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title: **Reactive transport simulations of geochemical processes induced by the ATEs operations in the Dogger aquifer (Paris Basin)**

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ABSTRACT

A project of Aquifer Thermal Energy Storage (ATES) in the deep carbonate Dogger aquifer in the Paris Basin (France) is under development. Before effective ATES operations, this study aims to identify the geochemical impacts of a cycle of heat storage and production on the properties of the aquifer and of the geothermal fluid.

A geochemical study using scenarios of different temperature perturbations is built up in three stages of complexity using reactive transport codes PHREEQC and MARTHE-REACT. The simulation results show potential occurrences of precipitation/dissolution processes that could damage the reservoir porosity and the ATES equipments. This study was done within the framework of the "GEOSTOCAL" Project co-funded by the French National Research Agency (ANR) of the call for proposals "Stock-E".

BACKGROUND

Aquifer Thermal Energy Storage (ATES) offers a promising solution to store excess energy into the ground when available for later use when needed. A previous study revealed that Ivry-sur-Seine (Ile-de-France, France) has attractive potential for an ATES technology: an excess of heat production in summer, a relevant heat networks adapted to the winter demand and a suitable aquifer (Dogger aquifer, 1500 m deep)

(http://www.colloques-2009-anr.fr/pdf/2/STOCKE_3_GEOSTOCAL_poster.pdf).

The excess energy and the use of the stored energy are managed by the district heating network of CPCU (Compagnie Parisienne de Chauffage Urbain). The heat vehicle used in the geothermal loop is the aquifer native water. Due to the temperature variation (between 40 to 95-110°C) the consequences of the disturbance of the initial thermodynamic equilibrium between reservoir phases (water - rock) could be dramatic if they lead to reservoir porosity decrease or damaging the storage equipments (clogging/corrosion of well casings, etc.). The study of detailed geochemical processes aims to identify the geochemical reactivity changes of carbonate reservoir submitted to a cycle of ATES exploitation. This step is crucial to evaluate the scaling risks to be considered and integrated in the development of the management strategies of the system.

SITE DESCRIPTION AND ATES OPERATIONAL DETAILS

The proposed storage site is located within the city of Ivry-sur-Seine (Ile-de-France, France); near an abandoned low enthalpy geothermal doublet. The targeted aquifer is the oolitic limestones of the Dogger reservoir which are situated approximatively 1500 m depth. Its main physical and petrophysical characteristics, derived from drilling reports of the abandoned geothermal doublet, are listed in Table 1.

Table 1. Physical and petrophysical properties of the oolitic limestones aquifer.

Depth	~ 1470	m (vertical)
Productive thickness	10	m (vertical)
Temperature	65	°C
Porosity	15	%
Intrinsic permeability	3.5	D
Formation heat conductivity	2.5	W/m/K
Wall heat conductivity	2	W/m/K
Longitudinal thermal dispersivity	20	m
Transverse thermal dispersivity	10	m
Salinity	18.5	g/L
Reservoir pressure	~ 160	kg/cm ²

No cutting sample is available within or close to the storage area. Therefore, the mineralogy used for the modelling (Table 2) is based on the literature (Rojaz et al., 1989 and Azaroual et al., 1997). It consists mainly of carbonates (80% in mass fraction) with some silicates. Minerals allowed to precipitate as secondary phases during the ATEs operations are also introduced (with a mass fraction as 0).

Table 2. Oolitic limestones mineralogy and minerals allowed to precipitate in the reservoir during the ATEs operations.

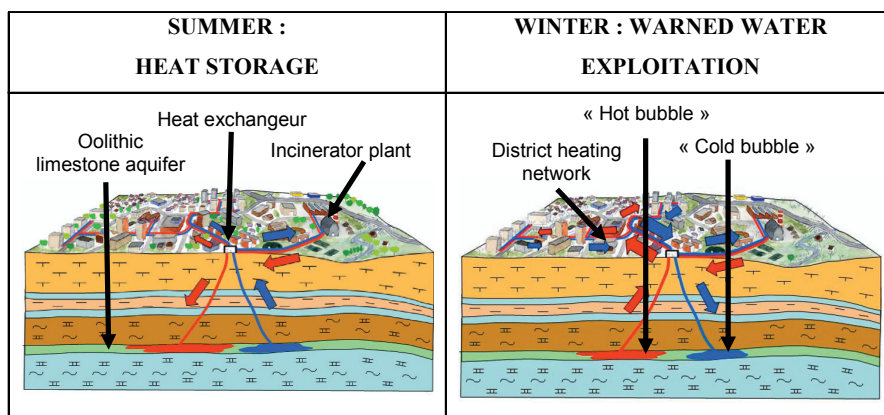
	Mass percent	Minerals introduced in the model		Mass percent	Minerals introduced in the model
Calcite	70	Calcite	Anhydrite	0	Anhydrite
Disordered dolomite	10	Dolomite-dis	Chalcedony	0	Chalcedony
Quartz	5	Quartz,alpha	Magnesite	0	Magnesite (Natur)
Albite	5	Albite_low	Gibbsite	0	Gibbsite
K-Feldspar	5	Microcline	Kaolinite	0	Kaolinite
Barite	5	Barite	Illite	0	Illite-Al
			Smectite	0	BeidelliteNa

In contrast, several samples of the formation water were taken during the geothermal exploitation of the doublet. Thus, the water sample collected in the geothermal production well (GIV2) for the Rojaz et al. (1989) study is selected as a representative for the oolitic limestones reservoir. However, in order to overcome the unreliability of the aluminium concentrations data, this water is equilibrated with albite (one of the supposed Dogger mineral) by means of geochemical software (*i.e.* PHREEQC). The physical chemical characteristics of the native fluids used for the modelling are given in Table 3.

Table 3. Initial composition of the formation water.

T (°C)	65	Cl	3.04E-01
pH <i>in situ</i>	6.29	K	2.35E-03
Alcalinité	5.68E-03	Li	2.79E-04
Al	3.91E-08	Mg	8.26E-03
B	1.24E-03	Mn	1.86E-05
Ba	1.41E-06	Na	2.60E-01
Br	8.18E-04	S	8.71E-03
C	8.97E-03	Si	5.76E-04
Ca	2.38E-02	Sr	4.87E-04

The considered ATEs technology operates through two artificial heat sources, a “cold bubble” and a “hot bubble”, generated and regenerated in the Dogger aquifer using geothermal wells. During the heat storage phase (summer season), water is extracted from the cold area, warmed by transfer of excess energy from an incinerator plant (heat exchanger) and finally re-injected into the warm storage area (Figure 1). Then, during the winter season (heat exploitation phase), the hot water is extracted, transferred in the heat exchanger to supply the district heating network. To close the geothermal loop, the cooled water down is finally re-injected into the cold storage area.

**Figure 1.** Sketch of the ATEs technology examined (courtesy of IFP).

MODELLING APPROACH

The carried out modelling method involves three stages of analysis: (1) equilibrium batch modelling; (2) kinetic batch modelling and (3) a 1D reactive transport model integrating thermo-kinetic processes of mineral dissolution/precipitation reaction. The three approaches focus on the geochemical changes occurring both in the wells and in the “bubbles”. The modelling is performed using the database Thermoddem (Blanc et al., 2009) and the numerical codes PHREEQC (Parkurst, Appelo, 1999) for the two first stages and MARTHE-REACT for the last stage.

Two scenarios are used in each of the stages. Both concern the first geothermal loop of the ATEs operations and differ by the heat storage temperature (Table 4).

Table 4. Operational details of the two scenarios tested differing by the heat storage temperature (95 or 110°C).

	Heat storage phase (summer season)	Warmed water exploitation phase (winter season)	Units
Duration	17	31	week
Flow rate	300	165	m ³ /h
Temperature	95 / 110	40	°C

In the stages two and three, kinetic rate laws of the following form (equation (1)) are used for mineral dissolution and precipitation (Palandri and Kharaka, 2004):

$$r_n = \pm m_n k_n A_n \left| 1 - \Omega_n^\theta \right|^\eta \quad (1)$$

Parameters m , k and A are the instantaneous mass of mineral n (in mol), the rate constant (in mol/m²/S) and the reactive surface area (in m²/mol), respectively. Ω_n represents the saturation index of the mineral n ($\Omega_n = Q/K$). θ and η are two empirical positive parameters assumed equal to 1 (Palandri and Kharaka, 2004).

Dependency of k_n with temperature and pH is given by:

$$k_n = k_{25}^N \exp\left[\frac{-Ea^N}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] + k_{25}^A \exp\left[\frac{-Ea^A}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] a_H^{n_A} + k_{25}^B \exp\left[\frac{-Ea^B}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] a_H^{n_B} \quad (2)$$

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), T is the temperature (in K) and a_H is the activity of H⁺. The indices N , A and B refer to neutral, acid and alkali mechanisms, respectively.

Precipitation rate laws only consider the neutral mechanism.

The parameters of the precipitation kinetics are assumed equal to the parameters of the dissolution kinetics. Moreover, the precipitation of feldspar (albite and K-feldspar) and then of quartz are inhibited in favour of the precipitation of clays and chalcedony respectively.

The values of the kinetic parameters (Table 5) and the reactive surface areas used for the modelling come from the literature.

Table 5. Kinetic parameters used for the modelling. The mechanisms for which the values are in grey are negligible at the pH conditions simulated. Thus, they are not considered in the simulations.

	Acid Mechanism			Neutral Mechanism		Carbonate Mechanism		
	log k25 [mol/m ² /s]	Ea [kJ/mol]	n [-]	log k25 [mol/m ² /s]	Ea [kJ/mol]	log k25 [mol/m ² /s]	Ea [kJ/mol]	n [-]
Calcite	-0.30	14.40	1.000	-5.81	23.50	-3.48	35.40	1.000
Disordered dolomite	-3.19	36.10	0.500	-7.53	52.20	-5.11	34.80	0.500
Quartz	–	–	–	-13.99	87.60	–	–	–
Albite	-10.16	65.00	0.457	-12.56	69.80	-15.60	71.00	-0.572
K-Feldspar	-10.06	51.70	0.500	-12.41	38.00	-21.20	94.10	-0.823
Barite	-6.90	30.80	0.220	-7.90	30.80	–	–	–
Anhydrite	–	–	–	-3.19	14.30	–	–	–
Chalcedony (as quartz)	–	–	–	-13.99	87.60	–	–	–
Magnesite	-6.38	14.40	1.000	-9.34	23.50	-5.22	62.80	1.000
Gibbsite	-7.65	47.50	0.992	-11.50	61.20	-16.65	80.10	-0.784
Kaolinite	-11.31	65.90	0.777	-13.18	22.20	-17.05	17.90	-0.472
Illite	-11.71	46.00	0.600	-15.05	14.00	-12.31	67.00	0.600
Beidellite (Smectite)	-10.98	23.60	0.340	-12.78	35.00	-16.52	58.90	-0.400

RESULTS AND DISCUSSION

The equilibrium batch modelling highlights that the ATEs operations may induce clogging problems due to the following trend:

- Calcite and calcium sulfate tend to precipitate when the fluid is heated and dissolved when the fluid is cooled down. Thus, these minerals may precipitate before and after injection of the fluid in the “hot bubble” and dissolve in the “cold bubble”.
- Chalcedony, gibbsite and clays (kaolinite, illite and smectite) may precipitate when the fluid reaches a temperature of 40-50° C. These minerals are likely to precipitate before and after injection into the “cold bubble”.

The second step of the modelling involves kinetic reactions in contrast to previous equilibrium batch models. Results of the kinetic batch modelling are summed up in Table 6 and in Table 7. These tables present the consequences of the ATEs operations on the wells and on the “bubbles” (near wellbore) in terms of precipitation or dissolution risk which is illustrated by the amount of mineral that could precipitate or dissolve.

Table 6. Processes of precipitation and dissolution involved during the heat storage phase.

	Amount (order of magnitude) precipitated or dissolved in moles/kgw		Risk: precipitation dissolution	(+) (-) (0)
	Hot well	Hot bubble		
Calcite	10^{-12}	10^{-4}		+
Disordered dolomite	$10^{-10} - 10^{-8}$	10^{-4}		+
Quartz	0.0	10^{-5}	0	-
Albite	0.0	10^{-5}	0	-
K-Feldspar	0.0	10^{-5}	0	-
Barite	0.0	10^{-7}	0	-
Magnesite	10^{-14}	10^{-13}		+
Chalcedony	0.0	0.0	0	
Anhydrite	$10^{-13} - 10^{-11}$	$10^{-14} - 10^{-4}$		+
Beidellite	0.0	10^{-5}	0	+
Illite	0.0	10^{-14}	0	+
Kaolinite	0.0	10^{-14}	0	+
Gibbsite	0.0	$10^{-19} - 10^{-18}$	0	+

Table 7. Processes of precipitation and dissolution involved during the heat exploitation phase.

	Amount (order of magnitude) precipitated or dissolved in moles/kgw		Risk: precipitation dissolution	(+) (-) (0)
	Cold well	Cold bubble		
Calcite	0.0	10^{-4}	0	-
Disordered dolomite	0.0	10^{-4}	0	-
Quartz	0.0	0.0	0	
Albite	0.0	10^{-11}	0	-
K-Feldspar	0.0	0.0	0	
Barite	10^{-14}	10^{-6}		+
Magnesite	0.0	0.0	0	
Chalcedony	10^{-20}	10^{-18}		+
Anhydrite	0.0	0.0	0	
Beidellite	10^{-7}	$0.0 - 10^{-15}$		+
Illite	10^{-14}	0.0	+	0
Kaolinite	10^{-16}	0.0	+	0
Gibbsite	$10^{-19} - 10^{-17}$	0.0	+	0

The quantities involved in the wells are negligible except for the beidellite (risk of precipitation, up to 10^{-7} mol/kgw). In contrast, in the “bubbles”, amount of mineral that could precipitate/dissolve are more significant (up to 10^{-4} mol/kgw). Feldspars, quartz and barium sulfate dissolve in the “hot bubble” while carbonates, calcium sulfate and clays (specifically beidellite) precipitate. Carbonates (calcite and disordered dolomite) and albite dissolve in the “cold bubble” whereas barium sulfate and beidellite precipitate. In each “bubble”, the formation of clays is related to the feldspars alteration that notably releases Al^{3+} (Figure 2). Finally, during the first ATEs operations cycle, both in wells and “bubbles”, most of the secondary phases could precipitate in small quantity ($< 10^{-10}$ mol/kgw) except beidellite and calcium sulfate that would precipitate in larger quantities. The kinetic batch modelling confirms the results of the previous equilibrium study. Additionally, they inform of the potential reaction paths and allow distinction between short term reactions (as calcite and dolomite reactions) and long term reactions (as aluminosilicate reactions). The last stage of the study (reactive transport modelling) is in process. The results of this undergoing work will be detailed during the conference.

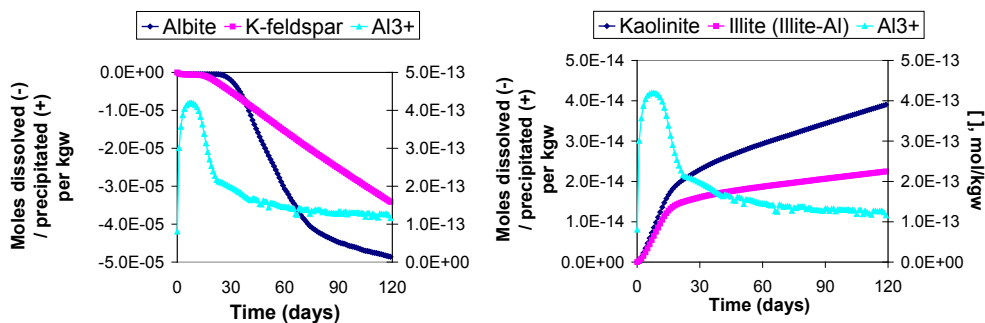


Figure 2. Evolution of Al³⁺ concentration and amounts precipitated and dissolved of feldspars and clays (kaolinite and illite) during the heat storage phase at 95°C as a function of time (Kinetic batch modelling approach).

CONCLUSION

Reactive modelling study simulating different scenarios of temperature perturbation highlights some potential clogging risks (*i.e.* precipitation of carbonate, calcium sulfate and clays minerals in the “hot bubble” and precipitation of barium sulfate and clay minerals in the “cold bubble”). Once the last stage will be completed, operating rules of the ATEs technology will be defined allowing operators to plan out management strategies for future ATEs sites in the Dogger aquifer.

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