SULFATE-REDUCTION STATE OF THE GEOTHERMAL DOGGER AQUIFER, PARIS BASIN (FRANCE) AFTER 35 YEARS OF EXPLOITATION: ANALYSIS AND CONSEQUENCES OF BACTERIAL PROLIFERATION IN CASINGS AND RESERVOIR

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ABSTRACT

Most geothermal installations exploiting the Dogger aquifer of the Paris Basin have encountered corrosion and scaling problems. The well casings are made of carbon steel and therefore do not resist geothermal water which is an anaerobic, slightly acidic medium characterized mainly by the presence Cl^-, SO_4^{2-}, CO_2/HCO_3^- and H_2S/HS^-.

The implementation of anti-corrosion treatments by bottom hole injection of surface-active cationic agents (effective corrosion inhibitors at very low concentrations, 2.5 mg/l), has enabled operators of geothermal installations to resolve most of these corrosion and scaling problems. New problems are, however, now arising on some sites.

This article presents the current state of knowledge of microbiological activity in this geothermal environment. It concerns identification of strains, and the localizing and evolution of bacterial activity in casings and reservoir. In order to study this evolution, two experimental methods were tested based on monitoring the composition of the water at production wellheads, at variable flow-rates. These methods enabled us to distinguish origin (and the respective amount) of the total sulfide content in the water sampled at certain production wellheads, $[S^{2-}]_T$: sulfide produced in the casings or sulfide coming from the reservoir.

Since 1989, the evolution of $[S^{2-}]_T$, has been observed in water sampled at certain production wellheads. For a constant flow-rate, this content has increased regularly since the commissioning of these wells, and for a variable flow-rate, it varied. It was suggested that the increase in $[S^{2-}]_T$ with decreasing flow-rate was due to current and increasing activity of sulfate-reducing bacteria (SRB) on well casings. The

evolution of the isotopic composition of sulfur ($^{34}S/^{32}S$) in sulfide, $\delta^{34}S(S^{2-})$, as a function of the flow-rate was used to verify and confirm the previous explanations. Then, at certain wells (those with low initial content in sulfide), $[S^{2-}]_T$ progressively increases before reaching a plateau in the early 2000s. Studies in 1991 and 1996 revealed that the reservoir produced water increasingly rich in sulfide. This behavior, well-known for years, is due to the presence of SRB in the Dogger water and on the wells tubing. SRB strains were identified in the water and in the scale deposited on corrosion samples.

After 2001, the high content of dissolved sulfide (and largely injected back into the reservoir for decades) stay quasi stable at the production wellheads. The reservoir contribution to the $[S^{2-}]_T$ is currently (2011) predominant, meaning that a major part of the Dogger reservoir is transformed and currently produces water in a more reduced state.

Consequently, the operators of geothermal installations need currently higher concentrations of corrosion inhibitors (more than 8 mg/l) to resolve most of their corrosion and scaling problems.

Keywords: geothermal water, Dogger, Paris Basin, sulfide, sulfate-reducing bacteria, thermophiles, anaerobes, deep ecosystem, deep biosphere

INTRODUCTION

Geothermal waters of the carbonate Dogger formation of the Paris Basin (France) is exploited as a source of energy for district heating since 1970s, usually by geothermal well doublets. The Dogger aquifer (Middle Jurassic) of the Paris Basin is predominantly a limestone assemblage, 200-300 m thick, confined between the Liassic and Upper Callovian marls. It is a deep (around 1,500-2,000

meters below land surface) low salinity aquifer. In such geothermal operations, the warm water (57-85°C) from the Dogger reservoir is extracted by a production well, cooled down in a heat exchanger (till about 40°C), and re-injected into the same aquifer via an injection well located about 1 km away from the production one (Figure 1). This technology allows protecting the surface environment from the Dogger fluids which are relatively saline (5 to 35 g/l), and maintaining the reservoir pressure.

Most geothermal installations exploiting the Dogger aquifer of the Paris Basin have encountered corrosion and scaling problems. Made of carbon steel, the well casings do not resist geothermal water, which is an anaerobic, slightly acidic medium characterized mainly by the presence of Cl^-, SO_4^{2-}, CO_2/HCO_3^- and H_2S/HS^-. These compounds are present since the aquifer was first exploited. Sulfur is mainly present in the form of hydrogen sulfide, H_2S and HS^-, (between 0 and 100 mg/l), mercaptans (organic sulfides), RSH/RS^- (between 0 and 10 mg/l) and sulfate SO_4^{2-} (between 300 and 1200 mg/l). Total sulfide content at production wellhead is defined as:

$$[S^{2-}]_T = [H_2S]_g + [H_2S]_{aq} + [HS^-]_{aq} + [S^{2-}]_{aq} \quad (1)$$

Where suffixes g at aq indicate respectively gaseous and dissolved species.
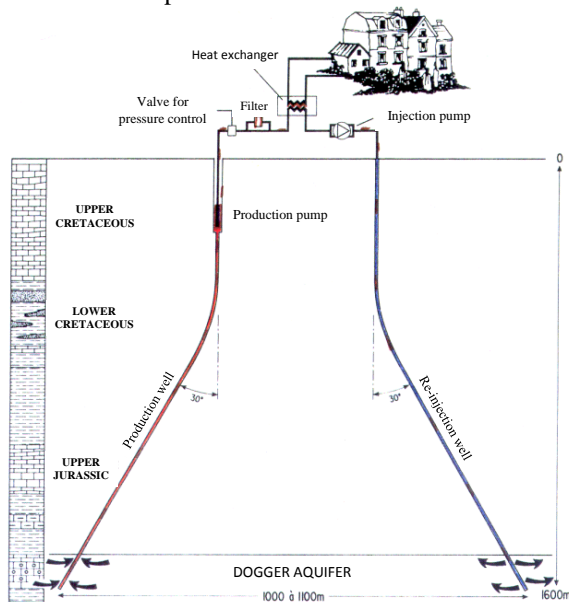

Figure 1: Sketch of the Dogger geothermal heating system, the "doublet" technology.

Systematic analytical studies showed the existence of a zone, which extends from the north to the west of Paris, that is particularly rich in sulfide, $[S^{2-}]_T$ values range from 30 to 100 mg/l, the rest of the aquifer having much lower values (0-10 mg/l). A map of $[S^{2-}]_T$ in the geothermal fluids was drawn in 1985 (Figure 2). The geographic distribution of $[S^{2-}]_T$ corresponded to the stable sulfur isotope ^{34}S of sulfate (Fouillac *et al.* 1990) showing a confined zone (reduced fluid) in the north and west and a less reduced fluid south and east of Paris. Zones with high sulfide content correspond to those where there is extensive corrosion and clogging in the wells (Ignatiadis et al., 1998). Indeed, in other studies (Amalhay et al., 1995; Ignatiadis, 1994; Ignatiadis et al.,1998) the electrochemical behavior of carbon steel was monitored in natural and modified geothermal media (sulfide contents ranging from 0 to 100 mg/l). The higher the sulfide content in the water, the higher the corrosion rate, the greater the thickness of scale and the rate of crystallization of mackinawite from amorphous FeS, and the lower the effectiveness of inhibitors. The sulfide 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: inhibition of iron coming from corrosion and understanding of sulfide production coming from reservoir and/or from actual activity of sulfate-reducing bacteria.
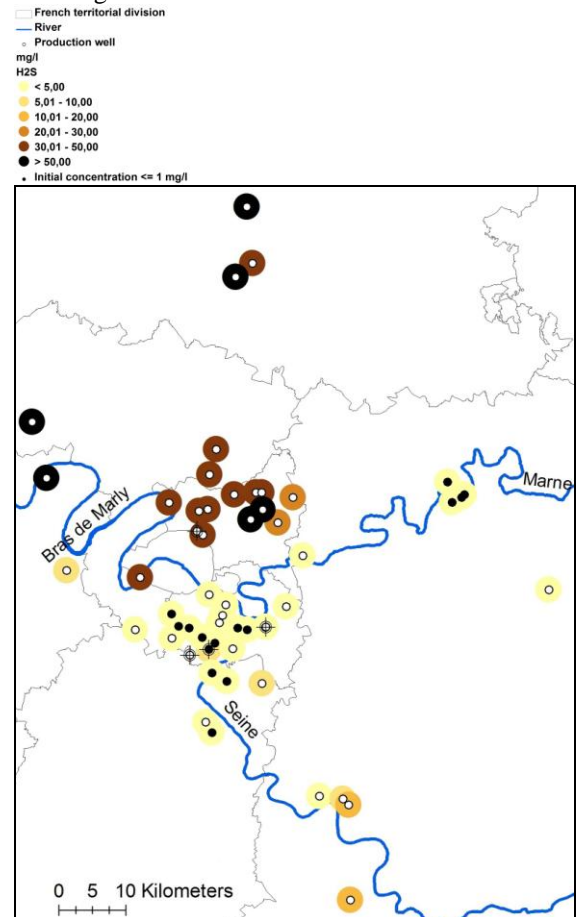

Figure 2: Map of the initial $[S^{2-}]_T$ of the geothermal Dogger fluids in the Paris basin.

During the last twenty years, several thousands of water samples from geothermal boreholes, oil fields and groundwater wells, tapping the Dogger limestone reservoir, were analyzed for their chemical

compositions and stable isotopes (Matray et al. 1994; Ignatiadis et al. 1998).

The microbiological activity of the Dogger geothermal waters has been previously studied (Daumas et al., 1986; Ignatiadis et al., 1998) showing evidences of sulfate reduction from fluid chemistry and sulfur isotopic compositions and a strong predominance of autotrophic sulfate-reducing microflora.

As early as 1988, analyses also showed that the $[S^{2-}]_T$ progressively increased in the fluids at certain geothermal wellheads, those with low initial content in sulfide (to the south and the east zone). This behavior, well-known for years, is due to the presence of SRB in the Dogger water and on the wells tubing. Since 2000s, the $[S^{2-}]_T$ is quasi stable at the production wellheads.

Studies in 1991 and 1996 revealed that the reservoir produced water increasingly rich in sulfide. The reservoir contribution to the $[S^{2-}]_T$ is currently (2011) predominant, meaning that a major part of the Dogger reservoir is transformed and at present produces water in a more reduced state.

We decided to carry out a historical and comprehensive study on the concentration and development of sulfide contents in the fluids at production wellheads during more than two decades. The aim of this study was: 1) to map the distribution and classify zones by their sulfide contents, 2) to highlight variations in sulfide contents caused by variations in the well flow-rate, 3) interpret and quantify sulfide production phenomena, and finally, 4) to determine the origin of the increases in sulfide contents found. This study ran from 1990 to 2011.

MATERIALS AND METHODS

Analytical techniques
Gases and dissolved species and bacteria collection
The sampling and analytical methods have been described in detail by Marty et al. (1988) for gases and by Criaud et al. (1989) for dissolved species. Briefly, gas/liquid ratios were directly measured on site by volumetry, the gases were analysed by gas phase chromatography after alkaline trapping of CO_2, whereas the aqueous species were analyzed partly by liquid phase chromatography performed on acidified aliquots, or by ICP/MS. The most important features and developments of the methods are also presented in Matray et al. 1994 and Ignatiadis et al. 1998) Especially, total dissolved sulfide was determined (detection limit 0.5 mg/l) by potentiometric titration, using Tacussel TIM 900 Titralab (Radiometer Analytical, Villeurbanne, France) with a titrating solution of $Hg(NO_3)_2$ (5. 10^{-3} or 5.10^{-4} mol/l), using a

specific silver sulfide electrode ($Ag-Ag_2S$) coupled to a Ag-AgCl reference electrode.

For isolation of bacteria strains, the samples were collected at the geothermal wellheads at certain flow-rates in sterile plastic bottles and kept at 4 °C until used.

Sulfur and oxygen isotope determinations.
All isotope analyses are reported in δ units, which are defined as deviations in ‰ of $^{18}O/^{16}O$ and $^{34}S/^{32}S$ from international standards: the sea mean ocean water (SMOW) for oxygen, and the Canyon Diablo Troilite (CDT) for sulfur. The ^{18}O values (‰ vs. SMOW) were determined using the gas-water equilibration method described by Epstein and Mayeda (1953), and isotopic ratios were measured on a Finnigan MAT 252 mass spectrometer (Finnigan MAT, Orsay, France) equipped with an automatic equilibration unit similar to the device used by Horita et al. (1989). Solutions were filtered at 0.45 µm, acidified with HCl 12 N, and then filtered again down to 0.025 µm. Sulfate was precipitated as $BaSO_4$ with a $BaCl_2$ solution. One aliquot of the dried $BaSO_4$ precipitate was reduced to H_2S by a boiling mixture of $HI-HCl-H_3PO_2$ (Thode et al. 1961). The H_2S, swept out with a stream of nitrogen, was precipitated as CdS by reaction with a cadmium acetate solution. Then, the dried CdS reacted under vacuum with O_2 to produce SO_2, on which the sulfur isotopic composition was determined, using a Delta S mass spectrometer (Thermo Finnigan, Orsay, France). Another aliquot of $BaSO_4$ was mixed with pure graphite (in excess) and heated at 1050°C under vacuum (Sakai and Krouse 1971; Caron et al. 1986). CO and CO_2 were both produced during the reaction. While CO_2 was trapped in liquid N_2, CO was converted to CO_2 by a high voltage electrical discharge. Isotope measurements were made on the total CO_2 using a Delta S mass spectrometer (Thermo Finnigan).

Methodology for triggering and studying water composition evolutions
In order to provoke and then study the evolutions in the composition of the waters sampled at the production wellheads, a methodology was defined. Based on some preliminary definitions and theoretical considerations (Ignatiadis, 1994), it was possible to determine two methods of triggering and studying variations in the production wellhead fluid: i) by monitoring of the fluid composition at various stabilized production flow-rates, during short period of time (few days) and during long period of time (few years or decades) and ii) by monitoring of the fluid composition before and after bactericidal treatment of the production well.

The total sulfide content at the production wellhead can be also written:

$[S^{2-}]_T = [S^{2-}]_{aquifer} + (\Phi_{bacter\ sulf} - \Phi_{deposited\ sulf})/Q_T$ (2)

where $[S^{2-}]_{aquifer}$ is the sulfide content of the aquifer, Q_T is the total flowrate at production wellhead, $\Phi_{bacter\ sulf}$ is the part of the sulfide flux currently produced at a given time by bacteria in the casing, $\Phi_{deposited\ sulf}$ is the part of sulfide flux deposited in the form of Fe_XS_y, on the casing walls. All measurements and analyses are carried out at the wellhead where the fluid composition results from both reservoir and production well casings contributions. It was established by Ignatiadis (1990; 1994), since a plot of the $[S^{2-}]_T$ against the reciprocal of the flow rate is always a straight line (according to the equation 2), the ordinate at the origin of this straight line represents $[S^{2-}]_{aquifer}$, while the slope of the lines represent the difference $\Phi_{bacter\ sulf} - \Phi_{deposited\ sulf}$).

In anaerobic water, such as that of Paris Basin Dogger aquifer, SRB can reduce sulfates into sulfides. This reaction increases the ^{34}S in residual sulfates (meaning that their $\delta^{34}S(SO_4^{2-})$ increases) and decreases the ^{34}S in the sulfides produced (i.e. $\delta^{34}S(HS-)$ decreases). Consequently, the ^{34}S in the residual sulfates increases as the fluid is reduced.

Similarly that the sulfide content, $\delta^{34}S(HS-)_T$ can be written:

$\delta^{34}S(HS-)_T = \delta^{34}S(HS-)_{aquifer} + \delta^{34}S(HS-)_{casing}/Q_T$ (3)

It was established by Ignatiadis (1994), since a plot of the $\delta^{34}S(HS-)_T$ against the reciprocal of the flow rate is always a straight line (according to the equation 3), the ordinate at the origin of this straight line represents $\delta^{34}S(HS-)_{aquifer}$, while the slope of the lines represent the $\delta^{34}S(HS-)_{casing}$, the last indicates the casing contribution (the ^{34}S mixing proportion between the bacterial production of sulfide and sulfide precipitation or other sulfide alterations (Ignatiadis, 1994). In other words,

RESULTS AND DISCUSSION

The Dogger aquifer of the Paris basin

Samples have been collected from the Dogger aquifer (Middle Jurassic) of the Paris Basin, France. The Dogger is predominantly a limestone assemblage, 200-300 m thick, confined between the Liassic and Upper Callovian marls. It is an oolithic limestone with an average porosity of 15 %, an average particular density of 2.7 and an average specific surface of 0.8 m^2/g. The Dogger is a deep (around 2,000 meters below land surface) low salinity aquifer.

Bacteria in wells exploiting the Dogger aquifer of the Paris basin

Current state of knowledge of microbiological activity in this geothermal environment

The microbiological activity of the Dogger geothermal waters has been previously studied (Daumas et al. 1986; Matray et al. 1994; Ignatiadis 1994 and Ignatiadis et al. 1998) showing evidences of sulfate-reduction from fluid chemistry and sulfur isotopic compositions and a strong predominance of autotrophic sulfate-reducing microflora.

Various types of bacteria have been found in the fluids sampled at geothermal sites. Daumas et al. (1984; 1986) showed the predominance of anaerobic over aerobic, and of thermophilic over mesophilic microflora. The measurement of autotrophic and heterotrophic microbial activity using radioactive tracers in the water showed that the predominant biological activity is of the chemolithotrophic type. The microflora responsible for this activity is for the most part thermophilic (Daumas et al. 1985). This greater autotrophic activity is probably due to a reduction or depletion in the initial organic reserves with time in this deep Dogger aquifer, poorly recharged (De Marsily 1986; Gonçalvès et al. 2004; Fouillac et al. 1990)) and isolated from all photosynthetic production. Heterotrophic bacteria are therefore poorly adapted to these conditions with little organic potential (Daumas et al. 1985). Furthermore, the latter seem to be mesophilic (optimum development at 20 to 44 °C), thus their poor adaptation to the high aquifer temperatures (65-70 °C). This inadaptation to the environment makes us wonder what the origin of these bacteria, which are furthermore aerobic, might be.

Since the Dogger fluids are very reducing (anaerobic), we assume that parts of these bacteria are allochthonous, most probably introduced during drilling operations and/or by percolation of surface waters. On the other hand, the autotrophic microflora turn out to be thermophilic (optimum temperature >45 °C) and anaerobic. These thermophilic chemolithotrophic anaerobic bacteria, particularly well adapted to the aquifer conditions (T, pH, anaerobic conditions, salinity, redox potential, presence of sulfate and electron donors), capable of proliferating and being metabolically active in the aquifer, could be autochthonous (Daumas et al. 1984). Few studies have been done to identify species. A few strains of sulfate reducing bacteria (SRB) have, however, been identified: *Desulfovibrio desulfuricans* and *Desulfotomaculum geothermicum* (Daumas et al. 1988). More recently (Fardeau et al., 2009) anaerobic and thermophilic microorganisms with the ability to reduce sulfur compounds (e.g. sulfate and/or thiosulfate) were isolated from water samples collected from about 2000 meters depth at in

situ temperatures of 70°C in the geothermal well of Melun L'Almont from the Paris Basin. Two strains were characterized by both DNA/DNA hybridization and 16S rRNA gene sequence analysis, which revealed that they are most closely related to *Thermotoga elfii*, a thiosulfate-reducing bacterium, and to *Archaeoglobus fulgidus*, a sulfate- and thiosulfate-reducing archaeon.

Other types of iron bacteria such as the genera *Leptothrix*, *Gallionella*, and *Thiobacillus* were sought. Only the species *Thiobacillus denitrificans* was detected in an unsystematic manner in the Dogger fluids. However, Magot et al. (1993) identified 36 species of SRB in brut emulsion/water at petroleum wellheads of the Dogger aquifer.

Significance of T. elfii and A. fulgidus in geothermal waters

These two microorganisms, *T. elfii*, and *A. fulgidus,* were indeed previously isolated from petroleum reservoirs in the Paris Basin (L'Haridon et al. 1995). It is known that *A. fulgidus* strains are widely distributed in shallow marine hydrothermal systems and their occurrence has also been demonstrated in deep oil field waters where they may be important contributors of biogenic H_2S generation (Magot et al., 2000; Stetter et al. 1988; Amalhay et al., 1995). *T. elfii* has also been frequently isolated from deep oil reservoirs throughout the world (Magot 1996) where it may be active also in oil souring as it is recognized as a thiosulfate-reducing microorganism producing sulfide (Ollivier and Cayol 2005). It is thus noteworthy that *T. elfii* and *A. fulgidus* may be also common inhabitants of deep terrestrial water environments. The presence of both *T. elfii* and *A. fulgidus* within the deep geothermal water environment reported in this study could result from hydrological connections over large timescales between oil reservoirs and deep aquifers. Such connections are reflected by the presence of hydrocarbon compounds in the investigated geothermal waters. In this respect, the H_2 oxidizing/producing capabilities of *T. elfii* together with the chemolithotrophic CO_2 assimilation capabilities of *A. fulgidus* using H_2 as energy source could make the consortium of these two species in geothermal waters of great significance. Finally, since Fe(III) and sulfate-reducing microorganisms are known to promote precipitation of solid carbonates from CO_2-rich waters, both *T. elfii* and *A. fulgidus* could be used as laboratory deep-biosphere model organisms for investigating the microbiological response of such aquifers at temperatures of about 70°C upon injection of CO_2. Specific adaptations of *A. fulgidus* to these environments in comparison to reference strains, such as enhancement of capabilities to use the H_2/Fe(III) couple, deserve further investigations and are to be kept in mind in such studies.

Evidence for more intense bacterial activity on well casings of the geothermal wells

In surface water samples only the bacteria brought up with the water were counted. Little is known about the activity of bacteria attached to surfaces (scale, reservoir). Bacteria counted on corrosion coupons are abundant (compared to those circulating in the fluid) and variable (from several to several millions of cells per cm²). For example, bacterial densities of around 10^9 cells/g of corrosion product were recorded for geothermal sites north of Paris. A significant difference was observed between the number of bacteria counted on carbon steel coupons and those on corroded stainless steel coupons with a layer of scale (*Table 1*). This scale when examined by X-ray diffractometry, revealed the very abundant presence of mackinawite on carbon steel and its scarce presence on stainless steel. This shows that the number of bacteria is linked to the presence of abundant scale. It is now possible to say that this scale constitutes a preferential site for both the attachment and development of bacteria. Indeed, observation of polished sections with a metallographic microscope revealed that mackinawite forms within dead bacteria cells and that it is a result of bacterial activity (Amalhay et al. 1995).

Table 1: Bacteriological analysis of water and scale (Fontainebleau untreated fluid). Scale obtained after 30 days exposure. Bacterial densities are expressed in number of bacteria per ml for the water and per cm^2 for the coupons.

Sample	Density of bacteria	
	Sulfate reducing microflora	Anaerobic hetero-trophic microflora
Geothermal water	$0.2500 \ 10^6$	$0.0005 \ 10^6$
carbon steel API K55	$50.0000 \ 10^6$	$2.0000 \ 10^6$

Evolution of the total sulfide content in the geothermal fluids and origin of this evolution

Since 1989, analyses of water sampled at the production wellheads have revealed an increase in the total sulfide content of certain wells (south and east of Paris) (Figure 3). At a constant exploitation flow rate, this content has increased regularly since the commissioning of these wells. At variable flow rates, it varied. This increase seemed to concern only those wells in which the initial sulfide content had been nil or low (< 5 mg/l). Investigations, performed between 1989 and 1998 on sulfide concentration, revealed (Figure 4 to Figure 6) two distinct zones (high sulfide and low sulfide) and two types of vari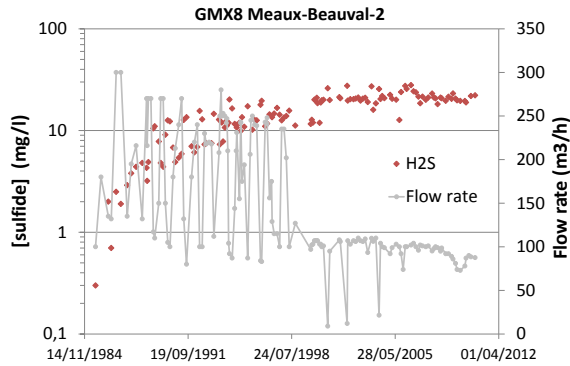ation (regional and local) (Ignatiadis et al., 1998). Investigations, performed between 1989 and 1998 on sulfide concentration, revealed (Figure 4 to Figure 6) two distinct zones (high sulfide and low sulfide) and two

types of variation (regional and local) (Ignatiadis et al., 1998).

Figure 3: Temporal variation of total sulfide concentration at the production wellhead $[S^{2-}]_T$ of Meaux-Beauval-2 (east of Paris).

A zone of high sulfide concentration (25 to 100 mg/l) lied to the north and west of Paris. In this zone, where the initial sulfide content was already high, it was found that the concentration did not vary significantly over time nor with the flow rate (Figure 5). A zone with lower initial sulfide concentrations lied to the south and east of Paris, where sulfide concentrations at wellheads increased in time and with the inverse of the flow rate (local variation, Figure 6). For instance, the sulfide content measured in 1990 at the wellhead of Meaux-Beauval-2 increased from 7.21 to 26.15 mg/l between 150 and 40 m³/h. The sulfide concentrations varied by several orders of magnitude between certain wells to the south and east and a few sites in north and west (regional variation), even though the total dissolved salts (TDS) only vary by a factor of 5 to 6 (5.8 to 35 g/l) over all geothermal wells (Figure 4). There is no general correlation between sulfide concentration and fluid temperature and/or TDS.
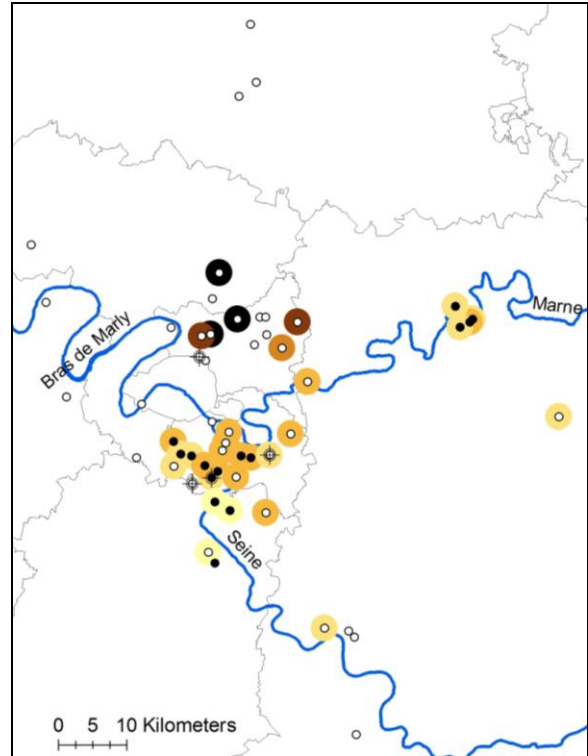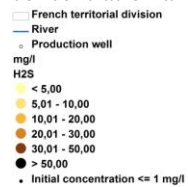

Figure 4: Map of the $[S^{2-}]_T$ of the geothermal Dogger fluids between 1995 and 1997 (data measured or extrapolated at a reference flow rate of 150 m³/h).
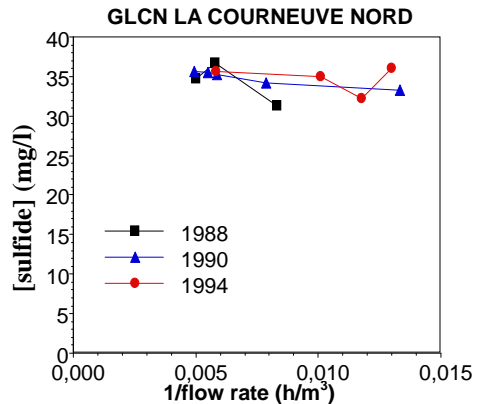

Figure 5: Variation of the $[S^{2-}]_T$ of "La Courneuve Nord" (north of Paris) as a function of the flow rate and time.
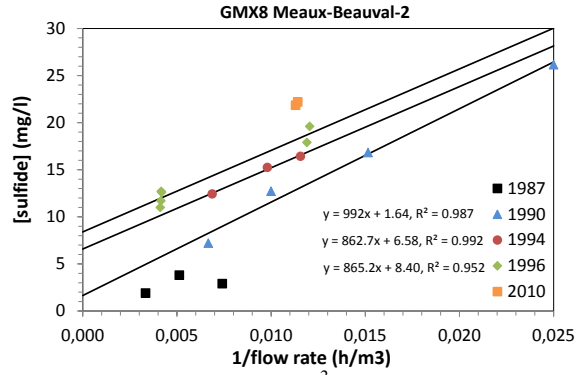
Figure 6: Variation of the [S²⁻]_T of "Meaux-Beauval-2" (east of Paris) as a function of the flow rate and time.

These works also showed that, since 1994, bacterial activity on well casings is not totally responsible for the increase in sulfide content measured in the water of south and east sites. Indeed, it has been determined that, in this zone, the reservoir produced a water more and more rich in sulfide (see the ordinate at the origin Figure 6 and Table 2), thus illustrating the recirculation of the water (already produced and re-injected) in the geothermal loop. To confirm this hypothesis and estimate the quantities of sulfide which originate from bacterial activity and from aquifer respectively, these works used an isotopic tool based on measuring how the isotopic composition of sulfur (^{34}S and ^{32}S isotopes) varies in sulfides and sulfates with time and the flow rate. They showed that δ^{34}(HS⁻) varied considerably with the flow rate ; it increases with the flow rate due to the higher contribution of the aquifer (rich in δ^{34}(HS⁻)). Then, they observed that δ^{34}(HS⁻) have decreased with time for a fixed flow rate (about 2‰ between 1990 and 1995 at the production wellheads of Meaux-Beauval, Table 3). Thus, they concluded that the quantity of sulfide which reaches the production wellhead largely results from recent bacterial activity. The effect of the flow rate on δ^{34}(SO$_4^{2-}$) is the reverse of that on δ^{34}(HS⁻) but is far weaker because of the high initial sulfate concentration in the aquifer.

Table 2: Variation of the reservoir sulfide content [S²⁻]_aquifer with time (n.a =not available)

Production well	Well commis-sioning before 1989 (Rojas et al.,1989)	1990	1994	2011
Créteil	0.00	2.93	7.00	18.18
Fresnes	2.90	0.14	4.49	13.27
Meaux-Beauval-1	0.90	1.24	2.58	14.00
Meaux-Beauval-2	0.30	1.64	6.58	20.52
Orly-1	0.24	5.80	6.08	10.38
Chevilly-Larue	0.87	1.41	4.35	13.06
Bonneuil-sur-Marne	0.00	2.70	7.69	n.a. since 2008
Alfortville	3.10	5.58	11.15	16.54
Maisons-Alfort-2	1.39	4.30	10.10	14.96
Hay-les-Roses	0.66	5.30	5.90	13.7
Coulommiers	1.60	4.03	5.60	12.29

Table 3: Variation of the δ^{34}S(HS-) and the δ^{34}S(SO$_4^{2-}$) with time

Production well	Date	flow rate (m³/h)	[S²⁻]_T	δ^{34}S (HS⁻)	δ^{34}S (SO$_4^{2-}$)
Meaux-Beauval-1	82/86	-	0.90	-	23.5
	1990	120	11.05	7.1	24.5
	1995	132	7.70	5.3	24.3
	2011	65	22.62	n.a.	n.a.
Meaux-Beauval-2	1990	150	7.21	7.5	24.2
	1994	145.5	12.43	6.1	
	1995	155	11.90	5.1	24.3
	2011	85	21.00	n.a.	n.a.
Chevilly-Larue	1986	180	0.87	4.1	23.4
	1994	142	8.03	0.7	25.2
	2011	180	13.65	-5.2	28.0
Coulom-miers	83/87	150	1.60	9.6	24.0
	1995	143	10.00	5.3	24.3
	1996	185	9.96	4.9	24.6
	2010	113	13.55	n.a.	n.a.

The present study, carried on this year, confirms and completes these first observations. The map produced to illustrate the current [S²⁻]_T shows that the two sulfide zones always exist, even if the sulfide content of the south and east zone is more and more elevated (Figure 7). It approaches 20 mg/l or equals it (e.g. of Meaux-Beauval and Chelles sites). In fact, as already observed in 1990's, in this zone, the reservoir produces a fluid increasingly rich in sulfide (Figure 8 and Table 2).
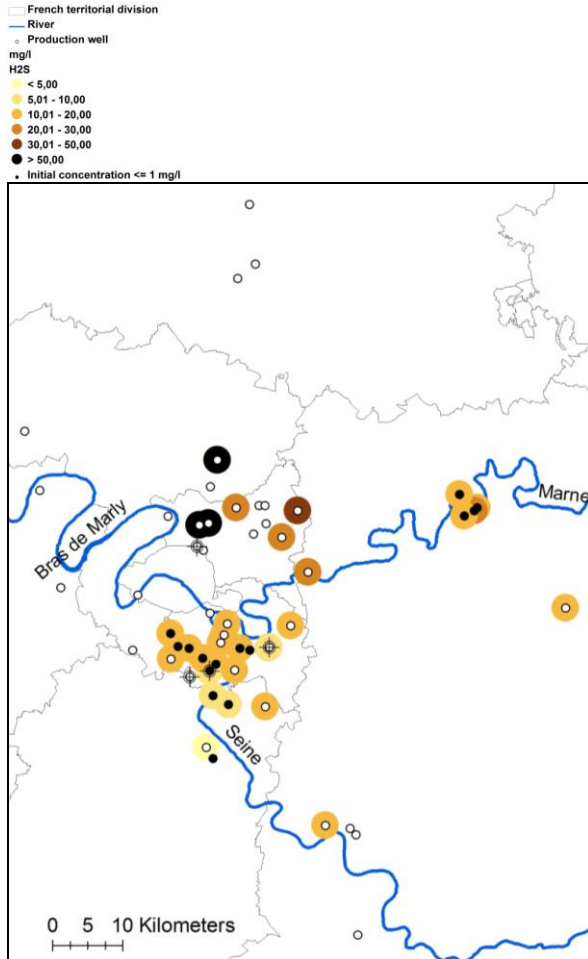
Figure 7: Map of the $[S^{2-}]_T$ of the geothermal Dogger luids between 2008 and 2010 (data measured or extrapolated at a reference flow rate of 150 m3/h).
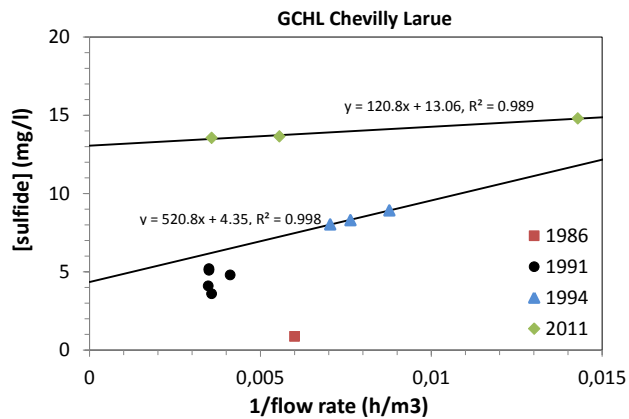

Figure 8 : Variation of the $[S^{2-}]_T$ of "Chevilly-Larue" (south of Paris) as a function of the flow rate and time.

About 1 mg/l at the commissioning of the wells (on average), the $[S^{2-}]_{aquifer}$ is now higher than 10 mg/l (about 14.7 mg/l on average, against 6.1 in 1994). The $[S^{2-}]_T$ continues to vary with the flow rate but tends to stabilize. For instance, $\Phi_{bact.\ sulf.} - \Phi_{deposited\ sulf.}$ has been divided by 4 since 1994 at the wellhead

of "Chevilly Larue" (south of Paris) (see the slope in Figure 8). It indicates that bacterial activity is declining in the casings and the near reservoir. Thus, the sulfide content currently measured in the water at wellhead is mainly produced by the reservoir as it is the case for years in the north and west sites. Regarding the sulfur isotopes, $\delta^{34}S(HS^-)$ continues to decrease (about 4‰ in 1986, it is now equal to -5.2‰ at Chevilly-Larue). Thus, the fluid produced by the wells located in the south and east zone is more and richer in bacterial sulfide. The bacterial activity declines for a few years, thus, this evolution doesn't reflect a current and strong bacterial activity but rather the recirculation of the water (already produced and re-injected, so already depleted in ^{34}S) in the geothermal loop.

To simplify, the illustrations of this paper concerned only a few production wells. But, all are representative of the zone (high or low sulfur) where it is localized.

CONCLUSION

This article presents the current state of knowledge on microbiological activity in this geothermal environment. It concerns identification of strains, the localizing and evolution of bacterial activity in casings and reservoirs. Sulfide producing strains were identified in the water and in the scale deposited on corrosion coupons. Since 1989, an evolution of the HS- content in water sampled in wellheads of certain production wells has been observed. At a constant exploitation flow-rate, this content has increased regularly since the commissioning of these wells. At variable flow-rates, it varied. In order to study these evolutions, two methods were tested based on monitoring of the composition of the water at variable flow-rates. These experiments enabled us to explain the increase in the sulfide content when the flow-rate decreases and confirm that this increase is due to current and increasing SRB activity on well casings. An isotopic tool based on the evolution of the isotopic composition of sulfur ($^{34}S/^{32}S$) in sulfide as a function of the flow-rate, was used to verify and confirm the previous explanations. Recent studies showed that in the zone known to have a low initial sulfide concentration the $[S^{2-}]_{aquifer}$ increases as a function of time. This is the result of sulfide producing bacteria proliferation either in the reservoir near the production well or a recirculation in the geothermal loop of the fluid already produced and re-injected.

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