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GRANITE-SALINE FLUID INTERACTIONS IN A DYNAMIC EXPERIMENTAL SYSTEM AT 200 DEGREES C AND 50 BARS

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ABSTRACT

Granite dissolution experiments were performed in a dynamic system at 200 ºC and 50 bars on fresh granite from Soultz-sous-Forets (NE of France). Two different saline fluids were used for these experiments: about 1 and 10 g·l^{-1} for the low salinity (LS) fluid and high salinity (HS) fluid, respectively.

SEM observations after the experiments showed that K-spars and plagioclase were the most reactive granite minerals with the LS and the HS fluids, respectively. The precipitation rate was high whatever the salinity of the percolative fluids, but the precipitates were of different types: mainly zeolite for the LS fluid and illite for the HS fluid. Measurements of the outlet fluid concentrations of some relevant elements have helped to identify the main chemical processes that occur between granite and hot saline fluids at such a high temperature and pressure.

The experimental results (morphological observations and chemical monitoring of the outlet fluid) provided constraints for a geochemical model that was used to simulate the reaction pathway of the experiments. In this study, the geochemical code EQ3NR (Wolery, 1992) was used to estimate the saturation state of the outlet fluids with granite minerals and a number of potentially precipitating minerals.

1. INTRODUCTION

In a Hot Dry Rock system (HDR), there are always some saline fluids that initially fill up the porosity of the rock. The chemical composition of these fluids is suspected to strongly affect the Water-Rock interactions (WRI) during the deep circulation of water between the injection and production wells. Recently, several studies have been conducted to improve the knowledge of the origin and evolution of these saline brines in crystalline rocks. This topic has been studied for HDR research projects (Milodowski et al, 1989) as well as for the storage of nuclear wastes in deep granitic environments (Andrew and Fontesís work at Stripa in Sweden; in Fritz, 1997).

In the work reported herein, several evaluations of WRI were conducted on granite from Soultz-sous-Forets (NE of France), the candidate site for the future European Hot Dry Rock geothermal heat exchanger, in order to investigate chemical reactions at a depth of 3000m. Experiments have also been carried out at the National Institute for Resources and Environment (NIRE), in Japan.

As the natural formation fluids in Soultz deep reservoir are very saline (~100 g·l^{-1}), the experiments were conducted with saline fluids in order to simulate the interactions that occur in that natural environment. Two different saline fluids were used:

1) A low salinity fluid (~400 mg·l^{-1} of Cl = less than 1% of the salinity of the natural brine), in order to estimate the influence of a small modification of the chemical composition of the circulating fluid.
2) A high salinity fluid (~5000 mg·l^{-1} of Cl = around 10% of the salinity of the natural brine), in order to more nearly simulate the natural environment at Soultz.

Another set of experiments carried out with distilled water under identical experimental conditions has already been completed and published (Plagnes et al, 2000, submitted). The comparison of these two sets of experiments allows a better understanding of the influence of the circulating fluid chemical composition on the evolution of the reservoir. In addition, our experimental work could provide some new data for the study of the processes, which create natural hydrothermal brines. Indeed, in addition to many other processes, WRI seem to be significantly involved in determining the geochemical composition of these fluids.

2. METHODS

2.1. Experimental apparatus

Laboratory experiments were conducted in an autoclave (plug-flow type), configured as a dynamic system (Figure 1). In this apparatus, the storage reservoir for the injection fluid is closed by a piston maintained by Ar gas at the experimental conditions in order to keep the fluid under stable temperature and pressure and to prevent contact with the ambient atmosphere. The fluid is circulated through the system using a high-pressure pump (0.01-9.99 ml·min^{-1}).

The percolation cell, filled with crushed rock or minerals, is a titanium cylinder (D=11mm, L=100mm). The fluid reaches the experimental temperature (<350 ºC) in the autoclave before percolating through the reactive cell. The temperature inside the cell is expected to be constant. The pressure and temperature inside the autoclave are recorded.

2.2. Starting materials

The experiments were carried out on crushed samples of fresh Soultz granite. Descriptions of the mineralogy and chemistry of this rock are presented in Tables 1 and 2. The petrography of cored samples from the GPK1 borehole has been described by Genter (1989), Traineau et al. (1991), Genter and Traineau (1992), and Ledéert (1993).

2.3. Experimental procedure

Two experiments were carried out with 2 different saline fluids according to the procedure described in Plagnes et al. (2000, submitted).

Based on the size of the cell, the instantaneous W/R mass ratio was calculated to be about 0.44-0.5. The experiments were performed over a period of 11 days at 200 ºC, which represents the temperature of the Soultz HDR reservoir at a depth of 5000m. Hydrostatic pressure was maintained at about 50 bars and the flow was 0.1ml·min^{-1}, corresponding to a mean advective speed of 2.52m·day^{-1}. Two different fluids (LS : low salinity and HS : high salinity) were percolated through the column. Table 3 gives the chemical composition of these fluids. The concentration of the high salinity fluid was about 1/10 the salinity of the natural brines found in the Soultz reservoir. The chloride content (around 5000 mg·l^{-1}) was the highest concentration that could be used without modification of the experimental equipment. Two complementary approaches were used to investigate the chemical reactions of dissolution and precipitation that occurred inside the column.

a) Chemical analysis of the outlet fluid was performed at the NIRE. Electric conductivity, pH and alkalinity were measured at the moment of sampling. Ca, Na K, Li, SO_4 and Cl were determined by ion chromatography. Si, Mg, Sr, Fe, Al, B, Ba, Zn, Mn, Li, Na, K and Ca were determined by ICP emission plasma spectrometry of acidified samples.
b) The mineral samples were observed using Scanning Electron microscopy at the Geological Survey of Japan before and after the experiments in order to evaluate morphological changes.

3. RESULTS and DISCUSSION

3.1. Morphological changes

The minerals contacted with the saline fluids show completely different features 1) compared to the experiments with pure water and 2) between the low and the high salinity fluids. Figure 2 shows several SEM photos of the weathered surfaces of the minerals and precipitates.

K-feldspars show the greatest degree of reaction with the LS fluid. Dissolution features are very strong and precipitation rate is largely higher than with pure water. Photo 2a shows the surface of K-spar almost completely covered by precipitates. Different kinds of precipitates can be distinguished, the more abundant being zeolite, but with albite and smectite also present. With the HS fluid (SEM photo not shown), the dissolution was as intense as for the LS fluid but the precipitates were mainly illite and albite.

Plagioclase presents an alteration (dissolution features and precipitates) less intense with the LS fluid than with pure water but it is the most intensively altered mineral with the HS fluid. In that case, the surfaces of plagioclase indicate a very highprecipitation rate of illite. Photo 2b shows that illite is concentrated in the etch pits arising from the earlier dissolution of plagioclase surfaces.

Concerning *quartz*, the alteration was more intense with the LS fluid. Typical features of dissolution controlled by the crystallography of the mineral are observed and they are more intensive with the saline fluids than with pure water. In addition, there are more precipitates on the surface of the mineral, especially for the LS fluid experiment (Photo 2c).

For *biotite*, dissolution seems to have been more active with saline fluids than with pure water even through the surfaces of the minerals are not so damaged and the precipitation rate not so high as with the other minerals examined (Photo 2d).

Finally, the study of the morphological changes of the minerals showed that the extent of the chemical reactions was greater with the LS fluid than with the HS fluid. The precipitation rate was particularly high with both saline fluids. While illite was the most important precipitate with HS fluid and pure water, other secondary mineral precipitates, primarily zeolite but also albite and smectite, were found in the LS fluid experiment.

3.2. Geochemistry of the outlet fluid

Only the temporal evolution of pH and contents of Si and Al are considered within the framework of this communication because they were not added to the system in the percolative fluid. These chemical data are presented in Figure 3 in concentration-time form and compared to data from an experiment conducted previously with distilled water (Plagnes et al., 2000, submitted).

While the *pH* increased from 7 to 8.2 (at 25°C) with the LS fluid (it reached 9.2 with distilled water), it exhibited a completely different behavior with the HS fluid, decreasing continuously from 6.5 to 5.5. This different behavior shows clearly that different mineral associations and precipitations may occur with variations in the initial composition of the percolative fluid. In the case of the LS fluid, the high pH caused the precipitation of zeolite minerals, since zeolite is a mineral characteristic of basic environments. On the other hand, precipitation of illite minerals was induced by the lower pH of the HS fluid.

Si concentration exhibited almost the same behavior at both salinities, but was higher for the distilled water experiments (around 40 mg·l^{-1}) compared to the LS and HS fluids experiments (33 to 30 mg·l^{-1} respectively). These contents are still low compared to the content which should be reached at equilibrium with quartz at 200°C in distilled water ($\text{Si} = 102 \text{ mg·l}^{-1}$). They reflect the high rate of precipitation of alumino-silicate minerals.

Al concentration showed different trends for the experiments conducted with distilled water and the saline fluids. While the concentration increased continuously with distilled water, it decreased with the saline fluids. In addition, while the values reached high concentrations ($2\text{-}8 \text{ mg·l}^{-1}$) with distilled water, they showed very low concentrations with saline fluids ($0.4 - 0.7 \text{ mg·l}^{-1}$). This strong difference shows that the precipitation of alumino-silicate secondary minerals is highly favored by the presence of alkaline elements in the percolative fluid, even at a low concentration (LS fluid).

3.3. Modeling approach

The mineralogical observations as well as the geochemical analyses of the outlet fluid provide important information to impose constraints on kinetic and thermodynamic models of the experimental system. The EQ3NR calculation code has been used at the BRGM. The EQ3NR model and its constraints are described in Azaroual and Fouillac (1997).

In this study, the saturation indexes of several potentially precipitating minerals were calculated for the two saline fluid experiments as well as for distilled water experiment. The results are presented in Table 4. For each experiment, two samples of fluid taken at the outlet of the test cell were analyzed. These data show the deviations of the measured concentrations of a number of minerals the equilibrium concentrations calculated with the model.

The first observation is that all initial main minerals (Table 1) were not present in equilibrium concentration in the outlet fluids for any of the experiments (saturation index values < 0.0). Consequently, these minerals would be expected to continue to dissolve even at the end of the reaction cell.

In general, it appears that the mineral dissolution results were very different depending on the salinity of the fluids involved. Boehmite, prehnite, mesolite, muscovite and scolecite minerals were over-saturated with respect to distilled water (DW experiment). The EQ3NR calculations suggest an equilibrium of the DW fluids with a Ca-Mg saponite and a clinozoisite. For the LS fluid experiment, prehnite and calcite minerals had a tendency to reach a local chemical equilibrium. Equilibrium with two solid solutions including grossular - andradite and Ca-Sr carbonate seem to have been achieved. Finally, boehmite, hematite and magnetite minerals were over-saturated with respect to the HS fluid. Smectite dominated by Ca, Mg and Na end members is predicted to be in equilibrium with the HS experiment fluids.

The *saturation indexes of quartz* was always negative, showing that the time-invariant silica concentrations correspond to a stationary state which was reached at the end of all the experiments.

Even if a poor agreement is obtained between observations and thermodynamic calculations, many characteristics of HDR system evolution have been identified. The nature of the precipitates was completely different for each of these 3 experiments showing the importance of the initial composition of the percolation fluid on the minerals associations and the chemical composition of the fluids after percolation.

The mineralogical observations showed that the DW system allowed precipitation of alumino-silicates (prehnite and mesolite) but the albite was not saturated. This discrepancy is probably due to the fact that in Soultz granite, the albite is an end member of the plagioclase (albite-84 – anorthite-16). The illite results (precipitates observed) contrasted with the muscovite (more stable at high temperature) as predicted by EQ3NR calculations. This interpretation is also valid for the HS experiment. In the LS experiment the dissolution/ precipitation due to the WRI is less intense as shown by the morphological and mineralogical study.

On the other hand, carbonates and some unexpected minerals (i.e. epidote, garnet, saponite, carbonates, not indicated in Table 4) are nearly in equilibrium with all or some of outlet fluids even through no precipitation of these species was observed. Thermodynamic model results reveal the limitation of the mineralogical observations. It is probably that traces of the above phase were precipitated but could not be detected.

A more detailed modeling study will be undertaken (Azaroual et al., in prep.) to further constrain these systems (DW, LS and HS) in order to elucidate the major mechanisms in each experiment. The combination of experimental study via field observations and numerical modeling will allow the optimization of the initial fluid composition to be injected to ensure the economic viability of HDR projects.

4. CONCLUSION

The experiments presented in this communication provided new information about reactant and product mineral phases, as well as changes in the chemistry of the outlet fluids. The observed WRI were dominated by dissolution processes due to the short residence time of the fluids within the experimental apparatus. Morphological observations showed that K-spars and plagioclase were the most reactive minerals depending of the salinity of the percolation fluid. The produced mineral phases were mainly zeolite for the LS fluid, and illite for the HS fluid and distilled water experiments. The Si content and saturation indexes of quartz show that the chemical reactions were still far from the equilibrium state in respect to quartz at 200 degrees C for all the granite minerals.

The first results of the modeling approach confirmed that the potentially precipitating minerals are completely different for each of the three experiments, showing that mineralization is closely related to the initial composition of the percolation fluid. Even small modifications of the chemical contents of the fluid may induce strong differences in the evolution of the mineral associations and precipitates.

The reaction-path modeling work is still in progress. More detailed modeling results will be presented at the congress.

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REFERENCES

Azaroual, M. and Fouillac, Ch. (1997). Experimental study and modelling of granite-distilled water interactions at 180°C and 14 bars. *Applied Geochemistry*, 12: 55-73.

Fritz, P. (1997). Saline groundwater and brines in crystalline rocks: the contribution of John Andrews and Jean-Charles Fontes to the solution of a hydrogeological and geochemical problem. *Applied Geochemistry*, 12, 851-856.

Genter, A. (1989). Géothermie Roches Chaudes Séches : le granite de Soultz-sous-Forêts. Fracturation naturelle, altérations hydrothermales et interaction eau-roche. *PhD Thesis, University of Orléans*, 201 p.

Genter, A. and Traineau H. (1992). Borehole EPS-1, Alsace, France : preliminary geological results from granite core analyses for Hot Dry Rock research. *Scientific Drilling,* 3: 205-214.

Ledéert, B. (1993). Fracturation et paléocirculations hydrothermales. Application au granite de Soultz-Sous-Forêts. *PhD Thesis, University of Poitiers*, 219p.

Milodowski, A., Savage, D., Bateman,K., Hugues, C.R. (1989). The precipitation of solids from potential heat exchange fluids for use in HDR geothermal system in granite. *Geothermics,* 18, (1-2), 233-240.

Pauwels, H., Criaud, A., Vuataz, F.D., Brach, M., Fouillac, Ch. (1991). Uses of chemical tracers in HDR reservoir studies. *Geotherm.Sci. & Tech*., Vol. 3 (1-4), 83-103.

Plagnes, V., Matsunaga, I., Azaroual, M., Aquilina, L., Tao, H., Fujimoto, K. (1999). Granite-distilled water interactions in a dynamic experimental system at 200 degrees C and 50 bars. *Submitted to Chemical Geology*.

Traineau, H., Genter, A., Cautru, JP., Fabriol, H., Chevremont, P. (1991). Petrography of the granite massif from drill cutting analysis and well log interpretation in the geothermal HDR borehole GPK1 (Soultz, Alsace, France). *Geotherm. Sci. & Tech*., **3,** (1-4), 1-29.

Wolery T.J. (1992) EQ3NR, A computer program for geochemical aqueous speciation- solubility calculations: theoretical manual, user's guide and related documentation (Version 7.0). UCRL-MA-110662-PT-I, Lawrence Livermore National Laboratory, Livermore, California, pp. 246.

Table 1: Origin and mineralogy of the Soultz fresh granite

Borehole	Core	Depth	Grain size	Mineralogy
GPK1	K20	1995m	1-2mm	*Main minerals :* quartz, porphyritic K-feldspar, plagioclase, biotite *Minor components :* metal oxides, amphiboles, sphenes, apatite, zircon…

Table 2 : Chemical composition of the fresh granite used for experiments

SiO_2 (wt%)	65.91	**Sr (ppm)**	366
TiO_2	0.29	**Rb**	173
Al_2O_3	17.06	**Ba**	1133
Fe_2O_3	0.72	**Li**	51
FeO	2.08	**F**	748
MgO	1.74		
CaO	2.05		
MnO	0.09		
Na_2O	4.13		
K_2O	4.09		
P_2O_5	0.07		
H_2O(+)	1.42		
H_2O(-)	0.06		

Table 3: Chemical composition at 25°C of the two saline fluids used for the experiments
*composition of the natural brine of Soultz reservoir is from Pauwels and al. (1991).

	Low Salinity fluid		**High Salinity fluid**	
	mol/kgH_2O	**% of natural brine***	mol/kgH_2O	**% of natural brine***
NaCl	0.001914	0.16%	0.1152	10.01%
$CaCl_2$	0.00311	1.86%	0.0157	9.98%
$CaSO_4$	0.000019	0.83%	-	-
KCl	-	-	0.0079	10.00%
$MgCl_2$	-	-	0.00058	10.08%
$SrCl_2$	-	-	0.00029	5.65%

Table 4: Saturation indexes of a non-exhaustive list of potentially precipitating minerals. The calculated in situ pH values (at 200°C) are 7.71 – 7.73 (DW), 6.74 –6.76 (LS), and 5.38 – 5.53 (HS). (DW = Distilled Water experiment, LS and HS: Low Salinity and High Salinity fluids)

	Albite	**Anhydrite**	**Annite**	**Barite**	**Boehmite**	**Calcite**	**Gibbsite**	**Illite**	**K-feld**	**Hematite**
DW	-1.88,	-4.34,	<-10.0,	-3.90,	0.15,	-0.93,	-0.93,	-1.34,	-1.09,	<-10.0,
	-1.80	-4.28	-1.01	-3.60	0.20	-0.80	-0.87	-1.28	-1.00	<-10.0
LS	-3.30,	-1.44,	<-10.0,	-2.80,	-0.84,	-0.02,	-1.87,	-3.95,	-2.59,	<-10.0,
	-3.26	-1.00	<-10.0	-2.75	-0.79	0.01	-1.81	-3.84	-2.54	<-10.0
HS	-2.12,	-3.55,	-2.94,	<-10.0,	0.05,	-3.90,	-0.97,	-2.17,	-1.91,	0.41,
	-1.32	-3.41	-1.36	<-10.0	0.71	-2.21	-0.32	-0.45	-1.11	1.56

	Magnetite	**Mesolite**	**Muscovite**	**Phlogopite**	**Prehnite**	**Quartz**	**Scolecite**	**Strontianite**	**Zoisite**
DW	<-10.0,	0.40,	0.02,	-0.70,	0.35	-0.45	0.63,	-0.73,	-0.02,
	<-10.0	0.47	0.07	-0.63	0.45	-0.44	0.65	-0.67	-0.01
LS	<-10.0,	-1.13,	-3.40,	-2.02,	0.38,	-0.51,	-0.42,	-2.45,	-0.98,
	<-10.0	-1.10	-3.26	-1.96	0.41	-0.50	-0.35	-2.44	-0.90
HS	-0.06,	-0.68,	-0.95,	-3.18,	-2.43,	-0.50,	-0.93,	-3.84,	-2.91,
	1.89	0.75	1.16	-0.95	-1.02	-0.49	-0.44	-3.21	-0.84

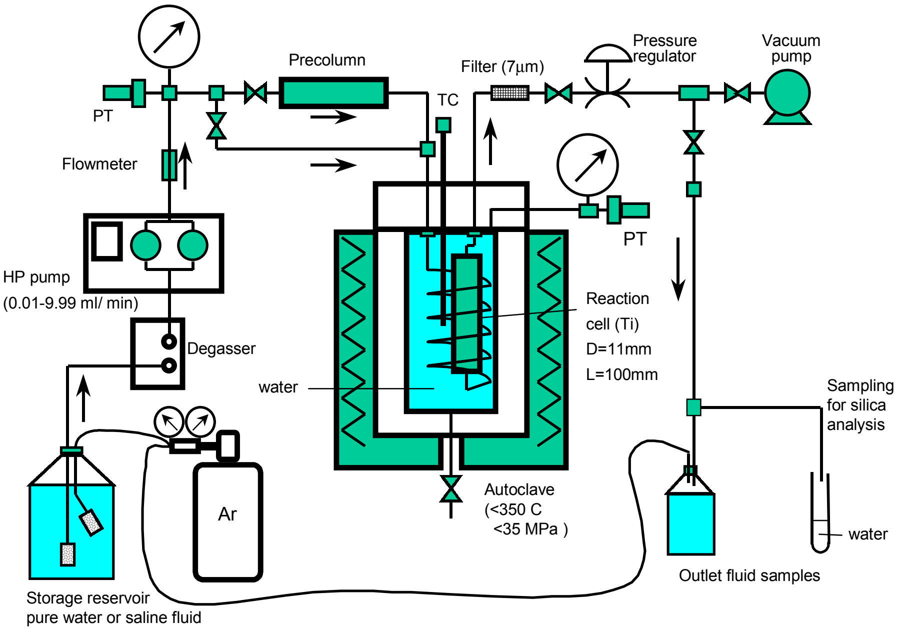

Figure 1: Experimental device

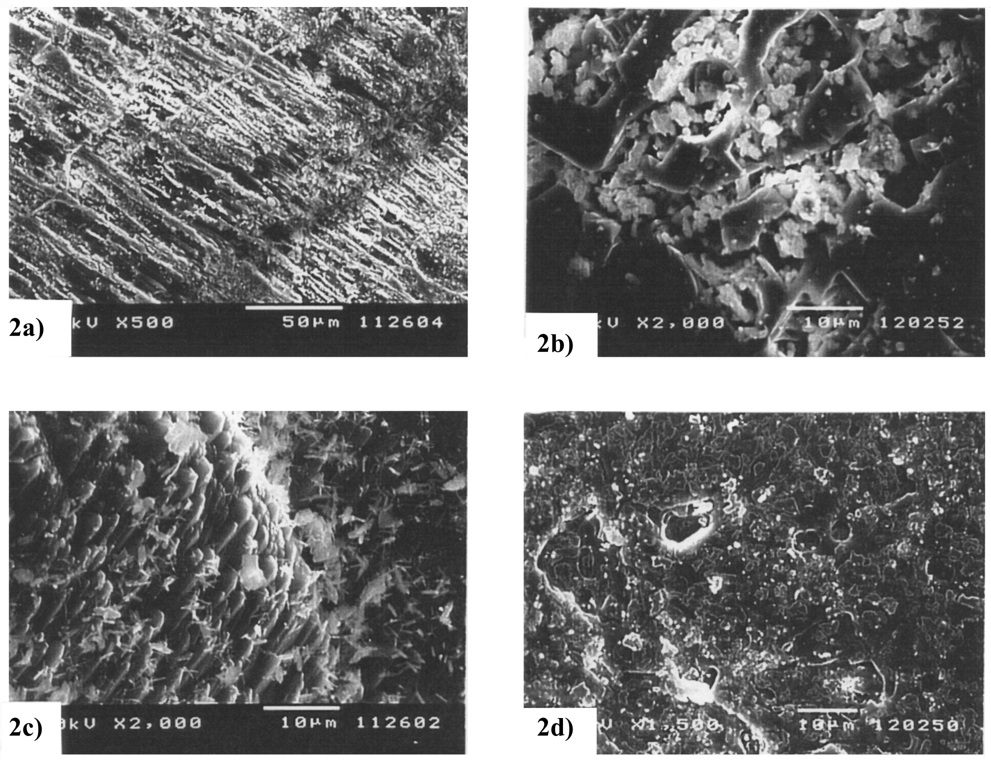

Figure 2 : SEM observations of the weathered state of the surface of the minerals and precipitates after experiments. 2a) Surface of K-feldspar covered by zeolite precipitates (LS). 2b) Surface of plagioclase with illite precipitates located in the holes of dissolution. 2c) Typical features of dissolution on surface of quartz mineral with a high precipitation rate of illite. 2d) Surface of biotite: dissolution features and precipitation rate limited.

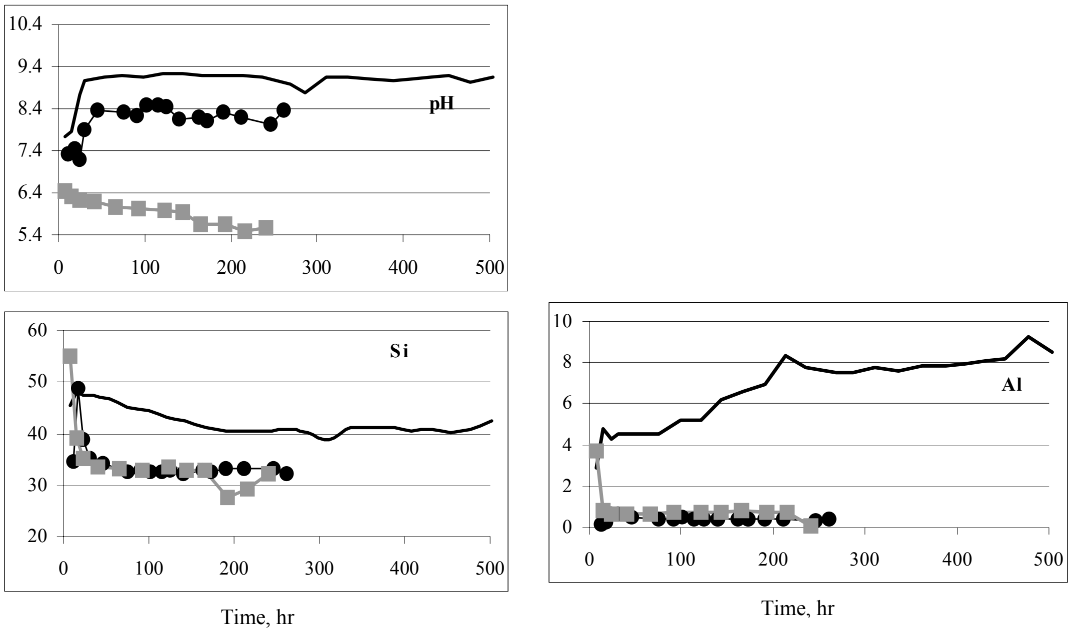

Figure 3: Evolution of the chemical composition of the outlet fluid with time at 200 ºC with a flow rate of 0.1 ml·min^{-1}. Contents in ppm. Black lines: DW, Black circles: LS, Grey squares: HS.