

PROCEEDINGS, Thirty-Sixth Workshop on Geothermal Reservoir Engineering  
Stanford University, Stanford, California, January 31 - February 2, 2011  
SGP-TR-191

## GEOCHEMICAL PARAMETERS AS PRECURSORS TO PREDICT THE DECLINE OF TEMPERATURE IN THE DOGGER AQUIFER (PARIS BASIN, FRANCE)

C. Castillo, M. Azaroual, I. Ignatiadis, O. Goyénèche

B.R.G.M  
3, avenue Claude Guillemin - BP 36009  
Orléans cedex 02, 45060, France  
e-mail: c.castillo@brgm.fr

### **ABSTRACT**

Geothermal energy of the carbonate Dogger aquifer of the Paris Basin is exploited for heating since 1970s using geothermal well doublet technology where the warm produced waters (57-85°C) is extracted by a production well and re-injected after used as cooled waters (about 40°C) in the same aquifer via a different well. The injection of the cooled waters into the Dogger reservoir disturbs the initial thermodynamic equilibrium between the Dogger aquifer phases. This creates a cold and growing bubble around the injection well which risks propagating toward the production wells. This study, based on geochemical monitoring and field data analyses, aims to identify chemical precursor(s) of the thermal decrease in the production well field. Ca and HCO<sub>3</sub> concentrations do not appear to be relevant precursors, because they are linked to fast mineral dissolution/precipitation reactions (carbonates). However Si concentration could be an appropriate precursor of the temperature drop, because it depends only on slow mineral reactions (silicates dissolution/precipitation). The results of this analysis are presented and discussed in this paper.

### **INTRODUCTION**

Geothermal waters of the carbonate Dogger formation of the Paris Basin (1.500-2.000 m deep) is exploited as a source of energy for district heating since 1970s, usually by geothermal well doublets. In such 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 1km 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. However, it causes the progressive decline of the Dogger's geothermal resource. Thus, one doublet cannot be exploited endlessly staying economically viable. Consequently, predict the temperature decline of the produced fluids is a crucial issue for geothermal exploitation.

Temperature measurements are regularly performed on the produced fluids during production. However, these measures strongly depend on flow rate. Consequently, establish a pattern of temperature drop from this field data is not simple. Nevertheless, previous hydro-thermal modeling of the Dogger formation has revealed that the temperature of produced waters should start to decrease soon (Lopez *et al.*, 2010). This decrease has not been observed yet: a small drop in temperature (2-3°C) has been recently measured in one of the 35 production wells in operation (GAL2, Alfortville, Figure 2 and Table 1).

The injection of the cooled waters back into the Dogger reservoir disturbs the initial thermodynamic equilibrium between the Dogger aquifer phases (water and rock). It creates a chemical front that will progressively propagate within the aquifer and must reach the production wells. It is currently assumed that the chemical front travel faster (3-5 times) than the thermal front (Goyénèche *et al.*, 2005), due to relative delay in thermal exchanges between reservoir phases (rock and flowing water). This study, based on field data analyses, aims to identify chemical precursor(s) of the thermal decrease in the production well field.

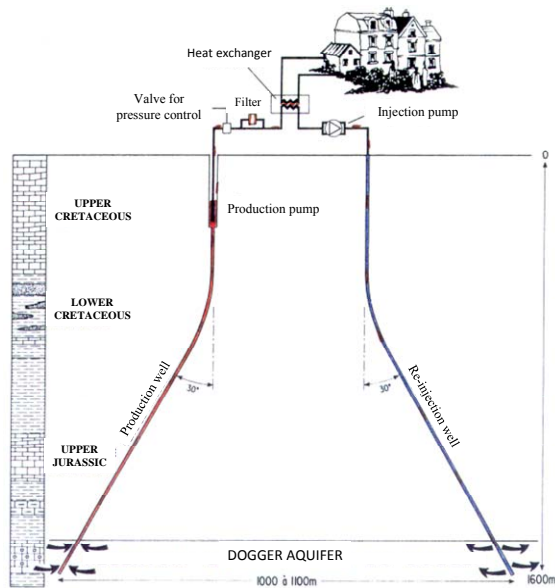


Figure 1 : Sketch of the Dogger geothermal heating system, the "doublet" technology.

### GENERAL SETTING

Since the beginning of geothermal exploitation of the Dogger aquifer, several studies were performed on the Dogger formation waters. Consequently, the initial composition of the Dogger formation waters, and their initial thermodynamic properties, are well established (Azaroual *et al.*, 1997; and herein references).

The Dogger formation waters is warm (57 to 85°C) and relatively saline (5 to 35 g/L). They are initially at thermodynamic equilibrium with respect to seven minerals: calcite, disordered dolomite, chalcedony, fluorite, gibbsite (or kaolinite), albite and K-feldspar. Additionally, aqueous solutions collected from the east part of the Dogger aquifer (EAST group, see below) are at equilibrium with respect to anhydrite as well (Michard and Bastide, 1988; Rojaz *et al.*, 1989; Coudrain-Ribstein and Gouze, 1993). Consequently, amounts of SiO<sub>2</sub>, Na, K, Ca, Mg, HCO<sub>3</sub>, Al and F in the Dogger fluids are controlled by temperature, chloride and sulfate concentrations (except in the East area where they are only controlled by temperature and chloride contents as waters are at equilibrium with anhydrite).

Currently, the Dogger geothermal waters are exploited by 35 operations which are divided into 4 groups (Figure 2):

- Val-de-Marne (VDM).
- Melun (SOUTH),
- Seine-Saint-Denis (SSD),
- Meaux-Coulommiers (EAST).

The SSD group has the lowest temperature (57-70°C) and the highest initial sulfide concentration (up to 20 mg/l). In contrast, the EAST group has the highest temperature (up to 75°C), the highest salinity (31-35g/l) and a low initial sulfide concentration (0.1-0.5mg/l). The VDM and the SOUTH groups have similar characteristics than the EAST group with high measured temperature (74°C on average) and low initial sulfide concentration (2-3 mg/l). The VDM group is characterized by a high density of wells while the SOUTH group contains only few well (Goyénèche *et al.*, 2004).

All the geothermal exploitations of the Dogger aquifer have to face corrosion and scaling phenomena (Ignatiadis *et al.*, 1998). The casing of the wells, generally in carbon steel, does not resist to geothermal fluids. Thus, corrosion inhibitors are continuously injected since 1980s into the producing wells to reduce these damaging processes.

### MATERIELS AND METHOD

#### Water analysis data

French geothermal operations are governed by a mining Law: the "Code Minier" which imposes on operation managers to collect and to analyze water samples every 2-3 months at wellheads or along the geothermal loop. Parameters usually measured are pH, Eh, temperature and SiO<sub>2</sub>, Na, K, Ca, Mg, HCO<sub>3</sub>, Cl, SO<sub>4</sub>, Fe, H<sub>2</sub>S, Al, B, NH<sub>4</sub>, Ba, F and Mn concentrations. Thus, chemical compositions of the produced fluids from the Dogger aquifer are very well-informed though, samples do not systematically cover all the operating period.

The water samples used in this study are collected between 1980s and 2010 at the wellheads of 11 production wells still in operation (Figure 2 and Table 1). The selected wells are located in the center of the Paris basin and distributed throughout the 4 groups of the Dogger geothermal operations previously described.

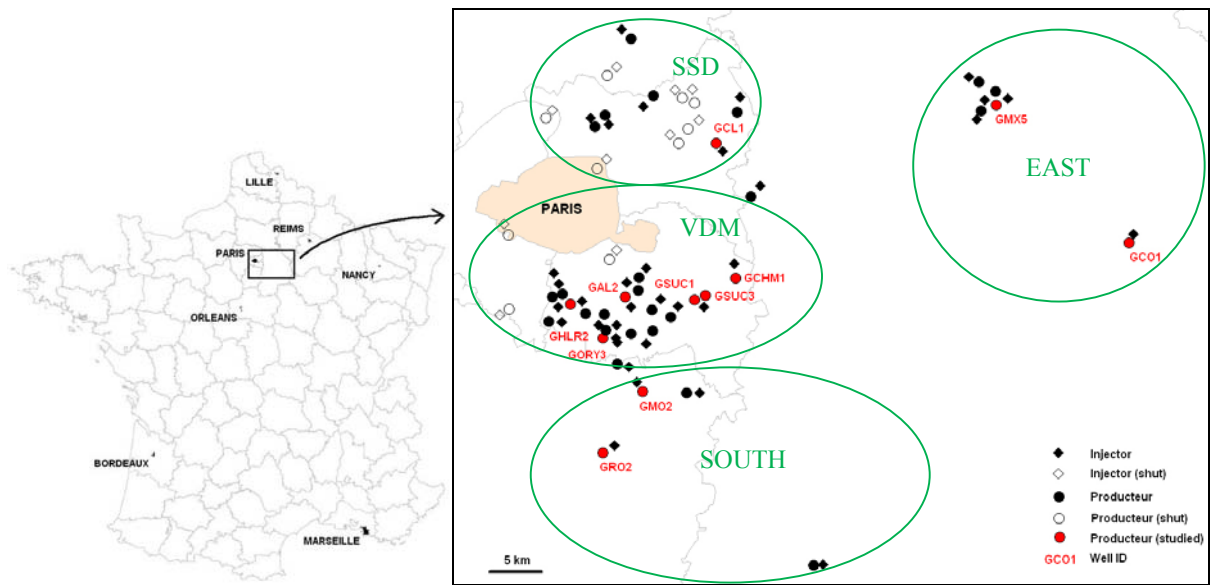


Figure 2: Location map of the sampling wells used in this study.

Table 1: Details on the production wells examined.

Operation group	Well ID	Location	X* (m)	Y* (m)	Depth(m)	Average wellhead temperature (°C)	Covered period
SOUTH	GRO2	Ris-Orangis	604229	2404572	1519	70	1985-2001 2007-2009
	GMO2	Montgeron	608158	2410624	1595	71	1997-2009
VDM	GAL2	Alfortville	606422	2419882	1620	73	1989-2010
	GCHM1	Champigny	617243	2421761	1664	75	1992-2010
	GHLR2	L'Hay-les-Roses	601009	2419187	1572	71	1991-2003 2007-2010
	GOR5	Orly	604207	2415837	?	75	2007-2010
	GSUC1	Sucy-en-Brie	613220	2419600	1671	75	1992-2008
	GSU3	Sucy-en-Brie	614318	2420030	1703.1	78	2008-2010
	CGO1	Coulommiers	655951	2425247	1941	83	1985-2010
EAST	GMX5	Meaux	642888	2438779	1792	76	1985-2007 2009-2010
	GCL1	Clichy-sous-Bois	615325	2434978	1690	70	1987-2010
*Lambert II "étendu" coordinates							

## Methodology

This study consists of temporal analyses of physico-chemical (pH, Eh, concentrations, *etc.*) and thermodynamic parameters (saturation indexes) of produced fluids.

### Temporal study of the Dogger fluids physico-chemistry

The first step of this study is dedicated to identify physico-chemical changes occurring in the Dogger fluids due to thirty years of geothermal energy exploitation. It uses the chemical analyses obtained between 1980s and 2010 from the 11 examined boreholes. All the available physico-chemical parameters are considered with a special consideration given to Ca, HCO<sub>3</sub> and Si concentrations as they are controlled by minerals sensitive to temperature changes (such as calcite, anhydrite or silica as presented on Figure 3).

### Temporal study of the Dogger fluids thermodynamic state and mineral reaction fastness

A second step is used to determine the thermodynamic state of the produced fluids over the operating period. It consists of aqueous speciation calculations performed with the geochemical code PHREEQC, the database phreeqc.dat (Parkurst and Appelo, 1999) and all the measured parameters previously detailed. We examine saturation indexes of minerals related to the Dogger context, either as primary or secondary phases, having an equilibrium constant strongly dependent on temperature (Figure 3). We especially focus on minerals with slow kinetic rates such as chalcedony (Figure 4).

The dependency of the rate constant *k* with temperature illustrated in Figure 4 is established using the following equation:

$$k_n = k_{25}^N \exp\left[\frac{-E_a^N}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \quad \text{Equation 1}$$

where  $E_a$  is the activation energy (in J/mol),  $k_{25}$  is the rate constant at 25°C,  $R$  is the gas constant (8.314 J/mol/K) and  $T$  is the temperature (in K). The indices  $N$  refer to neutral mechanism. Kinetic rate parameters used are extracted from Palandri and Kharaka (2004) and Xu *et al.* (2006) (Table 2). Dissolution and precipitation kinetic parameters are assumed equals.

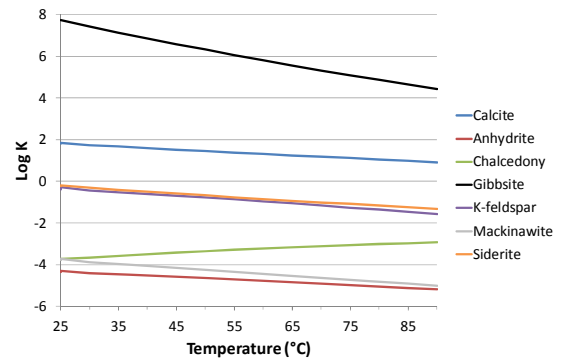


Figure 3: Variations of the equilibrium constants of the minerals examined with temperature.

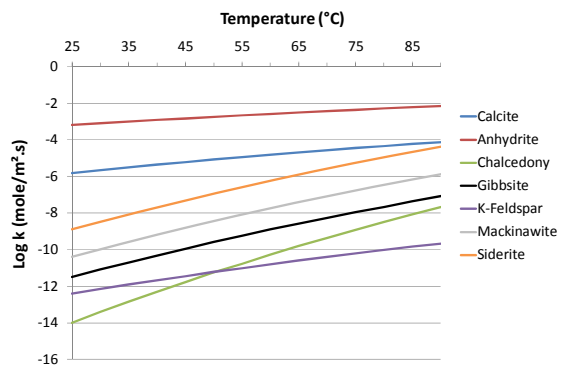


Figure 4: Dependency of rate constants of minerals examined with temperature.

Table 2: Kinetic parameters used for the calculations of the rate constants temperature dependency.

Minerals	Neutral Mechanism		Source
	log k25 [mol/m <sup>2</sup> .s]	Ea [kJ/mol]	
<b>Calcite</b>	-5.81	23.50	Palandri and Kharaka (2004)
<b>K-feldspar</b>	-12.41	38.00	
<b>Anhydrite</b>	-3.19	14.30	
<b>Chalcedony</b>	-13.99	87.60	
<b>Gibbsite</b>	-11.50	61.20	Xu <i>et al.</i> (2006)
<b>Mackinawite (as pyrite)</b>	-10.40	62.76	
<b>Siderite</b>	-8.90	62.76	

## RESULTS

All available information related to operation life events (drilling, production stop, well tubing maintenance, *etc.*) and to chemical treatments are used to interpret the operating histories examined (pH, Eh, concentrations, wellhead temperature, flow rate, *etc.*).

General tendencies of examined parameters are similar at all the studied sampling sites. To simplify, the illustrations concerned only two representative wells: GMX5 (Meaux) and GAL2 (Alfortville).

### Evolution of wellhead concentrations

Since the beginning of the geothermal exploitation, concentrations of dissolved major ions are stationary. Only dissolved sulfide and iron concentrations present large temporal variations over years (Figure 5).

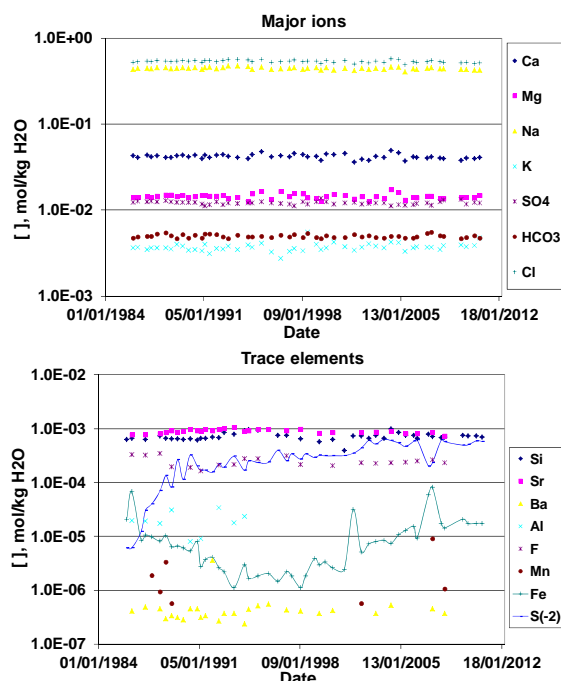


Figure 5: Temporal variations of major ions and trace elements concentrations at geothermal production wellheads – Example of the production well of Meaux (GMX5, EAST group).

At all the studied sampling sites, concentrations of dissolved sulfide progressively increase before reaching a plateau in the early 2000s (Figure 5 and Figure 6). This behavior, well-known for years, is due to the presence of sulfide-producing bacteria (SPB) in the Dogger fluid and, most often on the wells tubing, which reduce sulfates to sulfides.

Concentrations of dissolved iron decrease until 2001 (Figure 5 and Figure 6). This decline is likely due to

the progressive increase in dissolved sulfide concentrations which leads to iron sulfide precipitation on wells tubing and to the set-up of well treatment (injection of corrosion inhibitors). After 2001, the dissolved iron concentrations increase or stay stable. The rise mostly concerns geothermal operations progressively exploited at artesian flow rate (as Meaux one). Indeed, the corrosion of wells tubing, and therefore the mobilization in solution of Fe(2), is higher when the flow decreases as residence time increases.

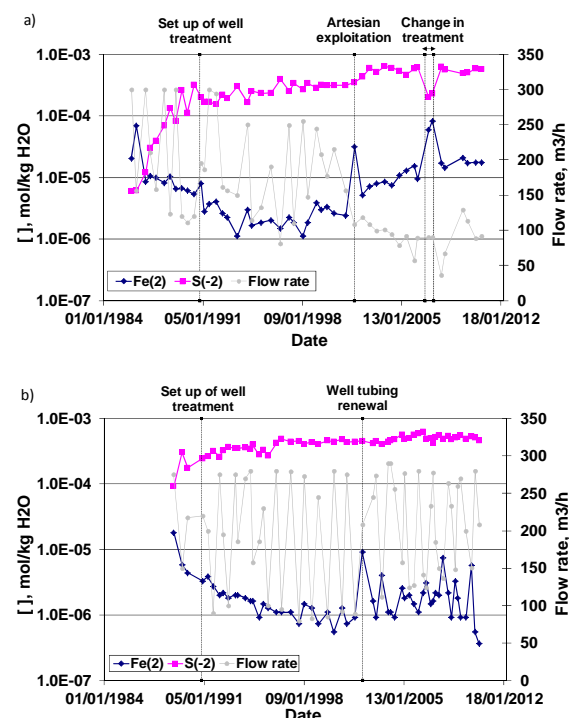


Figure 6: Temporal variations of dissolved sulfide and iron concentrations at the geothermal production wellheads – Examples of the production wells of a) Meaux (GMX5, EAST group) and b) Alfortville (GAL2, VDM group).

### pH evolution

Since the beginning of the geothermal energy exploitation, pH is quite stable in all considered produced fluids with however a small average decrease of 0.15 observed since 2001 (Figure 7 and Figure 8). Four processes can impact the pH of the geothermal fluids within the well:

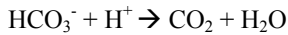
- bacterial reduction of sulfates ions to sulfides  

$$\text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{HS}^- + 2\text{O}_2$$
- well tubing corrosion  

$$\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$$
- iron sulfides precipitation  

$$x \text{Fe}^{2+} + y \text{HS}^- \rightarrow \text{Fe}_x\text{S}_y + y \text{H}^+$$

$$\text{Fe}_x\text{S}_y + z \text{HS}^- \rightarrow \text{Fe}_x\text{S}_{y+z} + z \text{H}^+$$
- and CO<sub>2</sub> degassing



But, only the deposition of iron sulfides can explain its decrease. In addition, it is possible that the pH of the Dogger formation waters has decreased since the beginning of geothermal exploitations. Actually, since their commissioning, geothermal operations of the Dogger reservoir produce huge concentrations of dissolved sulfide which are largely injected back into the reservoir. In the reservoir, these dissolved sulfides can precipitate with iron ( $\text{Fe}^{2+}$ ) and others dissolved divalent cations present in the Dogger fluid, and thus produce protons.

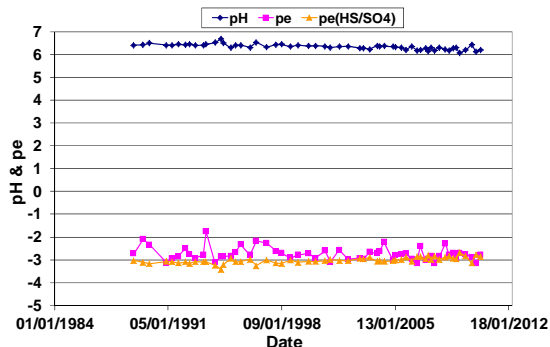


Figure 7: pH and pe evolutions – Example of the production well of Alfortville (GAL2, VDM group).

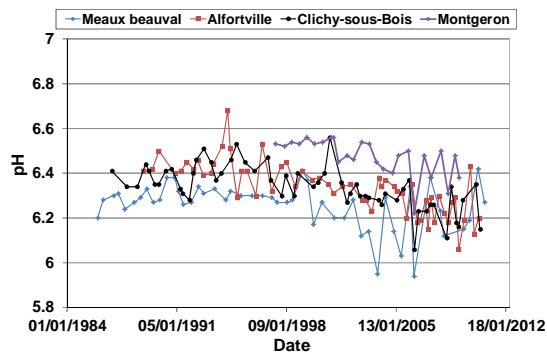


Figure 8: pH evolution.

### Evolution of the redox conditions

Since the beginning of the geothermal operation, the redox potential  $pe$  remains stable in all the sampling sites. It is about -3 and seems to be controlled by the redox couple  $\text{HS}^-/\text{SO}_4^{2-}$  (Figure 7).

### Evolution of Dogger fluid saturation state

The saturation index (SI) of calcite decreases over the exploitation period (Figure 9). Indeed, the aqueous solutions sampled between the 1980s and the early 2000s are slightly over-saturated with respect to calcite (SI around 0.38 on average) whereas those collected later are closer to equilibrium. This decrease is likely due to the decline in pH previously discussed. In addition, the saturation index of calcite is relatively unstable since 1980s. The instabilities are likely due to  $\text{CO}_2$  degassing which is an

ubiquitous phenomenon in the geothermal exploitation of the Dogger reservoir (Goyénèche *et al.*, 2005). Finally, calcite precipitation is thermodynamically feasible in the production wells over all the exploitation period. However, since the early 2000s and the decrease in pH, calcite precipitation is probably limited to  $\text{CO}_2$  degassing periods.

The saturation index of chalcedony and anhydrite are stable over the exploitation period (Figure 9). Thus, all the solutions studied are at thermodynamic equilibrium with respect to chalcedony since 1980s. Moreover, the aqueous solutions collected from wells of the EAST group are also at equilibrium with respect to anhydrite since 1980s whereas, those obtained from wells of others group are under-saturated.

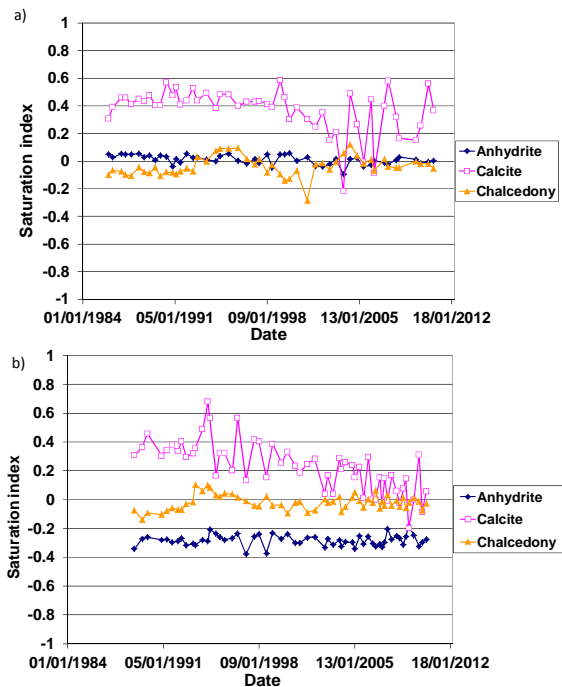


Figure 9: Saturation indexes of anhydrite, calcite and chalcedony versus time – Examples of the production wells of a) Meaux (GMX5, EAST group) and b) Alfortville (GAL2, VDM group).

The solutions examined are generally over-saturated with respect to K-feldspar, gibbsite and mackinawite (Figure 10). Thus, as discussed in a previous study by Ignatiadis *et al.* (1998), mackinawite precipitation is thermodynamically feasible on the wells tubing. The evolution of the mackinawite saturation index is strongly correlated to the variation of dissolved iron concentration. Since the early 2000s, the concentration of dissolved iron increases in few wells, especially in those exploited with artesian flow rates. Therefore, the precipitation tendency of the

mackinawite has increased in these wells since the early 2000s (Figure 11).

All the aqueous solutions studied are under-saturated with respect to siderite since 1980s (Figure 10). However, as mackinawite SI, the siderite saturation index is strongly controlled by the dissolved iron concentration. Thus, since the early 2000s, the precipitation risk of siderite has increase, in particular in the production wells under artesian conditions (as Meaux one), though it stays negligible (Figure 11).

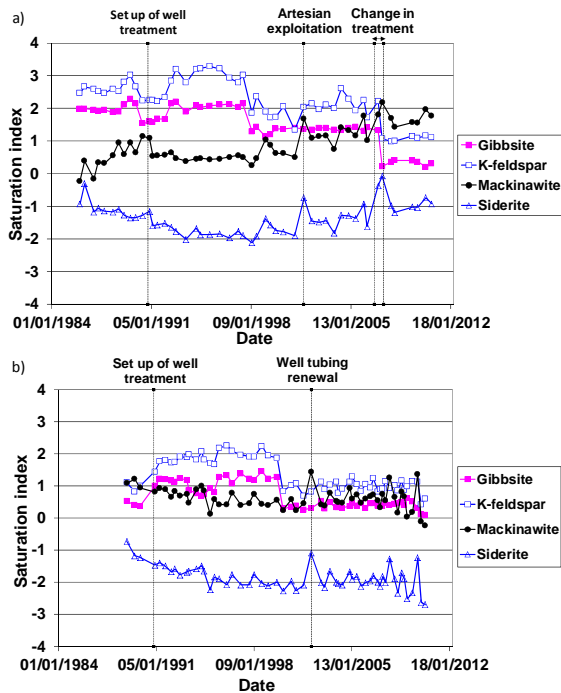


Figure 10: Saturation indexes of gibbsite, K-feldspar, mackinawite and siderite versus time – Examples of the production wells of a) Meaux (GMX5, EAST group) and b) Alfortville (GAL2, VDM group).

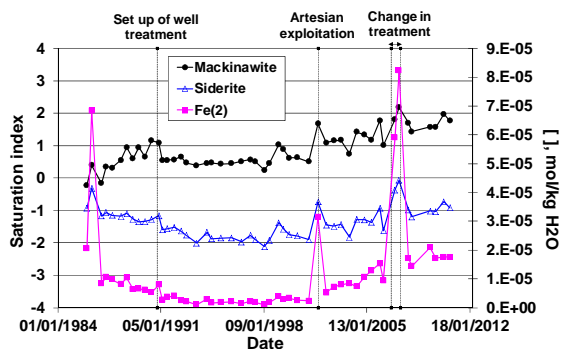


Figure 11: Comparison between the temporal evolutions of the mackinawite saturation indexes, the siderite saturation index and the dissolved iron concentrations - Examples of the production wells of Meaux (GMX5, EAST group).

## DISCUSSION & MAIN REMARKS

None of the geochemical parameters studied suggest a decline in temperature in the production well fields, though a small drop (2-3°C) has been recently measured in one of the 11 production wells studied (GAL2, VDM group). Actually, the only variations observed (dissolved sulfide and iron concentrations, mackinawite and siderite SI) are independent of temperature; they depend mostly on operational management (as flow rates, chemical treatments, etc.). Thus, it is valuable to discuss here the choice of the parameters specifically studied to detect the decrease of the temperature in the production well fields (such as Ca and HCO<sub>3</sub> concentrations). Ca and HCO<sub>3</sub> concentrations do not appear to be relevant precursors, because they depend on fast reactions (as carbonates precipitation/dissolution, Figure 4) and on pH variations. In contrast, Si concentration could be an appropriate precursor of the temperature drop, because it depends only on slow reactions (silicates dissolution/precipitation, Figure 4). However, analytical errors in the measurement of Si concentration are assumed to be about 10% in this study. Thus, the average uncertainty in Si concentration  $\Delta[\text{Si}]$  is about  $3.6 \cdot 10^{-5}$  mol/kgw for the fluids examined. This uncertainty is illustrated in **Erreur! Source du renvoi introuvable.** for the fluids produced at the production well of Alfortville (GAL2). According to Figure 13, a temperature decrease of 3 degrees of the geothermal solutions would lead to a variation of Si concentrations of about  $6 \cdot 10^{-5}$  mol/kgw. This variation is smaller than the total uncertainty on Si concentration measurement. Therefore, Si concentrations do not suggest any decline in temperature in the production well field of Alfortville operation, though a drop has been recently measured.

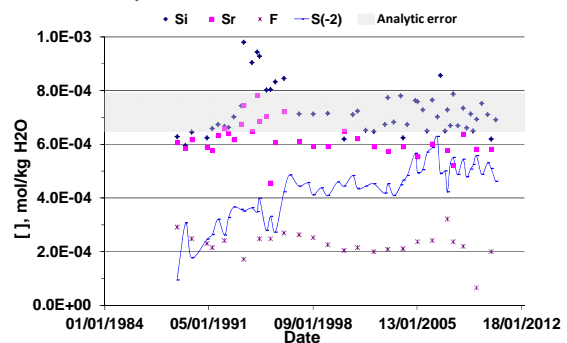


Figure 12: Illustration of the analytical errors in the measurement of Si concentrations – Example of the production well of Alfortville (GAL2, VDM group).

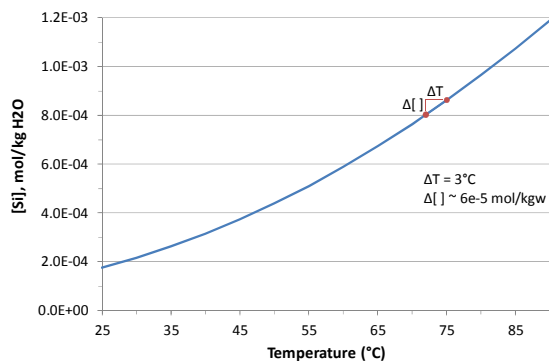


Figure 13: Solubility of chalcedony in pure water versus temperature.

Similar remarks can be made for minerals controlling Ca and HCO<sub>3</sub> concentrations of the Dogger fluids. Finally, the saturation indexes of minerals controlling the Si concentrations of the aqueous solutions, i.e. silicates and aluminosilicates, could be relevant precursors if analytical errors in measurements of chemical concentrations are sufficiently constrained.

#### **ACKNOWLEDGEMENTS**

This study was carried out within the framework of the “Gestion du réservoir du Dogger 2010” project, co-funded by the French Environment and Energy Management Agency (ADEME) and BRGM.

#### **REFERENCES**

- Azaroual, M., Fouillac, C. and Matray, J., M. (1997), “Solubility of silica polymorphs in electrolyte solutions, II. Activity of aqueous silica and solid silica polymorphs in deep solutions from the sedimentary Paris Basin”, *Chemical Geology*, 140, 167-179.
- Coudrain-Ribstein, A. and Gouze, P. (1993), “Quantitative study of geochemical processes in the Dogger aquifer, Paris basin, France”, *Applied Geochemistry*, 8, 495-506.
- Goyénèche, O., Desplan, A., Bretteville, V., Fabris, H., Menjot, A., Azaroual, M., Sbai, A., Unguemach, P., Antics, M. and Scalisi, G. (2004), “Mise en œuvre d’un système de gestion de la ressource géothermique du Dogger de la région Ile-de-France, phase 1”, BRGM report RP-52927-FR, 82p.

- Goyénèche, O., Desplan, A., Bretteville, V., Fabris, H., Menjot, A., Azaroual, M., Sbai, A., Unguemach, P., Antics, M. and Scalisi, G. (2005), “Mise en œuvre d’un système de gestion de la ressource géothermique du Dogger de la région Ile-de-France, phase 2”, BRGM report RP-53782-FR, 110p.
- Ignatiadis, I., Amalhay, A., Abou, A. and Cotiche, C. (1998), “Analyse et conséquences de la prolifération bactérienne dans les puits géothermiques du Bassin de Paris”, in: EDP Sciences (Ed.), “Biodétérioration des matériaux”, chap. 16, 231-257.
- Lopez, S., Hamm, V., Le Brun, M., Schaper, L., Boissier, F., Cotiche, C. and Giuglaris, E. (2010), “40 years of Dogger aquifer management in Ile-de-France, Paris Basin, France”, *Geothermics*, 39, 339-356.
- Michard, G. and Bastide, J., P. (1988), “Etude géochimique de la nappe du Dogger du Bassin parisien”, *Journal of Volcanology and Geothermal Research*, 35, 151-153.
- Palandri, J. L. and Kharaka, Y. K. (2004), “A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modelling”, U.S. Geological Survey Report 2004-1068.
- Parkurst, D. L. and Appelo, C. A. J. (1999), “User’s guide to PHREEQC (version 2). A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations”, *Water-Resources Investigations Report 99-4259*, 312p. Rojatz, J., Giot, D., Le Nindre, Y., M., Criaud, A., Fouillac, C., Brach, M., Menjot, A., Martin, J., C. and Lambert, M. (1989), “Caractérisation et modélisation du réservoir géothermique du Dogger, Bassin parisien, France”, BRGM report RR-30169-FR.
- Xu, T., Sonnenthal, E., Spycher, N. and Pruess K. (2006), “TOUGHREACT—A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO<sub>2</sub> geological sequestration”, *Computers & Geosciences*, 32, 145–165.