs données par HIMMELBLAU sont sensiblement supérieures.

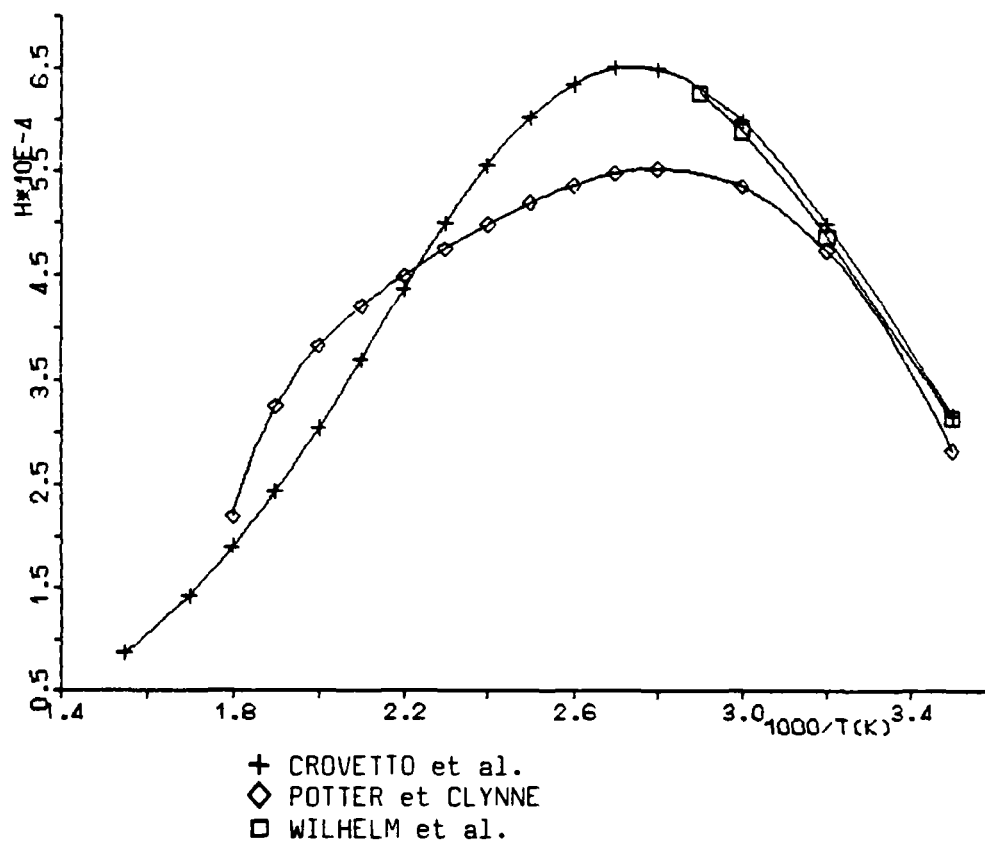


Figure 31 - Constantes de Henry de l'argon en fonction de la température (bars/fraction molaire)

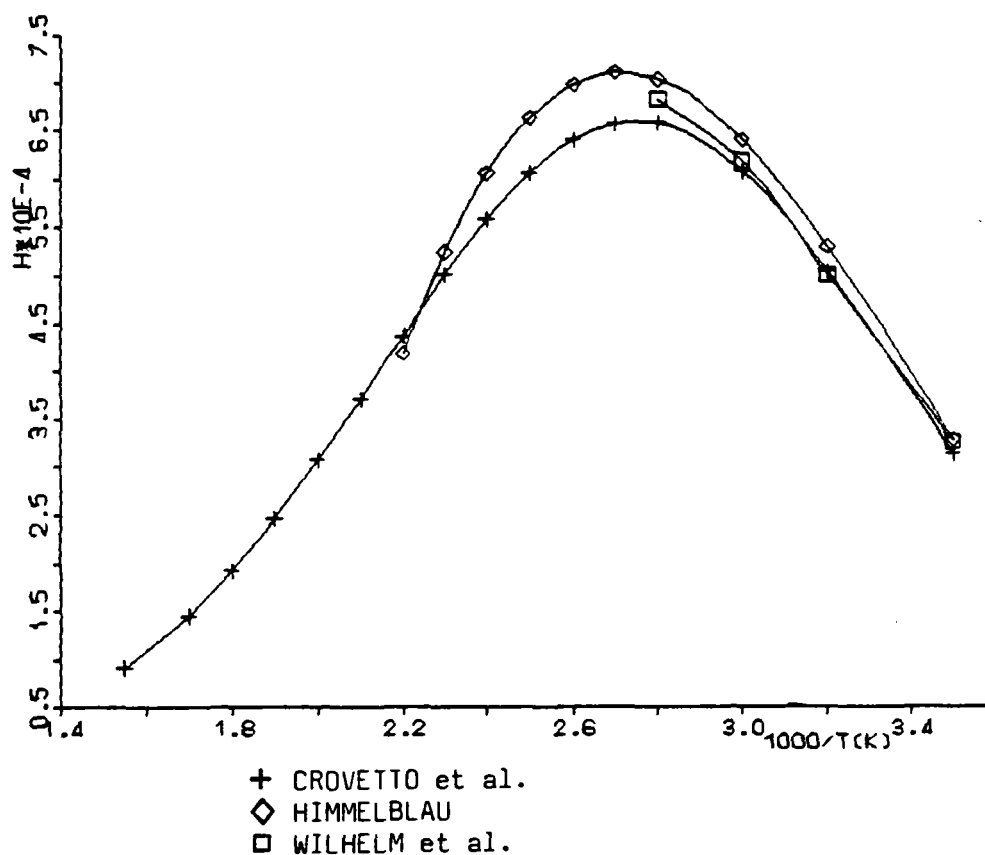


Figure 32 - Constantes de Henry du méthane en fonction de la température (bars/fraction molaire)

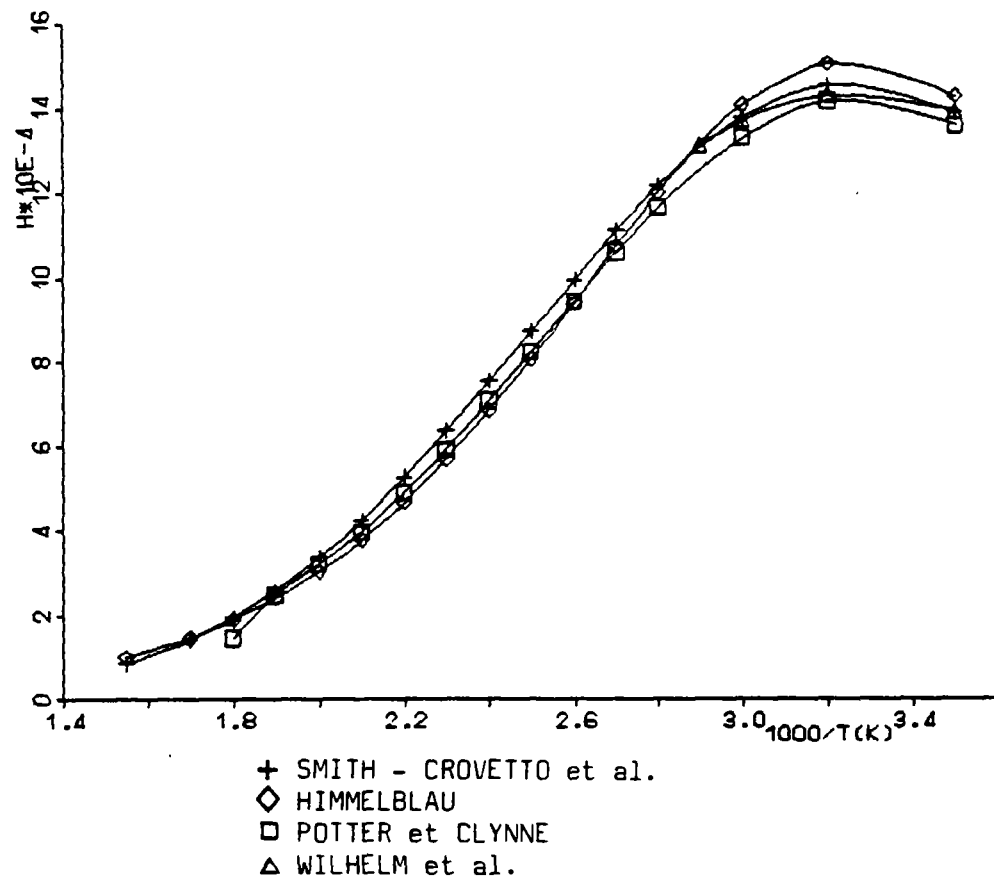


Figure 33 - Constantes de Henry de l'hélium en fonction de la température (bars/fraction molaire)

La corrélation de CROVETTO *et al.* s'avérant la plus satisfaisante, c'est elle qui a été retenue. Elle a en plus l'avantage d'être valable jusqu'à 320°C, ce qui couvre l'ensemble du domaine de température rencontré en géothermie. Elle s'exprime de la façon suivante (CROVETTO *et al.*, 1981) :

$$\ln H(T) = \sum_{i=0}^3 [A_i / (10^{-3}T)^i]$$

avec H : constante de Henry (GPa / fraction molaire)

T : température (K)

Les valeurs de A_i pour le méthane et l'argon sont les suivantes :

	A_0	A_1	A_2	A_3
CH ₄	-8.681	7.837	-1.5090	0.0206
Ar	-9.520	8.830	-1.8959	0.0698

La constante de Henry de l'hélium est déterminée par la formule suivante (SMITH, 1985) :

$$F_{He} = \left(X_{He} / X_{36Ar} \right)_{\text{liquide}} / \left(X_{Ar} / X_{36Ar} \right)_{\text{gaz}}$$

$$\text{ou } F_{He} = H_{Ar} / H_{He}$$

avec F_{He} : facteur de fractionnement de l'hélium

X : fraction molaire

K : constante de Henry

Cette formulation requiert la connaissance de la constante de Henry de l'argon, que l'on aura calculé d'après l'expression de CROVETTO *et al.*. Le facteur de fractionnement de l'hélium s'exprime de la façon suivante :

$$\ln F_{He} = a_0 + a_1 \left(\frac{T}{1000} \right)^{-1} + a_2 \left(\frac{T}{1000} \right)^{-2} + a_3 \left(\frac{T}{1000} \right)^{-3}$$

avec T : température (K)

$$a_0 = -0.727194$$

$$a_2 = -0.322123$$

$$a_1 = 0.982054$$

$$a_3 = -0.0057407$$

Les valeurs des constantes a_0 à a_3 proviennent d'un rectificatif établi par D.R. HILTON.

b) N_2

La constante de Henry de l'azote pour une température donnée est calculée par la relation suivante, applicable jusqu'à 350°C (HIMMELBLAU, 1960) :

$$A (\log \bar{H})^2 + B \left(\frac{1}{T}\right)^2 + C \log \bar{H} \frac{1}{T} + D \log \bar{H} + E \frac{1}{T} - 1 = 0$$

$$\text{où } \bar{H} = H \times 10^{-4} \quad \text{et} \quad \frac{1}{T} = \frac{1}{T} \times 10^3$$

avec H : constante de Henry (atm / fraction molaire)

T : température (K)

La résolution de cette équation du second degré en $\log H$ donne :

$$\text{DELTA} = \left(\frac{C}{T} + D \right)^2 - 4A \left[B \left(\frac{1}{T} \right)^2 + E \left(\frac{1}{T} \right) - 1 \right]$$

$$\log \bar{H} = \frac{-\left(\frac{C}{T} + D \right) - \sqrt{\text{DELTA}}}{2A}$$

Les valeurs des constantes sont les suivantes :

$$A = -0.1021$$

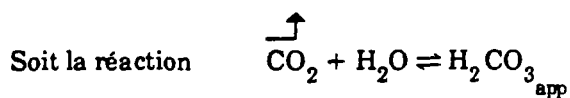
$$B = -0.1482$$

$$C = -0.01900$$

$$D = -0.03741$$

$$E = 0.8510$$

c) CO_2



La constante d'équilibre K_{CO_2} de cette réaction s'exprime par :

$$K_{CO_2} = \frac{(H_2CO_3)_{app}}{pCO_2 (H_2O)}$$

l'indice app indiquant qu'il s'agit de la somme indifférenciée de $H_2CO_{3(aqueux)}$ et de $CO_{2(aqueux)}$.

L'expression de K_{CO_2} en fonction de la température est donnée par la relation suivante, proposée par J. BUTZ et M.C. MICKLEY (1981) d'après les données de H.C. HELGESON (1969) :

$$\log K_{CO_2} = -1.3181 - 0.008442 T + 0.00002277 T^2$$

avec T en °C et K_{CO_2} en atm^{-1}

Cette relation est applicable jusqu'à 300°C.

La constante de Henry est déduite de cette constante d'équilibre par :

$$H_{CO_2} \approx \frac{55.51}{K_{CO_2}}$$

Une option permettant de prendre en compte l'effet de la salinité sur la solubilité du gaz carbonique a été introduite dans le programme pour des molalités voisines de 0,5 m NaCl :

$$H_{CO_2, m} = H_{CO_2} \times 10^{mk}$$

avec m : molalité de la solution (moles NaCl / kg H_2O)

k : coefficient de Setschenow

Le lissage des valeurs de k reportées à plusieurs températures par A.J. ELLIS et R.M. GOLDING (1963) donne :

$$k_{m=0.5} = 0.722 - 3.221 \cdot 10^{-3} T + 3.981 \cdot 10^{-6} T^2$$

avec T en °K

d) H_2S

Soit la réaction $H_2S_{\text{gazeux}} \rightleftharpoons H_2S_{\text{dissous}}$

La constante d'équilibre de cette réaction s'exprime par :

$$K_{H_2S} = \frac{(H_2S)}{p_{H_2S}}$$

L'expression de K_{H_2S} en fonction de la température est donnée par la relation suivante, proposée par J. BUTZ et M.C. MICKLEY (1981) d'après les données de H.C. HELGESON (1969) :

$$\log K_{H_2S} = -0.8866 - 0.006678 T + 0.00001619 T^2$$

avec T en $^{\circ}C$ et K_{H_2S} en atm^{-1}

Cette relation est applicable jusqu'à $300^{\circ}C$.

La constante de Henry est déduite de cette constante d'équilibre par :

$$H_{H_2S} = \frac{55.51}{K_{H_2S}}$$

4 - PRODUITS D'ACTIVITES IONIQUES ET DEGRES DE SATURATION

La réaction d'équilibre entre un minéral R_k et une solution aqueuse peut s'écrire en fonction des seules espèces simples de la façon suivante :

$$R_k = \sum_i n_k^i M_i$$

Le produit d'activité ionique, PAI, est une fonction des activités en solution des espèces impliquées dans la réaction considérée :

$$PAI_k = \prod_i (M_i)^{n_k^i}$$

Le produit de solubilité $K_{s,k}(T, P)$ du minéral considéré est une donnée thermodynamique spécifique de la réaction d'équilibre. A l'équilibre thermodynamique, le produit d'activité ionique est égal au produit de solubilité.

Le degré de saturation Ω_k de la solution vis-à-vis du minéral R_k est défini par :

$$\Omega_k = \log \frac{PAI_k}{K_{s,k}(T, P)}$$

$$\text{Si } \Omega_k \quad \begin{cases} < 0 & : \text{ la solution est sous-saturée vis-à-vis du minéral } R_k \\ = 0 & : \text{ la solution est en équilibre thermodynamique avec le minéral } R_k \\ > 0 & : \text{ la solution est sursaturée vis-à-vis du minéral } R_k \end{cases}$$

5 - COEFFICIENTS D'ACTIVITE

Les coefficients d'activité γ_s des espèces aqueuses électriquement chargées sont calculés par la formule de DEBYE-HUCKEL étendue :

$$\log \gamma_s = - \frac{A Z_s^2 \sqrt{I}}{1 + \hat{a}_s B \sqrt{I}} + D I$$

Pour la gamme de température et de pression rencontrée en géothermie, on considère que les paramètres $\hat{a}_s$ qui caractérisent la taille des espèces aqueuses sont des constantes et que A, B et D ne dépendent que de la température. I représente la force ionique de la solution et Z_s la charge de l'espèce s.

Les valeurs de $\hat{a}_s$, A, B et D retenues sont celles compilées par B. FRITZ (1981). Leur lissage pour ces dernières donne :

$$A = 0.4913 + 5.5114 \cdot 10^{-4} T + 7.3729 \cdot 10^{-6} T^2 - 4.1958 \cdot 10^{-8} T^3 + 3.1021 \cdot 10^{-10} T^4 - 1.1291 \cdot 10^{-12} T^5 + 1.7822 \cdot 10^{-15} T^6 \quad \text{pour } 0 \leq T (^{\circ}\text{C}) \leq 300$$

$$10^{-8} B = 0.32473 + 1.2240 \cdot 10^{-4} T + 7.6577 \cdot 10^{-7} T^2 - 2.9075 \cdot 10^{-9} T^3 + 5.5066 \cdot 10^{-12} T^4 \quad \text{pour } 0 \leq T (^{\circ}\text{C}) \leq 300$$

$$D = 3.409 \cdot 10^{-2} + 3.983 \cdot 10^{-4} T - 5.979 \cdot 10^{-6} T^2 + 4.395 \cdot 10^{-8} T^3 - 1.385 \cdot 10^{-10} T^4 + 1.317 \cdot 10^{-13} T^5 \quad \text{pour } 25 \leq T (^{\circ}\text{C}) \leq 300$$

Les valeurs de $\hat{a}_s$ sont reportées dans la table de données associée au programme (cf. Annexe 3).

Pour les espèces électriquement neutres, les mêmes approximations que celles utilisées par T.J. WOLERY (1983) sont adoptées :

- Les coefficients d'activité des espèces neutres polaires (CaCO_3^* , CaSO_4^* ...) sont pris égaux à 1.
- Les coefficients d'activité des espèces neutres non polaires (gaz dissous) sont pris égaux au coefficient d'activité de CO_2 dissous. Les valeurs prises par ce dernier sont obtenues par interpolation et extrapolation des données de H.C. HELGESON (1969), qui sont reportées intégralement ci-dessous pour différentes températures et pour des solutions de NaCl de molalités m différentes (FRITZ, 1981) :

T (°C)	m = 0	m = 1	m = 2	m = 3
0	1,0	1,31	1,67	2,06
25	1,0	1,27	1,57	1,93
60	1,0	1,23	1,49	1,78
100	1,0	1,20	1,44	1,74
150	1,0	1,19	1,40	1,70
200	1,0	1,23	1,47	1,74
250	1,0	1,34	1,67	1,86
300	1,0	1,50	2,00	2,29

6 - ACTIVITE DE L'EAU

L'activité de l'eau est calculée par la formule suivante (GARRELS et CHRIST, 1965, p. 66) :

$$a_{\text{H}_2\text{O}} = 1 - 0,036 I$$

I étant la force ionique de la solution.

7 - RECHERCHE DE LA REPARTITION A L'EQUILIBRE INITIALE

a) Constantes apparentes

Chaque espèce composée est en équilibre avec les ions simples qui la composent :

$$C_j = \sum_i n_j^i M_i$$

La constante d'équilibre K_j de la réaction est définie par :

$$K_j = \frac{\prod_i (M_i)^{n_j^i}}{(C_j)}$$

où les parenthèses représentent les activités des espèces considérées.

La constante apparente $KPRIM_j$ de la réaction est définie par :

$$KPRIM_j = \frac{K_j \gamma_{C_j}}{\prod_i (\gamma_{M_i})^{n_j^i}} \quad (\text{pour } M_i \neq H^+, OH^-, e^-)$$

les γ étant les coefficients d'activité des espèces considérées.

On peut tout aussi bien écrire :

$$KPRIM_j = \frac{\prod_i [M_i]^{n_j^i}}{[C_j]} \quad (\text{pour } M_i \neq H^+, OH^-, e^-)$$

où les crochets désignent les molalités des espèces considérées.

Si les espèces simples H^+ , OH^- ou e^- , qui ont des activités connues, interviennent dans la réaction, elles apparaissent sous forme d'activités dans l'expression de la constante apparente. Ainsi par exemple :

$$KPRIM_{HCO_3^-} = \frac{(H^+) [CO_3^{2-}]}{[HCO_3^-]}$$

b) Calcul des molalités des espèces simples

Les molalités des espèces simples sont initialement calculées à partir des molalités totales en éléments et des constantes d'équilibre apparentes. Pour plus de clarté, le principe de calcul est exposé pour le calcium, en ne considérant que 3 espèces, à savoir Ca^{2+} , CaCO_3° et CaHCO_3^+ :

$$N_{\text{Ca}^{2+}} = N_{\text{tot,Ca}}$$

$$N_{\text{CO}_3^{2-}} = N_{\text{tot,carbonates}}$$

$$\begin{aligned}
 N_{\text{tot,Ca}} &= N_{\text{Ca}^{2+}} + N_{\text{CaCO}_3^{\circ}} + N_{\text{CaHCO}_3^+} \\
 &= N_{\text{Ca}^{2+}} \left[1 + \frac{N_{\text{CO}_3^{2-}}}{\text{KPRIM}_{\text{CaCO}_3^{\circ}}} + \frac{(\text{H}^+) N_{\text{CO}_3^{2-}}}{\text{KPRIM}_{\text{CaHCO}_3^+}} \right] \quad \left. \vphantom{\frac{N_{\text{CO}_3^{2-}}}{\text{KPRIM}_{\text{CaCO}_3^{\circ}}}} \right\} A \\
 \text{d'où} \quad N_{\text{Ca}^{2+}} &= \frac{N_{\text{tot,Ca}}}{1 + \frac{N_{\text{CO}_3^{2-}}}{\text{KPRIM}_{\text{CaCO}_3^{\circ}}} + \frac{(\text{H}^+) N_{\text{CO}_3^{2-}}}{\text{KPRIM}_{\text{CaHCO}_3^+}}}
 \end{aligned}$$

On initialise donc les molalités des espèces simples aux molalités totales des éléments chimiques correspondants. Puis on calcule les nouvelles molalités des espèces simples selon la procédure A et on compare ces valeurs aux valeurs précédentes. On répète cette procédure jusqu'à ce que l'écart relatif soit inférieur au seuil de tolérance fixé (0.5 %). Le nombre de boucles itératives ne doit pas dépasser 10 sinon la convergence est déclarée impossible.

c) Calcul des molalités des espèces composées

Une fois les molalités des espèces simples obtenues, les molalités des espèces composées se déduisent directement des constantes apparentes correspondantes.

8 - APPRECIATION DE LA PRECISION DES CALCULS

A chaque réaction d'équilibre entre une espèce composée et les espèces simples correspondantes M_i est associée une constante d'équilibre K_j définie par :

$$K_j(T, P) = \prod_i \frac{(M_i)^{n_j^i}}{(C_j)} \quad (I)$$

Les valeurs de $K_j(T, P)$ sont calculées par les relations thermodynamiques décrites au paragraphe 1 de cette même annexe.

Les activités des espèces simples et composées sont calculées à chaque étape de l'évolution considérée à l'aide de la formule approchée du développement en séries de Taylor du second ordre.

La précision des calculs est appréciée en comparant les deuxièmes termes de l'équation (I) aux constantes d'équilibre $K_j(T, P)$, par leurs logarithmes. Les erreurs relatives x sont calculées par la formule suivante :

$$x(\%) = \left[\frac{\log [K_j(T, P)]}{\log \left[\frac{\prod_i (M_i)^{n_j^i}}{(C_j)} \right]} - 1 \right] \times 100$$

9 - VOLUME SPECIFIQUE DE LA PHASE LIQUIDE

En géothermie basse énergie, où les températures sont inférieures à 80°C, la corrélation de M. VANDENBEUSCH (1976) est utilisée. La masse volumique ρ d'une solution aqueuse de salinité S à la température T et soumise à une pression effective P , est calculée à l'aide de l'expression :

$$\rho(T, P, S) = \rho_t(T) \times f(S, T) \times h(T, P)$$

avec

- $\rho_t(T) = 0.999973 \left[1 - \frac{(T - 3.982)^2}{466700} \times \frac{T + 273}{T + 67} \times \frac{350 - T}{365 - T} \right]$

- $f(S, T) = 1 + \frac{S}{\alpha(T) + S \beta(T)}$

$$\alpha(T) = 1341.3 + 6.419 T - 9.366 \cdot 10^{-2} T^2 + 3.368 \cdot 10^{-4} T^3$$

$$\beta(T) = 0.5677 - 9.79933 \cdot 10^{-3} T + 1.3320 \cdot 10^{-4} T^2 - 5.16267 \cdot 10^{-7} T^3$$

$$\bullet \quad h(T, P) = \frac{1}{1 + \frac{dV}{V}(T, P)}$$

$$\frac{dV}{V}(T, P) = -10^{-5} P \left[1 + (0.739 - 1.23 \cdot 10^{-3} P) \exp\left(\frac{-T}{3.9 + 0.0136 P}\right) \right] \\ \times \left[\frac{8577}{1893 + P} + (1.806 \cdot 10^{-4} + 2.047 \cdot 10^{-8} P)(T - 55.5 + 0.0266 P)^2 \right]$$

- et
- $\rho(T, P, S)$: masse volumique de la solution (g/cm³)
 - S : salinité (g/l)
 - T : température (°C)
 - P : pression (atm rel.)
 - $\rho_t(T)$: masse volumique de l'eau pure à pression atmosphérique (g/cm³)
 - $f(S, T)$: facteur correctif de la masse volumique en fonction de la salinité
 - $h(T, P)$: facteur correctif de la masse volumique en fonction de la pression effective

Le volume spécifique v_1 de la phase liquide est égal à :

$$v_1(T, P, S) = \frac{1}{\rho(T, P, S)} \quad \text{en cm}^3/\text{g}$$

En géothermie haute énergie, où la température est supérieure à 80°C, c'est la corrélation de J.L. HAAS (1976) qui est utilisée. Elle est valable jusqu'à 325°C. La masse volumique ℓ d'une solution de chlorure de sodium à la pression de vapeur saturante, pour une température T et une molalité x données, est calculée par les expressions suivantes :

$$\rho = \frac{1000 + x W_2}{1000 v_o + x \phi}$$

$$\phi = \phi^* + k x^{0.5}$$

$$\phi^* = c_0 + c_1 v_o + c_2 v_o^2$$

$$k = (c_3 + c_4 v_o) [v_o / (v_c - v_o)]^2$$

$$v_o = \frac{v_c + c_5 \theta^{1/3} + c_6 \theta + c_7 \theta^4}{1,0 + c_8 \theta^{1/3} + c_9 \theta}$$

$$\theta = 647.27 - T$$

- ρ : masse volumique de la solution (g/cm³)
 x : molalité de la solution (moles NaCl / kg H₂O)
 T : température (K)
 v_o : volume spécifique de l'eau pure (cm³/g)

Les valeurs des constantes sont les suivantes :

$c_0 = -167.219$	$c_5 = -0.315154$
$c_1 = 448.55$	$c_6 = -1.203374 \cdot 10^{-3}$
$c_2 = -261.07$	$c_7 = 7.48908 \cdot 10^{-13}$
$c_3 = -13.644$	$c_8 = 0.1342489$
$c_4 = 13.97$	$c_9 = -3.946263 \cdot 10^{-3}$

$$v_c = 3.1975 \text{ cm}^3/\text{g}$$

Le volume spécifique v_l de la phase liquide est égal à :

$$v_l = \frac{1}{\rho} \quad \text{en cm}^3/\text{g}$$

10 - VISCOSITE DE LA PHASE LIQUIDE

La viscosité d'une solution saline à la température T est calculée par les expressions suivantes (MICHAELIDES, 1981) :

$$\log \frac{\mu(T, x)}{\mu_w(T)} = A(x) + B(x) \log \left[\frac{\mu_w(T)}{\mu_w(20)} \right]$$

$$A(x) = 0.3324 \cdot 10^{-1} x + 0.3624 \cdot 10^{-2} x^2 - 0.1879 \cdot 10^{-3} x^3$$

$$B(x) = -0.3961 \cdot 10^{-1} x + 0.102 \cdot 10^{-1} x^2 - 0.702 \cdot 10^{-3} x^3$$

$$\log \left[\frac{\mu_w(T)}{\mu_w(20)} \right] = \frac{20 - T}{96 + T} \left[1.2378 - 1.303 \cdot 10^{-3} (20 - T) + 3.06 \cdot 10^{-6} (20 - T)^2 \right]$$

$$\log \left[\frac{\mu_w(T)}{\mu_w(20)} \right] = \frac{20 - T}{96 + T} \left[1.2378 - 1.303 \cdot 10^{-3}(20 - T) + 3.06 \cdot 10^{-6}(20 - T)^2 + 2.55 \cdot 10^{-8}(20 - T)^3 \right]$$

$$\mu_w(20) = 1002 \mu \text{Pa.s}$$

- avec
- μ : viscosité de la solution (Pa.s)
 - μ_w : viscosité de l'eau pure (Pa.s)
 - T : température (°C)
 - x : molalité de la solution (moles NaCl / kg H₂O)

DONNEES THERMODYNAMIQUES ET LISTING DU FICHIER DE DONNEES DU PROGRAMME

Réaction	log K _{25°C, 1 bar}	ΔH°_r à 25°C (kcal/mole)	$\Delta C^\circ_{p,r}(T)$ (cal·K ⁻¹ ·mole ⁻¹) ($\Delta C^\circ_{p,r}(T) = CA + CB T + CC/T^2 + CD T^2$)				$\Delta V^\circ_r(T)$ (cm ³ /mole) ($\Delta V^\circ_r(T) = VA + VB T + VC T^2$)		
			CA	CB	CC×10 ⁻⁵	CD	VA	VB	VC
$H_2O \rightleftharpoons H^+ + OH^-$	-13,99 ^a	13,338 ^a	-783,85 ^a	4,380 ^a	0	-6,464.10 ⁻³ ^a	-134,8 ^a	0,708 ^a	-1,1.10 ⁻³ ^a
$HF^\circ \rightleftharpoons H^+ + F^-$	-3,17 ^a	-3,700 ^a	-36 ^a	-	-	-	-106,55 ^a	0,5066 ^a	-8,238.10 ⁻⁴ ^a
$H_4SiO_4^\circ \rightleftharpoons H^+ + H_3SiO_4^-$	-9,82 ^a	6,118 ^a	-37,99 ^a	0,0531 ^a	0	-1,12.10 ⁻⁴ ^a	-143,16 ^a	0,700 ^a	-10 ⁻³ ^a
$H_3BO_3^\circ \rightleftharpoons H^+ + H_2BO_3^-$	-9,23 ^a	3,218 ^a	-33,0 ^a	-	-	-	-116,6 ^a	0,51 ^a	-7,86.10 ⁻⁴ ^a
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	-10,33 ^a	-3,512 ^a	637,30 ^a	-4,213 ^a	0	6,233.10 ⁻³ ^a	-76,13 ^a	0,358 ^a	-6,35.10 ⁻⁴ ^a
$H_2CO_3^\circ \rightleftharpoons 2H^+ + CO_3^{2-}$	-16,68 ^a	5,700 ^a	-139,0 ^a	-	-	-	-186,73 ^a	0,923 ^a	-1,59.10 ⁻³ ^a
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	-1,98 ^a	-4,900 ^a	1523,40 ^a	-8,876 ^a	0	-1,321.10 ⁻² ^a	-139,60 ^a	0,774 ^a	-1,217.10 ⁻³ ^a
$H^+ + S^{2-} \rightleftharpoons HS^-$	17,10 ^b	-12,10 ^c	62,10 ^c	-	-	-	-65,7 ^d	0,572 ^d	-8,652.10 ⁻⁴ ^d
$H_2S^\circ \rightleftharpoons H^+ + HS^-$	-6,98 ^a	6,0 ^a	-80,00 ^a	-	-	-	-85,4 ^e	0,4548 ^e	-7,414.10 ⁻⁴ ^e
$NaCO_3^- \rightleftharpoons Na^+ + CO_3^{2-}$	-1,27 ^f	-8,911 ^f	-	-	-	-	-173,82 ^g	1,055 ^g	-1,666.10 ⁻³ ^g
$NaHCO_3^\circ \rightleftharpoons Na^+ + H^+ + CO_3^{2-}$	-10,08 ^f	3,512 ^f	-	-	-	-	-75,17 ^g	0,457 ^g	-7,186.10 ⁻⁴ ^g
$CaF^+ \rightleftharpoons Ca^{2+} + F^-$	-1,23 ^a	-2,60 ^a	-890,46 ^{g'}	5,317 ^{g'}	0	-7,807.10 ⁻³ ^{g'}	-181,54 ^a	1,09 ^a	-1,703.10 ⁻³ ^a
$CaCO_3^\circ \rightleftharpoons Ca^{2+} + CO_3^{2-}$	-3,16 ^a	-4,025 ^a	0 ^a	0 ^a	0	0 ^a	-240,38 ^a	1,493 ^a	-2,418.10 ⁻³ ^a
$CaHCO_3^+ \rightleftharpoons Ca^{2+} + H^+ + CO_3^{2-}$	-11,55 ^a	2,012 ^a	-439,06 ^h	1,979 ^h	0	-2,705.10 ⁻³ ^h	-208,01 ^a	1,167 ^a	-1,912.10 ⁻³ ^a
$CaSO_4^\circ \rightleftharpoons Ca^{2+} + SO_4^{2-}$	-2,43 ^a	-0,81 ^a	-2566,96 ⁱ	15,069 ⁱ	0	-2,215.10 ⁻² ⁱ	-203,38 ^g	1,233 ^g	-1,946.10 ⁻³ ^g
$MgF^+ \rightleftharpoons Mg^{2+} + F^-$	-1,91 ^a	-2,29 ^a	-248,38 ^a	1,777 ^a	0	-2,837.10 ⁻³ ^a	-98,85 ^a	0,607 ^a	-9,62.10 ⁻⁴ ^a
$MgCO_3^\circ \rightleftharpoons Mg^{2+} + CO_3^{2-}$	-2,99 ^a	-2,017 ^a	243,10 ^a	-1,56 ^a	0	2,265.10 ⁻³ ^a	-251,77 ^a	1,54 ^a	-2,452.10 ⁻³ ^a
$MgHCO_3^+ \rightleftharpoons Mg^{2+} + H^+ + CO_3^{2-}$	-11,40 ^a	2,32 ^a	183,24 ^a	-1,56 ^a	0	2,265.10 ⁻³ ^a	-233,03 ^a	1,30 ^a	-2,103.10 ⁻³ ^a
$MgSO_4^\circ \rightleftharpoons Mg^{2+} + SO_4^{2-}$	-2,40 ^a	-3,40 ^a	-1935,0 ^a	13,09 ^a	0	-1,944.10 ⁻² ^a	-209,47 ^a	1,254 ^a	-1,960.10 ⁻³ ^a
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	13,014 ^j	-10,179 ^k	77,01 ^l	-0,650 ^l	0	1,159.10 ⁻³ ^l	99,4 ^m	-0,4838 ^m	7,209.10 ⁻⁴ ^m
$Fe(OH)^+ \rightleftharpoons Fe^{2+} + OH^-$	-4,49 ⁿ	0,138 ⁿ	746,51 ^a	4,334 ^a	0	-6,394.10 ⁻³ ^a	-	-	-
$Fe(OH)_2^\circ \rightleftharpoons Fe^{2+} + 2OH^-$	-7,38 ⁿ	-2,724 ⁿ	-	-	-	-	-	-	-
$Fe(OH)_3^- \rightleftharpoons Fe^{2+} + 3OH^-$	-12,97 ⁿ	7,814 ⁿ	-	-	-	-	-	-	-
$Fe(OH)_4^{2-} \rightleftharpoons Fe^{2+} + 4OH^-$	-9,73 ^o	6,66 ^p	-	-	-	-	-	-	-
$Fe(OH)_2^{2+} + e^- \rightleftharpoons Fe^{2+} + OH^-$	1,214 ^q	-7,241 ^q	-	-	-	-	-	-	-
$Fe(OH)_2^+ + e^- \rightleftharpoons Fe^{2+} + 2OH^-$	-9,296 ^q	-0,6158 ^r	-	-	-	-	-	-	-
$Fe(OH)_3^\circ + e^- \rightleftharpoons Fe^{2+} + 3OH^-$	-15,358 ^a	3,600 ^r	-	-	-	-	-	-	-
$Fe(OH)_4^- + e^- \rightleftharpoons Fe^{2+} + 4OH^-$	-21,346 ^q	11,355 ^r	-2980,13 ^t	16,96 ^t	0	-2,576.10 ⁻² ^t	-	-	-
$FeF_2^+ + e^- \rightleftharpoons Fe^{2+} + F^-$	6,814 ^u	-12,879 ^u	-	-	-	-	-451,32 ^v	2,8482 ^v	-4,541.10 ⁻³ ^v
$FeF_2^+ + e^- \rightleftharpoons Fe^{2+} + 2F^-$	2,214 ^u	-14,979 ^u	-	-	-	-	-	-	-
$FeF_3^\circ + e^- \rightleftharpoons Fe^{2+} + 3F^-$	-0,986 ^u	-15,579 ^u	-	-	-	-	-	-	-

Réaction	log K _{25°C, 1 bar}	ΔH°_r à 25°C (kcal/mole)	$\Delta C^\circ_{p,r}(T)$ (cal K ⁻¹ mole ⁻¹) ($\Delta C^\circ_{p,r}(T) = CA + CB T + CC/T^2 + CD T^2$)				$\Delta V^\circ_r(T)$ (cm ³ /mole) ($\Delta V^\circ_r(T) = VA + VB T + VC T^2$)		
			CA	CB	CCx10 ⁻⁵	CD	VA	VB	VC
$FeCl^+ \rightleftharpoons Fe^{2+} + Cl^-$	-0,14 w	-7,501 z	-	-	-	-	-	-	-
$FeCl_2^+ + e^- \rightleftharpoons Fe^{2+} + Cl^-$	11,534 y	-18,089 y	-	-	-	-	-	-	-
$FeCl_2^+ + e^- \rightleftharpoons Fe^{2+} + 2Cl^-$	10,884 y	-18,149 y	-	-	-	-	-	-	-
$FeCl_3^+ + e^- \rightleftharpoons Fe^{2+} + 3Cl^-$	11,884 y	-20,469 y	-	-	-	-	-	-	-
$FeCO_3^+ \rightleftharpoons Fe^{2+} + CO_3^{2-}$	-4,73 z	0,070 z	-	-	-	-	-	-	-
$FeHCO_3^+ \rightleftharpoons Fe^{2+} + H^+ + CO_3^{2-}$	-12,5 z	2,472 z	-	-	-	-	-341,98 aa	1,968 aa	-3,178.10 ⁻³ aa
$FeSO_4^+ \rightleftharpoons Fe^{2+} + SO_4^{2-}$	-2,20 c	-0,56 c	-	-	-	-	-168,28 g	1,0207 g	-1,6107.10 ⁻³ g
$Fe(SO_4)_2^+ + e^- \rightleftharpoons Fe^{2+} + 2SO_4^{2-}$	7,594 bb	-14,779 bb	-	-	-	-	-	-	-
$FeSO_4^+ + e^- \rightleftharpoons Fe^{2+} + SO_4^{2-}$	8,864 cc	-16,379 cc	-	-	-	-	-196,03	1,3052	-2,104.10 ⁻³
$Fe(HS)_2^+ \rightleftharpoons Fe^{2+} + 2HS^-$	-8,94 c	-	-	-	-	-	-	-	-
$Fe(HS)_3^+ \rightleftharpoons Fe^{2+} + 3HS^-$	-10,97 c	-	-	-	-	-	-	-	-
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$ calcite	-8,52 a	-2,506 a	-107,19 a	-5,240.10 ⁻³ a	6,2 a	0	-305,7 a	1,564 a	-2,462.10 ⁻³ a
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$ aragonite	-8,35 a	-2,558 a	-102,34 a	-1,024.10 ⁻² a	3,34 a	0	-302,92 a	1,564 a	-2,462.10 ⁻³ a
$CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$ dolomite	-18,17 a	-7,286 a	1197,62 a	-8,444 a	10,95 a	1,247.10 ⁻² a	-596,88 a	3,105 a	-4,914.10 ⁻³ a
$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$ fluorite	-10,97 a	6,0 a	-60,89 a	7,28.10 ⁻³ a	0,47 a	0	-307,34 a	1,65 a	-2,61.10 ⁻³ a
$SiO_2 + 2OH^- + H^+ \rightleftharpoons H_3SiO_4^-$ quartz	14,16 a	-14,588 a	1519,60 a	-8,675 a	2,7 a	1,279.10 ⁻² a	140,95 a	-0,817 a	1,260.10 ⁻³ a
$SiO_2 + 2OH^- + H^+ \rightleftharpoons H_3SiO_4^-$ calcédoine	14,45 a	-14,958 a	1519,60 a	-8,675 a	2,7 a	1,279.10 ⁻² a	140,95 a	-0,817 a	1,260.10 ⁻³ a
$SiO_2 + 2OH^- + H^+ \rightleftharpoons H_3SiO_4^-$ silice amorphe	15,47 a	-17,668 a	1517,44 a	-8,671 a	3,45 a	1,279.10 ⁻² a	134,64 a	-0,817 a	1,260.10 ⁻³ a
$FeS + H^+ \rightleftharpoons Fe^{2+} + HS^-$ troilite	-5,31 dd	-2,298 ee	-666,58 ff	3,608 ff	0	-5,1646.10 ⁻³ ff	-214,3 gg	1,182 gg	-1,817.10 ⁻³ gg
$FeS + H^+ \rightleftharpoons Fe^{2+} + HS^-$ pyrrhotite	-5,19 dd	-2,218 hh	-666,58 ii	3,608 ii	0	-5,1646.10 ⁻³ ii	-213,68 gg	1,182 gg	-1,817.10 ⁻³ gg
$FeS + H^+ \rightleftharpoons Fe^{2+} + H_2S$ mackinawite	-3,6 dd	-	-	-	-	-	-214,3 jj	1,182 jj	-1,817.10 ⁻³ jj
$FeS + H^+ \rightleftharpoons Fe^{2+} + H_2S$ sulfure de fer amorphe	-2,95 dd	-	-	-	-	-	-	-	-
$FeS_2 + 2H^+ + 2e^- \rightleftharpoons Fe^{2+} + 2HS^-$ pyrite	-16,29 kk	10,564 hh	-962,48 ll	5,142 ll	3,05 ll	-7,385.10 ⁻³ ll	-293,642 gg	1,754 gg	-2,683.10 ⁻³ gg
$FeS_2 + 2H^+ + 2e^- \rightleftharpoons Fe^{2+} + 2HS^-$ marcassite	-15,956 mm	10,034 nn	-962,48 oo	5,142 oo	3,05 oo	-7,385.10 ⁻³ oo	-294,28 gg	1,754 gg	-2,683.10 ⁻³ gg
$Fe_2S_3 + 3H^+ + 2e^- \rightleftharpoons 2Fe^{2+} + 3HS^-$ sulfure de fer γ	-23,52 pp	10,246 qq	-	-	-	-	-	-	-
$Fe_3S_4 + 4H^+ + 2e^- \rightleftharpoons 3Fe^{2+} + 4HS^-$ greigite	-17,97 r	-	-	-	-	-	-	-	-
$Fe(OH)_3 + e^- \rightleftharpoons Fe^{2+} + 3OH^-$ hydroxyde de fer amorphe	-24,066 rr	14,760 c	-	-	-	-	-	-	-
$FeOOH + H^+ + e^- \rightleftharpoons Fe^{2+} + 2OH^-$ goethite	-14,296 aa	-0,087 tt	-1902,9 uu	-20,307 uu	0	-1,573.10 ⁻² uu	-366,92 gg	1,947 gg	-3,022.10 ⁻³ gg
$FeOOH + H^+ + e^- \rightleftharpoons Fe^{2+} + 2OH^-$ lépidocrocite	-11,696 aa	-3,635 tt	-1902,9 vv	-20,307 vv	0	-1,573.10 ⁻² vv	-368,47 gg	1,947 gg	-3,022.10 ⁻³ gg
$FeCO_3 \rightleftharpoons Fe^{2+} + CO_3^{2-}$ sidérite	-10,55 ww	-4,212 xx	-465,81 yy	-24,674 yy	0	-2,944.10 ⁻³ yy	-296,95 gg	1,540 gg	-2,452.10 ⁻³ gg

^a MICHARD (1983) - ^b GIGGENBACH (1971) - ^c NAUMOV *et al.* (1974) - ^d calculé à partir de $V_{HS}^{\circ}(T)$ (MICHARD, 1983) et $V_{S_2}^{\circ}(25^{\circ}C)$ (NAUMOV *et al.*, 1974) - ^e calculé à partir de $V_{HS}^{\circ}(T)$ (MICHARD, 1983) et $V_{H_2S}^{\circ}(T)$ obtenu en lissant les données de ELLIS et MacFADDEN (1972) - ^f PLUMMER *et al.* (1976) - ^g calculé d'après la théorie de FUOSS selon HEMMES (1972) - ^{g'} calculé à partir de $C_p^{\circ}Fe(T)$ et $C_p^{\circ}CaF_2(25^{\circ}C)$ (MICHARD, 1983) et de $C_p^{\circ}Ca_2(T)$ obtenu en lissant les données calculées à différentes températures d'après HELGESON *et al.* (1981) - ^h calculé à partir de $C_p^{\circ}CO_2(T)$ et $C_p^{\circ}CaHCO_3(T)$ (MICHARD, 1983) et de $C_p^{\circ}Ca_2(T)$ obtenu en lissant les valeurs calculées à différentes températures d'après HELGESON *et al.* (1981) - ⁱ calculé à partir de $C_p^{\circ}SO_2(T)$ et $C_p^{\circ}CaSO_4(25^{\circ}C)$ (MICHARD, 1983) et de $C_p^{\circ}Ca_2(T)$ obtenu en lissant les valeurs calculées à différentes températures d'après HELGESON *et al.* (1981) - ^j calculé à partir de $\Delta G_{Fe_2}^{\circ}$ et $\Delta G_{Fe_3}^{\circ}$ (HELGESON, 1985) - ^k calculé d'après $\Delta H_{Fe_2}^{\circ}(25^{\circ}C)$ et $\Delta H_{Fe_3}^{\circ}(25^{\circ}C)$ (HELGESON, 1985) - ^l obtenu en lissant les valeurs de $C_p^{\circ}Fe_2(T)$ et $C_p^{\circ}Fe_3(T)$ calculées d'après HELGESON *et al.* (1981) - ^m calculé à partir de $V_{Fe_2}^{\circ}(T)$ (MICHARD, 1983) et de $V_{Fe_3}^{\circ}(T)$ obtenu en lissant les valeurs calculées d'après HELGESON *et al.* (1981) - ⁿ BAES et MESMER (1981) (ainsi que les données concernant l'équilibre $H_2O \rightleftharpoons H^+ + OH^-$) - ^o calculé à partir de $\Delta G_{Fe(OH)_2}^{\circ}$ (NAUMOV *et al.*, 1974), ΔG_{OH}° (HELGESON *et al.*, 1981) et $\Delta G_{Fe_2}^{\circ}$ (HELGESON, 1985) - ^p calculé d'après BAES et MESMER (1981) en utilisant la valeur de log K de NAUMOV *et al.* (1974) (ainsi que les données concernant l'équilibre $H_2O \rightleftharpoons H^+ + OH^-$) - ^q BAES et MESMER (1976) (ainsi que les données concernant les équilibres $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ et $H_2O \rightleftharpoons H^+ + OH^-$) - ^r BAES et MESMER (1981) (ainsi que les données concernant les équilibres $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ et $H_2O \rightleftharpoons H^+ + OH^-$) - ^s BALL *et al.* (1980) (ainsi que les données concernant les équilibres $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ et $H_2O \rightleftharpoons H^+ + OH^-$) - ^t obtenu à partir de $C_p^{\circ}Fe(OH)_2$ (GUNNLAUGSSON et ARNORSSON, 1982) et de $C_p^{\circ}Fe_2(25^{\circ}C)$ et $C_p^{\circ}OH(T)$ (MICHARD, 1983) - ^u NORDSTROM et JENNE (1977) (ainsi que les données concernant l'équilibre $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$) - ^v calculé d'après la théorie de FUOSS selon HEMMES (1972) (avec également les données concernant l'équilibre $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$) - ^w DAVISON (1979) - ^x ARNORSSON *et al.* (1982) - ^y HELGESON (1969) (ainsi que les données concernant l'équilibre $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$) - ^z FOUILLAC et CRIAUD (1984) - ^{aa} calculé d'après la théorie de FUOSS selon HEMMES (1972) (avec également les données concernant l'équilibre $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$) - ^{bb} BALL *et al.* (1980) (ainsi que les données concernant l'équilibre $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$) - ^{cc} NAUMOV *et al.* (1974) (ainsi que les données concernant l'équilibre $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$) - ^{dd} DAVISON (1988) - ^{ee} calculé à partir de $\Delta H_{troilite}^{\circ}$ (NAUMOV *et al.*, 1974), $\Delta H_{Fe_2}^{\circ}$ (HELGESON, 1985) et ΔH_{HS}° (HELGESON *et al.*, 1981) - ^{ff} supposé égal à la pyrrhotite - ^{gg} calculé à partir de $V_{minéral}^{\circ}(25^{\circ}C)$ (ROBIE *et al.*, 1978) et de $V_{Fe_2}^{\circ}(T)$ et $V_{HS}^{\circ}(T)$ (MICHARD, 1983) - ^{hh} calculé à partir de $\Delta H_{minéral}^{\circ}$ (HELGESON *et al.*, 1978), $\Delta H_{Fe_2}^{\circ}$ (HELGESON, 1985) et ΔH_{HS}° (HELGESON *et al.*, 1981) - ⁱⁱ calculé à partir de $C_p^{\circ}pyrrhotite(T)$ (HELGESON *et al.*, 1978) et de $C_p^{\circ}Fe_2(T)$ et de $C_p^{\circ}HS(T)$ obtenus en lissant les valeurs calculées d'après HELGESON *et al.* (1981 et 1985) - ^{jj} supposé égal à la troilite - ^{kk} calculé à partir de $\Delta G_{pyrite}^{\circ}$ (HELGESON *et al.*, 1978), $\Delta G_{Fe_2}^{\circ}$ (HELGESON, 1985) et ΔG_{HS}° (HELGESON *et al.*, 1981) - ^{ll} calculé à partir de $C_p^{\circ}pyrite(T)$ (HELGESON *et al.*, 1978) et des valeurs $C_p^{\circ}Fe_2(T)$ et $C_p^{\circ}HS(T)$ obtenues en lissant les valeurs calculées d'après HELGESON *et al.* (1981 et 1985) - ^{mm} calculé à partir de $\Delta G_{marcasite}^{\circ}$ (ROBIE *et al.*, 1978), $\Delta G_{Fe_2}^{\circ}$ (HELGESON, 1985) et ΔG_{HS}° (HELGESON *et al.*, 1981) - ⁿⁿ calculé à partir de $\Delta H_{marcasite}^{\circ}$ (ROBIE *et al.*, 1978), $\Delta H_{Fe_2}^{\circ}$ (HELGESON, 1985) et ΔH_{HS}° (HELGESON *et al.*, 1981) - ^{oo} supposé égal à la pyrite - ^{pp} calculé à partir de $\Delta G_{Fe_2S_3}^{\circ}$ (NAUMOV *et al.*, 1974), $\Delta G_{Fe_2}^{\circ}$ (HELGESON, 1985) et ΔG_{HS}° (HELGESON *et al.*, 1981) - ^{qq} calculé à partir de $\Delta H_{Fe_2S_3}^{\circ}$ (NAUMOV *et al.*, 1974), $\Delta H_{Fe_2}^{\circ}$ (HELGESON, 1985) et ΔH_{HS}° (HELGESON *et al.*, 1981) - ^{rr} SERREBRENNIKOV (1977) (ainsi que le log K de l'équilibre $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$) - ^{ss} calculé d'après LANGMUIR (1969) (avec également les données concernant les équilibres $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ et $H_2O \rightleftharpoons H^+ + OH^-$) - ^{tt} calculé à partir de $\Delta H_{minéral}^{\circ}$ (GUNNLAUGSSON et ARNORSSON, 1982), $\Delta H_{Fe_2}^{\circ}$ (HELGESON, 1985) et ΔH_{OH}° (HELGESON *et al.*, 1981) - ^{uu} calculé à partir de $C_p^{\circ}goethite(T)$ (GUNNLAUGSSON et ARNORSSON, 1982), $C_p^{\circ}OH(T)$ (MICHARD, 1983) et $C_p^{\circ}Fe_2(T)$ obtenu en lissant les valeurs calculées d'après HELGESON *et al.* (1981 et 1985) - ^{vv} supposé égal à la goethite - ^{ww} LANGMUIR (1969) - ^{xx} calculé à partir de $\Delta H_{siderite}^{\circ}$, $\Delta H_{Fe_2}^{\circ}$ et $\Delta H_{CO_2}^{\circ}$ (HELGESON, 1985) - ^{yy} calculé à partir de $C_p^{\circ}siderite(T)$ (HELGESON *et al.*, 1978), $C_p^{\circ}CO_2(25^{\circ}C)$ (MICHARD, 1983) et $C_p^{\circ}Fe_2(T)$ obtenu en lissant les valeurs calculées d'après HELGESON *et al.* (1981 et 1985)

LISTING DU FICHIER DE DONNEES DU PROGRAMME

	5	Espèce	2	$\delta_g (\times 10^8)$	Masse molaire
Espèces simples	1	H	+1.	9.0	1.008
	2	Na	+1.	4.0	22.990
	3	K	+1.	3.0	39.102
	4	Ca	+2.	6.0	40.080
	5	Mg	+2.	8.0	24.312
	6	Fe	+2.	6.0	55.847
	7	OH	-1.	3.5	17.007
	8	F	-1.	3.5	18.998
	9	H3SiO4	-1.	4.0	95.107
	10	Cl	-1.	3.0	35.453
	11	H2BO3	-1.	2.5	60.825
	12	CO3	-2.	4.5	60.009
	13	SO4	-2.	4.0	96.062
	14	HS	-1.	3.5	33.072
	15	E	-1.	0.0	0.000
	16	N2	0.	0.0	28.013
	17	CH4	0.	0.0	16.043
	18	He	0.	0.0	4.003
	19	Ar	0.	0.0	39.948
	20	H2O	0.	0.0	18.015
Espèces composées	21	HF	0.	0.0	20.006
	22	H4SiO4	0.	0.0	96.107
	23	H3BO3	0.	0.0	61.833
	24	HCO3	-1.	4.5	61.009
	25	H2CO3	0.	0.0	62.009
	26	HSO4	-1.	4.0	97.062
	27	S	-2.	5.0	32.064
	28	H2S	0.	0.0	34.080
	29	NaCO3	-1.	5.4	82.999
	30	NaHCO3	0.	0.0	83.991
	31	CaF	+1.	5.0	59.078
	32	CaCO3	0.	0.0	100.080
	33	CaHCO3	+1.	6.0	101.080
	34	CaSO4	0.	0.0	136.142
	35	MgF	+1.	4.5	43.310
	36	MgCO3	0.	0.0	84.320
	37	MgHCO3	+1.	4.0	85.320
	38	MgSO4	0.	0.0	120.374
	39	Fe	+3.	9.0	55.847
	40	Fe(OH)	+1.	5.0	72.855
	41	Fe(OH)2	0.	0.0	89.862
	42	Fe(OH)3	-1.	5.0	106.869
	43	Fe(OH)4	-2.	5.0	123.877
	44	Fe(OH)	+2.	5.0	72.855
	45	Fe(OH)2	+1.	5.4	89.862
	46	Fe(OH)3	0.	0.0	106.869
	47	Fe(OH)4	-1.	5.4	123.876
	48	FeF	+2.	5.0	74.845
	49	FeF2	+1.	4.0	93.843
	50	FeF3	0.	0.0	112.841
	51	FeCl	+1.	5.0	91.300
	52	FeCl	+2.	5.0	91.300
	53	FeCl2	+1.	5.0	126.753
	54	FeCl3	0.	0.0	162.206
	55	FeCO3	0.	0.0	115.856
	56	FeHCO3	+1.	4.0	116.864
	57	FeSO4	0.	0.0	151.909
	58	Fe(SO4)2	-1.	4.0	247.970
	59	FeSO4	+1.	4.0	151.909
	60	Fe(HS)2	0.	0.0	121.991
	61	Fe(HS)3	-1.	4.0	155.063

j	Espèce	log k		ΔH° (cal/mole)		CA	CB	CC(*10E-5)	CD	VA	VB	VC
		(25 C, 1 atm)										
20	H2O	-13.99	13338	-783.85	0.4380E+01	0.000	-0.6454E-02	-134.80	0.708	-0.1100E-02		
21	HF	-3.17	-3700	-36.00	0.0000E+00	0.000	0.0000E+00	-106.55	0.507	-0.8238E-03		
22	H4SiO4	-9.82	6118	-37.99	0.5310E-01	0.000	-0.1120E-03	-143.16	0.700	-0.1000E-02		
23	H3BO3	-9.23	3218	-33.00	0.0000E+00	0.000	0.0000E+00	-116.60	0.510	-0.7860E-03		
24	HCO3	-10.33	3512	637.30	-0.4213E+01	0.000	0.6233E-02	-76.13	0.358	-0.6350E-03		
25	H2CO3	-16.68	5700	-139.00	0.0000E+00	0.000	0.0000E+00	-186.73	0.323	-0.1590E-02		
26	HSO4	-1.98	-4900	-1523.40	0.8676E+01	0.000	-0.1321E-01	-139.60	0.774	-0.1217E-02		
27	S	17.10	-12100	62.10	0.0000E+00	0.000	0.0000E+00	-65.70	0.572	-0.8652E-03		
28	H2S	-6.98	6000	-80.00	0.0000E+00	0.000	0.0000E+00	-85.40	0.455	-0.7414E-03		
29	NaCO3	-1.27	-8911	0.00	0.0000E-00	0.000	0.0000E-00	-173.82	1.055	-0.1666E-02		
30	NaHCO3	-10.08	3512	0.00	0.0000E-00	0.000	0.0000E-00	-75.17	0.457	-0.1946E-03		
31	CaF	-1.23	-2600	-890.46	0.5317E+01	0.000	-0.7807E-02	-181.54	1.090	-0.1703E-02		
32	CaCO3	-3.16	-4025	0.00	0.0000E+00	0.000	0.0000E+00	-240.38	1.493	-0.2418E-02		
33	CaHCO3	-11.55	2012	-439.06	0.1980E+01	0.000	-0.2705E-02	-208.01	1.167	-0.1912E-02		
34	CaSO4	-2.43	-810	-2566.96	0.1507E+02	0.000	-0.2215E-01	-203.38	1.233	-0.1946E-02		
35	MgF	-1.91	-2290	-248.38	0.1777E+01	0.000	-0.2837E-02	-98.85	0.607	-0.9620E-03		
36	MgCO3	-2.99	-2017	243.10	-0.1560E+01	0.000	0.2265E-02	-251.77	1.540	-0.2452E-02		
37	MgHCO3	-11.40	2320	183.24	-0.1560E+01	0.000	0.2265E-02	-233.03	1.300	-0.2103E-02		
38	MgSO4	-2.40	-3400	-1935.00	0.1309E+02	0.000	-0.1944E-01	-209.47	1.254	-0.1960E-02		
39	Fe3	13.014	-10179	77.01	-0.6504E+00	0.000	1.1588E-03	99.40	-0.484	0.7209E-03		
40	Fe(OH)	-4.49	138	746.51	4.3335E+00	0.000	-0.6394E-02	0.00	0.000	0.0000E+00		
41	Fe(OH)2	-7.38	-2724	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
42	Fe(OH)3	-12.97	7814	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
43	Fe(OH)4	-9.73	6660	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
44	Fe(OH)	1.214	-7241	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
45	Fe(OH)2	-9.296	-616	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
46	Fe(OH)3	-15.358	3600	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
47	Fe(OH)4	-21.346	11355	-2980.13	0.1696E+02	0.000	-0.2576E-01	0.00	0.000	0.0000E+00		
48	FeF	6.814	-12879	0.00	0.0000E+00	0.000	0.0000E+00	-451.32	2.848	-0.4541E-02		
49	FeF2	2.214	-14979	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
50	FeF3	-0.986	-15579	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
51	FeCl	-0.14	-7501	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
52	FeCl2	11.534	-18089	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
53	FeCl3	10.884	-18149	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
54	FeCl3	11.884	-20469	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
55	FeCO3	-4.73	70	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
56	FeHCO3	-12.500	2472	0.00	0.0000E+00	0.000	0.0000E+00	-341.98	1.968	-0.3178E-02		
57	FeSO4	-2.20	-560	0.00	0.0000E+00	0.000	0.0000E+00	-168.28	1.021	-0.1611E-02		
58	Fe(SO4)2	7.594	-14779	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
59	FeSO4	8.864	-16379	0.00	0.0000E+00	0.000	0.0000E+00	-196.03	1.305	-0.2104E-02		
60	Fe(HS)2	-8.94	0	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
61	Fe(HS)3	-10.97	0	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
62	Aragonit	-8.35	-2558	-102.34	-0.1024E-01	3.340	0.0000E+00	-302.92	1.564	-0.2462E-02		
63	Calcdoit	14.45	-14958	1519.60	-0.8675E+01	2.700	0.1279E-01	140.95	-0.817	0.1260E-02		
64	Calcite	-8.52	-2506	-107.19	-0.5240E-02	6.200	0.0000E+00	-305.70	1.564	-0.2462E-02		
65	Dolomite	-18.17	-7286	1197.62	-0.8444E+01	10.948	0.1247E-01	-596.88	3.105	-0.4914E-02		
66	Quartz	14.16	-14588	1519.60	-0.8675E+01	2.700	0.1279E-01	140.95	-0.817	0.1260E-02		
67	SiAmorph	15.47	-17668	1517.44	-0.8671E+01	3.450	0.1279E-01	134.64	-0.817	0.1260E-02		
68	Troilite	-5.31	-2298	-666.58	3.6084E+00	0.000	-5.1646E-03	-214.30	1.182	-0.1817E-02		
69	Pyrrothol	-5.19	-2218	-666.58	3.6084E+00	0.000	-5.1646E-03	-213.68	1.182	-0.1817E-02		
70	Mackinaw	-3.60	0	0.00	0.0000E-00	0.000	0.0000E-00	-214.30	1.182	-0.1817E-02		
71	Fe2S3	-23.52	10246	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
72	Marcassi	-15.956	10034	-962.48	5.1420E+00	3.050	-7.3852E-03	-294.28	1.754	-0.2683E-02		
73	Pyrite	-16.29	10564	-962.48	5.1420E+00	3.050	-7.3852E-03	-293.64	1.754	-0.2683E-02		
74	FeS Amor	-2.95	0	0.00	0.0000E-00	0.000	0.0000E-00	0.00	0.000	0.0000E+00		
75	Fe(OH)3A	-24.066	14760	0.00	0.0000E-00	0.000	0.0000E-00	0.00	0.000	0.0000E+00		
76	Goethite	-14.296	-87	-1902.90	-2.0307E+01	0.000	-0.1573E-01	-366.92	1.947	-0.3022E-02		
77	Greigite	-17.97	0	0.00	0.0000E+00	0.000	0.0000E+00	0.00	0.000	0.0000E+00		
78	Siderite	-10.55	-4212	-465.81	-2.4674E+01	0.000	-2.9440E-03	-296.95	1.540	-0.2452E-02		
79	Lepidocr	-11.696	-3635	-1902.90	-2.0307E+01	0.000	-0.1573E-01	-368.47	1.947	-0.3022E-02		
80	Fluorite	-10.97	6000	-50.89	0.7280E-02	0.470	0.0000E-00	-307.34	1.650	-0.2610E-02		

DESCRIPTEURS DES REACTIONS

Numéro de l'espèce composée	Numéro des espèces simples associées	Coefficients stoéchiométriques correspondants	Nombre d'espèces en jeu dans la réaction
20	1 7 0	-1 1 1 0	3
21	1 8 0	-1 1 1 0	3
22	1 9 0	-1 1 1 0	3
23	1 11 0	-1 1 1 0	3
24	1 12 0	-1 1 1 0	3
25	1 12 0	-1 2 1 0	3
26	1 13 0	-1 1 1 0	3
27	1 14 0	-1 -1 1 0	3
28	1 14 0	-1 1 1 0	3
29	2 12 0	-1 1 1 0	3
30	2 1 12	-1 1 1 1	4
31	4 8 0	-1 1 1 0	3
32	4 12 0	-1 1 1 0	3
33	4 1 12	-1 1 1 1	4
34	4 13 0	-1 1 1 0	3
35	5 8 0	-1 1 1 0	3
36	5 12 0	-1 1 1 0	3
37	5 1 12	-1 1 1 1	4
38	5 13 0	-1 1 1 0	3
39	6 15 0	-1 1 -1 0	3
40	6 7 0	-1 1 1 0	3
41	6 7 0	-1 1 2 0	3
42	6 7 0	-1 1 3 0	3
43	6 7 0	-1 1 4 0	3
44	6 7 15	-1 1 1 -1	4
45	6 7 15	-1 1 2 -1	4
46	6 7 15	-1 1 3 -1	4
47	6 7 15	-1 1 4 -1	4
48	6 8 15	-1 1 1 -1	4
49	6 8 15	-1 1 2 -1	4
50	6 8 15	-1 1 3 -1	4
51	6 10 0	-1 1 1 0	3
52	6 10 15	-1 1 1 -1	4
53	6 10 15	-1 1 2 -1	4
54	6 10 15	-1 1 3 -1	4
55	6 12 0	-1 1 1 0	3
56	6 12 1	-1 1 1 1	4
57	6 13 0	-1 1 1 0	3
58	6 13 15	-1 1 2 -1	4
59	6 13 15	-1 1 1 -1	4
60	6 14 0	-1 1 2 0	3
61	6 14 0	-1 1 3 0	3

Numéro du minéral	Numéro des espèces simples associées	Coefficients stoéchiométriques correspondants	Nombre d'espèces en jeu dans la réaction
62	4 12 0 0	-1 1 1 0 0	3
63	7 1 9 0	-1 -2 -1 1 0	4
64	4 12 0 0	-1 1 1 0 0	3
65	4 5 12 0	-1 1 1 2 0	4
66	7 1 9 0	-1 -2 -1 1 0	4
67	7 1 9 0	-1 -2 -1 1 0	4
68	6 14 1 0	-1 1 1 -1 0	4
69	6 14 1 0	-1 1 1 -1 0	4
70	6 14 1 0	-1 1 1 -1 0	4
71	6 14 15 1	-1 2 3 -2 -3	5
72	6 14 15 1	-1 1 2 -2 -2	5
73	6 14 15 1	-1 1 2 -2 -2	5
74	6 14 1 0	-1 1 1 -1 0	4
75	6 7 15 0	-1 1 3 -1 0	4
76	6 7 1 15	-1 1 2 -1 -1	5
77	6 14 15 1	-1 3 4 -2 -4	5
78	6 12 0 0	-1 1 1 0 0	3
79	6 7 1 15	-1 1 2 -1 -1	5
80	4 8 0 0	-1 1 2 0 0	3

Numéro du gaz	Numéro des espèces simples associées	Coefficients stoéchiométriques correspondants	Nombre d'espèces en jeu dans la réaction
81	7 1 12	-1 -1 1 1	4
82	1 14 0	-1 1 1 0	3
83	16 0 0	-1 1 0 0	2
84	17 0 0	-1 1 0 0	2
85	18 0 0	-1 1 0 0	2
86	19 0 0	-1 1 0 0	2

APPENDIX 4

LIST OF REPORTS (BRGM/IMRG) AND THESIS

ACADÉMIE DE MONTPELLIER
UNIVERSITÉ MONTPELLIER II
SCIENCES ET TECHNIQUES DU LANGUEDOC

THÈSE

présentée à l'Université des Sciences et Techniques du Languedoc
pour obtenir le diplôme de DOCTORAT

spécialité

Énergétique (Génie des Procédés)

**TRAITEMENT DES FLUIDES GÉOTHERMAUX DU DOGGER
(Bassin parisien - France)
PAR OXYDATION CHIMIQUE DES SULFURES DISSOUS
ET MICROFILTRATION TANGENTIELLE**

par

Sylvie DETOC-KARIMI
(Ingénieur ISIM)

Soutenue le 10 décembre 1990 devant le jury composé de :

M.	C. BOCQUILLON	Président
M.	C. FOUILLAC	Examineur
M.	I. IGNATIADIS	Examineur
M.	M. RUMEAU	Examineur
Mme	F. PERSIN	Examineur
M.	F.D. VUATAZ	Examineur

RESUME

L'analyse du contexte de la géothermie basse enthalpie en France et des connaissances acquises concernant les problèmes des centrales géothermiques exploitant les eaux géothermales du réservoir du Dogger (du Bassin Parisien) a permis de définir une technique de traitement adaptée aux fluides exploités. Celle-ci a pour objectif l'amélioration des conditions d'exploitation par réduction de la formation de dépôts de sulfures de fer. Le choix s'est porté sur le procédé d'oxydation chimique des sulfures dissous couplé à la microfiltration tangentielle sur membrane minérale.

L'étude de l'oxydation des sulfures dissous par le peroxyde d'hydrogène a été réalisée grâce à la mise au point de techniques d'analyse des espèces du soufre qui ont rendu possible la mise en oeuvre d'études cinétiques sur deux fluides géothermaux du Dogger, Fontainebleau et Tremblay-lès-Gonesse. Les résultats ont montré qu'il n'est pas aisé de déduire une loi de vitesse de réaction simple décrivant précisément l'ensemble des phénomènes observés. L'évolution de la vitesse de la réaction est complexe et dépend principalement du rapport de la concentration de l'oxydant sur la concentration de sulfures dissous, du pH et du catalyseur. L'analyse des produits de réaction a permis de dégager les étapes possibles de l'oxydation qui peuvent intervenir en milieu neutre ou acide et en milieu alcalin.

Le travail de mise au point de la seconde phase de traitement représente la première approche de l'étude de la microfiltration tangentielle sur un fluide géothermal exploité en basse enthalpie. Les résultats obtenus démontrent la faisabilité technique du procédé en géothermie.

Une évaluation économique globale montre que ce type de traitement ne pourrait pas être envisagé actuellement, en géothermie basse enthalpie du Dogger. Néanmoins, cette étude peut constituer le point de départ d'applications de ces procédés dans d'autres contextes géothermaux (exploitation des fluides géothermaux de haute enthalpie et des roches chaudes sèches).

MOTS CLES

Géothermie basse enthalpie

Dogger du Bassin Parisien

Sulfures dissous

Oxydation chimique

Peroxyde d'hydrogène

Catalyse

Microfiltration tangentielle

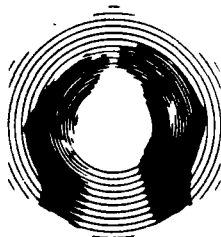
SOMMAIRE

	Pages
INTRODUCTION GÉNÉRALE	9
PREMIERE PARTIE : CONTEXTE DE L'ÉTUDE	13
1- LES EXPLOITATIONS GÉOTHERMIQUES DU DOGGER	15
2- LES FLUIDES EXPLOITÉS	21
3- LES PROBLÈMES D'EXPLOITATION	31
4- LES SOLUTIONS AUX PROBLÈMES D'EXPLOITATION	39
DEUXIÈME PARTIE : OXYDATION CHIMIQUE DES SULFURES	45
1- INTRODUCTION	47
2- ÉTUDE THÉORIQUE	49
3- PARTIE EXPÉRIMENTALE - ETUDES CINÉTIQUES	87
4- DISCUSSION	173
TROISIÈME PARTIE :	
TRAITEMENT DES FLUIDES GÉOTHERMAUX OXYDÉS	
PAR MICROFILTRATION TANGENTIELLE	189
1- INTRODUCTION	191
2- PRINCIPE DE LA MICROFILTRATION TANGENTIELLE	193
3- MISE AU POINT DE LA MÉTHODE EXPÉRIMENTALE ET DE L'APPAREILLAGE	201
4- ESSAIS SUR SITE	215
5- CONCLUSION	225
QUATRIÈME PARTIE :	
ÉLABORATION DU TRAITEMENT DES FLUIDES GÉOTHERMAUX	
PAR OXYDATION CHIMIQUE ET MICROFILTRATION TANGENTIELLE	227
1- CONTRAINTES D'EXPLOITATION	229
2- MISE EN PLACE DU TRAITEMENT	231
3- DIMENSIONNEMENT DES INSTALLATIONS	235
4- ÉVALUATION ÉCONOMIQUE DU PROCÉDÉ DE TRAITEMENT	239
CONCLUSION GÉNÉRALE	241
RÉFÉRENCES BIBLIOGRAPHIQUES	245
ABRÉVIATIONS UTILISÉES	255
TABLE DES MATIÈRES	257
ANNEXES	



BRGM

L'ENTREPRISE AU SERVICE DE LA TERRE



AGENCE FRANÇAISE
POUR LA MAÎTRISE DE L'ÉNERGIE

**INSTITUT MIXTE
DE RECHERCHES GÉOTHERMIQUES**
Service "Chimie Appliquée à la Géothermie"

dosage des sulfures et mercaptans dissous dans les fluides géothermaux du Dogger du bassin parisien

travaux cofinancés par :
CCE DG XII et l'IMRG
(contrat n° GE-0005-C)

projet "Exploitation basse enthalpie"
sous la direction de : Ph. Bray

I. Ignatiadis
M. Amalhay
M. Lafforgue
M. Brach

septembre 1991
R 33 488

BRGM-IMRG

B.P. 6009 - 45060 ORLÉANS CEDEX 2 - France - Tél. : (33) 38.64.31.72

RESUME

Dans ce rapport sont présentés les résultats d'une étude sur le dosage des sulfures et mercaptans dissous dans les fluides géothermaux du réservoir du Dogger du bassin parisien.

Les sulfures et mercaptans sont présents dans ces fluides géothermaux à de teneurs allant de 0 à 150 mg/l. Ils sont en partie responsables des difficultés rencontrées lors de l'exploitation de certaines installations géothermiques : pertes de débit, percement des tubages, colmatage... Ces problèmes sont liés essentiellement au caractère corrosif du fluide, qui attaque les tubages en acier doux et solubilise le fer. Ce fer ferreux réagit alors sur les sulfures d'hydrogène (H_2S , HS^-) pour donner des sulfures de fer, à l'origine des dépôts colmatants. La présence des sulfures d'hydrogène dans le fluide géothermal est due à la réduction bactérienne des sulfates.

Cette étude s'est effectuée dans le cadre d'un programme de recherche de l'Institut Mixte de Recherches Géothermiques (IMRG). Les travaux ont été co-financés par la Commission des Communautés Européennes (Contrat CCE DG XII n° GE-0005-C).

La teneur en sulfures et mercaptans dissous contenus dans les fluides géothermaux du réservoir du Dogger du bassin parisien a été un des paramètres suivis systématiquement par les maîtres d'oeuvres et les conseillers sous-sol.

Les sulfures et mercaptans dissous sont dosés régulièrement sur les sites géothermiques par une méthode de titration potentiométrique par un sel de mercure +II, le nitrate mercurique ou le chlorure mercurique. Compte tenu de la nature non conservative des sulfures et mercaptans, qui s'oxydent par l'oxygène de l'air, le dosage doit être effectué sur site.

Le dosage se fait sur site manuellement, ce qui nécessite une présence permanente de l'opérateur et une attention particulière durant toutes les étapes de la manipulation. De plus, sur site, il est impossible de traiter les données, d'où un retard dans la valorisation du travail et éventuellement l'interprétation des résultats.

Le but de cette étude était d'examiner cette méthode manuelle et éventuellement de la substituer par une méthode automatisée. En particulier, il était primordial d'essayer de mettre au point une méthode basée sur le même principe, mais plus rapide et plus fiable donnant des résultats immédiats qui permettent de traiter les données sur place, et valoriser le travail en interprétant de suite les résultats.

En introduction de ce rapport sont présentés le contexte, les problèmes de la géothermie liées aux sulfures dissous et les objectifs de cette étude.

Dans le chapitre 2, la méthode de dosage manuelle est tout d'abord présentée et discutée (principe, matériels et produits).

Ensuite, à travers des études de suivi antérieures et actuelles, la méthode est examinée précisément sur des bases statistiques. Le grand nombre d'analyses effectuées a permis et conditionné des approches statistiques sur la validité et la précision de la méthode. L'exploitation statistique des résultats a montré que ceux-ci sont homogènes et que, dans presque tous les cas, l'erreur relative de la méthode utilisée est faible. Ses limites et sa précision sont discutées et quelques critiques sont émises.

Dans le chapitre 3 le dosage des sulfures et mercaptans dissous est mis en oeuvre avec une chaîne de titration automatique. La faisabilité du dosage a été démontrée.

Le principe du dosage est le même. Le mode opératoire de la chaîne est présenté et quelques dosages sont effectués en parallèle avec la méthode manuelle. Ainsi, les deux méthodes sont comparées et discutées sur la base de leurs précision, limites et rapidité dans le dosage.

En conclusion, la nécessité de remplacer la méthode manuelle par la méthode automatique de dosage des sulfures et mercaptans est démontrée.

En annexes, des résultats en rapport avec la méthodologie analytique et le mode opératoire de la chaîne de titration sont exposés.

MOTS-CLES

géothermie, fluide géothermique, réservoir, Dogger, analyse chimique minérale, sulfure d'hydrogène, mercaptans, titration potentiométrique.

TABLE DES MATIERES

	Page
1 - INTRODUCTION.....	7
1.1 - PRESENTATION DU CONTEXTE.....	7
1.2 - PROBLEMES DE LA GEOTHERMIE LIES AUX SULFURES DISSOUS.....	8
1.3 - OBJECTIFS ET PRESENTATION DE L'ETUDE.....	9
1.3.1 - OBJECTIFS	9
1.3.2 - PRESENTATION DE L'ETUDE.....	10
2 - DOSAGE DES SULFURES SUR SITE PAR LA METHODE MANUELLE.....	11
2.1 - MATERIELS ET PRODUITS DE LA METHODE.....	11
2.2 - PRINCIPE ET MODE OPERATOIRE DE LA METHODE.....	12
2.3 - EXAMEN DE LA METHODE MANUELLE DE DOSAGE.....	14
2.3.1 - ETUDES ANTERIEURES.....	14
2.3.2 - ETUDES ACTUELLES.....	20
2.4 - LIMITE ET PRECISION DE LA METHODE MANUELLE.....	25
2.4.1 - LIMITE SUPERIEURE.....	25
2.4.2 - LIMITE DE DETECTION.....	25
2.4.3 - PRECISION.....	25
2.4.4 - CRITIQUES DE LA METHODE.....	25
3 - DOSAGE DES SULFURES AVEC LA CHAINE ORION 940/960.....	27
3.1 - MATERIELS, PRODUITS ET PRINCIPE DE LA METHODE.....	27
3.2 - MODE OPERATOIRE ET EXEMPLES DE DOSAGES AUTOMATIQUES.....	28
3.2.1 - LE MODULE EA 940.....	28

3.2 1.1 - OPERATEUR MENU.....	28
3.2 1.2 - CALIBRATION.....	29
3.2 1.3 - MESURE.....	29
3.2.2 - LE MODULE ORION 960.....	29
3.2.2.1 - DESCRIPTION DU MODULE ET PROCEDURES D'ENTREE DES DONNEES.....	29
3.2.2.2 - LES TECHNIQUES D'ANALYSE DE L'ORION 960 UTILISEES DANS LE CADRE DE CETTE ETUDE.....	33
3.2.2.2.1 - FONCTION DE GRAN.....	33
3.2.2.2.2 - DERIVEE(S) PREMIERE (ET SECONDE).....	33
3.3 - RESULTATS DES DOSAGES AUTOMATIQUES ET COMPARAISON DES RESULTATS ANALYTIQUES DE DEUX METHODES: MANUELLE ET AUTOMATIQUE.....	36
3.4 - CHOIX DE LA CONCENTRATION DU TITRANT.....	38
3.5 - LIMITE ET PRECISION.....	38
3.5.1 - LIMITE SUPERIEURE.....	38
3.5.2 - LIMITE DE DETECTION.....	38
3.5.3 - PRECISION.....	38
3.5.4 - CRITIQUES DE LA METHODE.....	39
4 - CONCLUSION.....	41
5 - REFERENCES BIBLIOGRAPHIQUES.....	43
6 - LISTE DES TABLEAUX.....	47
7 - LISTE DES FIGURES.....	49
ANNEXES.....	51
ANNEXE I - Diagramme de répartition des sulfures d'hydrogène en fonction du pH.....	52
ANNEXE II - Réactions d'oxydation des sulfures d'hydrogène par l'oxygène.....	53
ANNEXE III - Interprétations possibles des faibles évolutions des concentrations des espèces H ⁺ , Fe ²⁺ , fer total et sulfures dissous.....	54
ANNEXE IV - Définition et signification des termes utilisés pour l'exploitation statistique des résultats.....	55
ANNEXE V - Description détaillée de la procédure d'entrée de données pour la titration des sulfures et mercaptans.....	57



BRGM
L'ENTREPRISE AU SERVICE DE LA TERRE



AGENCE FRANÇAISE
POUR LA MAÎTRISE DE L'ÉNERGIE

document public

INSTITUT MIXTE
DE RECHERCHES GÉOTHERMIQUES
Service "Chimie Appliquée à Géothermie"

évolution des concentrations en sulfures dissous dans les fluides géothermaux du Dogger du bassin parisien

travaux cofinancés par :
CCE DG XII et l'IMRG
(contrat n° JOUG-0005-C)

projet "Exploitation basse enthalpie"
sous la direction de Ph. Bray

I. Ignatiadis
J.-M. Chéradame
M. Lafforgue
S. Castagné

novembre 1991
R 33 518

RESUME

Dans ce rapport sont présentés les résultats d'une étude sur les teneurs en sulfures dissous contenus dans les fluides géothermaux du réservoir du Dogger du Bassin parisien. L'étude porte plus particulièrement sur la répartition des teneurs en sulfures dissous sur l'ensemble du Bassin et sur leur évolution dans le temps et en fonction du débit d'exploitation.

En introduction de ce rapport sont présentés le contexte, les problèmes de production d'eau géothermale liés à la présence des sulfures dissous et les objectifs de l'étude.

Il est rappelé qu'une cartographie des sulfures a été effectuée par l'IMRG en 1985. Elle a permis de distinguer principalement, une zone à forte teneur en sulfures (de 30 à 100 mg/l) située au Nord, Nord-ouest et Ouest de Paris et une zone à faible teneur en sulfures située au Sud et Est de Paris. Il a été remarqué que les zones de fortes concentrations en sulfures dissous correspondent à celles où le colmatage des puits est rapide et que la répartition de la concentration en sulfures dissous correspond à celle de l'isotope stable du soufre ^{34}S des sulfates.

Il est noté que depuis 1987, les analyses montraient une évolution de la teneur en sulfures pour certains puits géothermiques situés au Sud et à l'Est de Paris. Compte tenu de l'importance des évolutions, il a été décidé que l'IMRG entreprenne une étude globale de l'importance et du développement des sulfures contenus dans les fluides géothermaux prélevés en tête des puits de production. Les objectifs de cette étude consistaient :

- 1) à établir une cartographie de répartition et un classement par zones homogènes, des sulfures,
- 2) à mettre en évidence les variations des concentrations en sulfures (et éventuellement en fer) liées au débit d'exploitation des puits, à interpréter et à quantifier les phénomènes de production de sulfures et finalement, à déterminer l'origine de la hausse des concentrations en sulfures observée.

Le chapitre 2, est une brève étude bibliographique sur la nature des espèces du soufre présentes dans les fluides du Dogger, ainsi qu'un bref rappel sur la méthodologie d'analyse des sulfures.

Dans le chapitre 3 est présentée la nouvelle cartographie des teneurs en sulfures dissous dans les fluides du Dogger. Cette cartographie a été réalisée en 1990-91 après collecte des données chimiques disponibles et quelques expériences de vérification des données sur certains sites.

Les teneurs en sulfures retenues après critique et validation des données collectées ont permis d'établir une carte qui fait apparaître deux zones et deux types de variations :

Une zone à forte teneur en sulfures (de 30 à 100 mg/l) située au Nord et Ouest de Paris (départements 93, 95) et secteur Melun-Fontainebleau dans le sud. Dans cette zone qui présentait déjà une forte teneur en sulfures initiale, on constate qu'il n'y pas de variation significative de la teneur en sulfures en fonction du temps et du débit d'exploitation.

Une zone à faible teneur en sulfures, située au sud et à l'est de Paris (départements 91, 94 et 77 sauf secteur Melun - Fontainebleau), à faible concentration initiale, où les concentrations en sulfures mesurées en tête de puits évoluent en fonction du temps et du débit d'exploitation.

Les deux types de variations sont :

A l'échelle régionale, les concentrations en sulfures dissous varient de plusieurs puissances de dix entre certains puits du sud et est de Paris et quelques sites de la Seine-Saint-Denis ou Beauvais (jusqu'à 100 mg/l) alors que la salinité totale sur l'ensemble des puits géothermiques ne change que d'un facteur 5 à 6 (5,8 à 35 g/l). Il n'y a pas de corrélation globale entre les concentrations en sulfures, les températures et/ou les salinités des fluides.

A l'échelle locale, les concentrations en sulfures d'hydrogène dissous ne sont pas constantes au cours du temps, surtout dans les zones dites à taux de sulfures faibles, le Val de Marne et la Seine et Marne.

Dans le chapitre 4 sont présentées les études réalisées pour mettre en évidence des évolutions des teneurs en sulfures dissous. Les résultats de ces études sont relatifs à l'origine de l'augmentation des teneurs en sulfures dissous dans les zones sud et est du Bassin parisien.

Deux méthodes ont été utilisées pour provoquer et étudier les évolutions éventuelles de la composition du fluide prélevé en tête des puits de production :

- 1) le suivi physico-chimique de la composition du fluide à débits d'exploitation variables (4 puits du Sud et Est de Paris),
- 2) le suivi physico-chimique de la composition du fluide avant et après un traitement bactéricide du puits de production (ORLY 1).

Conformément à la seconde méthode, dans la zone sud, à faible concentration initiale en sulfures, une expérience décisive de traitement bactéricide des parois internes du doublet géothermique d'ORLY 1 a permis de mettre en évidence la contribution des bactéries sulfato-réductrices dans l'augmentation des concentrations en sulfures dissous en tête du puits.

Conformément à la première méthode, un suivi physico-chimique de la composition du fluide en fonction du débit d'exploitation a été réalisé sur deux puits de l'Est parisien (**Meaux Beauval 1 (GMX5) et Meaux Beauval 2 (GMX7)**) et deux autres puits du Sud-est parisien (**Créteil (GCRT1) et Fresnes (GFR2)**) entre le 9 et le 12 juillet 1990 et de nouveau entre le 6 et le 12 septembre 1990.

Les concentrations en sulfures dissous y sont affectées de variations très importantes en fonction du débit d'exploitation. Parallèlement, le flux de sulfures dissous reste relativement constant, comme si le débit d'exploitation n'intervenait que sur la dilution plus ou moins grande des sulfures présents (et produits) par unité de temps.

Trois hypothèses, toutes à priori possibles, ont été considérées et explorées pour expliquer ces variations. Après discussion et confrontation des résultats obtenus au cours de cette étude, il en ressort que la seule hypothèse raisonnable est celle ayant trait à l'activité bactérienne actuelle dans les puits.

Bien que les expériences du traitement bactéricide du puits d'Orly et les raisonnements logiques sur les variations des concentrations en fer et en sulfures en fonction du débit de production sur certains puits géothermiques soient suffisantes pour indiquer la présence d'une activité bactérienne actuelle, un nouvel outil original, les mesures isotopiques $\delta^{34}\text{S}(\text{SO}_4^{2-})\text{‰}$ et $\delta^{34}\text{S}(\text{HS})\text{‰}$ a été utilisé et a permis de s'en assurer complètement.

Cette nouvelle méthode pourrait être parfois utilisée pour la mesure de l'activité bactérienne actuelle au même titre que l'analyse bactériologique du fluide.

En chapitre 5 quelques conclusions et recommandations sont émises concernant cette étude, qui ont leurs importance parce qu'elles ont trait avec la survie et l'avenir des installations géothermiques.

Dans les annexes I et II sont exposés respectivement les résultats de la collecte des données chimiques et quelques rappels relatifs à l'exploitation statistique de données.

Cette étude s'est effectuée dans le cadre d'un programme de recherche de l'Institut Mixte de Recherches Géothermiques (IMRG) avec la collaboration de la Compagnie Française pour le développement de la Géothermie et des énergies nouvelles (C.F.G.). Les travaux ont été co-financés par la Commission des Communautés Européennes DG XII (n° JOUG-0005-C).

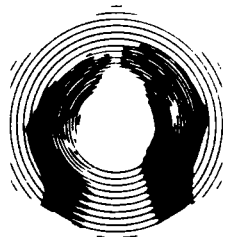
MOTS-CLES :

géothermie - fluide géothermal - Dogger - Bassin parisien - sulfures d'hydrogène - sulfures dissous - fer dissous - isotopes du soufre - bactéries sulfato-réductrices - débit d'exploitation - sulfure de fer - corrosion - dépôts -

TABLE DES MATIERES

	Page
1 - INTRODUCTION.....	9
1.1 - PRESENTATION DU CONTEXTE.....	9
1.2 - PROBLEMES DE LA GEOTHERMIE LIES AUX SULFURES.....	10
1.3 - OBJECTIFS ET PRESENTATION DE L'ETUDE.....	12
1.3.1 - OBJECTIFS	12
1.3.2 - PRESENTATION DE L'ETUDE.....	13
2 - LES SULFURES : NATURE ET ANALYSE.....	15
2.1 - NATURE DES ESPECES DU SOUFRE PRESENTES DANS LES EAUX EN GENERAL ET DANS LES FLUIDES GEOTHERMAUX EN PARTICULIER.....	15
2.1.1 - LES DIFFERENTES ESPECES DU SOUFRE PRESENTES OU POUVANT EXISTER EN SOLUTION AQUEUSE.....	15
2.1.2 - LES DIFFERENTES ESPECES DU SOUFRE PRESENTES OU POUVANT EXISTER DANS LES FLUIDES GEOTHERMAUX.....	16
2.1.2.1 - LES SULFURES.....	16
2.1.2.2 - LES MERCAPTANS.....	18
2.1.2.3 - LE SOUFRE ELEMENTAIRE.....	19
2.1.2.4 - LES SULFATES.....	19
2.1.3 - REPARTITION DES ESPECES DU SOUFRE.....	19
2.2 - METHODOLOGIE D'ANALYSE DES SULFURES DANS LES FLUIDES GEOTHERMAUX.....	24
2.2.1 - DEFINITIONS.....	24
2.2.2 - DETERMINATION DE LA CONCENTRATION EN SULFURES TOTAUX	
2.2.2.1 - PRELEVEMENT SUR SITE (EN TETE DE PUIITS OU AU POINT LE PLUS PROCHE AVANT L'ECHANGEUR DE CHALEUR) DE DEUX ECHANTILLONS POUR LE DOSAGE DES GAZ LIBRES ET DISSOUS.....	25
2.2.2.2 - MESURE SUR SITE (EN TETE DE PUIITS OU AU POINT LE PLUS PROCHE AVANT L'ECHANGEUR DE CHALEUR) DU RAPPORT DES VOLUMES OU DEBITS GAZ/LIQUIDE OU G.L.R.....	25
2.2.2.3 - PRELEVEMENT (EN TETE DE PUIITS OU AU POINT LE PLUS PROCHE AVANT L'ECHANGEUR DE CHALEUR) D'UN ECHANTILLON POUR LE DOSAGE SUR SITE DES SULFURES DISSOUS.....	26
2.3 - COMMENTAIRES SUR LES SULFURES PRESENTS DANS LES FLUIDES GEOTHERMAUX DU DOGGER DU BASSIN PARISIEN..	28
3 - CARTOGRAPHIE DES TENEURS EN SULFURES DISSOUS..	29
3.1 - HISTORIQUE - OBJECTIFS.....	29
3.2 - COLLECTE DES DONNEES EXISTANTES.....	30
3.3 - CRITIQUE ET VERIFICATION DES DONNEES.....	31
3.3.1. - CRITIQUE DES DONNEES.....	31
3.3.2 - VALIDATION DES DONNEES.....	32

3.4 - TENEURS EN SULFURES RETENUES ET CARTOGRAPHIES PROPOSEES.....	34
3.4.1 - ZONE NORD ET OUEST DE PARIS (DEPARTEMENTS 93, 95) ET SECTEUR MELUN-FONTAINEBLEAU DANS LE SUD.....	34
3.4.2 - ZONE SUD ET EST DE PARIS (DEPARTEMENTS 91, 94 ET 77 SAUF SECTEUR MELUN - FONTAINEBLEAU).....	37
3.4.3 - REPARTITION GEOGRAPHIQUE DES TENEURS EN SULFURES.....	40
3.4.4 - COMMENTAIRES.....	43
4 - MISE EN EVIDENCE DE L'EVOLUTION DES TENEURS EN SULFURES DISSOUS EN TETE DES PUIITS DE PRODUCTION. ORIGINE DE CETTE EVOLUTION.....	45
4.1 - SUIVI PHYSICO-CHIMIQUE JOURNALIER A DEBIT D'HIVER ET D'ETE DE QUATRE PUIITS GEOTHERMIQUES DE LA SEINE-SAINT-DENIS (FORTE TENEUR EN SULFURES).....	53
4.2 - SUIVI PHYSICO-CHIMIQUE D'UN PUIITS ARTESIEEN DE LA ZONE SUD AVANT ET APRES UN TRAITEMENT BACTERICIDE.....	61
4.3 - SUIVI PHYSICO-CHIMIQUE EN FONCTION DU DEBIT D'EXPLOITATION DANS LA ZONE A FAIBLE CONCENTRATION INITIALE EN SULFURES (SEINE ET MARNE ET VAL DE MARNE).....	65
4.3.1 - EVOLUTION DES PARAMETRES SUIVIS EN FONCTION DU DEBIT D'EXPLOITATION.....	65
4.3.1.1 - EVOLUTION DE LA SALINITE TOTALE DES FLUIDES ET DE LA COMPOSITION CHIMIQUE EN ELEMENTS (ANIONS OU CATIONS) MAJEURS EN FONCTION DU DEBIT D'EXPLOITATION.....	65
4.3.1.2 - EVOLUTION DE LA CONCENTRATION EN FER DISSOUS ET FER TOTAL EN FONCTION DU DEBIT D'EXPLOITATION.....	67
4.3.1.3 - EVOLUTION DE LA CONCENTRATION EN SULFURES DISSOUS EN FONCTION DU DEBIT D'EXPLOITATION.....	67
4.3.1.4 - EVOLUTION DES RAPPORTS ISOTOPIQUES DU SOUFRE ³⁴ S/ ³² S DES SULFURES ET DES SULFATES EN FONCTION DU DEBIT D'EXPLOITATION.....	67
4.3.2 - COMMENTAIRES SUR L'EVOLUTION DES CONCENTRATIONS OU AUTRES PARAMETRES SUIVIS EN FONCTION DU DEBIT D'EXPLOITATION MISE EN EVIDENCE DE LA CONTRIBUTION DE L'ACTIVITE BACTERIENNE DANS L'AUGMENTATION DES CONCENTRATIONS EN SULFURES DISSOUS.....	83
4.3.2.1 - SALINITE TOTALE ; ANIONS-CATIONS MAJEURS.....	83
4.3.2.2 - FER DISSOUS ET FER TOTAL.....	83
4.3.2.3 - SULFURES DISSOUS.....	84
4.3.2.4 - RAPPORTS ISOTOPIQUES ³⁴ S/ ³² S DES SULFURES ET DES SULFATES ET CONCENTRATION EN SULFATES.....	89
5 - CONCLUSION GENERALE.....	95
6 - REFERENCES BIBLIOGRAPHIQUES.....	97
7 - LISTE DES TABLEAUX.....	105
8 - LISTE DES FIGURES.....	109
ANNEXES.....	113



AGENCE FRANÇAISE
POUR LA MAÎTRISE DE L'ÉNERGIE

document non public

INSTITUT MIXTE
DE RECHERCHES GÉOTHERMIQUES
Service "Chimie Appliquée à la Géothermie"

évaluation de l'action d'un inhibiteur organique de corrosion sur les dépôts des sulfures de fer en milieu géothermal reconstitué et réel

travaux cofinancés par :
CCE DG XII et l'IMRG
(contrat n° GE-0005-C)

projet "Exploitation basse enthalpie"
sous la direction de : Ph. Bray

I. Ignatiadis
S. Teton
M. Lafforgue

novembre 1991
R 33 945

RESUME

Dans ce rapport sont présentés les résultats d'une étude sur l'action d'un inhibiteur organique de corrosion sur les dépôts des sulfures de fer en milieu géothermal reconstitué au laboratoire et réel sur site.

Certaines installations géothermiques du Dogger du Bassin parisien sont actuellement soumises à des difficultés d'exploitation : perte de débit, percement des tubages, colmatage... Celles ci sont liées essentiellement au caractère corrosif du fluide, particulièrement chargés en Cl^- , CO_2 et H_2S , qui attaque les tubages en acier doux et solubilise le fer. Ce fer ferreux réagit alors sur le sulfure d'hydrogène (H_2S , HS^-) pour donner des sulfures de fer, à l'origine des dépôts colmatants. Il est actuellement généralement admis que les dépôts de sulfures de fer présents sur un acier au carbone ne le protège pas totalement de la corrosion, le dépôt formé peut être plus ou moins poreux. Il est certain qu'en leur présence la corrosion est diminuée, mais n'est pas arrêtée pour autant.

Du fait de l'absence de traitement contre la corrosion dès le début de l'exploitation des puits géothermiques, les tubages ont été corrodés et sur leur surface interne subsistent des dépôts. Les opérations de réhabilitation des puits mettent en oeuvre des techniques lourdes : curage mécanique des puits à l'aide d'outils de forage. Mais, rien ne permet d'être sûr que l'on obtient une élimination totale des dépôts sur tout l'intérieur des casings. La majorité des puits géothermiques sont actuellement traités par injection d'inhibiteur de corrosion au fond du puits de production. Ces produits sont des agents tensio-actifs cationiques de type sels d'ammonium quaternaires. Ils ont une durée de rémanance de quelques heures et permettent de créer un film protecteur à l'interface entre parois des tubages et fluide.

Dans les puits géothermiques curés la présence des dépôts, qui subsistent après curage, est gênante et conditionne cette étude qui porte sur l'évaluation de l'efficacité des traitements par inhibiteur.

En introduction de ce rapport sont présentés, tout d'abord, le contexte et les objectifs de cette étude et en particulier les questions essentielles que l'on se pose actuellement et les expériences que l'on envisage pour y répondre. En effet, il sera recherché des réponses aux questions suivantes:

- Les inhibiteurs ont-ils une action particulière sur les dépôts ?
Peuvent-ils, par exemple, les remettre en solution ou en suspension ?
- Quelle est l'efficacité des inhibiteurs de corrosion organiques sur un casing où subsistent des dépôts ? En particulier, la protection par l'inhibiteur est-elle réelle vis-à-vis d'une corrosion sous dépôts ?

Evaluation de l'action d'un inhibiteur organique de corrosion sur les dépôts des sulfures de fer en milieu géothermal reconstitué et réel

Pour répondre à ces questions, il est nécessaire de faire une démonstration expérimentale en deux phases complémentaires :

- en laboratoire, étudier le comportement d'un dépôt, sous forme de poudre, en l'exposant sous atmosphère contrôlée, à une solution géothermale partiellement reconstituée, en absence ou en présence d'inhibiteur,
- sur site géothermique, étudier le comportement d'une sonde de corrosion en l'exposant au fluide corrosif en absence et en présence d'inhibiteur.

Le chapitre 2, est une étude bibliographique sur la corrosion, sur la nature et la structure des dépôts et sur les traitements anti-corrosion actuellement utilisés.

Dans le chapitre 3 sont présentés les matériels et méthodes utilisés pendant cette étude, en particulier le dépôt et l'inhibiteur choisis, les dispositifs de mesure, et les méthodes d'analyse mise en oeuvre.

Dans le chapitre 4 sont présentés les expériences effectuées au laboratoire et sur site. Les résultats d'expériences réalisées ont permis de répondre, en partie, aux questions soulevées.

Il s'avère que l'inhibiteur de corrosion organique, la Solamine 129®, employé dans les expériences de laboratoire dans cette étude, ne semble pas avoir le pouvoir de dégrader les dépôts. Il n'a donc pas d'action chimique sur les dépôts. Toutefois, ces travaux ont été menés au laboratoire et ne sont pas tout-à-fait représentatifs des conditions réelles. En effet, dans les puits géothermiques dont le fonctionnement particulier comporte des conditions hydrodynamiques sévères, notamment en ce qui concerne la vitesse de circulation du fluide (jusqu' à 3 m/s) et la pression exercée sur les parois des tubages (et des dépôts), l'on pourrait avoir une action physique importante sur un dépôt. On peut imaginer dans un premier temps, la fixation par adsorption des grosses molécules cationiques de l'inhibiteur sur les dépôts, puis le détachement de ces molécules qui en se détachant décrocheraient de petites particules de dépôt. Ainsi, le tandem "cation de l'inhibiteur-particule de dépôt" remonterait le long du puits de production jusqu'en surface, puis serait réinjecté dans le puits d'injection.

Les expériences sur site à l'aide d'un dispositif muni d'une sonde de corrosion montrent que l'inhibiteur peut agir physiquement sur les dépôts.

On constate, dans un premier temps, que même si le fluide n'est pas traité la vitesse de corrosion diminue en fonction du temps d'exposition au fluide dès les premiers instants de l'expérience. Lors de l'injection de Solamine 129®, on observe, dans tous les cas (métal nu ou après exposition et déposition préalable), une diminution de la vitesse de corrosion plus ou moins importante en fonction du temps d'exposition préalable au fluide non traité. La Solamine 129® présente incontestablement un effet très important sur la vitesse de corrosion.

Evaluation de l'action d'un inhibiteur organique de corrosion sur les dépôts des sulfures de fer en milieu géothermal reconstitué et réel

Si la Solamine 129® est injectée directement (sans contact préalable de la sonde avec le fluide non traité, la vitesse de corrosion chute très rapidement. Mais, cette vitesse diminue beaucoup moins fortement lorsque les sulfures de fer ont le temps de se déposer. Le fait que la vitesse de corrosion diminue lors de l'injection de Solamine 129®, malgré les dépôts, pourrait tout-à-fait être la preuve d'une action physique de cet inhibiteur : il parviendrait soit à filmer les dépôts, soit à atteindre le métal, en assurer la protection et permettrait ainsi une diminution de la vitesse de corrosion. A ce stade, les expériences réalisées ne permettent pas de conclure sur l'une ou l'autre de ces actions.

Ce travail a mis en évidence la transparence pour la Solamine 129® d'un **dépôt jeune et très fin** (de 30 à 150 nm). En effet, cette notion d'épaisseur semble jouer un rôle primordial dans l'action de l'inhibiteur. La texture des dépôts pourrait également être importante : c'est en fonction de cette texture qu'il existera un plus ou moins grand obstacle à une action efficace du produit inhibiteur.

Ces résultats ne peuvent pas être extrapolés directement à la situation réelle des tubages en acier des puits géothermiques, où les dépôts sont épais probablement de plusieurs millimètres et ont subis un vieillissement qui les a stabilisé thermodynamiquement (mackinawite → pyrite → pyrrhotite) et mécaniquement (structure, texture et porosité).

Des études complémentaires doivent être entreprises pour que l'on puisse réaliser une extrapolation fondée. Il est très important de connaître, maintenant que tous les puits exploitant l'aquifère du Dogger du Bassin parisien sont ou seront traités par inhibiteur en fond de puits de production, le rôle du dépôt en présence et en absence de traitement et d'évaluer l'efficacité des inhibiteurs vis-à-vis de la poursuite de la corrosion sous dépôts.

En conclusion, sont rappelés les points principaux de cette étude et la nécessité d'effectuer d'autres études analogues et plus poussées est démontrée.

En annexes sont présentés les résultats d'analyse chimiques du fluide géothermal de Fresnes, la fiche technique de l'inhibiteur utilisé, les analyses métallographiques du dépôt et les courbes granulométriques des échantillons des échantillons de dépôt.

Cette étude s'est effectuée dans le cadre d'un programme de recherche de l'Institut Mixte de Recherches Géothermiques (IMRG). Les travaux ont été co-financés par la Commission des Communautés Européennes (Contrat CCE DG XII n° GE-0005-C).

MOTS-CLES :

géothermie - fluide géothermal - Dogger - chimie analytique inorganique - sulfure d'hydrogène - sulfure de fer - traitement physico-chimique - corrosion - inhibiteur de corrosion - amines - sel d'ammonium quaternaires

TABLE DES MATIERES

Page

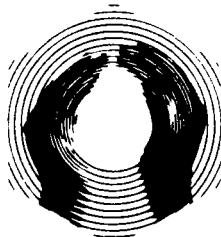
1 - INTRODUCTION.....	7
1.1 - PRESENTATION DU CONTEXTE.....	7
1.2 - OBJECTIFS ET PRESENTATION DE L'ETUDE.....	9
1.2.1 - OBJECTIFS	8
1.2.2 - PRESENTATION DE L'ETUDE.....	10
2 - ETUDE BIBLIOGRAPHIQUE.....	11
2.1 - PRESENTATION DE LA CORROSION.....	11
2.1.1 - CORROSION ANAEROBIE.....	11
2.1.2 - LES PHENOMENES SECONDAIRES DE LA CORROSION.....	13
2.1.2.1 - CORROSION PAR LES GAZ DISSOUS.....	13
2.1.2.2 - CORROSION PAR LES SELS DISSOUS.....	15
2.1.3 - LA CORROSION BACTERIENNE.....	18
2.1.3.1 - LES BACTERIES METHANOGENES.....	19
2.1.3.2 - LES BACTERIES SULFATO-REDUCTRICES.....	20
2.2 - NATURE ET STRUCTURE DES DEPOTS.....	22
2.2.1 - NATURE DES DEPOTS.....	22
2.2.2 - FORMATION DES DEPOTS.....	23
2.3 - TRAITEMENTS ANTI-CORROSION ANTI-BACTERIES ET ANTI-DEPOTS.....	23
2.3.1 - LA PROTECTION CATHODIQUE.....	23
2.3.2 - LES PEINTURES ANTI-CORROSION.....	24
2.3.3 - LES PRODUITS CHIMIQUES ORGANIQUES OU MINERAUX.....	25
2.3.3.1 - LES INHIBITEURS DE CORROSION.....	25
2.3.3.2 - BACTERICIDES - BACTERIOSTATIQUES.....	30
2.3.3.3 - INHIBITEURS DE DEPOTS.....	30
2.3.3.4 - MODES DE TRAITEMENT ACTUELS PAR PRODUITS INHIBITEURS.....	31
3 - MATERIELS ET METHODES.....	33
3.1 - DEPOTS CHOISIS : ORIGINE, COMPOSITION ET STRUCTURE.....	33
3.2 - CHOIX DE L'INHIBITEUR : LA SOLAMINE 129®.....	34

3.3 - DISPOSITIFS DE MESURE.....	37
3.3.1 - DISPOSITIF UTILISE EN LABORATOIRE.....	37
3.3.2 - DISPOSITIF DE MESURE SUR SITE.....	37
3.3.2.1 - SCHEMA ET FONCTIONNEMENT.....	37
3.3.2.2 - DESCRIPTION DU CORROSIMETRE ET DE LA SONDE.....	40
3.4 - METHODOLOGIES D'ANALYSE UTILISEES.....	42
3.4.1 - METHODES D'ANALYSE UTILISEES EN LABORATOIRE.....	42
3.4.1.1 - DOSAGE DU FER DISSOUS.....	42
3.4.1.2 - DOSAGE DES SULFURES.....	42
3.4.1.3 - DOSAGE DES IONS CHLORURES.....	44
3.4.1.4 - DOSAGE DES IONS CALCIUM.....	44
3.4.2 - METHODES D'ANALYSE UTILISEES PAR D'AUTRES LABORATOIRES DU BRGM: LA GRANULOMETRIE LASER.....	45
4 - EXPERIENCES ET INTERPRETATIONS.....	47
4.1 - EXPERIENCES EN LABORATOIRE AVEC LA SOLAMINE 129®.....	48
4.1.1 - EXPERIENCES REALISEES.....	48
4.1.2 - INTERPRETATION DES RESULTATS - DISCUSSION.....	49
4.1.2.1 - DEGRADATION DES DEPOTS.....	49
4.1.2.2 - RESULTATS DES ANALYSES GRANULOMETRIQUES.....	50
4.1.2.3 - DISCUSSION.....	50
4.2 - EXPERIENCES SUR SITE AVEC LA SOLAMINE 129®.....	53
4.2.1 - POSSIBILITES THEORIQUES D'ACTION.....	53
4.2.2 - CHOIX DU SITE ET EXPERIENCES REALISEES.....	54
4.2.2.1 - CHOIX DU SITE.....	54
4.2.2.2 - EXPERIENCES REALISEES.....	54
4.2.2.3 - INTERPRETATIONS DES RESULTATS.....	58
4.2.2.4 - DISCUSSION DES RESULTATS.....	60
4 - CONCLUSION GENERALE.....	61
5 - REFERENCES BIBLIOGRAPHIQUES.....	63
6 - LISTE DES TABLEAUX.....	68
7 - LISTE DES FIGURES.....	69
ANNEXES.....	71
ANNEXE I - Analyse physico-chimique de l'eau géothermale de Fresnes (GFR-2).....	72
ANNEXE II - Etude métallographique du dépôt de Cergy Pontoise.....	74
ANNEXE III - Fiche technique de la SOLAMINE 129® de SEPPIC.....	82
ANNEXE IV - Courbes d'analyse granulométriques des échantillons.....	85



BRGM

L'ENTREPRISE AU SERVICE DE LA TERRE



AGENCE FRANÇAISE
POUR LA MAÎTRISE DE L'ÉNERGIE

**INSTITUT MIXTE
DE RECHERCHES GÉOTHERMIQUES**
Service "Chimie Appliquée à la Géothermie"

évaluation de l'action de différents produits chimiques sur les dépôts des sulfures de fer et sur l'acier au carbone en milieu géothermal partiellement reconstitué

travaux cofinancés par :
CCE DG XII et l'IMRG
(contrat n° GE-0005-C)

projet "Exploitation basse enthalpie"
sous la direction de : Ph. Bray

**I. Ignatiadis
S. Teton
M. Lafforgue**

**novembre 1991
R 33 946**

BRGM-IMRG

B.P. 6009 - 45060 ORLÉANS CEDEX 2 - France - Tél. : (33) 38.64.31.72

RESUME

Dans ce rapport sont présentés les résultats d'une étude sur l'action de différents produits chimiques sur les dépôts des sulfures de fer et sur l'acier au carbone en milieu géothermal partiellement reconstitué au laboratoire. L'objectif principal de cette étude est de mettre au point un procédé de nettoyage chimique des parois des doublets géothermiques. Il s'agit d'essayer de mettre en solution (dissoudre) ou dégrader les dépôts (principalement constitués de sulfures de fer) présents sur les parois des puits géothermiques grâce à un traitement chimique. L'intérêt d'un tel procédé réside dans le fait qu'il pourrait être utilisé directement sur un puits faiblement encrassé ou en complément d'un traitement mécanique (à l'outil de forage seul ou couplé avec le jetting) pour améliorer l'efficacité du nettoyage.

En introduction de ce rapport est présenté, tout d'abord, le contexte et les objectifs de l'étude :

Certaines installations géothermiques du Dogger du Bassin parisien sont actuellement soumises à des difficultés d'exploitation : perte de débit, percement des tubages, colmatage... Celles ci sont liées essentiellement au caractère corrosif du fluide, particulièrement chargé en Cl^- , CO_2 et H_2S , qui attaque les tubages en acier doux et solubilise le fer. Ce fer ferreux réagit alors sur le sulfure d'hydrogène (H_2S , HS^-) pour donner des sulfures de fer, à l'origine des dépôts colmatants. Du fait de l'absence de traitement contre la corrosion dès le début de l'exploitation des puits géothermiques, les tubages ont été corrodés et sur leurs surfaces internes subsistent des dépôts.

Les premières opérations de réhabilitation qui datent de 1986, mettaient en oeuvre des techniques lourdes : curage mécanique des puits à l'aide d'outils de forage. Celles de 1990 et de 1991 utilisent les mêmes techniques et parfois des techniques mixtes comme le curage hydraulico-mécanique. Toutefois, rien ne permet d'être sûr que l'on obtient une élimination totale des dépôts sur tout l'intérieur des tubages.

Il est actuellement généralement admis que les dépôts de sulfures de fer présents sur un acier au carbone ne le protège pas totalement de la corrosion, le dépôt formé pouvant être plus ou moins poreux. Il est certain qu'en leur présence la corrosion est diminuée, mais n'est pas arrêtée pour autant. Il est également certain que les inhibiteurs de corrosion en quantité suffisante filment très bien une surface métallique propre sans dépôt et peuvent filmer un dépôt jeune et fin. Mais nous ne connaissons pas l'efficacité des inhibiteurs de corrosion organiques sur

un casing où subsistent des dépôts, et en particulier, s'il y a protection par les inhibiteurs vis-à-vis d'une corrosion sous dépôts épais et vieillis.

Dans les puits géothermiques curés (réhabilités) la présence des dépôts, qui subsistent après curage, est donc gênante et conditionne cette étude. En effet, ne connaissant pas ce qui se passe sous dépôts, il est préférable de s'en débarrasser par un traitement chimique directement ou en complément d'un curage mécanique, hydraulique ou mixte.

La question essentielle que l'on se pose actuellement est la suivante :

- Peut-on éliminer les dépôts, directement dans un puits ou les dépôts qui restent après un curage mécanique ou hydraulique ou même mixte, par un traitement chimique qui va les remettre en solution ou en suspension, sans altérer le métal sain et sans produire des nuisances secondaires ?

Pour répondre à cette question, il est nécessaire de faire une démonstration expérimentale en deux phases complémentaires :

- en laboratoire, étudier le comportement d'un dépôt en l'exposant sous atmosphère contrôlée à une solution géothermale partiellement reconstituée, en absence ou en présence de différents produits chimiques,
- sur site géothermique et sur pilote, étudier le comportement des dépôts en les exposant à différents produits chimiques en milieu géothermal réel.

Dans cette étude seule la première phase est visée, dont le but principal est la recherche d'une solution scientifiquement possible. Après avoir sélectionné et testé différents produits sur la base de leur réactivité sur les dépôts, les produits qui peuvent donner, seuls ou ensemble, une cinétique d'attaque des dépôts acceptable, une agressivité vis-à-vis du métal sain nulle et une production de produits de réaction agressifs ou toxiques inexistante ou très faible, seront proposés à la seconde phase. Cette dernière ne pourra être entamée qu'ultérieurement, suivant les résultats de la première phase, et permettra de proposer un procédé de dégradation-dissolution des dépôts des parois des puits.

Le chapitre 2, est une brève étude bibliographique sur la nature et la structure des dépôts que l'on rencontre dans les puits géothermiques exploitant l'aquifère du Dogger du Bassin parisien ainsi, que sur les différents traitements que l'on peut envisager pour les combattre avant et après leur formation.

Dans le chapitre 3 sont présentés les méthodes et les matériels utilisés pendant cette étude. En particulier, sont présentés les

échantillons des dépôts, les produits chimiques choisis suivant un certain nombre de critères de sélection, le dispositif expérimental utilisé au laboratoire et les méthodes d'analyse.

Dans le chapitre 4 sont exposés les expériences réalisées en laboratoire, les résultats obtenus, ainsi que les interprétations proposées. Les résultats ont permis de répondre, en partie, aux questions soulevées. Les produits chimiques employés dans les expériences de laboratoire dans cette étude ont tous une action chimique sur les dépôts.

L'acide chlorhydrique (concentration de 0,0206 à 0,4114 mol/l) associé ou non au glyoxal attaque très fortement les dépôts en dégageant du sulfure d'hydrogène et en produisant du fer dissous. La quantité de fer dissous en solution après réaction est considérable et représente de 82 à 98% (suivant les conditions) de la quantité de fer initialement présent dans le dépôt en 24 heures d'attaque.

Avec l'agent oxydant fort, le peroxyde d'hydrogène (concentration 0,2 et 0,3 mol/l), les dépôts sont plus modérément attaqués. La quantité de fer dissous en solution après réaction représente environ 10% en poids de la quantité de fer initialement présent dans le dépôt, en 24 heures d'attaque. Ce mécanisme d'attaque (oxydation) semble très complexe. Il y a production du soufre élémentaire, qui représente environ 15 à 19 % en poids du soufre présent initialement dans le dépôt.

La dégradation des sulfures de fer par l'emploi d'acide paraît tout-à-fait concluante. Mais, ce produit ayant une action très énergique (et corrosive vis-à-vis du métal), il est certain qu'il attaquerait également les tubages en acier au carbone des puits géothermiques.

Il nous a semblé donc astucieux de combiner deux traitements. A savoir, l'emploi d'inhibiteur de corrosion, qui pénétrerait jusqu'au métal et le protégerait, tout en ne gênant pas l'action du produit acide qui lui, dégraderait les dépôts.

Pour tester cette hypothèse, deux sortes d'expériences ont été réalisées au laboratoire, la première consistait à étudier le comportement d'un acier au carbone en présence de Solamine 129® et d'acide chlorhydrique, la seconde expérience consistait à étudier le comportement d'un dépôt mis en présence des deux composés afin de déterminer qui, de l'attaque acide ou du filmage l'emporte.

L'action de l'acide sur un acier au carbone en présence d'un agent tensio-actif a montré une protection (une corrosion acceptable) de l'acier à partir d'une certaine concentration de tensio-actif.

Le dépôt en présence de tensio-actif est attaqué par l'acide, mais sa vitesse d'attaque (de corrosion) est ralentie suffisamment par l'inhibiteur lorsque celui-ci est présent en quantité suffisante. Toutefois, sous la même solution réactive et pendant le même temps, le dépôt se dégrade beaucoup plus vite que l'acier. Il a été remarqué que la

teneur optimale en Solamine 129®, déterminée précédemment pour le bon filmage de l'acier n'est pas suffisante pour celui du dépôt. Le problème de curage est ainsi théoriquement résolu : les dépôts seraient dégradés par l'acide, tandis que l'acier resterait protégé.

L'idée première peut être réalisée et ces résultats peuvent ouvrir une voie de recherche qui aboutirait à un procédé de curage chimique des puits géothermiques. En effet, on peut envisager une attaque acide des dépôts accompagnée de l'injection d'inhibiteur organique pour stopper cette attaque au niveau de l'acier.

Ces résultats ne peuvent pas être extrapolés directement à la situation réelle et aboutir tout de suite à un procédé de curage. Il s'agit avant tout des résultats scientifiques bruts de laboratoire, très prometteurs, qui ne traitent que quelques aspects du problème.

Des études complémentaires de laboratoire doivent être entreprises pour que l'on puisse réaliser une extrapolation fondée. Il faudrait mener une étude cinétique qui déterminerait la vitesse d'attaque des dépôts par l'acide. On déterminerait ainsi le temps au bout duquel l'apport d'agent tensio-actif est nécessaire et à quelle concentration exactement.

Ensuite il serait convenable de passer au stade d'expérimentation sur pilote et sur site pour quantifier les réactions, penser à la neutralisation correcte des rejets liquides et/ou gazeux (pH, inhibiteur, H_2S) et finalement évaluer la faisabilité technique et économique du (ou des) procédé(s). La suite logique du travail actuel est la poursuite des travaux au laboratoire et ensuite les essais sur pilote.

En chapitre 5, la conclusion générale, quelques conclusions et recommandations sont émises concernant ces travaux, qui ont leur importance parce qu'elles préconisent de nouvelles expériences pour la meilleure compréhension des phénomènes ici traités.

En annexes sont présentés : la corrosion en milieu aqueux géothermal, les traitements anti-corrosion, anti-dépôts et anti-bactériens envisagés, le système Fe/S/ H_2O , les résultats des études métallographiques des dépôts et la fiche technique de l'agent tensio-actif utilisé.

Cette étude s'est effectuée dans le cadre d'un programme de recherche de l'Institut Mixte de Recherches Géothermiques (IMRG). Les travaux ont été co-financés par la Commission des Communautés Européennes (Contrat CCE DG XII n° GE-0005-C).

MOTS-CLES :

géothermie - fluide géothermal - Dogger - curage chimique - corrosion - dépôts - acide chlorhydrique - peroxyde d'hydrogène - glyoxal - inhibiteur de corrosion - sulfure d'hydrogène - sulfure de fer - fer - soufre

TABLE DES MATIERES

Page

LISTE DES ABREVIATIONS UTILISEES.....	9
1 - INTRODUCTION.....	11
1.1 - PRESENTATION DU CONTEXTE.....	11
1.2 - OBJECTIFS ET PRESENTATION DE L'ETUDE.....	13
1.2.1 - OBJECTIFS	13
1.2.2 - PRESENTATION DE L'ETUDE.....	15
2 - ETUDE BIBLIOGRAPHIQUE.....	17
2.1 - NATURE ET STRUCTURE DES DEPOTS.....	17
2.1.1 - NATURE DES DEPOTS.....	17
2.1.2 - FORMATION DES DEPOTS.....	18
2.1.2.1 - ORIGINE DES SULFURES.....	18
2.1.2.2 - ORIGINE DU FER.....	20
2.1.2.3 - FORMATION DES DEPOTS : REACTIONS, EQUATIONS ET FACTEURS REGISSANT L'EQUILIBRE ENTRE LES ESPECES Fe^{2+} , H_2S/HS^- , fer total et pH.....	21
2.2 - NATURE DES TRAITEMENTS.....	23
2.2.1 - TRAITEMENTS CONTRE LES DEPOTS AVANT LEUR FORMATION.....	23
2.2.1.1 - ACTION SUR LE pH.....	23
2.2.1.2 - ACTION SUR LE FER.....	23
2.2.1.3 - ACTION SUR LES SULFURES D'HYDROGENE.....	24
2.2.1.4 - LES SOLUTIONS DÉJÀ ENVISAGÉES DANS LE DOGGER.....	24
2.2.2 - TRAITEMENTS CONTRE LES DEPOTS APRES LEUR FORMATION.....	26
2.2.2.1 - TRAITEMENTS CONTRE LES DEPOTS APRES LEUR FORMATION PAR PRODUIT ACIDE.....	26
2.2.2.2 - TRAITEMENTS CONTRE LES DEPOTS APRES LEUR FORMATION PAR PRODUIT OXYDANT.....	27
3 - MATERIELS ET METHODES.....	31
3.1 - DEPOTS CHOISIS : ORIGINE, COMPOSITION ET STRUCTURE.....	31
3.1.1 - DEPOTS DU Puits de CERGY PONTOISE.....	31
3.1.2 - DEPOTS DU Puits de LA COURNEUVE NORD.....	33
3.2 - CRITERES DE SELECTION ET AGENTS CHIMIQUES.....	33
3.2.1 - CRITERES DE SELECTION DE PRODUITS.....	33
3.2.2 - AGENTS CHIMIQUES CHOISIS POUR L'ETUDE AU LABORATOIRE DE L'ACTION SUR LES DEPOTS ET L'ACIER.....	34
3.2.2.1 - ACIDE CHLORHYDRIQUE ET GLYOXAL.....	34
3.2.2.2 - PEROXYDE D'HYDROGENE.....	34
3.2.2.3 - ACIDE CHLORHYDRIQUE ET SOLAMINE 129®.....	35

3.3 - DISPOSITIF UTILISE EN LABORATOIRE.....	36
3.4 - METHODOLOGIES D'ANALYSE UTILISEES.....	38
3.4.1 - METHODES D'ANALYSE UTILISEES EN LABORATOIRE.....	38
3.4.1.1 - DOSAGE DU FER DISSOUS.....	38
3.4.1.2 - DOSAGE DES SULFURES.....	38
3.4.1.3 - DOSAGE DES IONS CHLORURES.....	40
3.4.1.4 - DOSAGE DES IONS CALCIUM.....	40
3.4.1.5 - DOSAGE DU SOUFRE ELEMENTAIRE.....	41
3.4.2 - METHODES D'ANALYSE UTILISEES PAR D'AUTRES LABORATOIRES DU BRGM....	41
4 - EXPERIENCES ET INTERPRETATIONS.....	43
4.1 - EXPERIENCES DE DEGRADATION DE DEPOT EN LABORATOIRE AVEC L'ACIDE CHLORHYDRIQUE ASSOCIE OU NON AU GLYOXAL.....	43
4.1.1 - MODE OPERATOIRE.....	43
4.1.2 - INTERPRETATION DES RESULTATS - DISCUSSION.....	45
4.2 - EXPERIENCES DE DEGRADATION DE DEPOT EN LABORATOIRE AVEC LE PEROXYDE D'HYDROGENE: OXYDATION PAR H₂O₂..	47
4.2.1 - MODE OPERATOIRE.....	47
4.2.2 - INTERPRETATION DES RESULTATS - DISCUSSION.....	48
4.3 - EXPERIENCES DE DEGRADATION DE DEPOT ET DE L'ACIER AU CARBONE EN LABORATOIRE AVEC L'ACIDE CHLORHYDRIQUE ET LA SOLAMINE 129®.....	50
4.3.1 - ACTION D'HCl ET DE TENSIO-ACTIF SUR UN ACIER AU CARBONE.....	50
4.3.1.1 - MODE OPERATOIRE.....	50
4.3.1.2 - INTERPRETATION DES RESULTATS - DISCUSSION.....	52
4.3.2 - ACTION D'HCl ET DE TENSIO-ACTIF SUR UN DEPOT DE SULFURES DE FER...54	
4.3.2.1 - MODE OPERATOIRE.....	54
4.3.2.2 - INTERPRETATION DES RESULTATS - DISCUSSION.....	54
4 - CONCLUSION GENERALE.....	57
5 - REFERENCES BIBLIOGRAPHIQUES.....	69
6 - LISTE DES TABLEAUX.....	65
7 - LISTE DES FIGURES.....	66
ANNEXES.....	67
ANNEXE I - Présentation de la corrosion.....	68
ANNEXE II - Traitements anti-corrosion, anti-dépôts et anti-bactéries..	79
ANNEXE III - Le système Fe/S/H ₂ O.....	88
ANNEXE IV - Etude métallographique du dépôt de Cergy Pontoise.....	91
ANNEXE V - Etude métallographique du dépôt de La Courneuve Nord.....	99
ANNEXE VI - Fiche technique de la SOLAMINE 129® de SEPPIC.....	101



Ademe



**INSTITUT MIXTE
DE RECHERCHES GÉOTHERMIQUES**
Cellule thématique "Chimie Appliquée à la Géothermie"

**prélèvement d'échantillons
de fluide géothermal
par le tube d'injection d'additifs
en fond de puits de production
sur le site d'ORLY I (GOR-2)**

projet "Exploitation basse enthalpie"
sous la direction de : Ph. Bray

I. Ignatiadis
A. Abou-Akar
M. Lafforgue
Ph. Bray

Travaux cofinancés par :
CCE DG XII et l'IMRG
(Contrat n° JOUG-005-C)

octobre 1992
R 34 513

RESUME

Dans ce rapport sont présentés les prélèvements d'échantillons de fluide géothermal, provenant du réservoir du Dogger du Bassin parisien, par un tube d'injection d'additifs en fond de puits de production, le TTFP de CFG-FORPLEX, sur le site d'ORLY 1 (GOR-2), les résultats d'analyse de ces échantillons ainsi que leur exploitation à la fois du point de vue géochimique et exploitation de la boucle géothermale (phénomènes de corrosion-dépôt). L'étude porte plus particulièrement sur l'utilisation des teneurs en sulfures et en fer dissous dosés dans les fluides prélevés simultanément en tête du puits de production et dans le TTFP afin de connaître la concentration en fer et en sulfures dans le fluide géothermal au niveau du réservoir du Dogger à l'aplomb d'ORLY 1 et pour caler un modèle de comportement du fluide (MODEP), qui tient compte de la corrosion et des dépôts dans les tubages.

En introduction de ce rapport sont présentés le contexte, les travaux antérieurs et les objectifs de l'étude.

Il y est signalé qu'avant la mise en oeuvre de ce prélèvement les concentrations en fer et en sulfures dans le fluide au fond du puits n'étaient pas connues et l'on supposait par défaut que le fer était en équilibre avec la pyrite.

Il y est rappelé que le prélèvement de fluides géothermaux est généralement réalisé, soit en surface par un piquage en tête du puits de production, soit dans les puits par un préleveur de fond lorsqu'il est possible de l'utiliser (absence de pompe immergée) et que ces deux méthodes ne permettent pas des mesures très fiables des teneurs en fer et en sulfures (pour les faibles teneurs), d'une part en raison des réactions du fluide géothermal avec l'acier du tubage ou du préleveur (dans le cas des préleveurs usuels), d'autre part à cause d'un "flashing" excessif ne permettant pas une conservation du fluide dans son état original (dans le cas des préleveurs de fond classiques).

Il y est également noté l'importance de prélever des échantillons provenant directement du réservoir (c'est-à-dire, non "pollués" par le tubage en acier), en particulier pour connaître les concentrations en fer,

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)

en sulfures et en bactéries sulfato-réductrices et pour caler les modèles de comportement du fluide au cours de sa remontée.

Enfin, une expérience antérieure est rappelée; elle a conditionné l'opération décrite et réalisée dans ce rapport dont les objectifs consistaient à:

- 1) prélever des échantillons en surface par le tube en matériau composite (fibre de verre + résine époxy), le TTFP de CFG-FORPLEX, avant la mise en service du traitement par inhibiteur de corrosion par ce même tubage.
- 2) évaluer la concentration en fer et en sulfures et le nombre de bactéries sulfato-réductrices au niveau de l'aquifère du Dogger à l'aplomb d'Orly 1.
- 3) caler un modèle de comportement du fluide (en cours de développement à l'IMRG) au cours de sa remontée.

Le chapitre 2, est une description du déroulement chronologique des expériences sur le site et des opérations au laboratoire. Un bref historique du puits avant cette opération est également présenté.

Dans le chapitre 3 sont présentés les résultats du suivi physico-chimique réalisé avant les prélèvements, les prélèvements, les traitements de données et les interprétations.

Avant d'échantillonner à travers le TTFP, un suivi de l'évolution des quelques paramètres physiques et des concentrations des espèces chimiques du fluide produit par le puits et par le TTFP a permis de s'assurer que le fluide produit était représentatif du fluide du réservoir (composition moyenne du fluide produit par ORLY 1 depuis plusieurs années). Quatre prélèvements ont été effectués et ont consisté en une prise d'échantillons en surface par le TTFP et par le casing à deux débits différents (100 m³/h et 60 m³/h) sur deux jours consécutifs (19/7/91 de 17h00 à 20h00 et 20/7/92 de 11h00 à 13h00).

Les concentrations en sulfures, fer et manganèse dosés dans le fluide provenant du TTFP sont discutées et assimilées comme celles du réservoir. Elles sont respectivement (en mg/l) pour le 1er prélèvement (débit=100 m³/h) : [Fe²⁺]_{TTFP} = 1,1 ; [S²⁻]_{TTFP} = 4,082 ; [Mn²⁺]_{TTFP} = 0,024 et pour le 2nd prélèvement (débit=60 m³/h) : [Fe²⁺]_{TTFP} = 0,73 ; [S²⁻]_{TTFP} = 2,841 ; [Mn²⁺]_{TTFP} = 0,021.

*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)*

Celles dosées en tête du puits de production sont discutées et assimilées comme étant celles résultant des phénomènes de corrosion-dépôt dans le cuvelage. Elles sont respectivement (en mg/l) pour le 1er prélèvement (débit=100 m³/h) : $[\text{Fe}^{2+}]_{\text{puits}}=3,0$; $[\text{S}^{2-}]_{\text{puits}}=3,016$; $[\text{Mn}^{2+}]_{\text{puits}}=0,054$ et pour le 2nd prélèvement (débit=60 m³/h) : $[\text{Fe}^{2+}]_{\text{puits}}=3,2$; $[\text{S}^{2-}]^{2+}=2,128$; $[\text{Mn}^{2+}]_{\text{puits}} = 0,045$.

La comparaison de la composition des fluides prélevés par le TTFP et par le puits de production a montré que seules les teneurs en fer, en sulfures, en manganèse et en cellules BSR varient significativement en fonction du débit de production et de la provenance de l'échantillon.

Il est remarqué que la teneur en fer au fond du puits n'est pas nulle. Sa valeur est voisine de 1 mg/l. La teneur en sulfures en fond du puits est supérieure à celle d'eau en tête du puits, ce qui prouve qu'il y a consommation des sulfures par précipitation de sulfures de fer.

Il a été possible de calculer approximativement la vitesse de corrosion dans le puits pendant les deux prélèvements en établissant le bilan en fer comme suit :

$$Q_T \cdot [\text{Fe}^{2+}]_T = \Phi_{\text{fer réservoir}} + \Phi_{\text{fer corrosion}} - \Phi_{\text{fer dépôts}}$$

Cette équation permet d'estimer le fer produit par la corrosion du tubage ($\Phi_{\text{fer corrosion}}$) connaissant le fer dosé en tête de puits de production ($[\text{Fe}^{2+}]_T$), le fer du réservoir ou $\Phi_{\text{fer réservoir}}$ (dosé dans le fluide issu du TTFP, soit $[\text{Fe}^{2+}]_{\text{TTFP}}$) et le fer déposé sous forme de sulfures. Ce dernier peut être estimé approximativement par la différence entre les sulfures dosés dans le TTFP et en tête du puits. Ainsi, les vitesses de corrosion évaluées sont V_{corr} (puits à 100m³/h) = 0,41 mm/an et V_{corr} (puits à 60m³/h) = 0,24 mm/an).

La même démarche avec les teneurs en manganèse conduit à des vitesses de corrosion du même ordre de grandeur: (V_{corr} (puits à 100m³/h) = 0,35 mm/an et V_{corr} (puits à 60m³/h) = 0,15 mm/an).

Il a été possible de tester les valeurs des vitesses de corrosion, évaluées dans le puits par le dosage du fer et des sulfures dissous lors des deux prélèvements, grâce à la modélisation de la remontée du fluide dans le puits de production au moyen des deux codes de calcul TPDEGAZ et MODEP (modélisation des phénomènes de dépôts). L'utilisation du code MODEP (qui est une extension du TPDEGAZ, puisqu'il permet de quantifier les sulfures de fer qui se déposent sur les parois du tubage d'un puits géothermique) pour le traitement des données physico-chimiques des fluides recueillis en tête du puits de production et en tête du TTFP permet d'une part de tester ce code et d'autre part de valider les vitesses de corrosion évaluées grâce à ces données.

*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)*

La composition du fluide au fond du puits est calculée à partir des analyses en tête du TTFP. La remontée dans le puits de production est simulée par le code MODEP pour effectuer les tests de validation, et ce par comparaison des compositions des deux fluides en tête du puits de production suivants : celui prélevé et analysé en tête du puits de production et celui simulé par MODEP.

Les calculs montrent que l'on obtient par l'utilisation du code de calcul MODEP des résultats plus proches des mesures réalisées pour l'intervention du 20/07/91, qui correspond d'ailleurs à une meilleure atteinte de l'état standard du fluide, même si le taux de fer dosé en tête du TTFP apparaît comme relativement élevé. Les écarts peuvent être attribués (en partie) aux hypothèses simplificatrices introduites dans le code MODEP. Toutefois, il existe une bonne corrélation entre le code MODEP et les résultats des analyses. Cependant des progrès restent à faire (ajout de paramètres cinétiques, prise en compte de la précipitation d'autres sulfures de fer, de carbonates etc..)

En chapitre 4 quelques conclusions et recommandations sont émises concernant cette étude. Il y est principalement exposé l'intérêt aussi bien du côté géochimique que du point de vue de l'exploitation géothermique d'effectuer ce type de prélèvement à chaque fois qu'une occasion se présente. Les données physico-chimiques sur les fluides ainsi recueillis en tête du puits de production et en tête du TTFP grâce à l'utilisation du code MODEP pour leur traitement permettent, désormais de valider les vitesses de corrosion évaluées grâce à ces données.

Dans l'annexe sont exposés les fichiers relatifs aux analyses effectuées en surface et au calcul de la composition du fluide au fond et qui ont servi à la modélisation de la remontée du fluide dans le puits de production par le code MODEP.

Cette étude s'est effectuée dans le cadre d'un programme de recherche de l'Institut Mixte de Recherches Géothermiques (IMRG). Les travaux ont été co-financés par la Commission des Communautés Européennes DG XII (n° JOUG-0005-C).

MOTS-CLES :

géothermie - fluide géothermal - Dogger - Bassin parisien - ORLY 1 - GOR-2
- sulfures d'hydrogène - sulfures dissous - fer dissous - isotopes du soufre - bactéries sulfato-réductrices - débit d'exploitation - sulfure de fer - corrosion - dépôts - TTFP - code de calcul géochimique - TPDEGAZ - MODEP.

TABLE DES MATIERES

	Page
1 - INTRODUCTION.....	9
1.1 - PRESENTATION DU CONTEXTE.....	9
1.2 - TRAVAUX ANTERIEURS.....	9
1.3 - OPERATION PROPOSEE ET OBJECTIFS.....	10
2 - DEROULEMENT CHRONOLOGIQUE DES EXPERIENCES SUR SITE ET DES OPERATIONS AU LABORATOIRE.....	11
2.1 - BREF HISTORIQUE DU PUIITS ET DES OPERATIONS EFFECTUEES AVANT LE CURAGE DU PUIITS ET L'INSTALLATION DU TTFP.....	11
2.2 - DEROULEMENT CHRONOLOGIQUE DES EXPERIENCES SUR SITE ET DU PRELEVEMENT PAR TUBE D'INJECTION D'ADDITIFS EN FOND DE PUIITS (TTFP CFG-FORPLEX).....	13
2.2.1 - DEGORGEMENT DU PUIITS DE PRODUCTION ET SUIVI PHYSICO-CHIMIQUE DU FLUIDE PRODUIT.....	15
2.2.2 - PRODUCTION PAR LE TTFP, CONDITIONNEMENT ET SUIVI PHYSICO-CHIMIQUE DU FLUIDE PRODUIT.....	16
2.2.3 - MESURES, PRELEVEMENTS ET ANALYSES D'ECHANTILLONS DE FLUIDE PRELEVE PAR LE TTFP ET PAR LA TETE DU PUIITS DE PRODUCTION.....	16
2.3 - TRAITEMENT DES DONNEES.....	17
2.4 - CODES DE CALCUL GEOCHIMIQUES.....	17
3 - RESULTATS DU SUIVI PHYSICO-CHIMIQUE ET DES PRELEVEMENTS. TRAITEMENTS DES DONNEES ET INTERPRETATIONS.....	19
3.1 - SUIVI PHYSICO-CHIMIQUE IN SITU DE L'EAU DU PUIITS	

*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)*

DE PRODUCTION ET DU TTFP AVANT ET PENDANT LES PRELEVEMENTS.....	19
3.1.1 - SUIVI DU DEBIT DE PRODUCTION DU PUIITS ET DU TTFP.....	25
3.1.2 - SUIVI DE LA TEMPERATURE DU FLUIDE PRODUIT PAR LE PUIITS DE PRODUCTION ET PAR LE TTFP.....	25
3.1.3 - SUIVI DE LA CONCENTRATION EN IONS CHLORURES DU FLUIDE PRODUIT PAR LE PUIITS DE PRODUCTION ET PAR LE TTFP.....	26
3.1.4 - SUIVI DE LA CONDUCTIVITE DU FLUIDE PRODUIT PAR LE PUIITS DE PRODUCTION ET DU TTFP.....	26
3.2 - COMPARAISON DE LA COMPOSITION DES FLUIDES PRELEVES PAR LE TTFP ET PAR LE PUIITS DE PRODUCTION, A UN JOUR D'INTERVALLE ET A DEUX DEBITS DIFFERENTS.....	33
3.2.1 - SALINITE TOTALE DES FLUIDES ET COMPOSITION CHIMIQUE EN ELEMENTS MAJEURS ET TRACES.....	33
3.2.2 - CONCENTRATIONS EN FER DISSOUS.....	35
3.2.3 - CONCENTRATIONS EN SULFURES DISSOUS.....	40
3.2.4 - POPULATION BACTERIENNE SULFATO-REDUCTRICE.....	45
3.2.5 - RAPPORTS ISOTOPIQUES DU SOUFRE $^{34}\text{S}/^{32}\text{S}$ DES SULFURES ET DES SULFATES.....	46
3.2.6 - CONCENTRATIONS EN MANGANESE.....	49
3.3 - MISE EN EVIDENCE DE LA CORROSION DU TUBAGE DU PUIITS DE PRODUCTION ET DE LA PRECIPITATION DES SULFURES DE FER DANS CE DERNIER GRACE AUX TENEURS EN SULFURES, EN FER DISSOUS ET EN MANGANESE.....	51
3.3.1 - VITESSE DE CORROSION DETERMINEE PAR LE DOSAGE DU FER ET DES SULFURES DISSOUS.....	51
3.3.2 - VITESSE DE CORROSION PAR LE DOSAGE DU MANGANESE.....	52
3.4 - MODELISATION DU COMPORTEMENT DU FLUIDE PAR TPDEGAZ ET MODEP. TEST PAR LE CODE MODEP DES VALEURS DES VITESSES DE CORROSION EVALUEES PAR LE DOSAGE DU FER ET DES SULFURES DISSOUS.....	55
3.4.1 - INTRODUCTION.....	55
3.4.2 - CALCUL DE LA COMPOSITION DU FLUIDE AU FOND DU PUIITS ET MODELIS- SATION DE LA REMONTEE DU FLUIDE DANS LE PUIITS DE PRODUCTION.....	57
5 - CONCLUSION.....	61
6 - REFERENCES BIBLIOGRAPHIQUES.....	63
7 - LISTE DES TABLEAUX.....	65
8 - LISTE DES FIGURES.....	67
ANNEXE.....	69

APPENDIX 5

LIST OF PUBLICATIONS

LIST OF PUBLICATIONS

IGNATIADIS I., FOUCHER J.C., FALGUERE P. (1990) - Poster : Determination of the solide suspended matter concentration in geothermal brine by Cross-Flow microfiltration using mineral membranes. 2nd International Conference on Inorganic Membranes, July 1-4, 1991, Montpellier, France.

DETOC-KARIMI S., FALGUERE P., FOUCHER J.C., PERSIN F., IGNATIADIS I. (1991) - Poster : Use of Cross-Flow microfiltration for the elimination of the sulfur produced by oxydation of dissolved sulfides in a geothermal brine. 2nd International Conference on Inorganic Membranes, July 1-4, 1991, Montpellier, France.

DETOC-KARIMI S., FALGUERE P., FOUCHER J.C., PERSIN F., IGNATIADIS I. (1991) - Use of Cross-Flow microfiltration for the elimination of the sulphur produced by oxydation of dissolved sulfides in a geothermal brine. Engineering Materials, Vol. 61-62, pp. 561-564.

IGNATIADIS I., DETOC-KARIMI S. (1992) - Poster : Utilisation de la microfiltration tangentielle pour le traitement d'un fluide géothermal. Séminaire Application des procédés de séparation par membrane, Ecole Nationale de l'Industrie Minérale du Maroc à Rabat.

IGNATIADIS I., DETOC-KARIMI S., FALGUERE P., FOUCHER J.C. (1992) - The use of Cross-Flow microfiltration for the determination of solid suspended matter concentration and for the elimination of the sulphur produced by oxydation of dissolved sulfides in a geothermal brine. Proceedings of the Euromembranes 92, October 5-8, 1992 à Paris, France, in Récents progrès en Génie des procédés, Membranes Processes, P. AIMAR and P. APTEL Editors (Lavoisier Press), n° 21, Vol. 6, pp. 141-146.

IGNATIADIS I., DETOC-KARIMI S., FALGUERE P., FOUCHER J.C. (1992) - The use of Cross-Flow microfiltration for the determination of solid suspended matter concentration and for the elimination of the sulphur produced by oxydation of dissolved sulfides in a geothermal brine. Communication in Euromembranes 92, October 5-8, 1992 à Paris, France.

IGNATIADIS I., TETON S. (1992) - Assessment of the chemical action of different agents on the iron sulphides constituting the scale formed by corrosion of carbon steels in geothermal environments. Geothermal Resources Council Transactions, Vol. 16, pp. 357-363.

LE DINH BAO B., IGNATIADIS I. (1992) - Anti-corrosion treatment of a carbon steel using sodium silicate to deposit a silica film. Analysis of films by photo-electron spectroscopy (ESCA). Article soumis pour publication in the Proceedings of the 6th International Conference on intergranular and interphase boundaries in materials, June 21-26, 1992, Thessaloniki, Greece. Trans. Tech. Publications Ltd in Materials Science Forum.

DETERMINATION OF SOLID SUSPENDED MATTER CONCENTRATION IN GEOTHERMAL BRINE BY CROSS-FLOW MICROFILTRATION USING MINERAL MEMBRANES

I. IGNATIADIS*, J.C. FOUCHER and P. FALGUERE

BRGM/AFME : Institut Mixte de Recherches Géothermiques (I.M.R.G.)
BP 6009 - 45060 ORLEANS CEDEX 2, FRANCE

* corresponding author

ABSTRACT

In the context of work on optimizing the exploitation of the geothermal fluids in the Dogger of the Paris Basin by physicochemical treatment, it is necessary to know accurately the solid suspended matter (SSM) content of the fluids before treatment in order to estimate the importance of the problems caused by scaling on well casing and in heat exchangers. It is also essential to know the effect of a treatment (by a surfactant dispersing agent, for example) on the suspended matter.

The solid suspended matter concentration in geothermal fluids is not well or not at all known on any geothermal well. The methods used up to now (staged filtration, laser granulometry, particle counting) have not given conclusive results, though they have often shown that the value is very low, less than 1 mg.l⁻¹.

Cross-flow microfiltration (CMF) on a mineral membrane of α aluminium of 0.2 μ m porosity has been applied to a raw brine on exit from the production well. The tests were carried out on a CMF pilot in a closed loop with a system of automatic declogging by flow reversal.

A large quantity (several cubic metres) of geothermal fluid is microfiltered, and the water from the filtration loop, which remains closed and clogging-free during the test, is recovered. Retention on the membrane is assumed to be total for particles larger than 0.2 μ m, while the total weight of particles smaller than 0.2 μ m is considered to be negligible. The water charged with the particles retained on the mineral membrane is evaporated in an oven at 70°C. When all the water from the loop has been evaporated, the residue, which consists of crystallized salts and solids formerly in suspension, is weighed. Since the precise composition of the fluid in dissolved salts is known, the weight of suspended matter in the quantity of fluid evaporated can be determined by subtraction.

The method is accurate provided that the total volume of filtered geothermal fluid, and its composition in dissolved salts are known. Repeated tests gave results that differed appreciably from each other in absolute terms (0.22-0.42 mg.l⁻¹), but were of the same order. From the point of view of procedure, these tests show the desirability of long-duration filtering, as this decreases the proportion of dissolved salts in the final residue and the SSM becomes predominant. After filtration for 90 hours the SSM represented 15% of the total weight of the residual deposit.

The use of CMF, on an α aluminium mineral membrane of porosity 0.2 μ m, is shown to be an efficient technique for quantitative analysis of SSM in raw geothermal brines. The method of continuous concentration in a closed loop and appropriate sampling can be applied to monitoring the hydraulic cleaning of geothermal wells by jetting, in order to estimate the total load extracted from clogged wells.

THE USE OF CROSS-FLOW MICROFILTRATION FOR THE ELIMINATION OF SULPHUR PRODUCED BY OXIDATION OF DISSOLVED SULPHIDES IN A GEOTHERMAL BRINE

S. DETOC-KARIMI, P. FALGUERE, J.C. FOUCHER, F. PERSIN*
and I. IGNATIADIS**

BRGM/AFME : Institut Mixte de Recherches Géothermiques, BP 6009
45060 ORLEANS CEDEX 2, FRANCE

*USTL : Laboratoire de Génie des Procédés, place Eugène Bataillon,
37060 MONTPELLIER CEDEX 1, FRANCE

** corresponding author

ABSTRACT

Oxidation of sulphides by hydrogen peroxide is currently being investigated as a method of treating geothermal fluids for the destruction of sulphides in the aqueous phase. The main object of the study is to resolve problems of scaling and clogging in geothermal wells. In this context, it was decided to test the feasibility of cross-flow microfiltration (CMF), on an α aluminium mineral membrane of 0.2 μm porosity, of a geothermal brine from the Paris Basin, in order to determine its efficacy in removing the by-products of oxidation of sulphides, in particular colloidal sulphur. The tests were made on a CMF pilot in a closed loop with a system of automatic declogging by flow reversal.

The CMF technique was first applied to the raw fluid, which contains 22 mg.l^{-1} dissolved sulphur on exit from the production well. Clogging of the membrane, both on and beneath its surface, was slight. The fall in filtrate flow rate remained small even after several days (20% after 4,5 days). Flow reversal is ineffective to declog the membrane and filtrate flow rate does not improve. It only reduces concentration in the filtration loop and momentarily destroys the polarization layer. In contrast, chemical cleaning of the membrane using 2% sodium hydroxide and 100 mg.l^{-1} Javel followed by 1% nitric acid returned flow rate and transmembrane pressure difference to their initial values. Raw fluid can be filtered for no more than 4-5 days without clogging. During this period, if filtration is done at a transmembrane pressure of about 1 bar, and a cross-flow rate reduced to only 3 m.s^{-1} , the filtrate flow rate remains in the interval 800 - 1000 $\text{l.h}^{-1}.\text{m}^{-2}$

The CFM technique was applied to the fluid oxidized by hydrogen peroxide in excess (3.6 to 18 times more than the dissolved sulphide content of the fluid). If the reaction goes to completion the hydrogen peroxide converts the sulphides into sulphates. In the present case an intermediate product, sulphur, was detected by nephelometry and UV absorption spectrophotometry at 276 nm. CMF tests on the oxidized fluid gave a loss in filtrate flow rate much greater than that recorded with unoxidized fluid, the rate falling from 1165 to 425 $\text{l.h}^{-1}.\text{m}^{-2}$ (i.e. a decrease of 64%) in 3,5 days, without declogging by flow reversal. Declogging reduced the rate of decrease in flow rate, but chemical cleaning is required in the short term to recover a filtrate flow rate near the initial rate. In order not to foul the membrane irretrievably, it appears necessary to do this every day or two. The cause of the large decrease in flow rate during filtration is the colloidal sulphur produced by the incomplete oxidation of the sulphides. The process of clogging with the oxidized fluid is different from that with the raw fluid - a film is adsorbed onto the surface of the membrane and can be slightly detached by flow reversal. Cross flow microfiltration renders the fluid clear and totally free of colloids, all that remains is the very small fraction ($<1 \text{ mg.l}^{-1}$) of dissolved elementary sulphur.

THE USE OF CROSS-FLOW MICROFILTRATION FOR THE ELIMINATION OF SULPHUR PRODUCED BY OXIDATION OF DISSOLVED SULPHIDES IN A GEOTHERMAL BRINE

S. Detoc-Karimi, P. Falguere, J.C. Foucher, F. Persin (a) and I. Ignatiadis (b)

BRGM/AFME: Institut Mixte de Recherches Géothermiques, BP 6009
F-45060 Orleans Cedex 2, France

(a) USTL, Lab. de Génie des Procédés, place Eugène Bataillon
F-37060 Montpellier Cedex 1, France

(b) corresponding author

ABSTRACT

Problems of scaling and clogging in geothermal wells are largely due to the presence of sulphides in the geothermal fluids. Oxidation of sulphides is currently being investigated in our laboratory as a means of treating geothermal fluids.

We report here, the use of cross-flow microfiltration (CFM) on a geothermal brine from the Dogger reservoir of the Paris Basin (Fontainebleau geothermal site) and we determine the efficiency of this method in removing the by-products of oxidation of sulphides, in particular colloidal sulphur. We used a CMF pilot in a closed loop with a system of automatic declogging by flow reversal and an α alumina mineral membrane of 0.2 μm pore size.

This is the first time that CFM has been applied to a low-temperature geothermal fluid. Our results show that the application of CFM technique is technically feasible. CFM technique can be used to successfully render the geothermal fluid (the raw fluid or the fluid oxidized by hydrogen peroxide) clear and totally free of colloids.

INTRODUCTION

Consideration of the setting of the low temperature geothermal system of the Paris Basin, and experience of the problems encountered during operations on geothermal projects caused by the fluids from the Dogger have enabled the development of a technique for dealing with these problems [1]. Problems of scaling and clogging in geothermal wells are largely due to the presence of sulphides (as hydrogen sulphide H_2S , HS^- et S^{2-} and mercaptans $\text{RR}'\text{S}$, RS^- , $\text{R}'\text{S}$ where R, R' = alkyl radical) in the geothermal fluids.

As a method of treating geothermal fluids, oxidation of sulphides is currently being investigated in our laboratory. The aim of this technique is to reduce the formation of iron sulphide scale by chemical oxidation of dissolved sulphides in the aqueous phase [1-3] and cross-flow microfiltration (CFM) on a mineral membrane [1, 4].

The development of analytical techniques for the determination of sulphur species made it possible to study the oxidation of sulphides by hydrogen peroxide [1]. The results of this latter study were in turn used to carry out kinetic studies on a Dogger reservoir geothermal fluid, from Fontainebleau, France. The studies showed that no simple rate law, describing all the observed phenomena, can be derived. Variations in reaction rate depend upon the ratio of concentration of oxidant to dissolved

sulphide, on pH and on catalysts. Identification of the products of reaction enabled stages to be recognised that could take place during oxidation in neutral or acidic and in alkaline solutions [1].

The second phase of the treatment, cross-flow microfiltration, has been applied here for the first time to a low-temperature geothermal fluid [1, 4].

It was decided first to test the feasibility of CFM, on an α alumina mineral membrane of 0.2 μm pore size, of a geothermal brine.

We report here the use of CFM on a geothermal brine from the Dogger reservoir of the Paris Basin (Fontainebleau geothermal site) and we determine the efficiency of this method in removing the by-products of oxidation of sulphides, in particular colloidal sulphur.

MATERIALS AND METHODS

Geothermal fluid

The Fontainebleau geothermal fluid comes from the Dogger limestone reservoir of the Paris Basin at depths between 1680 and 1780 m. The production temperature is 74.2°C. The pH at the surface is 6.73 and the salinity is 5.8 g.l⁻¹ (concentration, in mmol.kg⁻¹, of Na⁺ : 8.30, Cl⁻ : 72.30, HCO₃⁻ : 7.88, SO₄⁻ : 7.12). The fluid contains dissolved gases, principally CH₄ : 55%, CO₂ : 53.7% and N₂ : 24.1% by volume. The concentration in total sulphides is 7.10⁻⁴ mol.l⁻¹ [1]. Bubble point pressure is about 6 bar. The production flow rate varies during the year between 40 and 120 m³.h⁻¹.

Selection of technique and membrane

The geothermal fluid must be treated under conditions as close as possible to those of production, i.e. at a temperature not less than 74°C and, in order to avoid degasing the fluid, at a pressure above that of bubble point, which at times reaches 12 bar. These constraints imposed the choice of membrane and governed the design of the pilot setup. The configuration of the CFM pilot was selected for the advantages it presented, which are that it can be used at pressures up to 17 bar, temperatures of over 100°C, is resistant to corrosion and adaptable to the variations in flow rate of the fluid. The CFM process was thus tested in this pilot, installed on the production site.

The pilot treatment system possesses a mineral membrane, enables work to be carried out in a closed loop and includes a system of automatic declogging by flow reversal.

Inorganic membrane are the SCT multichannel membrane type P19 (SCT, Tarbes France). The main characteristics of this membrane are: nature: α alumina; length: 850 mm, filtration area: 0.2 m², pore size 0.2 μm . This inorganic membrane possess high degree of resistance to mechanical, thermal and chemical resistance (to corrosion) and they can operate in these extreme conditions [5-7].

The CMF technique was first applied to the raw fluid and second to the fluid oxidized by hydrogen peroxide.

EXPERIMENTAL, RESULTS AND DISCUSSION

Microfiltration of the raw fluid

The CMF technique was first applied to the raw fluid, which contains 22 mg.l⁻¹ dissolved sulphides on exit from the production well. The total load of suspended solids was evaluated at this time using a system of concentration in the closed loop [8], showing that the load was small, less than 0.5 mg.l⁻¹. The variation in flow rate of the filtrate shows that clogging occurred from the first hour of the experiment, reducing the flow rate by about 15% (Figure 1). Clogging of the membrane, both on and beneath its surface, was slight. The fall in filtrate flow rate remained small even after several days (20% after 4.5 days). Flow reversal is ineffective to declog the membrane and filtrate flow rate does not improve. It only reduces concentration in the filtration loop and momentarily destroys the polarization layer. In contrast, chemical cleaning of the membrane using 2% by volume sodium hydroxide and 100 mg.l⁻¹ Chlorine as NaOCl, followed by 1% by volume nitric acid returned flow rate and transmembrane pressure difference to their initial values (Figure 3). Raw fluid can be filtered for no more than 4-5 days without clogging. During this period, if filtration is done at a transmembrane pressure of about 1 bar, and a cross-flow rate reduced to only 3 m.s⁻¹, the filtrate flow rate remains in the interval 800 - 1000 l.h⁻¹.m². The turbidity of the fluid is reduced by 55% after microfiltration.

Microfiltration of the oxidized fluid

The CFM technique was applied to the fluid oxidized by hydrogen peroxide in excess (3.6 to 18 times more than the dissolved sulphide content of the fluid). If the reaction goes to completion the hydrogen peroxide converts the sulphides into sulphates. In the present case an intermediate product, sulphur [1,3,4], was detected by nephelometry and UV absorption spectrophotometry at 276 nm [1,9,10].

CMF tests on the oxidized fluid gave a loss in filtrate flow rate much greater than that recorded with unoxidized fluid, the rate falling from 1165 to 700 $\text{l.h}^{-1}.\text{m}^{-2}$ (i.e. a decrease of 40%) in an hour and from 1165 to 425 $\text{l.h}^{-1}.\text{m}^{-2}$ (i.e. a decrease of 64%) in 3.5 days, without declogging by flow reversal. Declogging every 30 minutes brings about a 10% increase in flow rate (Figure 3). Declogging reduced the rate of decrease in flow rate, but chemical cleaning is required in the short term to recover a filtrate flow rate near the initial rate. In order not to foul the membrane irremediably, it appears necessary to do this every day or two. After daily cleaning and declogging every 30 minutes, the filtrate flow rate can be maintained at close to 600 $\text{l.h}^{-1}.\text{m}^{-2}$, at a transmembrane pressure of 1 bar and a circulation rate of 4 m.s^{-1} . The difference in flow rate measured for the two types of fluid, raw and oxidized, demonstrates the clogging role of the colloidal sulphur.

The cause of the large decrease in flow rate during filtration is the colloidal sulphur produced by the incomplete oxidation of the sulphides. The process of clogging with the oxidized fluid is different from that with the raw fluid - a film is adsorbed onto the surface of the membrane and can be slightly detached by flow reversal.

Turbidity is virtually 100% eliminated, and colloidal sulphur about 80%. That part of the sulphur remaining in the fluid will correspond to newly formed particles that have not yet reached a size sufficient for them to be retained on the membrane [11].

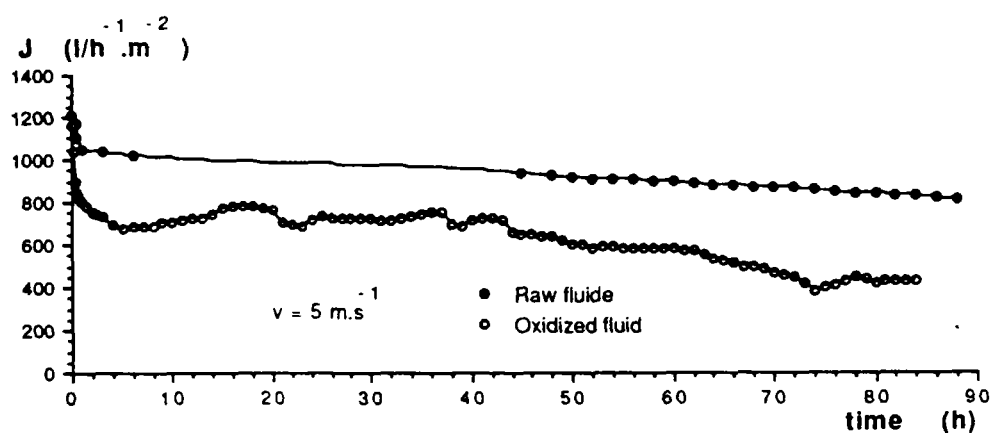


Figure 1. Comparison of the variation in the flow density of the permeate.

Raw and oxidized fluid. v =cross flow rate (m.s^{-1}),

J =flow density of the permeate ($\text{l.h}^{-1}.\text{m}^{-2}$)

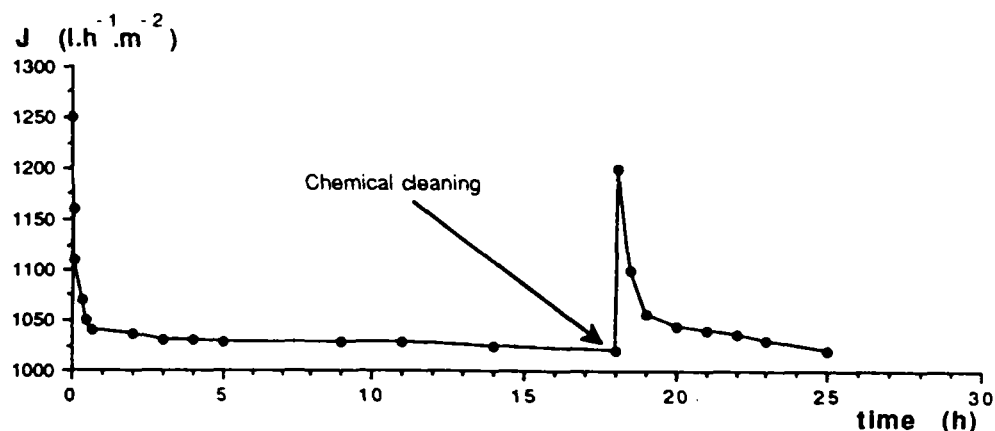


Figure 2. Efficiency of the chemical cleaning of the membrane. Raw Fluid.

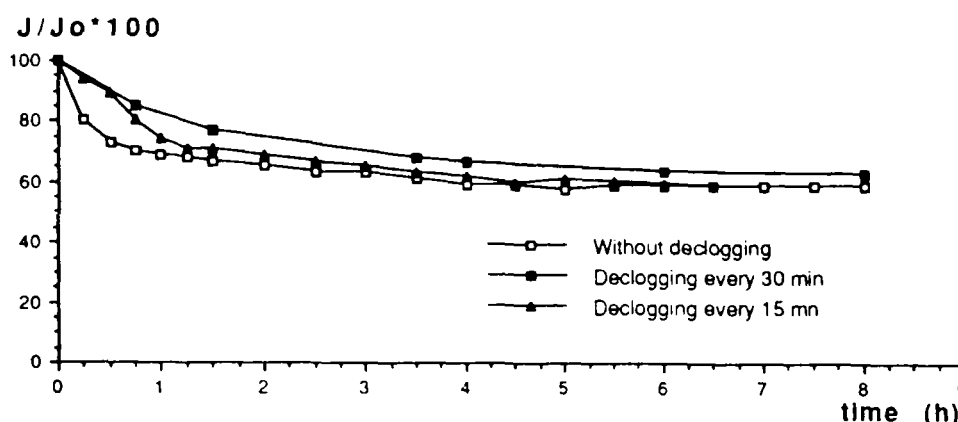


Figure 3. Influence of the frequency of declogging. Oxidized fluid.

J =flow density of the permeate ($\text{l.h}^{-1}.\text{m}^{-2}$),

J_0 =normalized flow density of the permeate ($\text{l.h}^{-1}.\text{m}^{-2}$)

CONCLUSION

This study made it possible to quantify the performances of this type of filtration of a raw fluid or the fluid oxidized by hydrogen peroxide. The results, both in flow rate and in retention of particles, clearly demonstrates the technical feasibility of using the CFM process on a geothermal fluid. The technique effectively eliminates turbidity and the retention of the by-products of oxidation. Cross flow microfiltration renders the fluids (the raw fluid or the fluid oxidized by hydrogen peroxide) clear and totally free of colloids.

These results, and the advantages in using this process on a geothermal fluid (maintenance of pressure and temperature, resistance to corrosion, adaptability to variations in fluid flow rate) should encourage and enable more detailed investigation of the geothermal applications of CFM. The CFM pilot has been shown to be of considerable interest as a tool for estimating the quantities of suspended solids in the raw geothermal fluid, a parameter little or unknown for any of the wells on the Dogger [8].

An overall economic assessment, however, shows that this type of treatment cannot at present be considered for the low-temperature fluids of the Dogger. Nevertheless, this study could be the starting point for the application of these processes to high-temperature geothermal fluids.

REFERENCES

- 1) Detoc - Karimi, S.: Thèse d'Université de Montpellier II - BRGM/Institut Mixte de Recherches Géothermiques. Traitement des fluides géothermaux du Dogger (Bassin parisien, France) par oxydation chimique des sulfures dissous et microfiltration tangentielle. BRGM/AFME, December 1990, 257 pp.
- 2) Avrahami, M. and Golding R.M.: J. Chem. Soc. (A), 1968, 647-651.
- 3) Gourmelon, C., Boulegue, J. and Michard G.: C.R. Acad. Sc. Paris, 1977, 284, série C, 269-284.
- 4) Falguere, P.: Rapport de stage d'ingénieur ISIM, Université de Montpellier II - BRGM/Institut Mixte de Recherches Géothermiques. Etude de la faisabilité technique en géothermie du procédé de microfiltration tangentielle sur membrane minérale, couplé ou non à l'oxydation des sulfures. June 1990, pp.80.
- 5) Aulas, F., Rumeau, M. and Tyburge, B.: Sciences et Techniques de l'Eau, 1983, 16, n° 3, 261-274.
- 6) Castelas, B., Rumeau, M., Cot, L., Guizard, C. and Allardy J.A.: FILTRA 84, 1984, Société Française de Filtration, Paris, 1984.
- 7) Galaj, S., Wicker, A., Dumas, J.P., Gillot, J. and Garcera, D.: Le lait, 1984, 64, 129-140.
- 8) Ignatiadis, I., Foucher, J.C. and Falguere P.: Communication submitted in the Second International Conference on Inorganic Membranes, July 1-4, 1991, Montpellier, France.
- 9) Friedman, H.L., Kerker, M.: J. Colloid. Sci., 1953, 8, 80-87.
- 10) Maurice, M.J.: Analytica Chimica Acta, 1957, 16, 574-577.
- 11) Zaiser, E.M. and La Mer, V.K.: J. Colloid. Sc., 1948, 3, 571-598.

UTILISATION DE LA MICROFILTRATION TANGENTIELLE POUR LE TRAITEMENT D'UN FLUIDE GEOTHERMAL

S. DETOC-KARIMI¹, P. FALGUERE, J.C. FOUCHER et I. IGNATIADIS*

BRGM/AFME : Institut Mixte de Recherches Géothermiques (I.M.R.G.)
BP 6009 - 45060 ORLEANS CEDEX 2, FRANCE

*corresponding author

RESUME

La géothermie en France est représentée par l'exploitation de fluides dont la température, comprise entre 47 et 85°C, permet principalement le chauffage de locaux.

Des problèmes d'exploitation sont apparus sur certaines installations géothermiques, liées à la corrosivité des fluides chargés notamment en Cl⁻, CO₂ et H₂S, qui corrodent les aciers (au carbone) constituant les tubages des puits géothermiques.

Un traitement de ces fluides géothermaux a été conçu dans le but de restaurer les conditions d'exploitation de ces centrales géothermiques. La première étape du traitement consiste à oxyder les sulfures dissous présents dans les fluides pour éviter la formation des sulfures de fer. La seconde étape du traitement a pour but d'éliminer les sous-produits de l'oxydation susceptibles de perturber l'exploitation, notamment le soufre colloïdal.

C'est dans cette deuxième partie du traitement qu'intervient le procédé de microfiltration tangentielle (MFT). Afin de tester sa faisabilité technique, un pilote, équipé d'une membrane minérale de diamètre de pores de 0,2 µm, a été mis au point. Ce pilote peut fonctionner éventuellement en boucle fermée et est muni d'un système de décolmatage automatique par inversion de flux. Il a permis d'effectuer des essais sur site.

Dans un premier temps, la MFT est appliquée au fluide brut, dont la teneur en sulfures dissous est de 22 mg/l, après sa sortie du puits de production. Le débit de filtrat se maintient entre 800 et 1000 l.h⁻¹.m⁻² pour une vitesse tangentielle de filtration de 3m.s⁻¹, une pression transmembranaire de 1 bar et un nettoyage chimique, par de la soude à 2% et de l'eau de javel à 100 ppm, puis de l'acide nitrique à 1%, tous les 4 jours. La turbidité du fluide chute alors de 55%.

Une deuxième série d'essais a permis de quantifier l'efficacité de la MFT pour l'élimination du soufre colloïdal formé après l'oxydation du fluide brut : 80% du soufre produit est retenu sur la membrane. Le débit de filtrat obtenu est de 600 l.h⁻¹.m⁻² avec un décolmatage d'une fréquence de 30 minutes et un nettoyage chimique quotidien.

Dans les deux cas, filtration de fluide brut ou de fluide oxydé, la MFT a montré son efficacité, les membranes de seuil de coupure 0,2 µm permettent d'éliminer dans le premier cas l'essentiel des matières en suspension, et dans le deuxième cas, la presque totalité du soufre colloïdal formé issu de l'oxydation des sulfures dissous.

Cette technique se révèle donc prometteuse dans le domaine de la géothermie et peut être étendue à tout autre type de fluides nécessitant une désulfuration en phase aqueuse.

¹ Adresse actuelle : ADI, 4, rue Ibn Abdoune, RABAT, MAROC

THE USE OF CROSS-FLOW MICROFILTRATION FOR THE DETERMINATION OF SOLID SUSPENDED MATTER CONCENTRATION AND FOR THE ELIMINATION OF SULPHUR PRODUCED BY OXIDATION OF DISSOLVED SULPHIDES IN GEOTHERMAL BRINES

I. Ignatiadis, S. Detoc-Karimi, P. Falguere, J.C. Foucher

< >

BRGM-AFME

Institut Mixte de Recherches Géothermiques

45060 ORLEANS Cedex 2 France

Abstract

Problems of scaling and clogging in geothermal wells are largely due to the presence of sulphides in the geothermal fluids. Oxidation of sulphides is currently being investigated in our laboratory as a means of treating geothermal fluids. We report here the first use of cross-flow microfiltration (CFM) on a geothermal brine, and we determine the solid suspended matter (SSM) concentration before oxidation of sulphides in the raw fluid and the efficiency of CFM in removing the by-products of oxidation, in particular colloidal sulphur. We used a CMF pilot, with an α -alumina mineral membrane of 0.2 μm pore size and a system of automatic declogging by flow reversal. Our results show that the application of CFM is technically feasible. The CFM has been shown to be of considerable interest as a tool for estimating the quantity of SSM in the raw fluid and can be used to successfully render the geothermal fluid (the raw fluid or the fluid oxidized by hydrogen peroxide) clear and totally free of colloids.

I. INTRODUCTION

Certain geothermal installations exploiting the Dogger aquifer in the Paris Basin are experiencing operational difficulties - loss of flow rate, perforation of casing, clogging - due essentially to the corrosivity of the fluid, which attacks the mild steel casings and solubilizes the iron. This ferrous iron then reacts with the sulphides (as hydrogen sulphide H_2S , HS^- and mercaptans RS^- , where R = alkyl radical) in the fluid to give iron sulphides of the type Fe_xS_y which form the clogging scale. This situation has enabled the development of a technique for dealing with these scaling and clogging problems (1). Various physicochemical treatments, and particularly oxidation of sulphides in the aqueous phase, are currently being investigated in our laboratory as a means of treating geothermal fluids. The aim of this technique is to reduce the formation of iron sulphide scale by chemical oxidation of dissolved sulphides in the aqueous phase (1-3) followed by cross-flow microfiltration (CFM) on a mineral membrane (1, 4).

The development of analytical techniques for the determination of sulphur species made it possible to study the oxidation of sulphides by hydrogen peroxide (H_2O_2) (1). The results of this latter study were in turn used to carry out kinetic studies on a Dogger reservoir geothermal fluid, from Fontainebleau, France. The studies showed that no simple rate law, describing all the observed phenomena, can be derived. Variations in reaction rate depend upon the ratio of concentration of oxidant to dissolved sulphide, on pH and on catalysts. Identification of the products of reaction enabled stages to be recognised that could take place during oxidation in neutral or acidic and in alkaline solutions (1). The second phase of the treatment, cross-flow microfiltration, has been

applied here for the first time to a low-temperature geothermal fluid (1, 4).

Optimizing the exploitation of the geothermal fluids in the Dogger of the Paris Basin by physicochemical treatment, needs also to know accurately the solid suspended matter (SSM) content of the fluids before treatment in order to estimate the importance of the problems caused by scaling on well casing and in heat exchangers. It is also essential to know the effect of a treatment (by a surfactant dispersing agent, for example) on the SSS. The SSM concentration in geothermal fluids is not well or not at all known on any geothermal brine. The methods used up to now (staged filtration, laser granulometry, particle counting) have not given conclusive results, though they have often shown that the value is very low, less than 1 mg/l.

It was decided first to test the feasibility of CFM, on an α -alumina mineral membrane of 0.2 μm pore size, of a geothermal brine.

We report here the use of CFM on a geothermal brine from the Dogger aquifer of the Paris Basin (Fontainebleau geothermal site) and we determine the efficiency of this method first in estimating the quantities of suspended solids in the raw geothermal fluid and second in removing the by-products of oxidation of sulphides, in particular colloidal sulphur.

II. MATERIALS AND METHODS

II.1. Geothermal fluid

The Fontainebleau geothermal fluid comes from the Dogger limestone reservoir of the Paris Basin at depths between 1680 and 1780 m. The production temperature is 74.2°C and the production flow rate varies during the year between 40 and 120 $\text{m}^3 \cdot \text{h}^{-1}$. The pH at the surface is 6.73 and the salinity is 5.8 $\text{g} \cdot \text{l}^{-1}$ (concentration, in $\text{mmol} \cdot \text{kg}^{-1}$, of Na^+ : 8.30, Cl^- : 72.30, HCO_3^- : 7.88, SO_4^{2-} : 7.12). The fluid contains dissolved gases, principally CH_4 : 54%, CO_2 : 11% and N_2 : 24% by volume. The concentration in total sulphides is $7 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ (1). Bubble point pressure is about 6 bar.

II.2. Selection of technique and membrane

The geothermal fluid must be treated under conditions as close as possible to those of production, i.e. at a temperature not less than 74°C and, in order to avoid degasing the fluid, at a pressure above that of bubble point, which at times reaches 12 bar. These constraints imposed the choice of membrane and governed the design of the pilot setup. The configuration of the CFM pilot was selected for the advantages it presented, which are that it can be used at pressures up to 17 bar, temperatures of over 100°C, is resistant to corrosion and adaptable to the variations in flow rate of the fluid. The CFM process was thus tested in this pilot, installed on the production site. The CMF technique was first applied to the raw fluid and second to the fluid oxidized by hydrogen peroxide. The pilot treatment system possesses a mineral membrane, enables work to be carried out in a closed loop and includes a system of automatic declogging by flow reversal. Inorganic membrane are the SCT multichannel membrane type P19/40 (SCT, Tarbes France). The main characteristics of this membrane are: nature: α -alumina; length: 850 mm, filtration area: 0.2 m^2 , pore size 0.2 μm . This inorganic membrane possess high degree of resistance to mechanical, thermal and chemical resistance (to corrosion) and they can operate in these extreme conditions (5-7). Figure 1 shows a simplified flow scheme of the experimental CFM pilot which has been used for these studies.

III. EXPERIMENTAL RESULTS AND DISCUSSION

III.1. Microfiltration of the raw fluid

Cross-flow microfiltration (CMF) on a mineral membrane of α -alumina of 0.2 μm pore size has been applied to a raw brine, which contains 22 $\text{mg} \cdot \text{l}^{-1}$ dissolved sulphides on exit from the production well. The tests were carried out on the CMF pilot in a closed loop with a system of automatic declogging by flow reversal.

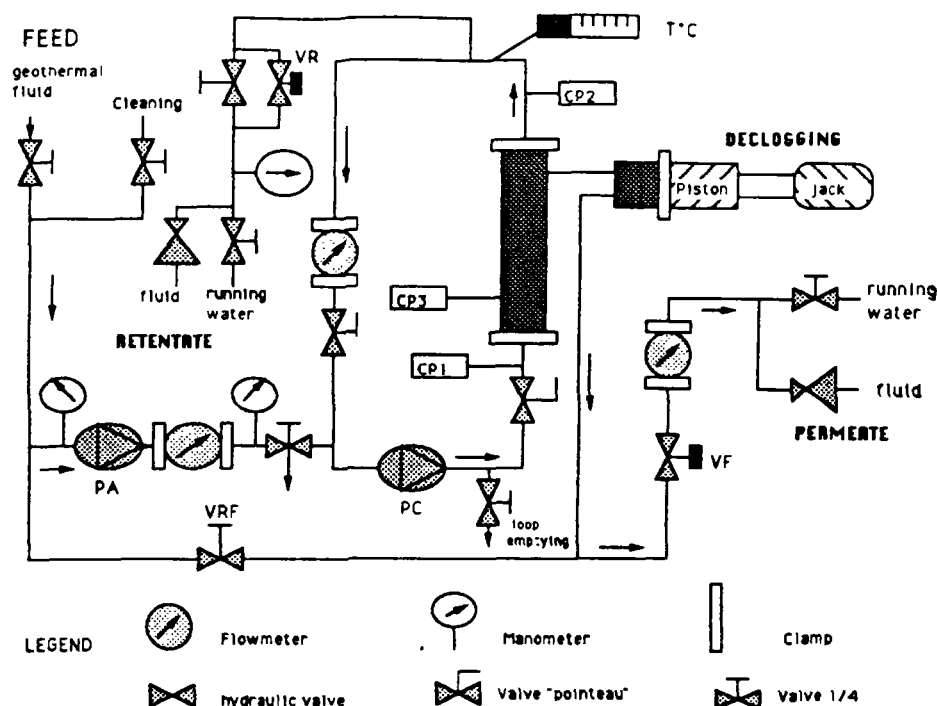


Figure 1: Simplified scheme of the experimental CFM pilot

The total load of suspended solids was evaluated at this time using a system of concentration in the closed loop (see III.2 below), showing that the load was small, less than 0.5 mg.l^{-1} (8). The variation in flow rate of the filtrate shows that clogging occurred from the first hour of the experiment, reducing the flow rate by about 15% (Fig. 2). The fall in filtrate flow rate remained small even after several days (20% after 4.5 days) (Fig. 2). Clogging of the membrane, both on and beneath its surface, was slight. Flow reversal is ineffective to declog the membrane and filtrate flow rate does not improve. It only reduces concentration in the filtration loop and momentarily destroys the polarization layer. In contrast, chemical cleaning of the membrane using 2% by volume sodium hydroxide and 100 mg.l^{-1} Chlorine as NaOCl, followed by 1% by volume nitric acid returned flow rate and transmembrane pressure difference to their initial values (Fig. 3). Raw fluid can be filtered for no more than 4-5 days without clogging. During this period, if filtration is done at a transmembrane pressure of about 1 bar, and a cross-flow rate reduced to only 3 m.s^{-1} , the filtrate flow rate remains in the interval $800 - 1000 \text{ l.h}^{-1}.\text{m}^{-2}$. The turbidity of the fluid is reduced by 55% after microfiltration.

III.2. Determination of the solid suspended matter

A large quantity (several m^3) of geothermal fluid is microfiltered, and the water from the filtration loop, which remains closed and clogging-free during the test, is recovered. Retention on the membrane is assumed to be total for particles larger than $0.2 \mu\text{m}$, while the total weight of particles smaller than $0.2 \mu\text{m}$ is considered to be negligible. The water charged with the particles retained on the mineral membrane is evaporated in an oven at 70°C . The residue, which consists of crystallized salts and solids formerly in suspension, is weighed. Since the precise composition of the fluid in dissolved salts is known, the weight of suspended matter in the quantity of fluid evaporated can be determined by subtraction. The method is accurate provided that the total volume of filtered geothermal fluid, and its composition in dissolved salts are known. Repeated tests gave results that differed appreciably from each other in absolute terms ($0.22 - 0.42 \text{ mg.l}^{-1}$), but were of the same order (see Table 1). From the point of view of procedure, these tests show the desirability of long-duration filtering, as this decreases the proportion of dissolved salts in the final residue and the SSM becomes predominant. After filtration for 90 hours the SSM represented 15% of the total weight of the residual deposit.

	Run N° 1	Run N° 2
Microfiltration time (h)	3,0	92,0
Volume microfiltered (l)	939,2	16812,0
Volume of the water recovered from the filtration closed loop (l)	5,091	5,105
Total dissolved salts (salinity) in water (g)	5,712 ± 0,050	5,712 ± 0,050
Weight of total dissolved salts in the recovered volume (g)	29,080	29,160
Weight of dry vessel (g)	292,241	479,152
Weight of scale + vessel (g)	321,713	512,020
Weight of recovered SSM (g)	0,392	3,708
concentration of SSM (mg/l)	0,42	0,22

Table 1: Conditions of the procedure and determination of SSM concentration in a geothermal brine (Fontainebleau, France) by Cross-Flow microfiltration.

III.3. Microfiltration of the oxidized fluid

The CFM technique was applied to the fluid oxidized by H_2O_2 in excess (3.6 to 18 times more than the dissolved sulphide content of the fluid). Oxidation conditions vary as a function of flow rate load: ratio $[H_2O_2]/[H_2S]$ vary between 3.6 and 18. According to the $[H_2O_2]/[H_2S]$ ratio, the concentration in different by-products of oxidation (sulphur, polysulphides, thiosulphates, sulphites, sulphates) varies. If the reaction goes to completion the H_2O_2 converts the sulphides into sulphates. In the present case an intermediate product, sulphur (1,3,4), was detected by nephelometry and UV absorption spectrophotometry at 276 nm (1,9,10).

CMF tests on the oxidized fluid gave a loss in filtrate flow rate much greater than that recorded with unoxidized fluid, the rate falling from 1165 to 700 $l.h^{-1}.m^{-2}$ (i.e. a decrease of 40%) in an hour and from 1165 to 425 $l.h^{-1}.m^{-2}$ (i.e. a decrease of 64%) in 3.5 days, without declogging by flow reversal. Declogging every 30 minutes brings about a 10% increase in flow rate (Fig. 4). Declogging reduced the rate of decrease in flow rate, but chemical cleaning is required in the short term to recover a filtrate flow rate near the initial rate. In order not to foul the membrane irretrievably, it appears necessary to do this every day or two. After daily cleaning and declogging every 30 minutes, the filtrate flow rate can be maintained at close to 600 $l.h^{-1}.m^{-2}$, at a transmembrane pressure of 1 bar and a circulation rate of 4 $m.s^{-1}$.

Concerning the performances in the retention of particles, we note that turbidity is virtually 100% eliminated, and colloidal sulphur about 80%. That part of the sulphur remaining in the fluid will correspond to newly formed particles that have not yet reached a size sufficient for them to be retained on the membrane (11).

The difference in flow rate measured for the two types of fluid, raw and oxidized, demonstrates the clogging role of the colloidal sulphur in the CFM process. The process of clogging with the oxidized fluid is different from that with the raw fluid - a film is adsorbed onto the surface of the membrane and can be slightly detached by flow reversal.

The cause of the large decrease in flow rate during filtration is the colloidal sulphur (produced by the incomplete oxidation of the sulphides), which seems to provokes two types of distinct phenomena: first the formation of a layer easily detachable on the surface of the membrane (that has been shown by the efficiency of declogging by flow reversal) and second a type of clogging more deep which hinders filtration and reduces flow rate.

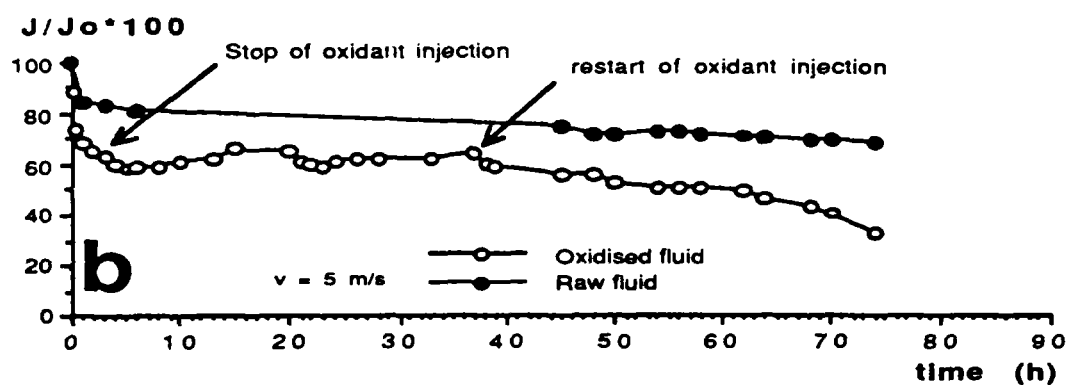
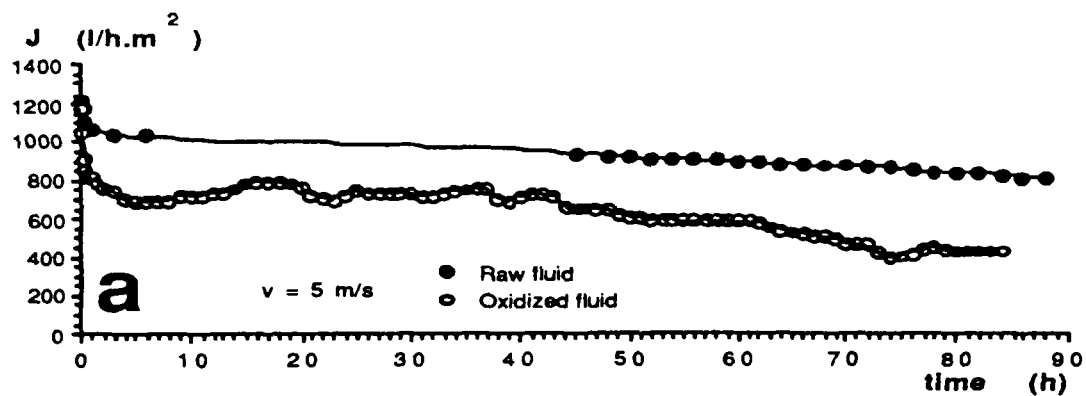


Figure 2: Comparison of the variation in the flow density of the permeate. Raw and oxidized fluid. v =cross flow rate (m.s⁻¹),
a: Flow density of the permeate J (l.h⁻¹.m⁻²)
b: Normalized flow density of the permeate $100 \cdot J/J_0$ (l.h⁻¹.m⁻²)

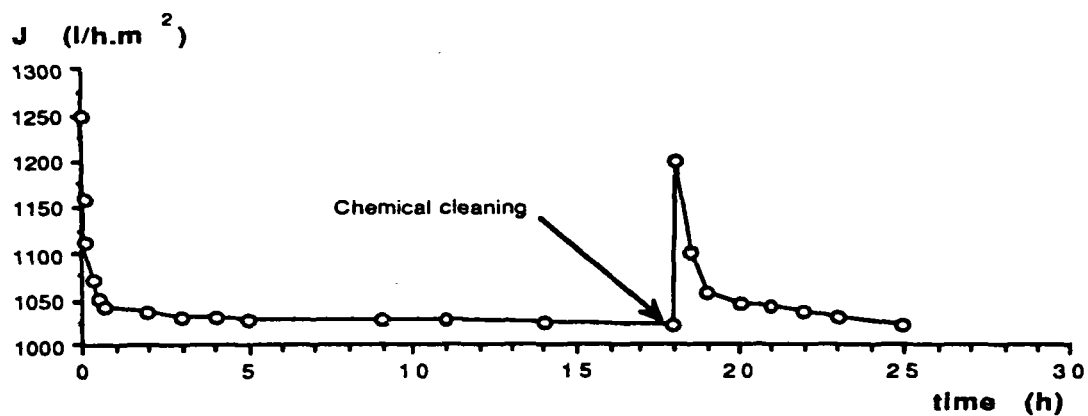


Figure 3: Efficiency of the chemical cleaning of the membrane. Raw Fluid.

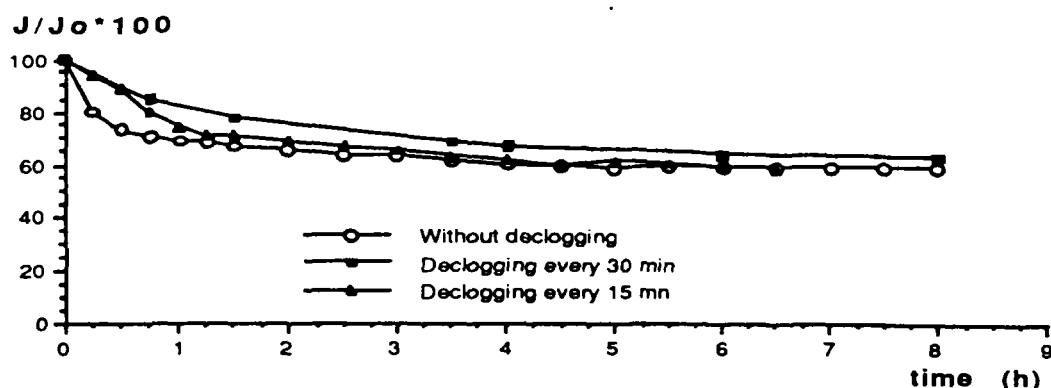


Figure 4: Influence of the frequency of declogging. Oxidized fluid.

J =flow density of the permeate ($\text{l.h}^{-1}.\text{m}^{-2}$),

$100 \cdot J/J_0$ =normalized flow density of the permeate ($\text{l.h}^{-1}.\text{m}^{-2}$)

IV. CONCLUSION

This study made it possible to quantify the performances of this type of filtration of a raw fluid or the fluid oxidized by hydrogen peroxide. The results, both in flow rate and in retention of particles, clearly demonstrates the technical feasibility of using the CFM process on a geothermal fluid. Cross flow microfiltration renders the fluids (the raw fluid or the fluid oxidized by hydrogen peroxide) clear and totally free of colloids. These results, and the advantages in using this process on a geothermal fluid (maintenance of pressure and temperature, resistance to corrosion, adaptability to variations in fluid flow rate) should encourage and enable more detailed investigation of the geothermal applications of CFM. The CFM pilot has been shown to be of considerable interest as a tool for estimating the quantities of suspended solids in the raw geothermal fluid, a parameter little or unknown for any of the wells on the Dogger (8). An overall economic assessment, however, shows that this type of treatment cannot at present be considered for the low-temperature fluids of the Dogger. Nevertheless, this study could be the starting point for the application of these processes to high-temperature geothermal fluids.

References

1. Detoc - Karimi S., Thèse d'Université de Montpellier II - BRGM/IMRG. Traitement des fluides géothermaux du Dogger (Bassin parisien, France) par oxydation chimique des sulfures dissous et microfiltration tangentielle, 257 pp., December 1990.
2. Avrahami M., Golding R.M., J. Chem. Soc. (A), 647-651 (1968).
3. Gourmelon C., Boulegue J., Michard G., C.R. Acad. Sc. Paris, 284, série C, 269-284 (1977).
4. Falguere P., Rapport de stage d'ingéniorat ISIM, Université de Montpellier II - BRGM/IMRG. Etude de la faisabilité technique en géothermie du procédé de microfiltration tangentielle sur membrane minérale, couplé ou non à l'oxydation des sulfures, pp.80, June 1990.
5. Aulas F., Rumeau M., Tyburge B., Sciences et Techniques de l'Eau, 16, n° 3, 261-274 (1983).
6. Castelas B., Rumeau, M., Cot, L., Guizard, C., Allardy J.A., FILTRA 84, 1984, Société Française de Filtration, Paris, 1984.
7. Galaj S., Wicker A., Dumas J.P., Gillot J., Garcera D., Le lait, 64, 129-140 (1984).
8. Ignatiadis I., Foucher J.C., Falguère P., Communication in the Second International Conference on Inorganic Membranes, July 1-4, 1991, Montpellier, France.
9. Friedman H.L., Kerker M., J. Colloid. Sci., 8, 80-87 (1953).
10. Maurice M.J., Analytica Chimica Acta, 16, 574-577 (1957).
11. Zaiser E.M., La Mer V.K., J. Colloid. Sci., 3, 571-598 (1948).

**ASSESSMENT OF THE CHEMICAL ACTION OF DIFFERENT AGENTS
ON THE IRON SULPHIDES CONSTITUTING THE SCALE FORMED BY
CORROSION OF CARBON STEELS IN GEOTHERMAL ENVIRONMENTS**

Ioannis Ignatiadis and Sophie Teton

**B.R.G.M. : Institut Mixte de Recherches Géothermiques
(I.M.R.G.), BP 6009 - 45060 ORLEANS CEDEX 2, FRANCE**

ABSTRACT

The purpose of this work is to find a way of removing scale by chemical treatment either directly or as a complement to mechanical, hydraulic or mixed mechanical/hydraulic cleaning. In order to test the efficacy of the breakdown of scale, different agents were tested in the laboratory under varying conditions, in a reconstituted geothermal environment and under a controlled atmosphere. HCl in varying concentrations, used with or without glyoxal, completely breaks down the scale. H_2O_2 in excess is less effective. HCl and a surface active agent were used together so that the latter would penetrate to the metal and protect it, while not impeding the action of the acid in breaking down the scale. This showed that both the carbon steel and the scale could be protected by the surface active agent despite the presence of the acid. But a marked difference exists in the rates of corrosion of the steel and of the scale that can be exploited so as to treat selectively the scale without corroding the steel.

1. INTRODUCTION

Certain of the geothermal projects exploiting the Dogger aquifer in the Paris Basin are experiencing operational difficulties - loss of flow rate, perforation of casing, clogging - that are due essentially to the aggressivity of the fluids, owing to the presence of mainly Cl^- , CO_2 and H_2S , which attack the carbon steel casings and solubilize the iron. The resulting ferrous iron then reacts with the H_2S and HS^- in the fluid to give iron sulfides of the type Fe_xS_y which form the clogging scale.

Because there has been no protective treatment against corrosion since the initiation of exploitation of the wells, the casings have been corroded, and scale remains on the internal surfaces. In the framework of maintenance of the geothermal installations, the internal walls of the casings are cleaned of scale once every few years. The purpose of this is to expose the clean metal, before continuing normal operation, with or without treatment of the geothermal fluid by introducing a

commercial cationic surfactant at the bottom of the production well in order to avoid renewed harmful scaling. The surface active agents used are mainly composed of nitrogen derivatives of quaternary ammonium salt type, and are supposed to have anti-corrosive, anti-scaling and bactericidal effects. The first rehabilitation operations, carried out in 1986, employed mechanical cleaning methods using drilling equipment. The 1990 and 1991 operations used the same techniques and sometimes mixed techniques such as hydraulic/mechanical, using a reverse-circulation device attached to standard drill rods, or hydraulic, using a jetting tool attached either to standard drill rods or to a continuous flexible tube. Total elimination of scale from the entire internal surface of the casing cannot, however, be guaranteed.

It is now generally accepted that sulfide scale coating carbon steel does not completely protect it from corrosion, as the scale may be porous to varying degrees. Corrosion is undoubtedly decreased when scale is present, but it is not arrested. In addition, corrosion can take place beneath scale, in particular when bacteria develop on and beneath the scale, producing hydrogen sulfide by reduction of the sulfates contained in the geothermal water. It is also certain that corrosion inhibitors in sufficient quantity produce an effective film on clean, non-scaled metal, and may do the same on new, thin scale (Ignatiadis et al., 1991a), but the efficacy of organic corrosion inhibitors on casing where scale persists, and in particular whether or not they can protect against corrosion beneath old, thick scale, is unknown.

The persistence of scale in rehabilitated geothermal wells is a nuisance and has conditioned this study. As it is not known what takes place beneath scale, it is preferable to eliminate it by chemical treatment, either directly or as a complement to mechanical, hydraulic, or mixed mechanical/hydraulic cleaning.

The main objective of this study was to develop a process for the chemical cleaning of the walls of geothermal doublets. This involved attempting to dissolve the scale, composed mainly of iron sulfides, on the casing by chemical treatment. The interest of such a process lies in the fact that it

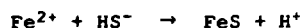
could be used directly, on a slightly fouled well, or additionally to mechanical treatment to improve the efficacy of the cleaning. The basic question to be answered at present is: can scale, remaining after mechanical, hydraulic or even mixed cleaning, be removed directly in a well by a chemical cleaning that puts the scale into solution or suspension, without producing secondary problems? In order to answer this question, an experimental demonstration needs to be made in two stages, in the laboratory, and on a pilot and on site. The laboratory study would bear on the behaviour of scale exposed, under a controlled atmosphere, to a partly reconstituted geothermal solution, in the presence or otherwise of certain chemicals. On the pilot and on site, the behaviour of the scale would be studied on exposure to different chemicals in an actual geothermal environment.

The present study concerned only the first stage, the principal aim of which was to find a scientifically possible solution. The study has been fully reported, in BRGM report No. 33946, by Ignatiadis et al. (1991b). After selection and testing of various chemicals for their reactivity to scale, those which, alone or in combination, are able to give an acceptable kinetic of attack on the scale, are completely non-aggressive towards clean metal, and produce no or very little aggressive or toxic products of reaction will be proposed for the second stage. This can only be commenced when the results of the first stage are known, and will enable the proposal of a process for the breakdown and dissolution of scale on well walls.

2. PRELIMINARY STUDIES

A literature search was made on the nature and structure of the scale encountered in the geothermal wells exploiting the Dogger of the Paris Basin (Ignatiadis et al. 1991b). The results are summarised below.

The formation of scale can be represented by:



The Ionic Activity Product (IAP) of the reaction can be written:

$$\text{I.A.P.} = \frac{(\text{HS}^-)(\text{Fe}^{2+})}{(\text{H}^+)}$$

where (Fe^{2+}) is the activity of ferrous iron in the solution, (HS^-) is the activity of dissolved sulfide HS^- in the solution, (H^+) is the activity of H^+ ions, which represents the pH of the solution $(-\log(\text{H}^+))$.

Iron sulfide can be precipitated if the IAP of the reaction becomes greater than the solubility product $K_s(P,T)$ of the mineral FeS . K_s is a thermodynamic value that is dependent only upon temperature and pressure.

It is obvious that by "treatment against iron

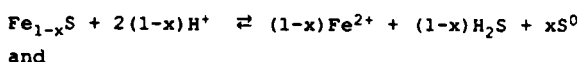
sulfide scaling" is meant the various types of attack such as breakdown, dissolution or oxidation of the scale. Literature in this field is scarce. A non-exhaustive literature review resulted in the selection of certain attack processes for testing on scale (Ignatiadis et al., 1991b), they are: redissolution of iron sulfides by the action of a strong acid and the oxidation of sulfides by a strong oxidant.

2.1. Redissolution of iron sulfides by a strong acid

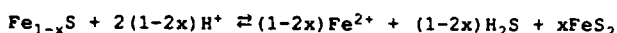
The addition of acid enables reduction of the IAP, thus favouring the dissolution of iron sulfides. The best known reaction for the laboratory preparation of hydrogen sulfide is cold hydrochloric acid attack on iron sulfide in a Deville's or Kipp's type apparatus, according to the reaction:



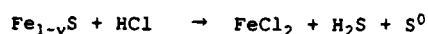
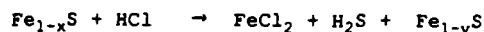
The process for a sulfide of the type Fe_{1-x}S can be described by the following reactions:



and



Experiments by Luganov and Shabalin (1985) gave results that could only be explained by the first equation. Their results also enabled a more precise identification of the mechanism, showing that the attack in fact takes place in two stages, an initial formation of an iron sulfide deficient in iron is in the next stage accompanied by the formation of elementary sulfur according to the reactions:

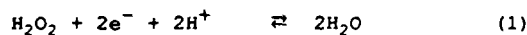


where y is greater than x , and of the order of 0.13 to 0.145.

2.2. Oxidation of iron sulfides by an oxidant

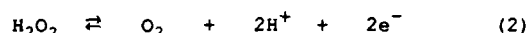
The corrosion of iron exposed to geothermal fluids is very strongly influenced by temperature and by the content of the fluid in sulfide compounds. The potential-pH electrochemical diagram of the system $\text{Fe-S-H}_2\text{O}$ makes it possible to represent the limits of thermodynamic stability of the metal and to identify the products of its corrosion. On the basis of the Pourbaix $\text{Fe/H}_2\text{O}$ diagram, Pound et al. (1985) were able to establish diagrams taking into account both temperature and the sulfur species. The different reactions considered, and the values of the coefficients of activity and of potential are given in the report of Ignatiadis et al. (1991b). It is thus possible to draw the diagram of the system $\text{Fe-S-H}_2\text{O}$ at 373°K,

which is the temperature closest to that of the Dogger fluids, and to superpose on this diagram the system corresponding to the selected oxidant, which in our case was hydrogen peroxide, H_2O_2 (Detoc-Karimi, 1990, 1991), which is a non-linear chain of polyoxides, the oxidizing power of which increases with acidity (Doré, 1989):



where $E_{H1}^0 = 1.776$ V

H_2O_2 can also be a reducer:



where $E_{H2}^0 = 0.700$ V

When the redox potential of E_{H1}^0 is greater than E_{H2}^0 , the H_2O_2 dismutation reaction can take place. This is the reaction:



which is none other than the spontaneous decomposition reaction of hydrogen peroxide. H_2O_2 is thus thermodynamically unstable.

The equilibrium conditions (at 25°C, i.e. at 373°K) corresponding to reactions (1) and (2) are:

$$E_{H1}^0 = 1.776 - 0.074 \text{ pH} + 0.038 \log(H_2O_2)$$

$$E_{H2}^0 = 0.700 - 0.074 \text{ pH} - 0.038 \log(H_2O_2)$$

The action of H_2O_2 on inorganic substrates takes different forms (Weres and Tsao, 1983; Doré, 1989):

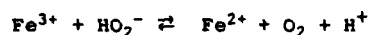
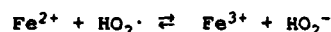
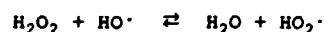
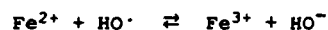
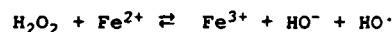
a) If the substrate is nucleophile, H_2O_2 behaves like an electrophile; for example:



b) Substitution by HOO^- may take place

c) H_2O_2 may form the radical ion $HO^\cdot$, a powerful oxidant which reacts with the substrate, initiating a series of reactions (Duke, 1959).

The dismutation of H_2O_2 to give water and oxygen according to the reaction $2 H_2O_2 \rightleftharpoons 2 H_2O + O_2$ is catalysed by many different metals. The couple H_2O_2 -Fe is of particular importance (Fenton's reaction), (Doré, 1989). The principal reactions taking part are:



In order that the reaction of oxidation of iron sulfides take place and be quantitative, it is necessary that the normal conditional potential of the hydrogen peroxide be greater than the normal conditional potentials of the sulfur species considered. By superposing the pH/Eh diagram for H_2O_2 upon that for the sulfur species, it can be deduced that the field of oxidation of H_2O_2 is substantially above the curves for the sulfur system being considered. The oxidation reactions given will therefore be thermodynamically possible.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The selected chemicals were hydrochloric acid with or without glyoxal or a commercial surfactant, Solamine 129 (Seppic Co., Paris, France) and hydrogen peroxide alone. Samples of two types of scale were used. The major element composition of sample 1 is given in Table 1 below. Sample 2 consisted essentially of arborescent pyrite.

Table 1. Composition, in wt %, of scale sample No. 1, from the Cergy Pontoise (Paris Basin, France) geothermal production well.

Element	Fe	S	Na	Cl	SiO ₂	Ca
wt %	49.3	21.55	1.07	0.27	1.17	0.87

3.1. Dissolution of scale by hydrochloric acid with and without glyoxal

The scale used was sample No.1, in the form of a powder of 100 μ m particle size. The experiments were carried out in the laboratory, in a glass cell under a controlled, oxygen-free atmosphere, at a thermostatically controlled temperature of 70°C, and at atmospheric pressure. The solution was agitated, the contact time was 24 hours and the ratio of sample weight to volume of solution was 1 g to 300 ml. The hydrochloric acid used was 37.5 wt %, and the oxidant used with it was glyoxal (glycol aldehyde - $C_2H_2O_2$).

The experimental conditions and results are given in Table 2. The acid and oxidant were used at various concentrations in order to determine the minimum concentrations necessary and to see whether or not any secondary reactions took place. The role of the glyoxal in the breakdown was also studied. In view of the chloride ions provided by the acid, no salts were added. One litre each of solutions E200, E50, E20, E20 without glyoxal, and E10 were prepared. The analytical procedure used is simple, consisting in weighing the dry scale before and after, and analysing for the chemical species in solution. The effects of the concentrations of acid and of glyoxal in the attack on the scale can be compared. The acid concentration varied from 0.0206 to 0.4114 mol/l (i.e. pH 0.38-1.69). The effect of duration of contact cannot be determined as the

time was fixed at 24 hours. When breakdown of the scale occurs, hydrogen sulfide and iron in solution should be produced. It can be seen in Table 2 that in fact the quantity of iron in solution after reaction is substantial and represents 82-98% (according to the conditions) of the amount of iron initially present in the scale. The breakdown with respect to iron proceeded to 89, 93, 82, 90 and 98% respectively in the five solutions. There were thus apparently no side reactions as the excess acid took no part. Elemental sulfur is not present in the scale, and neither is S^0 found as fine particles in the filtrate; only very small amounts of S^0 were found, i.e. 1.9%, 0.06% and 0.01% with respect to the sulfur initially present in the scale. The S^0 is undoubtedly oxidized in soluble form, such as sulfates, in the water. The glyoxal appears to have no effect on the decomposition reaction; the percentage breakdown with respect to iron, for solutions E20 and E20 without glyoxal are comparable - 82 and 89%.

Figure 1 below shows the results of the experiments in graphic form.

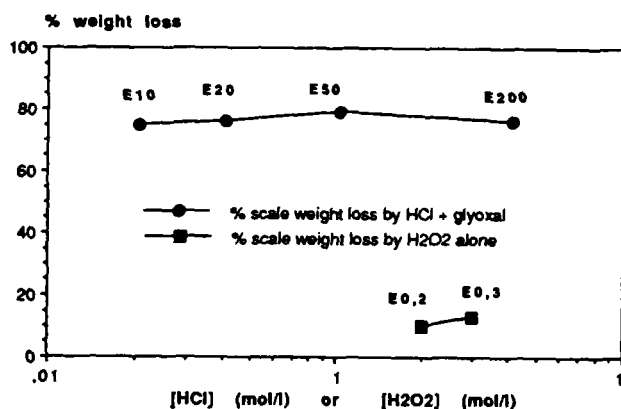
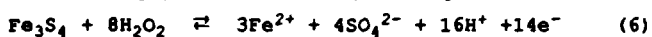
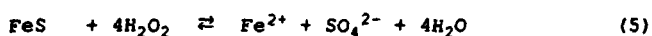
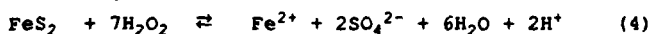


Figure 1. Percentage of weight loss with respect to the initial weight of scale against concentration of hydrochloric acid and hydrogen peroxide.

3.2. Oxidation of scale by hydrogen peroxide

The experiments were carried out in the same apparatus as before and the conditions were identical. Experimental conditions and results are given in Table 2. The hydrogen peroxide used was a 30 wt % aqueous solution.

Where the oxidation reaction of S^{2-} sulfides is total (the oxidation state of sulfur changing from -II to +VI) the reactions considered are the following:



According to the analyses of the powder, it contains about 80% iron sulfide equivalent of FeS type, i.e. for the test amount of 1 g, 0.01 mol of equivalent FeS . If H_2O_2 is taken in slight excess (10 times more than the iron sulfides as against 7, 4 and 8 respectively), the volume of hydrogen peroxide (30% solution) to be used is 38 ml. This is made up to 1000 ml with milli-Q water. The concentration of oxidizing agent is thus 0.3 mol/l, whence:

$$E_{H1}^0 = 1.756 - 0.074 \text{ pH and } E_{H2}^0 = 0.720 - 0.074 \text{ pH}$$

Two experiments were carried out, at concentrations of 0.2 mol/l and 0.3 mol/l, corresponding respectively to H_2O_2/FeS ratios of 6.66 and 10. The reacting medium had a much yellower appearance than that of the previous experiments (acid plus glyoxal), and bubbles were given off for about 30 minutes in the flask of 0.5N NaOH. The colour of the liquid indicates the presence of elemental sulfur during the reaction, and indeed 14.9% and 18.4% of the sulfur initially present was transformed into elemental sulfur (Table 2). In addition, the pH increased. If reaction (5) was dominant, the pH should not change, and furthermore reactions (4) and (6) should induce a lowering of pH. It is probable that in these cases the acid reaction, seen in the preceding paragraph, takes over from oxidation, whence a consumption of the H^+ ions produced and the formation of S^0 in the scale. Nevertheless, the oxidation reaction appears to be very complex. The reaction rate, based on dissolved iron, was only 9 and 11%, indicating that other reactions intervened. Figure 1 gives the results of this experiment and enables comparison with the results of the hydrochloric acid plus glyoxal experiments.

3.3. BREAKDOWN OF SCALE AND CARBON STEEL BY HYDROCHLORIC ACID AND A SURFACE ACTIVE AGENT

The breakdown of iron sulfide by the use of hydrochloric acid appears quite conclusive; its action is not only strong, however, but also corrosive to metal, so it would undoubtedly also attack the carbon steel casings of geothermal wells. It therefore seemed a good idea to combine the use of acid with a second proposed treatment, that of a surfactant corrosion inhibitor, which would penetrate down to the metal and protect it, while not affecting the action of the acid in breaking down the scale. In order to verify this hypothesis, two types of laboratory experiment were carried out:

a) The first was to investigate the behaviour of a carbon steel in the presence of Solamine 129, a cationic surfactant, and hydrochloric acid, in order to determine if the inhibitor prevented the acid from attacking the steel by creating a film on the bare metal.

Table 2 - Dissolution and/or oxidation of scale by hydrochloric acid (with or without glyoxal) and by hydrogen peroxide alone.

* [HCl]/[FeS] ratio : if iron sulphides in the scale sample are only assimilated to FeS

** [H2O2]/[FeS] ratio : if iron sulphides in the scale sample are only assimilated to FeS

Conditions	SAMPLES						
	E200	E50	E20	E20 without glyoxal	E10	E0,2 H2O2	E0,3 H2O2
[HCl] (mol/l)	0,4114	0,1028	0,0411	0,0411	0,0206	-	-
[HCl]/[FeS] ratio *	20	5	2	2	1	-	-
Glyoxal volume (ml) for 1 l of solution	200,00	50,00	20,00	0,00	10,00	-	-
[H2O2] (mol/l)	-	-	-	-	-	0,200	0,300
[H2O2]/[FeS] ratio **	-	-	-	-	-	6,66	10,00
contact time (h)	24	24	24	24	24	24	24
[Cl ⁻] (mol/l)	0,4114	0,1028	0,0411	0,0411	0,0206	-	-
weight loss (%)	76	79	76	79	75	9	13
breakdown/iron (%)	88,7	93,3	82,4	90,3	97,6	9,3	11,3
breakdown/sulfur (%)	1,9	0,1	0,1	0,1	-	14,9	18,4

Table 3 - Action of hydrochloric acid on a carbon steel and on a scale in the presence of a surfactant (Solamine 129®).

* in the carbon steel coupon (98,673% iron) placed in 300 ml aqueous solution

* in the scale coupon (90% pyrite FeS₂, molecular weight=119,967) placed in 300 ml aqueous solution

Conditions	SAMPLES								
	XC38 carbon steel coupon N° or scale coupon N°								
	coupon 1	coupon 2	coupon 3	coupon 4	coupon 5	coupon 6	coupon 7	scale 1	scale 2
[Solamine 129®] (mg/l)	0	2,5	10	50	100	500	2000	50	2000
[HCl] (mol/l)	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02
reaction time (h)	1,50	2	2	2	2	2	2	2	2
weight before reaction (g)	16,4776	16,4212	16,4244	16,4111	16,4322	16,4348	16,4895	6,3105	6,0679
weight before reaction (g)	16,1939	16,1662	16,3374	16,3982	16,4268	16,4341	16,4888	6,1829	5,9555
weight loss (g)	0,2837	0,255	0,087	0,0129	0,0054	0,0007	0,0007	0,1276	0,1124
weight loss (%)	1,722	1,553	0,530	0,079	0,033	0,004	0,004	2,022	1,852
corrosion rate (mm/day)	0,23393	0,15770	0,05380	0,00798	0,00334	0,00043	0,00043	0,54530	0,48034
corrosion rate (mm/year)	85,38487	57,56030	19,63822	2,91187	1,21892	0,15801	0,15801	199,03419	175,32479
iron initially present (mg/l) *	54196,47	54010,97	54021,49	53977,75	54047,15	54055,70	54235,61	8812,99	8474,18
[Fe ²⁺] in solution (mg/l)	892,00	764,00	261,00	48,00	16,00	15,00	21,00	27,00	31,00
breakdown/iron (%)	1,65	1,41	0,48	0,09	0,03	0,03	0,04	0,31	0,37

b) The second was to investigate the behaviour of a scale in the presence of the two components in order to determine whether the acid attack or the filming was predominant.

The analytical procedure consisted in weighing the dry steel before and after, and analysing the species in solution. The corrosion of the steel was expressed by its weight loss after exposure.

When the steel coupon comes into contact with the acid alone, it is attacked, and a slight "effervescence" can be distinguished on its surface. In contrast, in the presence of Solamine 129 (at 2000 ppm) this effect is not observed. The results (Table 3) show that the steel is attacked by the acid, but that the rate of corrosion is slowed by the inhibitor when present in sufficient quantity. The Solamine 129 resists the HCl and prevents steel XC38 from being attacked by the acid. The rate of breakdown with respect to iron is 40 times less when the inhibitor is present in concentrations greater than 50 mg/l.

Figure 2 shows the rate of corrosion of the carbon steel, in mm/day, against the concentration of Solamine 129.

As the results have been fairly conclusive at the experimental values, it would be interesting now to determine the minimum concentration of Solamine 129 that can be used effectively. Its practical use at a concentration of 2000 ppm cannot be envisaged, in particular from an economic point of view. A value of 50 ppm seems a reasonable compromise, as this is a low concentration and the loss of steel remains acceptable.

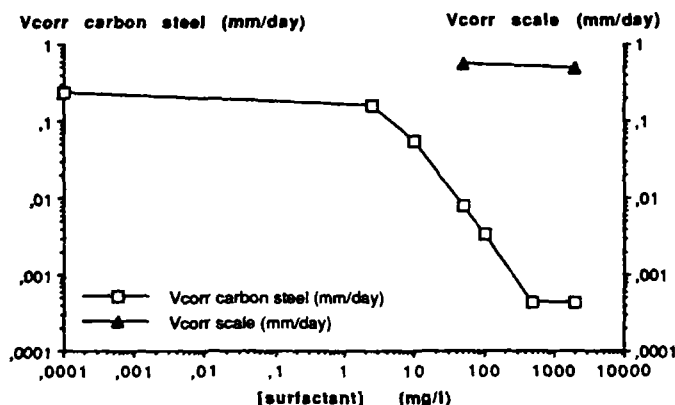


Figure 2. Rate of corrosion of carbon steel and raw scale in the presence of 0.02 M HCl and various concentrations of Solamine 129 at 70°C and one atmosphere.

The concentrations of acid and Solamine 129 were chosen according to the behaviour of the Solamine 129 in an acid medium. Solamine 129 still acts as an inhibitor at a concentration of 1-2 g/l in a solution of pH 1. It should create a film on bare metal protecting it from corrosion; its action on scale, however, is relatively poorly known. It is known to be a softening agent (i.e. it promotes the

spreading of the liquid over the surface of scale, or increases the rate of penetration into porous scale) and to be a detergent-dispersant (i.e. facilitates the dispersion of particles in water).

3.3.1. Effect of hydrochloric acid and surfactant on a carbon steel

The experiments were carried out in the same laboratory apparatus. The experimental conditions and results are reported in Table 3. The temperature was thermostatically controlled at 70°C and the pressure was atmospheric pressure. The solution was agitated by a magnetic agitator, contact time was 2 hours, and the ratio of steel to volume of solution was fixed at about 16.4 g steel to 300 ml of solution. The steel samples used were Anticor Co. (Thonon, France) type XC38 (0.38% C), in the form of coupons 44 x 24 x 3 mm with no middle orifice, rectified on both sides, grease-free, marked, dried, weighed and packed according to NACE standard RP 07-75. The total surface area of each coupon is 25.2 cm². The average composition of this steel is given in Table 4 below:

Table 4. Composition in wt % of steel XC38 (0.38 % C and 98.673% Fe).

Element	Mn	Si	P	S	Ni	Cr	Cu	Al
wt %	0.65	0.10	0.017	0.016	0.05	0.03	0.062	0.022

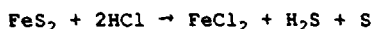
The acid used was 37.5 wt % hydrochloric acid; a single concentration was used - 0.02 mol/l (pH 1.69). The concentration of Solamine 129 was varied from 0 to 2000 mg/l.

The coupon of XC38 was placed in the bottom of the cell and plunged into a solution of 300 ml 0.02 mol/l acid and variable concentrations of Solamine 129, brought to 70°C and deoxygenated by nitrogen bubbling for about three quarters of an hour. The Solamine 129 was injected first in order to film the sample, and the acid was introduced half an hour later. The reaction time was fixed at a total of two hours. In order to test the efficacy of the Solamine 129, an experiment was first carried out without inhibitor.

3.3.2. Effect of hydrochloric acid and a surfactant on iron sulfide scale

The experiments were carried out in the same laboratory apparatus and under the same conditions as above (3.3.1), except that the ratio weight of scale to volume of solution is 6.2 g to 300 ml of solution. The experimental conditions and results are given in Table 3. The scale used was extracted from the extraction column of the production well at La Courneuve Nord (GCLN-2). The samples were in the form of plates 20 x 20 x 3 mm, giving a total surface area of 10.4 cm². A metallographic study showed that the scale consists of more than 90% arborescent pyrite (Ignatiadis et al., 1991b).

Only two experiments were done. The acid used was 37.5 wt % HCl. A single acid concentration was used (0.02 mol/l) with two concentrations of Solamine (50 and 2000 mg/l). The coupon of scale was placed in the bottom of the cell and plunged into a solution of 300 ml of 0.02 mol/l acid and Solamine 129, brought to 70°C and deoxygenated by bubbling nitrogen for about three quarters of an hour. The Solamine was injected first in order to film the sample, and the acid was added half an hour later. The reaction time was fixed at a total of two hours. No experiment was done without inhibitor, so the attack on scale without Solamine cannot be studied. The analytical procedure consisted in weighing the dry scale before and after, and analysing for the species in solution. The corrosion was expressed as weight loss after exposure. When the acid is introduced, half an hour after the Solamine, a slight "effervescence" appears on the surface of the scale and fine particles of scale are also present in suspension in the solution. Acid attack has thus taken place. The predominant reaction is usually written:



If reaction is complete, the amount of acid present in the solution would enable the breakdown of about 1.3 g of iron sulfide, i.e. 20-22% breakdown with respect to the quantity of scale used. If the theoretical and actual percentages are comparable, acid attack predominates, but if the actual percentage is appreciably lower than the theoretical one, this indicates that the Solamine has filmed the scale and prevented acid attack. In fact, according to the above, no secondary reaction seems to have intervened, so that only the inhibitor can have an effect. The loss of mass of the pyritic scale, which is very stable in air, is of the order of 2% for 2 hours of exposure. This would correspond to a loss of thickness of about 0.5 mm/day, or 180 mm/y. Thus, even at 2000 ppm the Solamine does not totally film the scale. Figure 2 shows the rate of corrosion of the scale, in mm/day, against the concentration of Solamine.

It has been shown that the carbon steel and the scale can be protected by the surfactant despite the presence of acid. The action of HCl on a carbon steel in the presence of a surfactant has shown an acceptable degree of corrosion of the steel above a certain concentration of the surfactant (fig.2). The scale in the presence of surfactant is attacked by the acid, but the rate of corrosion is sufficiently slowed down by the inhibitor when the latter is present in large amounts. Nevertheless, in the same reactive solution and exposed for the same length of time, the scale is broken down much more rapidly than the steel. A range of concentration of the surfactant from 50 to 2000 ppm has been determined, within which the steel resists acid attack whereas the scale is attacked. Within this range there exists a clear difference in the rates of corrosion of the steel and the scale that can be exploited in order to treat selectively the scale without corroding the steel.

4. CONCLUSIONS

The results of our experiments could open up a

line of research that would lead to a process of chemical cleaning of geothermal wells by acid attack of scale accompanied by injection of an organic inhibitor to prevent the acid from attacking the steel. Nevertheless, these results cannot be extrapolated directly and be expected immediately to achieve a cleaning process under real conditions. They are, above all, laboratory results, certainly very promising, but dealing only with certain aspects of the problem. Further laboratory studies need to be undertaken before a valid extrapolation can be made. It would then be possible to pass to the stage of pilot and on-site testing to quantify the reactions, pay attention to the correct neutralization of the liquid and/or gaseous discharges (pH, inhibitor, H₂S), and lastly to assess the technical and economic feasibility of the process. The logical extension of work at present is the continuation of laboratory experimentation, followed by pilot testing.

REFERENCES

- Doré M. (1989) - Chimie des oxydants et traitement des eaux. Editions Lavoisier, Tec et Doc, Paris, 504 p.
- Detoc - Karimi S., (1990) - Traitement des fluides géothermaux du Dogger (Bassin parisien, France) par oxydation chimique des sulfures dissous et microfiltration tangentielle. Thèse d'Université de Montpellier II - Institut Mixte de Recherches Géothermiques, BRGM/AFME, Décembre 1990, 257 p.
- Detoc - Karimi S., Falguère P., Foucher J.C. Persin F. and Ignatiadis I. (1991) - Use of Cross-flow Microfiltration for the elimination of the sulfur produced by oxydation of dissolved sulfides in a geothermal brine. Engineering Materials, Vol. 61-62 1991 pp. 561-564.
- Duke F.R. (1959) - Mechanisms of oxydation - reduction reactions in "Treatise of Analytical Chemistry", Part I, Vol.1, Kolthoff & Elving, Editions Interscience, pp. 629-660.
- Ignatiadis I., Teton S., Lafforgue M. (1991a) - Evaluation de l'action d'un inhibiteur organique de corrosion sur les dépôts des sulfures de fer en milieu géothermal reconstitué et réel. Rapport BRGM n°33945 IRG SGN 91, 90 p.
- Ignatiadis I., Teton S., Lafforgue M. (1991b) - Evaluation de l'action de différents produits chimiques sur les dépôts des sulfures de fer et sur l'acier au carbone en milieu géothermal partiellement reconstitué. Rapport BRGM n°33946 IRG SGN 91, 103 p.
- Luganov V.A., Shabalin V.I., (1985) - 15th Congrès international de minéralurgie, (CR), pp. 31-39.
- Pound B.G., Wright G.A., Sharp R.M., (1985) - Electrochemical phases diagrams for the iron/ sulfur/water under geothermal conditions. Australian Journal of Chemistry, Vol. 38 (5), pp. 643-657.
- Weres O., Tsao L., (1983) - Reaction of hydrogen sulfide with oxygen in the presence of sulfite. Report of the Lawrence Berkeley Laboratory L.B.L-11377, 76 p.

ANTI-CORROSION TREATMENT OF A CARBON STEEL USING SODIUM SILICATE TO DEPOSIT A SILICA FILM. ANALYSIS OF FILMS BY PHOTO-ELECTRON SPECTROSCOPY (ESCA).

Berthille LE DINH BAO and Ioannis IGNATIADIS

**BRGM/ADEME : Joint Geothermal Research Institute (I.M.R.G.)
BP 6009 - 45060 ORLEANS CEDEX 2, FRANCE**

Key Words: corrosion, carbon steel, sodium silicate, silica, iron sulphide, photo-electron spectroscopy

ABSTRACT

Problems of scaling and clogging in geothermal wells are largely due to the presence of sulphides in the geothermal fluids. The deposition of a silica-based film is here investigated as a means of protection against the corrosion of the steels in well casings. Sodium silicate was used in a reconstituted geothermal brine and the optimal conditions for effective deposition of films on samples of carbon steel were determined. It was possible to evaluate qualitatively the thicknesses of the films and to study their composition. The variation of the abundances of the elements Fe, Si, S, O and C was monitored as a function of the time of erosion of the films by photoelectron impact. Samples placed in a corrosive sulphide medium that were immediately treated with sodium silicate for 48 h were covered with a film, of the order of 360 nm thick, consisting of iron sulphides, silica and ferrous silicate, and were found to be well protected.

INTRODUCTION

Certain of the geothermal project exploiting the Dogger aquifer in the Paris Basin are experiencing operational difficulties - loss of flow rate, perforation of casing, clogging - that are essentially due to the aggressivity of the fluids mainly due to the presence of Cl^- , CO_2 et H_2S , which attack carbon steel casings and solubilize iron. The resulting ferrous iron then reacts with the hydrogen sulphide in the fluid to give iron sulphides of the type Fe_xS_y which form the clogging scale [1].

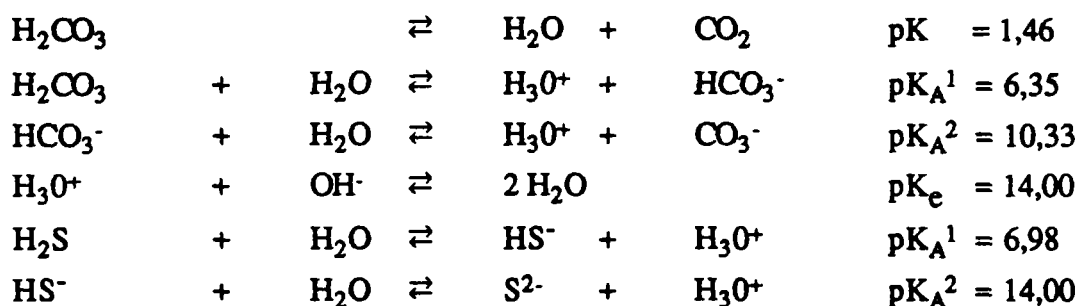
This situation has made possible the development of a technique for dealing with the resulting problems of corrosion, scaling and clogging. Various physicochemical treatments, in particular the injection of organic inhibitors, are currently being investigated in our laboratory as a means of treating geothermal fluids. The employment of organic corrosion-inhibitors in geothermal wells necessitates the use of well-bottom treatment tubes, and continuous or semi-continuous injection of the inhibiting agent. Although effective, this technique is expensive, complex and its application difficult.

We therefore decided to investigate mineral inhibitors, the principle being to create a permanent protective film thus avoiding the need to lower an injection device to the well bottom. The laboratory work on mineral corrosion-inhibitors is being restricted to sodium silicate [2,3,4,5] because of the presence of dissolved silica in the natural Dogger water, which suggests the possibility of maintaining the protective film. Furthermore, silica satisfies the requirements for a mineral inhibitor, i.e. low cost, non-toxicity, and compatibility with the environment.

The work programme deals with the investigation of the composition of protective films, and of the conditions and kinetics of their formation.

MATERIALS AND EXPERIMENTAL METHODS

Laboratory experiments carried out in a thermostated reactor (electrochemical type water-jacketed cell bottom), under controlled oxygen-free atmosphere, consisted in studying the creation of films on soft-steel samples under different conditions (reconstituted or not geothermal fluids, with or without addition of sodium silicate. Preliminary tests of the stability of the artificial aqueous solutions were carried out in order to simulate as closely as possible actual geothermal conditions. The solution used for the tests had a pH of 6.5, contained 35 g/l NaCl (0.6 M), 100 mg/l ($3 \cdot 10^{-3}$ M) of dissolved sulphides and it was saturated in CO_2 . Its composition is calculated accurately on the basis of the following equilibria (at 25°C):



and considering mass and electroneutrality balances. Precise quantities of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, NaCl, NaHCO_3 , HCl (which fixes the pH at 6.5) and of demineralized-deoxygenated water are thus used to reconstitute the geothermal fluid. In addition, the reconstituted solution must be free of O_2 , which necessitates working in a glove box and a deoxygenated water circuit. The H_2S content is maintained constant, and continuous ventilation is effected using a precisely calculated gaseous mixture of H_2S , CO_2 and N_2 .

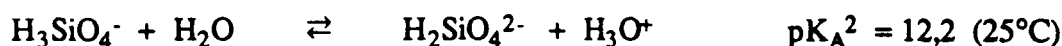
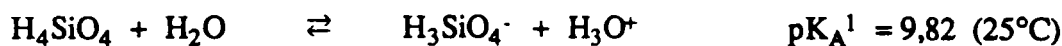
Comparative tests of fixation, anti-corrosion protection (i.e. decrease in rate of corrosion), and of film quality, thickness and composition were made on the film obtained in the different experiments. The parameters fixed at the outset were the time of fixation of the film (48 hours), temperature (70°C), pressure (1 atm) and the stirring rate.

The average weight per cent composition of the steel samples is as follows: C:0,42% ($\pm 0,04$); Mn:1,08% ($\pm 0,001$), Mo:0,014% ($\pm 0,01$); Si:0,34% ($\pm 0,04$), Ni:0,092% ($\pm 0,005$); Cr:0,100% ($\pm 0,005$). The samples are either cylindrical, with a surface area of 5 cm^2 , or flat, with a surface area of 4 cm^2 , and are rectified, de-greased, dried, weighed and conditioned according to NACE standard RP 07-75 [6]. Sodium silicates of the type $\text{Na}_2\text{O} \cdot x(\text{SiO}_2)$, with $x = 3.5$ (it may be between 2 and 5) were used.

The laboratory procedure for comparing the films in the artificial sulphide medium included both weight loss and electrochemical methods, the latter involving monitoring of potential as a function of time, measurement of corrosion rates from polarization resistance and by drawing Tafel polarization curves. The films obtained were also investigated by ESCA photoelectron spectroscopy, by means of which the composition and thickness of the film can be determined [7]. The ESCA analyses were made on a VG Instruments Escalab S MkII apparatus equipped with a VG Instruments electrostatic-dispersive analyser, on which angular measurements can be made (150° in this case). The photon source was $\text{AlK}\alpha$ with a kinetic energy of 1486.6 eV. Detection was by a Channeltron electron multiplier (factor 10^8) placed after the analyser exit slot. Data acquisition and processing was done on a Compaq 386.20 computer using an AEI Cybernetix software. The eroded surface was a disc of 6 mm diameter. The surface of the samples was subjected to bombardment by photons and the Channeltron received the photoelectrons emitted to give the energy spectra of the core electrons from the atoms, which is characteristic of the surface composition.

RESULTS AND DISCUSSION

The deposition of silica is based on the property of silicates of precipitating amorphous silica in aqueous media at pH values greater than 9.82:



the mass balance equation is: $\Sigma[\text{Si}] = [\text{H}_4\text{SiO}_4] + [\text{H}_3\text{SiO}_4^-] + [\text{H}_2\text{SiO}_4^{2-}]$ and the solubility is limited by the equilibrium: $\text{SiO}_2 \text{ (solid)} + 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$, with $K_s = [\text{H}_4\text{SiO}_4] = 10^{-2.69}$ at 25°C .

The first films obtained in a reconstituted geothermal fluid in the presence of sodium silicates showed good fixation and very good protection, but the deposit was not uniform. It was observed that the temperature and pH of the solution (modified by the addition of HCl after the injection of sodium silicate) play an important part in the fixation and quality of the film. It was thus evident that it was necessary to optimize the mode of deposition of silica in a reconstituted geothermal medium. The quantity necessary to prepare a solution of sodium silicates at concentrations of 100-5000 mg/l is injected into the reconstituted geothermal fluid and pH is adjusted to 10.5-11 by addition of NaOH. The solution is brought to a temperature between 25° and 95°C (optimum $70\text{--}75^\circ\text{C}$) at atmospheric pressure and agitated. The pH is next brought to 6.5 by rapid injection of HCl. Under these conditions the films in certain cases reached thicknesses of 3-5 μm .

Three types of film were deposited on the surfaces of the carbon steel samples and studied: 1) films obtained in the reconstituted geothermal fluid alone (sample 1), 2) films obtained in the reconstituted geothermal fluid containing in addition 400 mg/l of silicates (sample 2), and 3) films obtained in a solution of 400 mg/l silicates in de-ionized water at 25°C (sample 3).

Type 1 films (reconstituted geothermal fluid alone) give protection that is unacceptable even in the short term (Figure 1). Investigation of the film by ESCA shows it to consist mainly of iron sulphides with a minimum thickness of 120 nm. Traces of carbonates, oxides and hydroxides of iron were also present.

Type 2 films (reconstituted geothermal fluid with added silicates) give excellent protection of the steel sample (Figure 1). Electron microscopy showed that the film was uniformly distributed over the surface, and ESCA analysis showed it to be a mixture mainly of iron sulphides (Figs. 2a, b, film thickness 240-360 nm), silica (Figure 2c, film thickness 240-360 nm) and ferrous silicate (Figure 2d). At the start of deposition, traces of iron carbonates, oxides and hydroxides were also deposited. The density of iron sulphides in these samples was less than in the type 1 sample.

Type 3 films (silicates in de-ionized water) were shown by ESCA analysis to be very thin (2-20 nm), irregularly distributed and composed of silica with traces of iron oxides and hydroxides. The thickness and composition of this film suggested that the precipitation of silica is favoured by temperature and the presence of hydrogen sulphide.

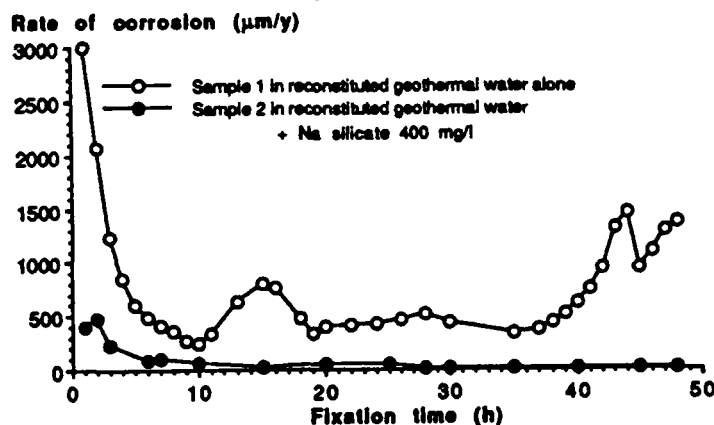


Figure 1. Corrosion rates of carbon steel in aqueous solution containing 35 g/l NaCl and 100 mg/l sulphides in presence and absence of sodium silicates at pH 6.5, temperature 70°C and pressure 1 bar.

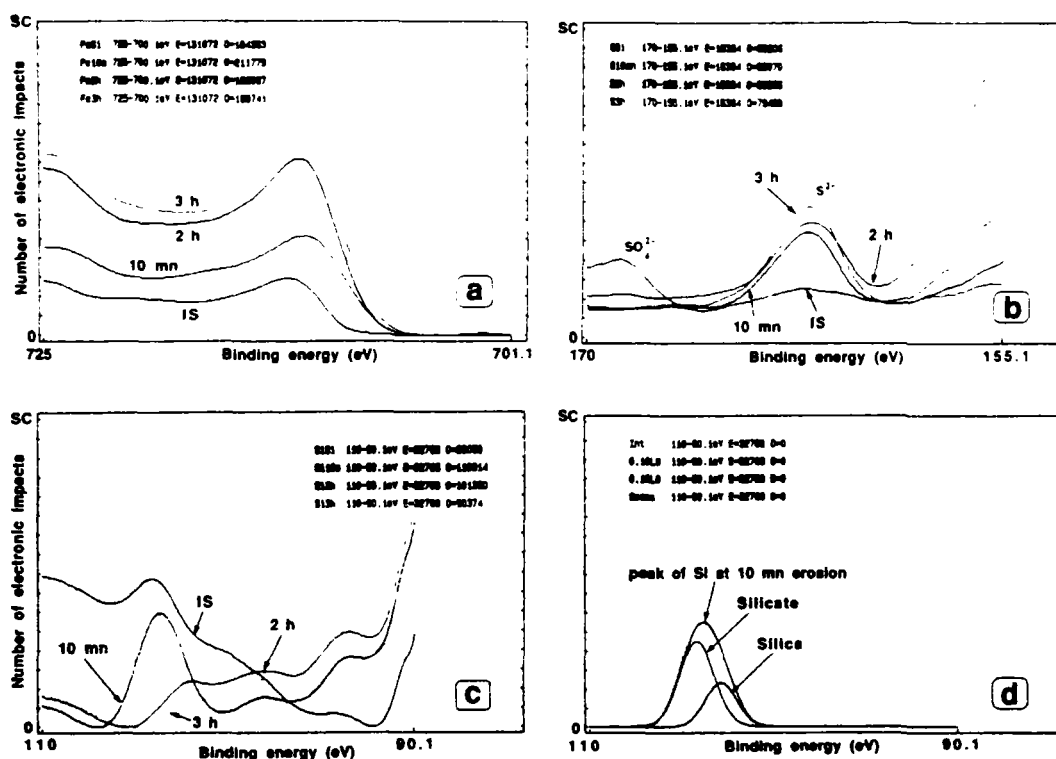


Figure 2. ESCA analysis of a sample treated with sodium silicates. Variation of peaks for Fe (Figure 2a), S (Figure 2b) and Si (Figure 2c) against erosion time (IS - initial surface, 10 mn, 2 h and 3 h; erosion approx. 2 nm/mn). Figure 2d shows the recomposition of the Si peak at 10 mn time of erosion. The abscissa of the ESCA spectra gives the binding energies in eV corresponding to the energy level of the element concerned, and the ordinate gives the number of photoelectron impacts received by the Channeltron. The erosion time determines approximately the thicknesses examined (the length of erosion corresponds to a thickness eroded). The thickness of the film on a sample can thus be calculated according to the disappearance or appearance of a substance after a known erosion time, e.g., disappearance of iron sulphides or silica and appearance of metallic iron. The state of oxidation of an element can be distinguished.

CONCLUSION

The tests performed have shown that the best protection against corrosion, over 48 h fixation time periods, is provided by sodium silicates. The formation of a silica film, protecting against corrosion, results from the adsorption of the silica onto the steel.

It was possible to evaluate qualitatively the thicknesses of the films and to study their composition. The variation of the abundances of the elements Fe, Si, S, O and C was monitored as a function of the time of erosion of the films by photoelectron impact. Samples placed in a corrosive sulphide medium that were immediately treated with sodium silicate for 48 h were covered with a film, of the order of 360 nm thick, consisting of iron sulphides, silica and ferrous silicate, and were found to be well protected.

This work demonstrates the use of a technique of local spectroscopic surface analysis for the purpose of determining the optimum conditions for the creation of films providing the best anti-corrosion protection.

REFERENCES

- 1) Criaud A., Fouillac C.: Geothermics, 1988, Special Issue, **18**, 10.
- 2) Lerhman L., Shuldener H.L.: Ind. Eng. Chem., 1952, **44**, 1765.
- 3) Shuldener H.L., Sussman S.: Corrosion, 1960, **16**, 126.
- 4) Lane R.W., Larson T.E. Neff C., Schilsky S.W.: Materials Performance, 1973, **12**, 32.
- 5) Rozenfield I.L.: Corrosion Inhibitors, 1981, McGraw-Hill, New York.
- 6) NACE Standard RP07-75, National Association of Corrosion Engineers, Houston, Texas, 1975.
- 7) Sastri V.S. Packwood R.H.: Werkstoffe und Korrosion, 1987, **38**, 77.