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High Temperature - High Pressure rated sensors and tools useful for geothermal purposes. Bibliographical Review

Final Report

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Study carried out as part of research activities BRGM GTHR-02, under 6th Framework Programme funding - HITI project (High temperature instruments for supercritical geothermal reservoir characterization and exploitation)

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Synopsis

This review is performed in the framework of the FP6 European project HITI (HIgh Temperature Instruments for supercritical geothermal reservoir characterization and exploitation). This research project, co-funded by UE and the different partners, aims to provide geophysical and geochemical sensors and methods to evaluate deep geothermal wells up to supercritical conditions (T > 375°C). The main objective in the Work Package 6 (WP6) is to examine and develop prospective strategies and new concepts in order to perform geophysical and geochemical measurements into wells at temperatures up to 500°C. This review is the first step of this objective.

Temperature and pressure resistant devices are strongly needed for high temperature geothermal applications. Achieving good temperature measurements at depth is a challenging task, as it requires sensors and materials that can survive in harsh environments or even under supercritical conditions (water critical point: 376°C – 221 bars). Other challenging tasks are the performing of reliable pressure, pH, electrical conductivity measurements under those high temperature - high pressure conditions. As a consequence and recently pointed out by the US Department Of Energy, there is a strong need to overpass those technological gaps in the forthcoming years.

Since all of those objectives have become more and more important to lot of industrial companies in the past years, lots of enhancements still are under development. This report intends to give a short overview of some of those developments, especially focusing on key parameters essential for realistic geochemical identification of geothermal systems. Temperature, pH, conductivity, dissolved gas species measurements, samples recovery as well as promising technologies that would become more and more developed in the near future will be the matter of discussion.

Contents

1. Introduction

This review is performed in the framework of the FP6 European project HITI (HIgh Temperature Instruments for supercritical geothermal reservoir characterization and exploitation). This research project, co-funded by UE and the different partners, aims to provide geophysical and geochemical sensors and methods to evaluate deep geothermal wells up to supercritical conditions (T > 375°C).

Supercritical geothermal wells are presently non-conventional but may provide a very efficient way to produce electricity from a clean, renewable source. A deep geothermal well is currently being drilled for this purpose into the Krafla area, Iceland as part of the IDDP ("Iceland Deep Drilling Project") and with joint funding from Icelandic industry and science. Another deep well will be drilled in the Reykjanes peninsula, Iceland, in the framework of this same project.

The main objective in the Work Package 6 (WP6) is to examine and develop prospective strategies and new concepts in order to perform geophysical and geochemical measurements (temperature, pressure, gamma radiation, acoustic signal, fluid conductivity, pH and Redox, etc.), at temperatures up to 500°C. This review is the first step of this objective.

Temperature and pressure resistant devices are strongly needed for high temperature geothermal applications. For example, up to date US Department of Energy grant applications do focus on some of those topics, to improve characterization of geothermal resources [1]. Achieving good temperature measurements at depth is a challenging task, as it requires sensors and materials that can survive in harsh environments for hours (5000 hours expected, [1]), even in supercritical conditions (water critical point: 376°C - 221 bars). There is also a strong need to perform other measurements at depth, such as pressure, pH, electrical conductivity ones..., as pointed out by US DOE [2]. Last, it would also be of primary interest to properly collect fluids at depth without disturbing them by applying strong pressure changes or sudden thermal cooling. All of these aspects are part of the technological gaps identified by US DOE.

All of those objectives have become more and more important to lot of industrial companies, so that enhancements still are or will in the forthcoming years become available on the market. This report intends to give a short overview of some of those developments, as well as to highlight promising technologies that would become more and more applied in the future. As temperature evaluation is the primary goal, this aspect will be discussed in details, other high temperature rated devices for complementary chemical determinations being viewed in a secondary section.

2. Temperature measurements

2.1. PRINCIPLES

In industrial processes as well as in geological purposes, there are two ways to measure temperature [3]:

- the "contact" method, which implies a contact between the sensor and the object;
- the "non-contact" method, which relies to the heat radiations emitted by the object.

Both methods have their own advantages and disadvantages. Establishing a contact between two objects needs time to attain thermal equilibrium between the two objects, frequently between 1 to 3 minutes, while measuring radiation emissions is quicker (2 to 3 seconds). At the opposite, the contact method allows very accurate data acquisition that can nevertheless be modified by the contact process between two objects at different temperatures (respective relative "cooling" or "heating" of the two objects). Non contact measurements refer only to surface ones, or to mean temperature of the medium and are therefore less accurate. Even if the relative accuracy of those two measurement methods is quite similar (between 0.5 and 1%), their domain applicability is different. Inherent to its own principle of working, contact measurement is limited to a smaller temperature range, from -200 to 1200°C, and could be enhanced with some refinements up to 2300°C [4]. Radiations measurements can be made over a wider range, from -50 to 3000°C.

2.1.1. Thermocouples and Resistance Temperature Detectors

Frequently, temperature measurement can be done either by using a thermocouple or by using a resistance thermometer [3]. A thermocouple is based on the Seebeck effect, induced by the welding of two conductors to form a closed circuit. If the two welded junctions are exposed at different temperature, then an Electro-Motive Force (EMF) is created, which will vary as function of the temperature. A Resistance Temperature Detector (RTD) is based on the metals' electrical resistivity, which varies with the temperature. Metals chosen for RTD's have well known resistance changes for a given temperature shift [5]. By measuring its resistance at some unknown temperature and comparing this value to the resistor's nominal value (pre-specified resistance value at a given temperature, expressed in ohms), the change in resistance is determined, and the change in temperature from the point initially specified can be therefore calculated. Platinum is the most frequent used metal, as its properties vary linearly with temperature over a wide operating range, and as platinum is not affected by oxidation or corrosion [5, 6]. Platinum RTD elements are available either as thin films or as wire wounds [6].

Contrary to thermocouple devices, RTD would rather give the average temperature of the medium than the temperature of a precise location. Nevertheless, they are more accurate and stable in the long term.

Depending on the required application, several enhancements can be brought to temperature sensors. For example, resistance to corrosion can be obtained by protecting the sensor with stainless steel tubing - PTFE coated in the range 0 to 250°C [3]. Titanium alloy should be used with highly corrosive waters (brines, sea water) under 500°C, whereas enamel can resist up to 1000°C [3]. Silicon Carbide (SiC) alloys can be used to monitor temperature of molten metals around 1000°C. For higher temperatures, double protection tubes are required, frequently with an external ceramic coating [3]. Those pressure-tight receptacles that extend the life of a temperature sensor in chemically aggressive environments are also known as thermowells (e.g. SiC, fused quartz) [4].

Platinum RTD's should be used in the range -200 to 650°C, but RTD's wiring insulation is often made of TFE that would not resist over 250°C, as epoxy used for moisture proof sealing [5]. Fibreglass wiring can be used up to 482°C [6] and ceramics up to 600°C [7]. External casing can resist to pressures up to 2000 atm, to accelerations up to 20 G's and to shock up to 70 G's [8].

2.1.2. Capacitive sensors

For specific requirements, other temperature sensors can be used. By them, capacitive proximity sensors can be used in high temperature media with or without contact with the hot material [9, 10]. Entire temperature range extends from -70 to 250°C. Those capacitive sensors are sensitive to objects (both metallic and non-metallic) that exceed a specific capacitance when approaching the sensor on the object's surface [10]. The sensing distance (between 0 to 50 mm) is a function of the dielectric constant of the material, and this kind of measurement can be used in liquid and bulk materials. For applications in aircraft industry, specific capacitive sensors can be designed to work up to 900-1000°C [11, 12, 13]. In gun tunnels [12], which use piston compression to rise up pressure before expanding the atmosphere, temperature sensors must resist to high pressure (up to 7.7 MPa) and also to high temperature (up to 727°C), as well as resist to sudden pressure and temperature changes. Transient thin film platinum heat flux gauges are thought to work well in such conditions [10], as they are robust and able to produce high bandwidth data (c.a. 100 kHz). Thermocouple assemblages can also be used for reactor experiment (CNRS Orleans, up to 10 atm and 620°C) [13].

2.1.3. Fibre optic sensors

For some industrial purposes, the temperature sensor is exposed to high temperature, but also to high pressure conditions. Specific temperature sensors have been designed for those applications. Fibre optic sensors, as the TP-02 probe proposed by [14], use the inherent temperature sensitivity of the fibre Bragg grating as well as the thermal expansion of its housing. High resolution measurements can be done (0.4°C accuracy) even in high pressure and harsh environments (max. 150 bars but only 85°C for this device [14]).

Indeed, fibre optic sensors do have lots of advantages for sensing temperature, pressure, mechanical strain, vibrations and even concentrations of chemical species [15]. They are built with insulating materials, immune to electromagnetic interferences, not subject to corrosion, have a wide temperature operating range and can be multiplexed. Moreover, laser detection is operated at the surface, without the need to have electronics at depth. Sensing can be based on the Bragg wavelength (the wavelength of maximum reflectivity [15]) that varies with strain and temperature. Refinements by adding many grating sensors in one fibre can provide measurement along the fibre (quasi-distributed sensing). Sensing can also be based on the Raman or Brillouin scattering (based on intrinsic fibre properties) sometimes allowing measurements over the full fibre length. Last, interferometric measurements, based on the Fabry-Pérot technique (light interference produced by two parallel reflecting surfaces either side of a small cavity [16]), can be performed with pairs of Bragg gratings [15].

As a consequence, lots of other fibre optic based sensors are available with greater functional ranges. In nuclear applications, optic fibres provide smart sensing capabilities, detailed self-diagnostic and multiple measurements processing [17]. Ceramic fibre optic pressure sensors can survive in high pressure (138 bars), high temperature (1400°C) and high radiation environments (1.6 $\times 10^{18}$ neutrons per cm^2 and 6.6 Grad γ irradiation) [17]. High-temperature, radiation-hardened fibre optic pressure and temperature sensors needing to operate at temperature of at least 800°C and pressure up to 70 bars are also under development by the same manufacturer [18], highlighting recent developments in fibre optic engineering [19]. A promising 1000°C rated temperature sensor based on silica fibre has just been made commercially available [20]. Some sensors can withstand very high pressure (up to 1000 bars) and temperature (range 1700 - 3300°C) if protected by adequate optical window [21].

Exposure to high pressure conditions can also be monitored by specific pressure sensors, which are not thermometer as well but can survive in very hot environments. For example, continuous monitoring in combustion processes or chemically active environments can be done using static and/or dynamic pressure sensors [22]. Those sensors are also built using optical fibres, the intensity of the reflected light being proportional to the pressure induced deflections. Such sensors are small (up to 1.7 mm in diameter) and can operate in harsh conditions (up to 2000 bars and 350°C) [22]. Thin film pressure transducers can also operate in such conditions or even hotter (up to 593°C [23]), depending on their self protection (stainless steel tubing, double isolation...).

As many sensors are built using silica fibre, questions have arisen about strength and durability of optical sensors exposed to harsh conditions. Indeed, measurement methods often rely on the modulation of the optical length path within the silica fibre. Some studies [24] tend to demonstrate that silica fibres can be damaged when exposed to high temperature and high pressure conditions, birefringence properties being strongly affected under 270 bars and 200 to 300°C. Another limitation is the cross-sensitivity between measured pressure and temperature that can lead to erroneous data [25]. A recent patent describing a low-cost sensor system capable of operating in high-temperature, high-pressure downhole environments and offering a better accuracy can be purchased from the University of Strathclyde [25]. Nevertheless, temperature records have been recently proven to be achievable at very high temperature (1295°C), with Bragg gratings operating even when the optical fibre has become brittle [26].

Despite some disrupting effects, optical properties of fibres are commonly used for monitoring temperatures over long distances, up to 30 to 50 km long [27, 28, 29]. Such temperature distributed sensing operates very fast and can bring useful information regarding pipeline safety for example. Measurements (Raman or Brillouin scattering) can either be done with a single fibre (mirror-ended) or a loop (two fibres), with spatial resolution of 3 m at 50 km distance. Temperature resolution is 0.1°C and operating range up to 700°C (limited by optical fibre) for 50 km long [27], and as fine as 0.004°C up to 30 km long but with considerably lower temperature resistance (40°C; [29]). A modified Fabry-Pérot cavities based fibre sensor has been recently demonstrated in South Korea, by splicing together three different types of fibres [30]. Temperature changes between 50 and 1000°C have been monitored with a 50°C stepping.

2.1.4. Phosphor thermometry

In the industry, another kind of thermometer is frequently used to follow steel manufacturing [31], heat transfer in gas turbine [32], aerospace [33] or engines [34] applications by measuring surface temperatures. The non-contact technique is based on the temperature dependence of fluorescing materials, such as phosphors, whose fluorescence decay time is a sensitive function of temperature. A thin layer of material is applied on the surface, illuminated with UV light (usually from a laser) and the subsequent luminescence interrogated.

As pointed out by [35] in their recent review, this method is more precise that pyrometric one, but requires bonding phosphors to the surface of interest. This is often done by coating phosphors onto ceramics that can survive in hazardous physical and chemical environments and are insoluble in water [33].

For some phosphor chemistries using rare earth elements, the ratio between two emission bands can vary by a factor of 40 for a 100°C temperature variation, thus enabling very sensitive measurements [36]. For example, [31] used thermographic phosphor thermometry to monitor temperatures ranging from 450 to 700°C with an accuracy of ± 5°C, but temperature up to 1400°C can be reached using the temperature-dependent luminescent properties of lanthanide-doped ceramics (e.g. dysprosium and samarium based ceramics) [32]. Nevertheless those authors report a quite worse repeatability, around 70% in the range 25-625°C. Rare earth content of the phosphors can be modified to account for gas compositional and pressure conditions. Some researchers [37] have tested compositions that survive up to 30 bars, but only at room temperature.

Nevertheless this technique doesn't seem to be used in geothermal wells, as it requires applying material onto a surface.

2.2. USE FOR GEOLOGICAL PURPOSES

Constrains on temperature sensors applicable for geothermal purposes are partly met by industrial devices, but as the sensors would be lowered in media becoming hotter (the minimal electrical power generation temperature is 180°C [38]), insulation or protection against warming should be more efficient. Conventional low-temperature electronic devices cannot withstand the ambient temperatures that may reach 300°C or greater within the well. Typically, a heat shield or a Dewar-flask is used to house the electronics and maintain the internal temperature below a design maximum. Due to the limited performance of such heat shield devices, the temperature inside the package gradually rises during the time that the tool remains downhole, thus limiting the total logging time. Such a flask adds significant cost as well as geometrical volume to the tool [38]. Moreover, it's not possible to work as in laboratory measurements, with an acquisition unit outside a HT-HP chamber that includes the temperature probe. Therefore, there are fewer devices available than can work in hot to very hot wells. Nevertheless, as the petroleum industry has noticed a greater demand for HT-HP applications and drillings, lot of work is currently under progress to produce newer tools at reasonable costs. In particular, Measurements While Drilling (MWD) and Logging While Drilling (LWD) are requiring such tools development. It's worth noting that frequently temperatures probes are associated with pressure probes, so that in the following sections some HP sensors would also be described.

2.2.1. In-situ logging

Data acquisition during drilling has become of great economical importance, as it allows quicker site characterization and therefore substantial cost reductions. Petroleum companies and associated engineering currently sell different probes and devices that can monitor many parameters, but the majority of them are limited to pressures under 200 Mpa and temperatures under 250°C [39]. Numerous research efforts are thus done to extend temperature range capacities. As a consequence, the following instrumentation could either be commercially available or currently under development:

- In-situ data recording sampler which monitors downhole temperature and pressure respectively up to 150°C and 138 MPa [39]. This recorder is programmed at surface and functions with self batteries, measurements being done using Unigage gauges. Those gauges are rated to work during well testing: a quartz sensor is used for high permeability reservoirs with no sudden pressure changes, whereas a sapphire sensor is preferred for HT-HP environments (acidic, or H_2S-, CO_2-rich). Lifetime is close to one year. Quartz gauges can also be devoted to the only pressure monitoring, with extended lifetime (10 years) and similar maximum pressure and temperature ratings (resp. 173 MPa and 177°C).
- A high-temperature MWD tool capable to operate in a 200°C environment during 50 hours and to survive during 5 hours in a 220°C environment has been built in

Japan and tested in 1997 and 1998 [40]. It can resist to 30 G's vibrations during 6 hours and to short 1000G's shocks. Outer probe diameter is 44.4 mm and the length is 12 m. Acquisition data include azimuth, inclination, tool face and borehole temperature. A pressure pulse device is utilized in order to transmit borehole information data from the bottom to the surface by emitting a positive pulse up signal to the mud. No new electronics were developed, rather chosen in those having a high heat-resistance performance. Lifetime of these screened high-temperature electronics is from 100 to 250 hours in a 200°C environment. The temperature sensor is made of PN-junction diodes.

- A Pressure, Temperature, Spinner (PTS) instrument designed to continuously measure and record downhole temperatures, pressures and flows in geothermal wells is also available [41]. This instrument is capable of operating at 315°C and up to 200 bars pressure, either operating on mono conductor cable in online mode (surface readout) or on slickline in downhole memory mode. The external diameter of the instrument is 45 mm. The memory module can be operated in wells where the temperatures exceed 315°C (successfully tested at 320°C), which is the maximum mono conductor cable working temperature. Measurement probes consist of a strain gauge pressure transducer and a platinum RTD. The electronics are designed to operate inside a pressure housing at atmospheric pressure and over a temperature range of -5°C to 90°C. The life of the RTD is dependent on the operating temperatures. Typical speeds are c.a. 0.6 $m.s^{-1}$ while logging.
- Fibre optic device has been used with success up to 249°C in deep well logging [39]. Temperature logging using fibre optic is less complex and time consuming than conventional temperature log [42]. Conventional logging requires to attach a probe at the end of a cable, and to lower it at reasonable speed to build a continuous log. At the opposite, fibre optic monitoring just requires to install a fibre optic cable into the borehole, with no active electronic component downhole [43]. When at equilibrium with the medium, then a temperature log for the whole depth range can be nearly immediately obtained. Moreover, fibre optic cable is resistant to aggressive water chemistries. It has been tested in EPS1 borehole (HDR site Soultz-sous-Forêts) in November 2006 and experiment should have ended in mid of 2007. The cable's central element is an Inconel 625 tube holding 3 OFS type fibres, which are a hydrogen resistant line of graded index optical fibres, specialized for performance in Distributed Temperature Sensing (DTS) applications. The tube is covered by an ETFE (Ethylene-tetrafluorethylene copolymer)-belt. The strength member of the cable consists of two layers of stranded galvanized improved plow steel. The fibre core and cladding are silica glass drawn. The primary coating is a very thin layer of carbon that chemically bonds with the glass to provide a hermetic seal against moisture at all temperatures. In order to allow the fibre to perform in environments ranging up to 300°C, a secondary coating of pyrocoat polyimide was added [42]. The fibre optic pressure sensor is based on non-contact deflection measurement of a stainless steel diaphragm (Fabry-Perot interferometry) [42, 43]. Pressure creates a variation in the length of a Fabry-Perot cavity consisting of the inner surface of the stainless steel diaphragm on one side and of a glass window on the other. Due to costs reasons, the pressure sensor is actually not active in the logging tool. This sensitive Raman scattering temperature measurement is also used in other commercially available tools such as the Instantaneous Temperature

Profile Log (ITPL), which can operate up to 300°C along 3000 m depth pathway in 50 mm diameter hole or less (cable resistance 300 to 350°C) [44]. The measurement principle is based on the temperature and the pulsed laser technique called OTDR, with temperature determination each meter at one minute interval or less.

- Fibre optic device has also been used with success with temperatures higher than 300°C, but with some size limitations induced by the use of flask shielding [38, 45]. This flasked high temperature tool is intended for the logging of pressure, temperature, percentage of water in the vapour phase, and the vapour phase flow rate in geothermal wells and steam injection wells. This tool uses a Dewar-flask to protect electronics and sensors from the downhole harsh environments, and may be operated up to 7 hours at 400°C before the internal temperature rises to an unacceptable level and the onboard battery power is exhausted. The tool is 4.57 cm on diameter and 183 cm long with the housing. The sensor package is used as a self-contained well logging tool in that all electronics including a battery power supply are enclosed onboard, and the tool is lowered into and recovered from steam injection wells using a passive steel wire slick line. Data is recorded in an onboard memory unit during the logging operation. Temperature range is 0-400°C with 0.5% resolution, and pressure range is 0-200 bars with the same resolution. This logging system has also been field tested without its housing for long term monitoring, but with smaller temperature range (up to 250°C) [38]. Electronics, based on SOI components, was designed to permit direct wireline data logging without the need for the thermal flask. SOI electronic components can survive over a full -55 to +225°C temperature range for a minimum of five years of operation, and for one year at 300°C. The key premise of the high temperature downhole logging tool is the HTASIC (High Temperature Application Specified Integrated Chip), which allows the integration of more functions. Outside tool diameter is reduced to 3.17 cm, with an overall length of 137 cm. Temperature range is 0-250°C with 0.5% resolution, and pressure range is 0-690 bars with the same resolution. TDS Range is 0 to 6,000 mg/l with 0.5% accuracy.
- Another way to measure temperature in wells is to deploy fibre optic distributed temperature sensing technology behind the casing [46], as proposed to long-term monitor a 4265 m depth and 143°C bottom temperature well in Germany (Groß Schönebeck Geothermal Lab) using Sensa technology (UK).
- Metal-coated fibre Bragg grating sensor has also been deployed for measuring under high-temperature and high-pressure conditions (oil wells, [47]). The metal coating allows improving bonding performance between metal material substrate and sensor and prolonging the lifespan of the sensor.
- Improving measurement techniques should also refer to improvements of electronic components found in MWD tools. An US research program launched in 2002 has for main objective to build a permanently installed pressure and temperature sensor in a 175-200°C well using Silicon-On-Insulator (SOI, see V.) technology and to demonstrate a 225°C MWD tool using a unique 225°C battery system that can operate up to 6100 m depth [48]. Field testing of the temperature sensor was realised at 192°C and the hybrid battery (VCO A/D circuit) lab tested at 250-300°C.

- Two new MWD systems have been recently developed [49]. The first system is the Hostile Environment Logging (HEL™) MWD system that comprises directional and gamma ray tools, with options for downhole pressure, vibration, and temperature sensors. The second system is the Precision LWD™ system that adds resistivity, neutron, and density tools to the tool string. The HEL MWD system is rated to a maximum operating temperature of 180°C and survival to 200°C, with associated bottomhole pressure rating of 207 MPa (drilling up to 9,754 m depth). The Precision LWD™ system is rated to a maximum operating temperature of 150°C (survival up to 165°C).
- Last, one currently available temperature gauge can record in geothermal environments up to 370 °C [50]. The KTG LV Temperature Recorder uses the principle of the multiple helical coil bourdon tube, with two metals reacting differently to temperature. This reaction creates rotation in the coil. The clock is used to regulate the travel of the chart carrier through the lead screw, lead nut and push rods. The recording section of the KTG LV and Bi-Metal transmits the rotation of the bourdon tube (or external coil) to the stylus shaft which is connected to the stylus assembly, rotating within the chart carrier. The stylus assembly scribes a mark on a coated chart within the chart carrier. The LV element uses an external coil on the top end which transfers temperature down through the sensing element. The Bi-Metal element uses a special housing that transfers well temperature to the sensing element. Both the LV and the Bi-Metal elements are quick responding, corrosive resistant and reliable. Diameter is 3.17 cm, length 140 cm, maximum pressure 1520 bars and maximum temperature 370°C (±1°C). The tool can withstand nine hours at 315.6°C and 5 to 6 hours at 370°C.

2.2.2. Oceanographic measurements

HT-HP temperature sensors have been used for many years for deep sea research along mid oceanic ridges, in order to better understand water dynamics and chemistry near black smokers. The Woods Hole Oceanographic Institution [51] holds all the drawings and assembly information since the production of the so-called "Hobo" high temperature fluid logger stopped in 2006. These self-recording temperature loggers have been used for more than ten years with lot of success (see related bibliography [51]) in Pacific and Atlantic oceans. They are rated for operating up to 6000 m depth with temperature between 152 and 417°C. Two designs were used for the assembly. The oldest is cylindrical and the latest spherical, this geometry allowing on-board refurbishment during cruses. A detailed report describing the operating protocol for high temperature measurements is available [52]. Temperatures of hydrothermal vents have been measured since 1993 using probes based on the Hobo and Stowaway 8-bitlogging chips made by Onset Computer Corp. The chips, housed in custom Grade 2 titanium pressure housings made by Deep Sea Power and Light, are connected to platinum resistance temperature device (RTD) sensors located at the end of a 61 cm or 72 cm long hollow, air-filled 6.35 mm diameter titanium tube. Two RTDs are encased in high-temperature ceramic for each logger, to prevent damage to the fine wires that connect them to the Onset™ chips. Batteries supplied with the logger are Lithium/thionyl chloride made by Tadiran Batteries Ltd [51]. All seal surfaces have been machined to tolerance and the entire housing is rated to 6000 m depth and certified for

Alvin operation [51]. When first developed, these probes allowed measurement periods ranging from 360 days with sample frequencies of 4.8 h, to periods as short as 1 day with sample frequencies of 4 s [52]. More recent models of these loggers (Stowaway), tested and deployed in 1995, have a 32k memory chip that permits sampling periods as short as 0.5 s and recording times as long as 5 years with data recorded every 1.5 h. The probes have been deployed and recovered by the deep submergence vehicle Alvin during five dive programs to the area. The sensors have a precision of 1°C between 153°C and 419°C and have been intercalibrated with Alvin's thermocouple probe. Oceanographic studies have also dealing with in situ high temperature pH measurements that will be described in section III.

2.2.3. Temperature logging using synthetic fluid inclusions

This method using the synthesis of fluid inclusions using known solutions has been deployed in hot wells since the beginning of the 90's, and has proven a good agreement with other logging tools (under 300°C). Temperatures up to 449°C are expected in the Kakkonda geothermal system [53], which is the melting point of tellurium. The highest temperature recorded in geothermal wells in Italy was 419°C, which is the melting point of zinc. As said before, conventional downhole instruments have lower temperature limits even using Teflon cable (tensile strength length limit of 3000 m at temperatures above 315°C). Practically, platinum RTD's, thermocouples and optical fibres used as wire-line tools to measure formation temperatures are limited to temperatures around 300°C [28]. Electronic devices can measure hotter temperatures, but this is only possible if the device is shielded against heating with an insulation vessel such as Dewar flask (limit 350 to 375°C [53, 54]). Temperatures above 400°C can be estimated by using metals or melting tablets whose melting points are known, such as Zn (419°C), but it only gives minimum values [53, 54].

Synthetic fluid inclusion logging should therefore be a tool for carrying out these measurements and also be a method for directly sampling fluids in high-temperature boreholes where conventional tools cannot be used. This technique is based on the formation of fluid inclusions in cracked minerals. Cracked crystals, soaked in saturated solutions in gold or platinum capsules, are placed in a geothermal borehole for days to several weeks and then recovered. The sealed capsules contain solutions of known pressure-volume-temperature (PVT) properties, used to synthesize fluid inclusions. The cracked crystals are soaked in these solutions in the sealed capsules, and fluid inclusions are easily formed through crack healing in host crystals. Borehole temperatures are determined by measuring the homogenization temperatures *(Th)* of the inclusions. In addition, geothermal fluids are directly sampled as fluid inclusions in cracked crystals in containers that can be opened at the required sampling depths in the boreholes [53].

However, major technical problems arise when using the synthetic fluid inclusion techniques, such as determining temperatures above the critical point of water (reduced accuracy) and the time taken to form the fluid inclusions [53]. Indeed, if producing cracked crystals able to form fluid inclusions at depth is a controlled process, the mechanism of crack healing at depth is not fully understand. Last, another technical problem is to obtain sufficient fluid for chemical analysis, and to reduce contamination of the fluid sample as much as possible.

Quartz is the most popular crystal used, as the silica solubility in various solutions and P-T ranges has been studied for many years. For example, α-quartz can be used as a synthetic fluid inclusion logging tool up to 573°C. Calcite and anhydrite can also be used, calcite stability being also sensitive to the CO_2 content whereas anhydrite becomes stable under geothermal conditions [53].

Trapping temperatures of the fluid inclusions are determined by means of isochors constructed from the *Ths* on the saturated vapour pressure curve, but also need borehole pressures measurements, either directly measured or extrapolated from solutions of different PVT properties placed in separate capsules. However, the accuracy of this second method is lower. Instrumental errors may also arise when using a heating stage, the thermal gradients in sample holders of the stages generally increasing with increasing temperatures [53].

Some refinements have been made to strengthen this method. Batch-autoclave experiments conducted to evaluate the potential use of synthetic those fluid inclusions as a simultaneous temperature - pressure (and fluid sampling) logging tool in deep-seated, high-temperature (> 350°C) geothermal systems are reported [54]. Fluid inclusions, up to 50 µm long, have been readily synthesized during 5-day autoclave experiments (conducted at 375-475°C and 39-62 MPa) in pre-fractured, inclusion- and impurity-free artificial quartz. Inferred fluid inclusion trapping conditions are calculated by deducing the intersection of isochores derived from microthermometric data for three sets of simultaneously trapped synthetic fluid inclusions in healed microfractures. Synthetic fluid inclusion logging offers a precise borehole temperature measurement technique without need of any pressure correction. Pressure estimates are less precise, although the method may be improved by using a combination of H_2O - NaCl and H_2O - KCl solutions/salinities, and fluid/quartz/amorphous silica systems that facilitate crack healing but trap fluids that do not homogenize at near-critical conditions. Synthetic fluid inclusions, unlike mechanical sampling, can also be applied when reservoir fluids are scarce, since minute amounts of fluid can be analyzed by Raman microspectroscopy, laser ablation inductively coupled plasma mass spectroscopy and secondary ion mass spectroscopy [54].

However, there are many practical and chemical limitations to understanding the characteristics of the reservoir fluid since reservoir conditions are typically inferred from the analysis of fluids contaminated by fluids introduced during drilling programs. In addition, a partial or complete phase change is likely to occur as a result of pressure decrease as the fluid moves towards the surface. For hypersaline fluids, sampling can induce phase separation to salt and liquid phases, while CO_2, CH_4, H_2S, N_2 and other gaseous constituents are likely to escape from the fluid [54]. There are also potential limitations to the use of synthetic fluid inclusions as a sampling tool. For example, the chemistry of the inclusion fluid may not be exactly the same as that of the primary reservoir fluid, as there will likely have been chemical exchange with the host mineral (e.g. modification of $\delta^{18}O$ of inclusion fluid). Equally challenging are the technical difficulties involved in using fluid inclusions as downhole fluid samplers, including how to lower into the geothermal borehole the fractured quartz crystals in which reservoir fluids are subsequently trapped. Crack healing could occur as the quartz is lowered into the borehole, thus trapping fluid inclusions with a range of density and chemical compositions. Using container fitted with rupture disks to avoid such unwanted entrapments should be a solution [53].

2.2.4. Other potential tools (laboratory development)

The US National Energy Technology Laboratory (NETL) initiates in 2005 the development of the UDS (Ultra Deep Single Cutter Drilling Simulator) to provide critical science needed to engineer effective and efficient drilling technologies viable at depths greater than 6.1 km. The test cell will be rated to 2070 bars and 300°C [55].

Pressure sensors that could survive in harsh environments are also progressively made available by [22] or [56]. Firsts ones are dedicated to continuous monitoring (up to 3 years) for high pressures (up to 2000 bars) in hot conditions (up to 350°C) [22]. The second one, based on silica piezoresistive gauges, can operate at 1500 bars under temperatures of 500 to 700°C (only for few minutes; [56]). New designs and new applications are welcomed by the inventor.

3. Measurements of other parameters

3.1. PH MEASUREMENTS

Despite the existence of several pH electrodes operating at high temperature (e.g. hydrogen concentration cell, palladium hybrid electrodes and ceramic membrane electrodes - [57] and reference therein), in-situ pH measurements at high temperature are often difficult to obtain, inducing the development of methods based on the chemical analysis of reservoir fluids discharged via deep geothermal wells, or surface features. A new tube-type flow-reactor has been developed, with a pH measurement system, to simulate fluid-rock interaction processes over a range of temperature up to 500°C and pressures between 10 and 50 MPa [57]. The pH of reacted hydrothermal fluid in the flow system may be measured under reaction conditions or at room temperature. The pH of the hydrothermal fluid at 'reservoir' conditions is assessed using SOLVEQ92, based on the potential difference between an external reference electrode and a Pt-hydrogen electrode, pH and potential difference of standard buffer solutions and major element chemistry of the solutions. HDR experiments were undertaken at 20 MPa and thermal gradient up to 425°C.

As for temperature measurements, fibre optic appears to be a promising technique that could in the future bring powerful information in geothermal wells. Optical sensors for pH monitoring in such environments must match several restrictive conditions. Moreover, there is a strong need to develop sensors suitable for in-situ long term measurements, e.g. through permanent downhole equipment [58]. Existing devices used for water logging and monitoring, such as potentiometric measurement of electromotive force based on glass electrodes, are poorly stable under elevated temperature and pressure and suffer from long time response to changes in ionic composition. Colorimetric methods using reactions with indicator dyes do react faster, but suffer from a lack of precision [58]. Nevertheless, entrapping dye molecules into thick polymeric films, or bonding them to a substrate for immobilization, can allow creating promising optical pH sensors, as those devoted to groundwater monitoring [59]. Fused silica fibres (7 bars, 220°C), holding colorimetric indicators (from phenol red to thymol blue, pH ranging from 6.5 to 12 pH units) acting either as transmissive or reflective ones, are available for long term monitoring [60]. Other indicators (bromocresol) have been employed for brines pH measurements where conventional electrodes (glass porous membrane) were dramatically affected by fouling [61].

Optic detection can then be based on the monitoring of the fluorescence signal, evanescent light, total internal reflection, surface Plasmon resonance, optical time domain reflectometry ... [58, 62, 63, 64, 65]. Fluorescein indicator has being proven to be reliable to pressures up to 250 MPa, but limited by pressure induced dissociation of weak acids [66]. Variations of -0.4 pH unit at 100 Mpa and -1.0 at 200 MPa of several acids and buffers are reported for this fluorescein method. Using plastic cladding, multi-point fibre sensors allowing measurements along the entire fibre with a spatial resolution of 2.5 m have been processed [63, 67]. Mercurochrome can also be monitored using fluorescence measurements for in-situ pH determinations [68].

Those statements lead to the recent patenting of an optical sensor for pH using a cross-linked network of bi-functional organosilane agents to immobilize a pH sensitive chromophore to a surface potentially exposed to a high pressure, high temperature environment [58]. Changes in the indicators' UV or visible spectra are thus pH related. The inventors suggest this kind of sensor could also be adapted to monitor P_{CO2}. Another newly patented apparatus, based on spectroscopic measurement of pH, has extended the applicability of such a method to high pressure - high temperature domains [69]. Indeed, inventors noticed that since the pH measurement is only dependent from the molecular properties of the indicator dyes, the need for calibration prior measurement can be cancelled if dye equilibrium dissociation constants are properly characterised. Standard salt buffer equilibrium models are used to calculate pH at temperatures and pressures higher than those reported by the International Union of Pure and Applied Chemistry. By determining acid dissociation constants of various dyes, temperatures up to 150°C, pressures up to 680 bars and ionic strengths up to 3 mol/kg can be monitored [69].

Apart from water logging with CTD probes[1] which is beyond the subject, deep sea research in hydrothermal areas has also lead in the last years to the development of in-situ pH electrodes that can survive in harsh environments. The challenge of determining pH of a chemically complex fluid at elevated temperatures and pressures indeed involved the need to account for temperature and pressure dependent changes in the distribution of aqueous species. First pH measurements using solid state electrochemical sensors are reported in the Pacific Ocean [70]. Vent fluid temperature and pressure ranged from 180 to 384°C and 220 to 250 bars, respectively. pH sensors for use in seafloor hydrothermal systems make use of solid-state YSZ (yttria-stabilized zirconia) ceramic, which has been used with success in laboratory studies to determine pH of aqueous fluids at high temperatures. This device is still the one that is known to be able to work in harsh environments [58]. In its initial seafloor deployment, however, the YSZ-sensor was configured in such a way that pH was not explicitly determined, but rather pH response served as a reference permitting measurement of dissolved H_2 and H_2S. In the present study [70], this configuration was changed in that the YSZ-sensor was combined with an Ag-AgCl reference electrode allowing $pH_{(in\ situ)}$ to be explicitly determined.

The pH electrode assembly is located at the tip of the sensor and housed in a titanium casing. The Ti-casing was designed to enhance the flow of fluid passing the electrodes, while at the same time protecting the electrodes from potential impact with rock or chimney structures. Uncertainties from the sensor are on the order of 0.02 pH units. Uncertainties on dissolved Cl concentration contribute to errors (0.05 pH unit for a 100 mM uncertainty), as well as more serious uncertainties associated with the thermodynamic database used to calculate chlorine activity. Overall errors in reported pH values can be as high as 0.1 units [70].

[1] See part 3.2 for temperature and pressure limitations for the use of such devices.

The pressure housings containing the transition unit and electronics package are constructed of titanium alloy. The titanium alloy housing prevents seawater access to the electrical contacts leading to the electrode assembly or the electronics package, where signal processing is carried out.

YSZ sensors are also used for pH measurements of deep fluids for geothermal purposes. Many natural geochemical systems (and industrial applications) are characterized by relatively HT, HP, high ionic strength and low pH. For example, most axial hot-spring fluids are acidic, with dissolved Cl concentrations ranging from 40 to 200% of the seawater value (0.55 mol*)*, and have temperatures as high as 400°C. Thus, to assess the viability of the YSZ (ZrO_2 with 9% Y_2O_3) membrane as a pH sensor in fluids with relatively high ionic strength (0.57 mol NaCl) and low to moderate pH, experiments are performed at supercritical conditions of water (400°C and 40 MPa) in a titanium flow reactor [71]. The measurements agree well with theoretical predictions, showing strong associations of HCl° and $NaOH^{\circ}$ complexes in high-temperature fluids. The pH sensor has an uncertainty lesser than 0.05 pH unit. Stated sensor life is 1500 hours under those HT-HP conditions. Nevertheless, the measured potentiometric changes associated to pH variations under supercritical conditions suffer from slow response time (20 minutes) and lack of stability if the reference electrode is in contact with the fluids [58].

Moreover, other limitations of those YSZ sensors have been highlighted in recent years, especially dealing with sensor durability when exposed to high temperatures [72]. This is a significant achievement over the typical durability of glass electrodes (only a few hours) at 90°C or above, but is still a question when operating sensors in harsh environments where the sensors can't be replaced. YSZ sensor durability may be limited by thermal shock, chemical leaching or insufficiency of internal buffer ([72] and references therein). During experiments performed at 91°C (minimum cell operating temperature of YSZ sensor is 83°C), [72] enhanced sensor durability by filling two to three times as much Hg-HgO paste as done in previous experiments. Liquid based internal buffers (e.g. Hg/HgO) provide quicker response time because their contact resistance, compared to hard contact (solid Cu/Cu_2O*)* buffers which will decrease the overall bulk resistance and increase response time.

This statement leads to the recent patenting of YSZ pH electrodes for applications at temperature up to 400°C and pressures up to 60 MPa. This Zr/ZrO_2 electrode is based on a Zr wire coated with Zr oxide and insulated [73]. Coupled with other newly patented Au and Ag/AgCl electrodes, this allows the HT-HP determination of pH, H_2, Eh and/or H_2S in solution. Indeed, the YSZ sensors are specific ion sensors and can be hard-wired to function as either an oxygen or hydrogen ion sensor. By hard wiring the sensor to preferentially detect an oxygen ion, the sensor can be made to detect the fugacity of oxygen in solid, melt, or vapour environments [72]. By choice of different circuitry, the YSZ sensor can also be used to measure hydrogen ion in a wide variety of geothermal and industrial aqueous solutions (e.g. palladium/platinum resistance sensor rated up to 410°C and 276 bars [74]. Some manufacturers sold YSZ pH sensors with Ag/AgCl reference electrode for applications at temperatures higher than 130 to 185°C [75, 76[2]]. Resolution is 0.01 pH units with an accuracy of ± 0.3 pH units. Operating temperature can extend up to 360°C but is practically limited by the reference electrode at 300°C. Pressure rating is limited by the one of the ZrO_2-based pH probe, around 138 bars (up to 355 bars for the reference electrode).

Last, CO_2 geological storage experiments match the same HT-HP conditions for pH monitoring, with supercritical carbon dioxide. Expected conditions under geological storage are then dependent on the aquifer chemistry and the reactive nature of the reservoir host rock. Very limited fundamental measurements of pH and aqueous speciation have been performed in water-salt-CO_2 mixtures at high pressure. A high-pressure view cell equipped with a pressure-capable glass combination pH probe was used to independently measure solution pH in H_2O–CO_2 brine mixtures to beyond supercritical conditions [77].

3.2. CONDUCTIVITY MEASUREMENTS

As for temperature and pH, conductivity sensors that could perform realistic measurements at high pressure and/or high temperature are frequently coming from industrial applications. For example, boiler sensors can handle 200°C but only 17 to 20 bars [78]. Other geometries based on stainless steel and ceramics can resist to 250°C and 40 bars, but the connection between the sensor plug and the cable can only handle temperatures up to 100°C [79]. Nevertheless it's worth noting that small conductivity changes are better recorded at high temperatures than at room temperature [80].

Temperature resistance of conductivity sensors should be much greater in steam turbines, reaching hundreds of Celsius degrees. In those harsh environments, it's of great importance to well monitor corrosion due to salt solution (mainly NaCl) occurring as a vapour phase. For those applications sensors includes a metal foil base over which is deposited a glass insulating layer [81]. Available corrosion resistant devices can operate up to 200°C and perform reliable measurements in the range 0-20,000 µS/cm depending on the chosen cell constant [82]. Research efforts have recently focussed on conductivity measurements in concentrated solutions (NaCl - H_2SO_4 - H_2O) [83]. Measurements were performed in the range 25 to 250°C with an electrode-less conductivity cell.

Two types of sensors geometries could be deployed depending on the monitoring focus. Sensors can either work by contact, which is the more common application, or allow flow circulation between the measuring electrode (toroidal conductivity sensor) [84]. Those sensor can be deployed to monitor water, wastewater, groundwater and also acid and base [85]. Depending on the sensor inside, those conductivity probes can withstand temperatures up to 200°C and pressures up to 21 bars, with a whole measurement range of 0 to 2,000 mS/cm. Transmission distance is around 100 m [86].

[2] This manufacturer also sells a platinum redox probe operating up to 305°C and 350 bars.

Last, as for above mentioned parameters, lots of conductivity sensors do exist for oceanographic applications and can be rated up to 10,000 m depth (e.g. [87, 88]). Nevertheless there are frequently limited to 50-60°C maximum temperature, bringing them unusable in hot environments. Moreover they are built using large scale electrodes, which can be a limiting factor for long-term monitoring in wells. This led to the recent patenting of a micro sensor system for liquid conductivity, temperature and depth [89]. This invention is based on the use of liquid crystalline polymer allowing manufacturing thin film sensors. Thus water salinity can be easily monitored with the conjoint use of pressure and temperature micro-sensors, all sensors being designed to have a flat planar shape.

3.3. OXYGEN AND OTHER GAS SENSORS

In the past ten years, lots of efforts have been made to build thin film gas sensors using gallium oxide Ga_2O_3. Because of oxygen vacancy in the crystal, this oxide behaves like a n-type semiconductor over 600°C and transforms into a very stable monoclinic crystal after an annealing process [90]. This kind of thin film operates as a surface-control-type sensor due to a reduced gas below 900°C and a bulk-type sensor due to an oxidized gas above 900°C. Oxygen sensors have been built using those specific properties, by deposing gallium oxide on a silica substrate [91]. Some refinements include a sandwich structure using platinum, allowing measurements at 1000°C for industrial purposes [92].

In coal-fired plants, combustion optimization has led to the development of oxygen sensors that avoid plumbing problems. Potentiometric internal reference oxygen sensors were then created by embedding a metal/metal oxide mixture within an yttria-stabilized zirconia oxygen-conducting ceramic superstructure [93]. Long-term operating and resistance to strains of thermal cycling are some of the sensor characteristics, temperature being limited to 800°C.

Other gaseous species implied in harsh environments (power plants, exhaust streams...) become nowadays important to monitor with great accuracy (levels of ppm): e.g. CO, CO_2, NH_3, NOx, hydrocarbons, H_2, H_2S, H_2O [94]. Researches currently under progress aim to develop micro-scale gas sensing devices for such applications, using, thin film gas sensitive layers in combination with SiC based micro hotplate devices. Two sensing techniques are envisaged, for investigations at temperature greater than 500°C:

- the first, based on electrochemical thin films, for sensing H_2O and H_2S. Materials of interest are $BaZrO_3$ doped with Y and $BaCe_2S_4$ doped with Ca to measure H_2O and H_2S concentrations, respectively;
- the second, based on metal oxide semi-conductive sensing, for H_2, CO, CO_2, NH_3, NOx and hydrocarbons. Materials of interest are In_2O_3, Ga_2O_3, and NiO, the first two of which are n-type semiconductors and the last of which is a p-type semiconductor.

Other sensing approach can be used to determine concentrations of CO_2 and NO [95]. It appears that sensors utilizing passive wireless resonant telemetry scheme are relevant to eliminate the need for onboard power and exposed interconnects. The wireless platform is based on an inductor capacitor resonator circuit, using nickel and ceramic dielectrics. Those dielectrics exhibit variations in electrical properties with exposure to different levels of CO_2 (changes in conductivity of a 1:1 mixture of $BaTiO_3$-La_2O_3) and NOx (changes in permittivity of a 1:1 mixture of ZnO-WO_3). CO_2 sensor can operate up to 675°C and NOx sensor up to 600°C, while detecting NO concentrations below 5 ppm [95].

Another set of sensors is based on bulk acoustic wave resonators for sensing CO and H_2 [96]. The system consists of CeO_2 coated langasite ($La_3Ga_5SiO_{14}$) resonators with a special electrode design to detect mechanical and conductivity changes in the sensor film. The aim is to be able to distinguish between those two species at high temperature (about 600°C). Bulk acoustic wave resonators allow the detection of resonance frequency shifts caused by changes in mechanical properties of the sensing layer. Langasite, a new high temperature stable piezoelectric material, can be excited to bulk acoustic waves at temperatures up to 1470°C [96].

Last, fibre optic can also be envisaged for gas sensing. [97] used a sol-gel-processing technique to bond a copper-exchanged zeolite fluorescence indicator onto the end of an all-silica optical fibre. Experimental results from prototype sensors show they can be used to measure either the oxygen concentration or the equivalence ratio for gas mixtures containing weak or strong reductants, respectively. Fabry-Perot fibre sensors are also attractive alternatives, because the optical path length in the cavity is related to the refractive index of the medium inside, and by extension to its chemical composition [16]. Changes in cavity length were measured up to 1100 °C, but suffer from thermally induced bending at very high temperatures. Nevertheless the cavity would enable to operate the fibre as a chemical sensor based on measurements of the solution's refractive index.

To end this part dedicated to chemical determinations, it should be mentioned that other kind of sensors do exist for quantification of some dissolved species, preferentially in freshwater environments [88]. Ammonia, nitrate, chloride and fluorine can be monitored in the 0-1000 bars range.

3.4. GEOPHYSICAL PARAMETERS

As HT-HP surviving sensors are needed for chemical applications, petroleum service companies have also conducted research to extend the working capacities of their geophysical sensors, especially for MWD (measurement while drilling) and LWD (logging while drilling) applications.

LWD commercially available tools have been rated up to 175°C in the beginning of the 2000's, with survival at 200°C [98]. Sensors for gamma ray, resistivity, neutron and density logging have been field tested at depth up to 4.5 km and temperatures up to 186°C [98]. Triaxial accelerometer and magnetometer have been successfully laboratory tested at 195°C for 700 hours, highlighting the need of more effective electronic components such as SOI [99, 100]. Those devices are currently under improvement for deepest applications (up to 230°C and 1380 bars [101]), close to temperature range of deep gas reservoirs in south Texas and the Gulf of Mexico [100], but some power limitations due to batteries lifetime do exist [101]. Primary tool modules that should be strengthen are those for telemetry, gamma ray, generator, battery and directional applications [100, 102]. Some manufacturers strengthen their existing devices using Dewar technology to shield the electronics: operating time of acoustic televiewers can thus reach 10 hours at 275°C, with maximum pressure around 800 bars [103].

Another important parameter considering MWD and LWD tools is the reliability of the sensor and the electronics. For example up to date SOI electronics are rated to operate 20 years at 150°C, 10 years at 200°C but only 5 years at 225°C [104].

For oil and gas applications, this factor is slightly less important than in geothermal applications, as approximately 95% of the existing wells have temperatures under 150°C. But for those geothermal applications, reservoir ambient temperature can reach 350°C or more. Several problems can then be encountered:

- when drilling, dealing with high reservoir temperature is less crucial, as the mud cools the fluid below 225°C, operating devices being rated to 250-350°C [104];
- when logging the well in its isothermal state, temperature becomes of great importance, needing sensors or devices that could really survive at 350°C. Moreover, during production, the flowing fluid causes vibration when rising up, so that logging tools must also resist to shocks [104];
- for temperature equal to or lesser than 300°C, which represents 75% of the geothermal market, operating life is close to 1000 hours (c.a. 10 logs before replacing electronics [104]). This duration is considerably lower than the typical operating lifetime of oil and gas electronics emplaced in casing or completions (3 to 5 years nowadays, sought to be extended to 10 to 30 years in the future).

3.5. IN-SITU SAMPLERS

As stated for other kind of measurements, petroleum industry has numerous devices that can perform in-situ sampling at depth, but often with temperature limitation around 200°C and maximum pressure between 103 and 138 MPa [39]. Sampling could either be done with bottom pressure compensation, punctual collection of pore formation water or with ultra low contamination by fluids used during drilling (Quicksilver probe [39]). Other tool geometry implies to lower a flow-through design chamber with open valves on each end, with closing at the desired depth (programmed at surface or mechanically activated) [50, 54]. Pressure is preserved for around 0.6 litre of sample (maximum salinity 300 g/l), at maximum temperature of 230°C and maximum pressure of 690 bars [50]. Another goal of petroleum industry is to perform in-situ downhole measurements in real time without interfering with production by using permanent remote sensors and fibre optic cable data transfer [105]. This newly developed device (2006) uses near-infrared spectroscopy and induced fluorescence measurement to accurately determine oil, water and gas concentrations over a broad range of water cuts (error less than 5%). The active components are located at the surface while the only downhole components are optical windows and fibre optic cable. Limit sensor deployment depth is 1.83 km and extendable to 3.05 km using non laser technology, and to virtually any depth with laser technology [105].

Researches applied to geothermal field characterization have to deal with higher temperature, currently 300°C or above. As for oil purposes, two sampling techniques can be used: the "flow through" and the "vacuum" types [106]. However with the first type the sample can be a mixture of the fluid encountered during the deepening of the device. The second type implies under HT-HP conditions a boiling of the sample when it enters the sampler. Therefore [106] have built a downhole system capable of operating up to 400°C with minimal sample alteration and zero contamination, using a Controlled Displacement Sampler (CDS). Field tests were performed at 1125 m depth under 200°C and 5.81 MPa conditions. This CDS is made of two coaxial chambers protected by a heat insulated pressure body. The inner chamber is divided into two sections by a movable piston which preserves the sample fluid from contamination by the piston working fluid. The outer coaxial chamber is connected to the working fluid chamber by an adjustable throttling valve. When a sample is collected the working fluid is transferred to the outer chamber under the control of the throttling valve. A sample is collected by perforating a thin rupture disk with a timer controlled piercing needle [106]. Nevertheless, as the sampler has to be lowered and recovered each time a sample is needed, it can create chemical disturbances especially in non pumped wells.

Note that the Lawrence Berkeley National Laboratory holds a downhole high temperature fluid sampler with downhole electronics rated up to 350°C [107].

Such high temperatures are also frequent near hydrothermal vents. Ten years ago a shape-memory alloy based sampler was designed to collect fluids on those structures [108]. Shape-memory alloy (SMA) serves as both sensor and actuator of relatively large power (Patented). Thus, the sampler senses hot fluid and generates pumping power from the heat energy of the fluid. A 50.18% Ni and 49.82% T alloy in spring is used to form the actuator and the high-temperature sensor, with a phase transformation temperature of 80°C (from martensite at low temperature to austenite at high temperature). A shape-memory alloy is also used to switch the intake valve of the sampler, the intention being to avoid missampling when the inlet is in low temperature water. Test sampling was performed at hydrothermal vents (1372-1374 m deep) with fluid temperatures between 138 and 298°C and ambient seawater temperature of 3.1°C [108]. Approximate dimension is 70 mm in diameter and 300 mm in length before suction, and 420 mm long after suction allowing the collection of about 100 ml of fluid sample.

Last, fluid sampling can also be made using synthetic fluid inclusions [54] but the amount of water is considerably lower. Moreover there is no control on the kinetic processes, so that fluid mixtures can be sampled. The advantage is the higher temperature range (up to 573°C with α-quartz).

In a complementary perspective, in-situ measurements on fluid phase could give additional information. Real-time downhole fluid composition (oil, water, gas) using fibre optic sensor (near-infrared detection) is available for well completions, allowing for example to detect gas or water breakthrough [109]. Temperature and pressure survivability are 200°C and 1380 bars respectively, with a 5 years long operating life and no downhole electronics. Moreover, based on their unique infrared absorption spectrum, carbon, hydrogen, oxygen or sulphur species can be monitored.

Last, fibre optic can also be used during tracer experiments in geothermal environments [110]. In the Hijiori HDR site in Japan (2200 m depth, 270°C), tests were conducted using potassium iodine, potassium bromide, and fluorescein. Despite some troubles, fibre-optic fluorometer detection of fluorescein has been continuously performed during a 2 years long term circulation test.

3.6. PROGRESS IN ELECTRONIC CAPABILITIES

Lot of work is also performed to enhance power capabilities of devices used in LWD or MWD applications. Batteries should be modified to work several weeks at high temperatures (up to 250°C), as classical lithium-magnesium/thionyl chloride batteries are limited to 200°C. Testing cells made of Pyrex glass with a tungsten wire-glass seal (oxidized tungsten surface) have been successfully laboratory tested [111]. Capacitors should also resist to high temperatures exposures up to 250°C that should be available in 2009 [112, 113]. Downhole microcomputer system used to perform in-situ real time data acquisition should also overcome to temperature around 275°C (295°C rated) during at least 1000 hours using Silica-On-Sapphire (SOS) components [114]. SOI components are also strengthened to work at such elevated temperatures [115, 116]. Piezo-resistive pressure sensors based on separation by implanted oxygen SOI (SIMOX) technology for pressure measurement (0-40 MPa) at high temperature (up to 220°C) were developed for oil drilling industry [117]. Memories rated up to 400°C have been developed for fluid density logging tools [118].

In recent reviews, [119, 120, 121] summarized the up to date developments and the postulated capabilities of each electronic devices. SiC can operate up to 500°C and SOI up to 300°C, without any heat shielding. Even a 600°C SiC pressure senor for future applications in Jupiter or Venus surfaces has yet been designed. New ceramic batteries are under development to withstand temperatures up to 500°C [120].

4. Conclusions and Perspectives

This review focuses on two main objectives. The first one is to examine existing temperatures sensors that can be used or adapted for sensing under high pressure – high temperature conditions (i.e. above water critical point). The second one is to identify strategies and concepts in order to perform other measurements (fluid conductivity, pH, Redox…) useful for geochemical and geothermal purposes.

Four principal techniques currently used for temperature measurements in industrial applications have been highlighted:

- Resistance Temperature Detectors, whose operating range extends from -250 up to 1000°C, depending on sensors' shapes and insulations. Pressure resistance can reach 2000 bars;
- capacitive sensors can perform measurements between -70 and 900 to 1000°C, but with associated maximum pressure only close to 76 bars;
- phosphor thermometry is also frequently used (from 25 to 1400°C and 30 bars), but needs the deposition of materials onto the surface to monitor;
- last, fibre optic sensors can withstand higher pressures (up to 1000 bars), similar temperatures (1400°C) and operate in harsh environments. Measurements can moreover be performed along the whole fibre, which is not achievable using other sensing techniques.

Some of these techniques have been or are currently in use for geological purposes. One particular limitation of in-situ temperature sensing is not directly linked to the sensor itself, but to the electronics that frequently need to be coupled with the sensor. As a consequence, previously mentioned temperature domains are rather limited, reaching 250 to 370°C for available logging tools even if electronics are heat shielded. Lifetime is considerably lowered under high temperature, reaching only few hours. At the opposite pressure does not seem to be a limiting factor, some instruments surviving at 10,000 m depth. Fibre optic sensors appear to be the most frequent sensing tool deployed for geological applications, and RTD sensors for oceanographic ones. An alternative technique is the in-situ synthesis of fluid inclusions, using appropriate metals whose melting points are well defined, but it suffers from relative uncertainty (melting temperature is not necessarily the maximum temperature reached at depth) and from other bias (mimicking bottom fluid chemistry is a challenging task).

The evolution of chemical parameters is also very important to monitor at depth. The following techniques could be deployed, but they all need further refinements to become fully operational:

- pH measurements are representative of the fluid 's chemistry, as well as its dissolved gas content. Fibre optic sensing appears to be a promising technique, e.g.

by entrapping colorimetric indicators into the fibre (within a 220°C - 2000 bars domain). Another approach directly comes from oceanographic applications, using solid-state Yttria-Stabilized Zirconia sensors (max. 380°C - 250 bars);

- conductivity measurements at high temperature at depth are less common, as corrosion by saline fluid can quickly damage sensors. Recent researches focus on monitoring conductivity using liquid crystalline polymers manufactured as thin films;
- the thin film technique is also used for building gas sensors, but to our knowledge no work has been reported for their use under geothermal conditions. Other approaches focus on bulk acoustic wave resonators, passive wireless resonant telemetry and fibre optic sensing.

As numerous works are aimed to better characterize fluids at depth, there is also a strong will to develop devices that could sample deep fluids and recover them at the surface with minimal disturbances. Indeed, recovering fluids is necessary to perform complementary laboratory measurements. Existing samplers can nowadays operate up to 230°C and 1400 bars, operating either by “flow through” or “vacuum”. Theoretical maximum temperature limitations are frequently higher (350-400°C) but testing at such high temperatures is not yet reported. Moreover their volume is quite limited (frequently less than 1 litre), leading to the emergence of “hybrid” devices that can determine in-situ concentrations of oil, water and gas. The oceanographic approach uses Shape-Memory Alloys acting both as sensor and actuator to collect fluids in a desired temperature range.

All of the previous mentioned devices or sensors are also dependent from progress in electronic capabilities. For example batteries' and memories' lifetime and strength must be improved. Electronic components (printed circuit ...) must also be enhanced, the most promising ones (Silica-On-Sapphire, implanted oxygen Silica-On-Insulator, Silicon Carbide ...) being nowadays intensely studied for their capacities and survivability under high temperature - high pressure conditions.

As oil and gas applications need to explore deeper and deeper sedimentary formations, as geothermal energy applications are continuously growing, there is then a strong willing to develop sensors and devices rated for higher temperature and pressure domains, which can survive during long time in harsh environments. To our mind, some of the key parameters will be:

- the development of high temperature electronics, or the extension of electronic durability under HT-HP conditions;
- the development, if necessary, of smaller and better heat shields, e.g. mimicking the thermal barrier coatings used in the gas turbines industry (ceramics based);
- strengthen the durability of fibre optics at depth;
- pursuing researches on rare earth zirconates as alternative to YSZ sensors.

As shown by this bibliographic report, done in the 2009 spring, evolution is very rapid, so that new devices will become available very soon.

As part of the HITI project, this review is also aimed to develop prospective strategies and concepts for monitoring under high temperature - high pressure conditions. In that way, BRGM's work will focus in the forthcoming months on working on and/or testing the following items:

- precisely identifying the most promising ways and materials that would help to build efficient thermal shields;
- focus on pH measurements, either by testing YSZ sensors if available on the market at reasonable cost, or by working on colorimetric methods and optic detection (usable molecules, stability ranges…).

5. References

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