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AND A TRANSPORT MODEL OF DISSOLVED ELEMENTS

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ABSTRACT

In order to assess the safety analysis of an underground repository, we have to model the transport of radioelements in groundwater and their interactions with the geological medium. The objective of this work is the setting up and experimental validation of the coupling of a geochemical model with a transport model of dissolved elements.
A laboratory experiment was developed at the CEA center of Cadarache.
Flow-through experiments were carried out on columns filled with crushed limestone, where several inflow conditions were taken into account as the temperature, the presence of a pollutant (strontium chloride) at different concentrations.
The results consist of the evolution of the chemical composition of the water at the outlet of the column. The final aim of the study is to explain these results with a coupled model where geochemical and transport phenomena are modelled in a two-step procedure.
This code, called STELE, was built by introducing a geochemical code, CHIMERE, into an existing transport code, METIS.
At this stage, the code CHIMERE can take into account :
- any chemical reaction in aqueous phase (complexation, acid-base reaction, redox equilibrium),
- dissolution-precipitation of minerals and solid phases,
- dissolution-degassing of gas.
The paper intends to describe the whole process leading to the coupling which can be forcasted over the next years between geochemical and transport models.

INTRODUCTION

In order to assess the safety analysis of an underground repository of radioactive waste, we have to calculate the transport of radioelements in groundwater and their interactions with the geological medium.
The scope of this paper is the setting up and the experimental validation of the coupling of a geochemical model with a transport model of dissolved elements.
For this purpose, flow-through experiments were carried out on columns filled with crushed limestone, where several inflow conditions were taken into account as the temperature, the presence of a pollutant.

EXPERIMENTAL WORK

Materials

Natural calcium carbonate from quarries of Banon (Alpes de Haut Provence) was used after crushing in the range : 0,250 - 0,315 mm. T. chemical analysis of this rock and its mineralogical composition are shown in table I.

Columns of 50 mm in diameter and 250 mm in length were filled with this crushed limestone. The columns were thermostatic controlled and the reference solution was distilled water.

Table I : Chemical composition (weight percentages) and mineralogical composition of the limestone from BANON

Ca^{++}	34.10	$CO_3^=$	51.10
Mg^{++}	0.43	Cl^-	< 0.02
Na^+	0.02	$SO_4^=$	0.28
K^+	0.05		
Si	11.90	Gd	< 0.001
Sr	0.11	U	< 0.002
Ba	0.001	Ce	< 0.004
Fe	0.14	La	0.006
Ni	< 0.001	Eu	< 0.001
Co	< 0.001	Sm	< 0.001
Al	0.33	Rb	< 0.1

$Ca CO_3$	> 90 %
Dolomite	0,5 - 1 %
Quartz	3 - 4 %
Clays (Smectite)	6 - 7 %

Experiments

Flow-through experiments were carried out at the nuclear center of Cadarache (IPSN-DERS-SERE). Experiments lasted between 30 and 80 hours and the conditions and variables were :
- the composition of water ; two independent conditions :
  . preestablished equilibrium or not with the crushed limestone,
  . presence or not (in certain cases, at different concentrations) of strontium chloride,
- the temperature of the water : near 25° C or near 40° C.
The flow rate was 100 ml/hour ; one experiment was carried out at 20 ml/hour.

The table II summarizes the flow-through experiments.

Table II : Summary of the carried out flow-through experiments

Temperature Water	Room temperature	38 or 40° C
Distilled	. Flow rate : 20 ml/h . Flow rate : 100 ml/h	. :
Distilled + Strontium chloride	. Concentration = 10^{-3} M/L . Concentration = 10^{-1} M/L	. Concentration = 10^{-3} M/L . Concentration = 10^{-1} M/L
Equilibrated	.	.
Equilibrated + Strontium chloride	. Concentration = 10^{-1} M/L	. Concentration = 10^{-1} M/L

Flow rate = 100 ml/h, each point corresponds to an experiment.

Measurements

The objective is to follow the evolution, versus time, of the temperature and of the water composition at the outlet of the column. For this purpose, temperature, pH, resistivity were measured continuously and samples of water were taken for analysis of major ions.

RESULTS AND DISCUSSION

Among the eleven experiments, six were carried out with strontium chloride. We decided to present the characteristic behaviour of strontium [1].

- Evolution of the concentration of strontium and chloride at the outlet of the column, with respect to the inlet concentration

We can notice two types of curves for the strontium.
1) When the inlet concentration of $SrCl_2$ is 10^{-3} mole per liter, during thirty hours the outlet concentration of strontium remains equal to about the hundredth of its inlet level. Then its concentration increases continuously. In the experiment with distilled water at 38° C, it reaches the inlet concentration at the end of eighty hours (figure 1). The curve remains identical at room temperature. At this date, chloride leaves the column with a concentration nearly two times higher than the injected water.
2) When the inlet concentration of $SrCl_2$ is 10^{-1} mole per liter, the outlet concentration of strontium is on the same order of magnitude as the inlet one, from the beginning of the curve (figure 2). In this experiment with water at 38° C, the concentration of strontium becomes higher than the inlet concentration.

Chloride outlet concentrations are higher than the inlet concentrations in several cases, including the two last mentioned. This phenomenon is observed only for heating experiments. A possible explanation is the evaporation. The injected water concentrates by evaporation during the experiment.

To explain the two behaviours of strontium, we can invoke precipitation of strontium carbonate at the surface of the calcium carbonate particles ; this is visible for low concentrations (10-³ molar).
Modelling will now be used as an help for the interpretation of these reactions.
- Sensitive species to the presence of chloride strontium and independent species

The table III presents the concentrations of different species at the end of each experiment. Except for strontium and calcium in a few cases, these values are unchanging.
This table allows us to distinguish two kinds of species : those for which the outlet concentration is independent of the presence of the pollutant and those for which this concentration is dependent of the concentration of strontium chloride.
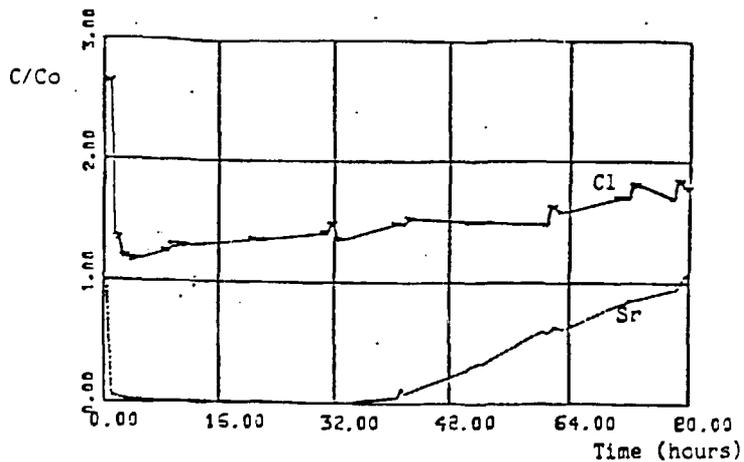

Figure 1 : Evolution versus time of the concentration of strontium and chloride at the outlet of the column, with respect to the inlet concentration (SrCl$_2$ 10^{-3} M distilled water, T = 38°C)
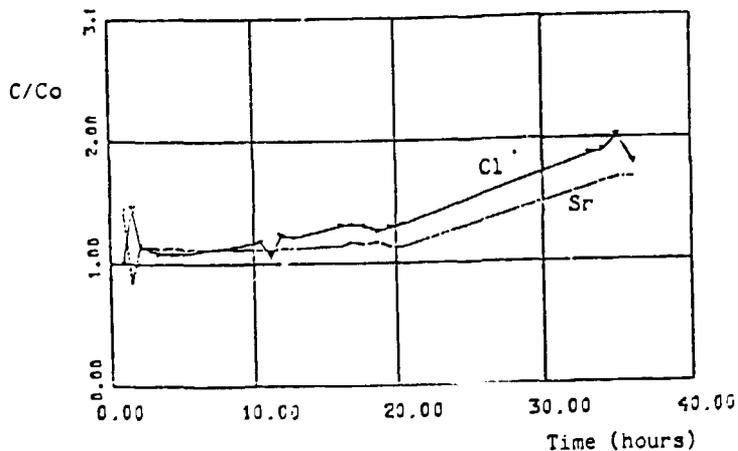

Figure 2 : Evolution versus time of the concentration of strontium and chloride at the outlet of the column, with respect to the inlet concentration (SrCl$_2$ 10^{-1}M, distilled water, T = 38°C)

Table III : Concentration of different species at the outlet of the column and at the end of the experiment

Experiment	T	pH	Sr	Cl	Calc	Ca	Mg	Na	K	SO$_4$	Si
distilled room T	21	9.1	-	0.05	0.3	0.2	0.06	0.05	0.03	0.03	0.1
distilled T = 40° C	28	8.9	-	0.01	-0.1	0.26	0.05	0.02	0.02	0.08	0.09
distilled + SrCl$_2$ 10-³ room T	23	9.0	0,25	1.9	0.8	0.9	0.09	0.006	0.01	0.01	0.04
distilled + SrCl$_2$ 10-³ T = 40° C	34	8.9	1	3.5	0.9	1.1	0.08	0.01	0.01	0.04	0.05
distilled + SrCl$_2$ 10-¹ room T	21	8.2	-	158	0.7	32.7	0.8	0.12	0.01	0.007	0.07
distilled + SrCl$_2$ 10-¹ T = 40° C	32	7.7	200	400	0.5	40	2.3	0.2	0.02	0.02	0.08
equilibrated room T	22	8.6	-	0.01	-0.1	0.3	0.07	0.02	0.02	0.06	0.08
equilibrated T = 40° C	30	8.3	-	0.03	0.1	0.5	0.1	0.02	0.02	0.18	0.07
equilibrated+ SrCl$_2$ 10-¹ room T	22	8.0	87	81	-2.4	0.03	11	0.2	0.02	0.01	0.11
equilibrated+ SrCl$_2$ 10-¹ T = 38° C	30	7.5	200	400	0.3	58.9	1.7	0.2	0.04	0.01	0.10

T : temperature ; calc : saturation index of calcite (0 = equilibrium) ;
Other variables : total concentrations, unit : 10-³ moles/l
Flow rate : 100 ml/h

- Species for which the outlet concentration is independent of the presence of strontium chloride :

• potassium, sulphate and silica,

- Species for which the outlet concentration is linked with the presence of strontium chloride :

• especially the case of the calcium.

   The following table summarizes these observations.

Table IV : Concentration of calcium at the end of the experiment

Experiment	Measured Calcium at the end
Distilled water	$0,2 \times 10^{-3}$ M
Equilibrated water	$0,3 \times 10^{-3}$ M
Distilled water + SrCl$_2$ 10^{-3} M	$0,9 \times 10^{-3}$ M
Distilled water + SrCl$_2$ 10^{-1} M	33×10^{-3} M
Equilibrated water + SrCl$_2$ 10^{-1} M	$0,03.10^{-3}$ M at room temperature 60.10^{-3} M for T = 38° C

With distilled water alone, the outlet calcium concentration is rather the same one as in the case with equilibrated water ($0,2$ to $0,3 \times 10^{-3}$M). With distilled water and 10^{-3} M of chloride strontium, the outlet concentration is three times higher ($0,9 \times 10^{-3}$M). With distilled water and 10^{-1} M of chloride strontium, it is one hundred times higher (33×10^{-3}M). With equilibrated water and 10^{-1} M of chloride strontium, we have two different concentrations, according to the heating or not.
The behaviour of calcium can be linked to the behaviour of strontium. It is planned to calculate by exchange ion reactions, the missing amounts of strontium (with respect to injected water) and the exceeding amounts of calcium (with respect to equilibrated water) and to correlate them, if possible, with the experimental data.

For this purpose, it is planned to use a coupled model. Let us present the main features of the geochemical code, called CHIMERE, and the coupled model, called STELE.

THE GEOCHEMICAL CODE : CHIMERE

Methodology - General features

This code was built to be coupled to a transport model /2/. The aims were :
- to compute the speciation of a static volume,
- to clearly write down the chemical constraints and equations,
- to minimize computer time and core storage.
The method of CHIMERE is based on the use of chemical components or master species as defined by Morel /3/. The components are species chosen among the set of species taken into account and such that each species of this set may be expressed as a linear combination of the components. It allows the second and third of the aims to be achieved. The advantages of this method become apparent when the components are chosen among the dominant species of the geochemical system under specific study.
Any chemical reaction could be taken into account, but at this stage, the code makes provisions only for the following ones :
- complexation, acid-base reaction, redox equilibrium,
- dissolution-precipitation of minerals and solid phases,
- dissolution-degassing of gas.
The adsorption-desorption are not yet taken into account within this code.

To solve a speciation problem, the number of unknowns is equal to the number, N, of components. The number of mass balance equations is also equal to N. The number of chemical constraints must be equal to N, too. For each component, one may choose :
- either to impose the activity of this component,
- or to impose the total amount of this component.
The activity of a component may be imposed, for example, to assign pH, Eh, equilibrium with respect to a mineral or partial pressure of a gas.
In a speciation problem, the number of unknowns, and thus the number of equations to be solved, is equal to the number of components. If the activity of one component is imposed, it is no longer an unknown.
To minimize the number of species, the user must specify each of the species he wants to take into account.
The temperature of the speciation may be anywhere in the validity range of the equilibrium constant database.
The activity coefficients are computed from the Davies equation, valid up to an ionic strength of 0,1 M. When the set of mass balance equations have been solved, the ionic strength is computed. If the ionic strength is sufficiently close to the preceding one, the speciation is achieved. Otherwise, the set of mass balance equations is again solved, taking into account the new activity coefficient values. The Newton-Raphson iterative method is used in CHIMERE to solve the non-linear mass balance equations.

THE COUPLED MODEL : STELE

The aim of this model was to compute the evolution in space and time of the chemical composition of a solution as well as the spatial distribution of the dissolved or precipitated (degassed) quantities for each mineral (gas).

The METIS code

STELE was built by introducing the CHIMERE features into an existing transport code : METIS (Goblet /4/) which solves the flow and transport equations in 1, 2 or 3 dimensions using the Finite Element Method.
The chemical reactions are described by the classical method of a global partition coefficient between the aqueous phase and the solid phase. The aim of STELE was to replace the empirical Kd approach by the description of the chemical reactions.

The STELE methodology

All the features of METIS and CHIMERE are included in STELE.
A two steps procedure is used in STELE. At each time step, two sets of equations are solved alternatively. The first one corresponds to the aqueous speciation and yields explicit geochemical source terms. The second one corresponds to the total mass balance equations, where the chemical source terms are known.
At each time step, the speciation is computed at each node at local tempe-rature. So the reactive element transport depends on the evolution of the temperature field.
Each total mass balance equation is set up for a total concentration in one component. The mass balance equations are solved in the following cases :
- the total mass balance of this component varies in space, and the activity of this component is not imposed,
- the activity of this component is imposed, it is a mineral or a gas, and the user wants to compute the dissolved or precipitated (degassed) quantities of this mineral (gas).

Local equilibrium is assumed for the aqueous phase reactions. For the hetero-
geneous reactions, a reaction kinetic may be taken into account, represented
by a common kinetic law of the first order.

The coupling is useful in four situations :
- in the case of adsorption-desorption,
- in the case of kinetics in chemical reactions, when chemical constant time
is on the same order of magnitude of the transport constant time,
- when there is an evolution of any physical or chemical parameter of the
solution,
- when there is mixing of waters of different chemical composition
(diffusion-dispersion).

CONCLUSION

The objective of this study is the experimental validation of the coupling of
a geochemical model with a transport model of dissolved elements. We have
presented flow-through experiments and their results.
We have obtained some interesting results, such as the behaviour of strontium
and its interaction with calcium. Now, we want to try to explain these
experimental results by the coupled model, STELE, where chemical reactions
are described explicitly.

AKNOWLEDGEMENTS

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