SKB TECHNICAL
KBS REPORT
84-10

Geochemical simulation of the evolution of granitic rocks and clay minerals submitted to a temperature increase in the vicinity ot a repository for spent nuclear fuel

Bertrand Fritz
Marie Kam
Yves Tardy
Université Louis Pasteur de Strasbourg
Institut de Géologie

Strasbourg, France July 1984

SVENSK KÄRNBRÄNSLEHANTERING AB
Swedish Nuclear Fuel and Waste Management Co
MAILING ADDRESS: SKB, Box 5864 S-102 48 Stockholm, Sweden
Telephone: 08-67 95 40

GEOCHEMICAL SIMULATION OF THE EVOLUTION OF GRANITIC ROCKS AND CLAY MINERALS SUBMITTED TO A TEMPERATURE INCREASE IN THE VICINITY OF A REPOSITORY FOR SPENT NUCLEAR FUEL

Bertrand Fritz
Marie Kam
Yves Tardy

Université Louis Pasteur de Strasbourg
Institut de Géologie
Strasbourg, France July 1984

A list of other reports published in this series during 1984 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28) and 1983 (TR 83-77) is available through SKBF/KBS.

UNIVERSITÉ LOUIS PASTEUR DE STRASBOURG
INSTITUT DE GÉOLOGIE
1, rue Blessig - 67084 STRASBOURG Cedex (FRANCE) - Tél. (88) 35.66.03

GEOCHEMICAL SIMULATION OF THE EVOLUTION OF GRANITIC ROCKS AND CLAY MINERALS SUBMITTED TO A TEMPERATURE INCREASE IN THE VICINITY OF A REPOSITORY FOR SPENT NUCLEAR FUEL

Bertrand FRITZ, Marie KAM and Yves TARDY

Université Louis Pasteur de Strasbourg
Institut de Géologie
F-67084 STRASBOURG Cedex
FRANCE

July 1984

CONTENTS

SUMMARY

The alteration of a granitic rock around a repository for spent nuclear fuel has been simulated considering the effect of an increase of temperature due to this kind of induced geothermal system. The results of the simulation have been interpreted in terms of mass transfer and volumic consequences. The alteration proceeds by dissolution of minerals (with an increase of the volumes of fissures and cracks) and precipitation of secondary minerals as calcite and clay minerals particularly (with a decrease of the porosity). The increase of the temperature from 10°C to about 100°C will favour the alteration of the granitic rock around the repository by the solution filling the porosity. The rock is characterized by a very low fissure porosity and a consequent very low water velocity. this too, favours intense water rock interactions and production of secondary clays and the total possible mass transfer will decrease the porosity. A combination of these thermodynamic mass balance calculations with a kinetic approach of mineral dissolutions gives a first attempt to calibrate the modelling in the time scale: the decrease of porosity can be roughly estimated between 2 and 20% for 100,000 years.

The particular problem of Na-bentonites behaviour in the proximate vicinity of the repository has been studied too. One must distinguish between two types of clay-water interactions:

- within the rock around the repository, Na-bentonites should evolute with illitization in slightly open system with low clay/water ratios,
- within the repository itself, the clay reacts in a closed system for a long time with high clay/water ratios and a self-buffering effect should maintain the bentonite type.

This chemical buffering effect is a positive point for the use of this clay as chemical barrier.

INTRODUCTION

From the conclusions of the first annual report (FRITZ et al., 1983) two major proposals have been extracted to drive this new year of research on the problem of evolution of the granitic rocks and clay minerals around a storage of spent nuclear fuel:

(1) What are the consequences of possible alterations induced in the granitic rock by the artificial geothermal system, on the physical properties of the rock (increase or decrease of the porosity)?

(2) What is the behaviour of clay minerals in these systems: in the fissures of the rock, but also in the repository itself (will Na-bentonites be transformed into non-swelling clays at higher temperatures?

The first point has been studied by simulating rock-solution interactions in order to answer the following questions:

- What is the effect of a theoretical alteration sequence on the volume of fissures concerned by the alteration?
    - o in a closed system ("one" alteration)
    - o in open system (water circulates from one rock unit to another and successive alteration sequences are cumulated).
- Are the effects equivalent for different temperatures (10 to 100°C)?
- What are the consequences of possible low redox potentials?

The modelling approach, using only chemical potential energy data, gives only tendencies of evolution, possible reactions and mass transfers. If one considers these results together with hydrologic and hydrodynamic data, it is possible to obtain a kind of time scale for these possible transformations. More, the recent evolution of mass transfers calculation models (HELGESON and

MURPHY, 1983) give us first indications on kinetic effects for the kind of processes playing here. This can help to begin to calibrate the thermodynamic alteration sequence in the time scale: the calculations presented here constitute a first attempt to combine thermodynamic, hydrodynamic and kinetic approaches of water-rock interactions in geothermal alterations.

The second point has been approached in two ways:

- simulation of clay solid solutions and aqueous solutions interactions; influence of the Clay/Water ratio on the transformation induced by a temperature increase ("self-buffering" against illitization of Na-bentonites?),

- experimental and theoretical study of the swelling properties of clay minerals. This last point has also been evaluated but will be reported later.

1 SIMULATION OF GRANITE ALTERATION AT 25, 60 AND 100°C

1.1 INITIAL CONDITIONS

1.1.1 The initial aqueous solution

The simulation have been made for 25, 60 and 100°C with the computer code DISSOL (FRITZ, 1975, 1981). At the respective temperatures, the initial conditions for the solution have been obtained by simulating the heating of a natural solution from 10 to 100°C (see previous report, FRITZ et al., 1983) using the computer code THERMAL (FRITZ, 1981). In this series of tests the solution selected was always the dilute well water from FINNSJÖN ("mean drilled well", see HULTBERG et al.). This water has been chosen in order to give an estimation of the maximum risk of alteration of the granite. The initial composition of the solution is given in Table 1. The initial quantities of less soluble elements (aluminium and iron) are limited by the saturation limit of kaolinite for aluminium and goethite (FeOOH) or pyrite (FeS_2) for iron, depending on redox conditions. The redox potential values have been chosen in order to be consistent with two values of oxygen fugacity:

- mean reducing conditions ($pO_2 = 10^{-45}$):
  - o Eh = +120 mV for pH = 7.40 at 25°C
  - o Eh = +2 mV for pH = 7.06 at 60°C
  - o Eh = -155 mV for pH = 6.79 at 100°C
- reducing conditions ($pO_2 = 10^{-60}$):
  - o Eh = -95 mV for pH = 7.40 at 25°C
  - o Eh = -260 mV for pH = 7.06 at 60°C
  - o Eh = -440 mV for pH = 6.79 at 100°C

These last reducing conditions may represent in situ conditions in the swedish deep granites as shown by WIKBERG et al. (1983).

Table 1. Chemical composition of the solutions used for the simulations of the alteration of granite at 25, 60 and 100°C.

Temperature		25°C	60°C	100°C
pH		7.400	7.065	6.790
Eh (mV)	(1)	+120	+2	-155
	(2)	-95	-260	-440
Na millimoles/l		0.634	0.634	0.634
K "		0.190	0.190	0.190
Ca "		1.525	1.320	1.022
Mg "		0.189	0.189	0.189
Al micromoles/l		0.001	0.100	1.000
Fe "	(1)	10^{-6}	10^{-4}	5.10^{-3}
Fe "	(2)	10^{-2}	10^{-3}	5.10^{-5}
Alkalinity (meq/l)		3.344	2.936	2.340
Si millimoles/l		0.185	0.185	0.185
SO_4 "		0.175	0.175	0.175
Cl "		0.556	0.556	0.556
log pO_2	(1)	-45.41	-44.27	-44.55
" "	(2)	-59.94	-60.13	-59.92
log pCO_2		-2.113	-1.560	-1.135
Calcite deposit from 10 to t°C (millimoles/l)		0.000	0.205	0.502

For the first set of values the aqueous iron solubility was always controlled by the goethite or 2:1 clay formation. For the second set, pyrite or 2:1 clay or ferrous chlorite control the aqueous iron species.

The carbon dioxide partial pressure was not fixed in the simulation as it is for simulating near surface weathering. The values given in Table 1 are only calculated from the alkalinity and the pH data within the aqueous speciation calculation routine.

1.1.2 The mineral "reactant" assemblage

The mineral assemblage chosen for the calculations fits the chemical composition of the granodiorite from borehole (1) at FINNSJÖ Lake (KBS Report 78-II, Geology) with quartz, Na-, K- and Ca-felspars, one ferrous mica (annite and one Mg-amphibole (Table 2).

Table 2. Mineralogical and chemical composition of the granite used in the simulation (consistent with the granodiorite of FINNSJÖN Lake, KBS Report II, 1978).

Mineral	Formula	Mole %	Oxides	Weight %	Oxides	Weight %
Quartz	SiO_2	64.4	SiO_2	66.5	K_2O	3.6
Microcline	$KAlSi_3O_8$	7.9	Al_2O_3	14.8	Na_2O	2.5
Albite	$NaAlSi_3O_8$	12.5	FeO	5.2	MgO	2.0
Anorthite	$CaAl_2Si_2O_8$	10.0	CaO	4.8	H_2O	0.6
Biotite	$Si_3AlFe(II)_3O_{10}(OH)_2$	3.7				
Tremolite	$Si_8Mg_5Ca_2O_{22}(OH)_2$	1.5				

1.1.3 Simulation conditions

The programs DISSOL and THERMAL have been used with the CLOSED SYSTEM option. All reactant and product minerals and the aqueous solution are considered as a closed system. Any mineral produced in an early stage of the simulation may be dissolved again later and transformed into another secondary phase (gibbsite into kaolinite, goethite and kaolinite into clays for example). This option is particularly convenient for simulating alteration in deep groundwater aquifers (low porosity, low water flux through the rock).

The six initial reactant minerals (Table 2) are dissolved in the solution as long as their saturation state is not reached in the solution. They have not been allowed to be precipitated after, even if this was thermodynamically possible for quartz, microcline and tremolite, the less "soluble" ones, at the end of the sequences.

The secondary minerals are produced at equilibrium with the solution: as pure minerals for goethite or pyrite, kaolinite, calcite, but as solid solution of multicomponent end members for 2:1 clays (TARDY and FRITZ, 1981) and binary solid solution for chlorite (clinochlore-daphnite).

The simulation itself does not include kinetic laws for the reactions and follows only the mass transfers due to irreversible dissolutions of several minerals (reactant) initially unstable with respect to the solution. The aqueous ions speciation and the production of secondary phases is supposed to be constrained by thermodynamic equilibrium conditions.

1.2 SIMULATED MINERALOGICAL STABILITY SEQUENCES

The previous results (FRITZ et al., 1983, Tables 8 to 10, Figure 15) will not be recalled here but major tendencies will be summarized, as they appear in Figure 1.

1.2.1 Sequences of stability of primary minerals

The six reactant minerals behave differently from 25 to 100°C and the less soluble ones at 25°C (quartz and microcline) become much more soluble and increase the alteration potential. Albite remains very soluble, while anorthite stability cannot be reached even at 100°C. Only tremolite shows a decrease of solubility with increasing temperature: this fact added to the frequent Mg control in the solution by chlorite formation may explain the systematically very low Mg concentration in geothermal waters in crystalline rocks (MICHARD, 1979; FRITZ, 1981). The solubility of the ferrous mica is sensitive to redox potentials but the saturation state was not reached at any temperature for $pO_2 = 10^{-45}$.

1.2.2 Sequences of stability of secondary minerals

In the early stages of alteration, the products are successively goethite, kaolinite and calcite for the whole temperature range. Smectites and/or Mg-Chlorites are produced later in the sequence: smectites only, at 25°C, and chlorites and 2:1 clays at 60 and 100°C. These clay minerals appear always between microcline and albite saturations: this part of the alteration sequence corresponds to the most important mass transfers. The composition of the 2:1 clays and the chlorite produced are given in Table 3. These results were obtained with an initial redox potential corresponding to near neutral conditions (+120 mV at 25°C and -155 mV at 100°C) and a low oxygen partial pressure (around 10^{-45}).

Table 3. Chemical composition of the total 2:1 clay produced by a simulated alteration of the granite at saturation point of albite.

Temperature	Clay formula		
	Tetrahedra	Octahedra	Interlayer
25°C	$Si_{3.352}Al_{0.648}$	$Al_{1.248}Fe^{III}_{0.582}Mg_{0.255}\ O_{10}(OH)_2$	$K_{0.027}Na_{0.0}Ca_{0.21}Mg_{0.101}$
60°C	$Si_{3.308}Al_{0.692}$	$Al_{1.238}Fe^{III}_{0.695}Mg_{0.101}\ O_{10}(OH)_2$	$K_{0.171}Na_{0.049}Ca_{0.197}Mg_{0.041}$
100°C	$Si_{3.480}Al_{0.520}$	$Al_{1.189}Fe^{III}_{0.628}Mg_{0.275}\ O_{10}(OH)_2$	$K_{0.452}Na_{0.024}Ca_{0.022}Mg_{0.00}$
	and Mg-Chlorite $Si_3Mg_5Al_2O_{10}(OH)_8$		

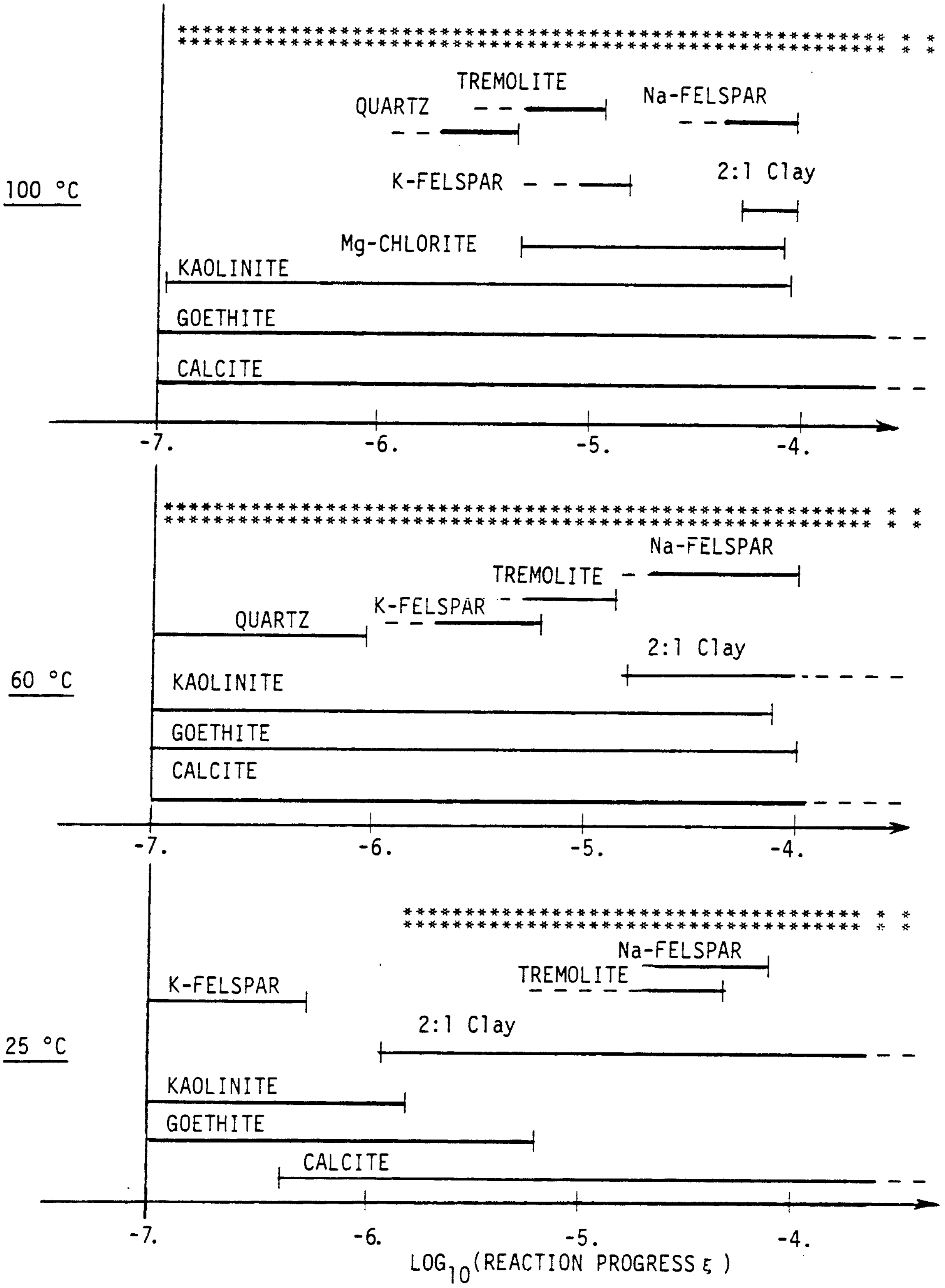

Figure 1. Mineralogical sequences along the simulated dissolution path of the granite in a diluted natural well water from FINNSJÖN at 25, 60 and 100°C. After FRITZ et al. (1983). ($\overset{***}{***}$ indicates the part of the sequence where the volume of precipitated minerals exceeds the volume of dissolved minerals.)

1.3 EFFECT OF A REDUCING ENVIRONMENT

All the calculations were repeated with lower initial redox potentials. The option (2) from Table 1 corresponds to a very low oxygen fugacity ($pO_2 = 10^{-60}$) and to Eh values about 200 mV lower at each temperature. These values are suggested by careful field measurements and by calculations of Eh values by WIKBERG et al., (1983) on different sites and groundwaters in granitic rocks. The comparison of the simulated sequences obtained with the two redox options (Table 4, 5 and 6) shows first that iron bearing minerals behave differently:

- at 25°C, the simulated sequence is only lightly altered. Goethite appears later in the sequence but still in an early alteration stage and the ferrous mica is not stabilized in the whole sequence,
- at 60°C, the differences appear more important. Pyrite is precipitated instead of goethite and the biotite is also rapidly stabilized in the sequence,
- at 100°C, pyrite is also precipitated instead of goethite, but maintains such a low ferrous ion activity in the solution that it prevents to stabilize the biotite.

These differences concern essentially the iron bearing minerals and the general sequences of alteration for the other minerals are maintained. However, one will see that the effect on the evolution of the porous volume can be much more important.

Table 4A. Sequence of events in the simulated dissolution of granite at 25°C (initial Eh = +120 mV; log pO_2 = -45).

Log ξ	$10^6 \cdot \xi$	Mineralogical events	pH	Log p^{CO_2}	Eh(mV)
- ∞	0	Quartz initially stable	7.40	-2.11	120
-12.58	ε	Goethite precipitates	7.40	-2.11	120
- 9.97	ε	Kaolinite precipitates	7.40	-2.11	120
- 6.37	0.43	Calcite precipitates	7.45	-2.16	117
- 6.27	0.54	K-spar becomes stable	7.45	-2.16	117
- 5.88	1.33	2:1 clay precipitates	7.46	-2.17	116
- 5.78	1.67	Kaolinite has been redissolved	7.46	-2.17	116
- 5.09	8.17	Goethite has been redissolved	7.54	-2.27	110
- 4.28	52.9	Tremolite becomes stable	8.05	-2.95	79
- 4.07	85.9	* Albite becomes stable	8.59	-3.61	47

* At this point anorthite and biotite are still unstable and Mg-chlorite has not been formed.

Table 4B. Sequence of events in the simulated dissolution of granite at 25°C (initial Eh = -95 mV; log pO_2 = -60; ξ = number of rock units dissolved).

Log ξ	$10^6 \cdot \xi$	Mineralogical events	pH	Log p^{CO_2}	Eh(mV)
- ∞	0	uartz initially stable	7.40	-2.11	- 95.0
- 9.97	ε	Kaolinite precipitates	7.40	-2.11	- 95.0
- 9.20	ε	Goethite precipitates	7.40	-2.11	- 95.0
- 6.37	0.43	Calcite precipitates	7.45	-2.16	- 97.8
- 6.27	0.54	K-felspar becomes stable	7.45	-2.16	- 97.9
- 5.87	1.36	2:1 clay precipitates	7.46	-2.17	- 98.6
- 5.76	1.72	Kaolinite has been redissolved	7.46	-2.17	- 98.6
- 5.55	2.81		7.47	-2.19	- 99.4
- 5.39	4.06		7.49	-2.21	-100.3
- 5.22	5.92		7.51	-2.24	-101.8

Table 5A. Sequence of events in the simulated dissolution of granite at 60°C (initial Eh = +2 mV; log pO_2 = -45).

Log ξ	$10^6 \cdot \xi$	Mineralogical events	pH	Log p^{CO_2}	Eh(mV)
- ∞	0	Calcite initially at equilibrium	7.07	-1.56	- 2.1
-11.71	ε	Goethite precipitates	7.07	-1.56	- 2.1
- 8.59	ε	Kaolinite precipitates	7.07	-1.56	- 2.1
- 5.98	1.06	Quartz becomes stable	7.08	-1.58	- 1.1
- 5.16	6.84	K-spar becomes stable	7.17	-1.69	- 4.9
- 4.82	15.15	Tremolite becomes stable	7.31	-1.87	-14.1
- 4.74	18.12	2:1 clay precipitates	7.35	-1.92	-16.5
- 4.10	80.27	Kaolinite has been redissolved	7.75	-2.44	-44.3
- 3.96	109.3	Goethite has been redissolved	8.17	-2.95	-74.4
- 3.93	118.5	* Albite becomes stable	8.36	-3.18	-91.8

* At this point anorthite and biotite are still unstable and Mg-chlorite has not been formed.

Table 5B. Sequence of events in the simulated dissolution of granite at 60°C (initial Eh = -260 mV; log pO_2 = -60; ξ = number of rock units dissolved).

Log ξ	$10^6 \cdot \xi$	Mineralogical events	pH	Log p^{CO_2}	Eh(mV)
-9.96	ε	Pyrite precipitates	7.06	-1.56	-260
-8.59	0.0026	Kaolinite precipitates	7.06	-1.56	-260
-5.98	1.06	Quartz becomes stable	7.09	-1.59	-262
-5.23	5.95	Biotite becomes stable	7.24	-1.77	-271
-5.21	6.20	Microline becomes stable	7.24	-1.78	-272
-4.90	12.53	Chlorite(Mg-Fe) precipitates	7.35	-1.92	-279
-4.89	13.00	Tremolite becomes stable	7.36	-1.93	-280
-4.62	23.78	2:1 clay precipitates	7.43	-2.03	-284

Table 6A. Sequence of events in the simulated dissolution of granite at 100°C (initial Eh = -155 mV; log pO_2 = -45).

Log ξ	$10^6 \cdot \xi$	Mineralogical events	pH	Log p^{CO_2}	Eh(mV)
$-\infty$	0	Calcite initially at equilibrium	6.79	-1.11	-155.6
-9.48	ε	Goethite precipitates	6.79	-1.11	-155.6
-6.94	0.11	Kaolinite precipitates	6.79	-1.11	-155.6
-5.30	5.02	Quartz becomes stable	6.85	-1.18	-160.2
-5.27	5.43	Mg-chlorite precipitates	6.86	-1.19	-160.6
-4.90	12.62	Tremolite becomes stable	6.90	-1.24	-163.7
-4.76	17.56	K-spar becomes stable	6.93	-1.28	-166.1
-4.23	58.31	2:1 clay precipitates	7.30	-1.72	-193.5
-4.09	81.76	Mg-chlorite has been redissolved	7.67	-2.16	-222.2
-3.98	105.0	* Albite becomes stable	7.94	-2.50	-244.9

* At this point anorthite and biotite are still unstable

Table 6B. Sequence of events in the simulated dissolution of granite at 100°C (initial Eh = -440 mV; log pO_2 = -60; ξ = number of rock units dissolved).

Log ξ	$10^6 \cdot \xi$	Mineralogical events	pH	Log p^{CO_2}	Eh(mV)
-11.49	ε	Pyrite precipitates	6.79	-1.14	-440
- 6.94	0.11	Kaolinite precipitates	6.79	-1.14	-440
- 6.09	0.79		6.80	-1.15	-441
- 5.50	3.13		6.83	-1.19	-444
- 5.38	4.17	Clinochlore precipitates	6.86	-1.21	-445
- 5.30	5.05	Quartz becomes stable	6.86	-1.22	-445
- 5.14	7.28		6.88	-1.24	-447

2 EFFECT OF ALTERATION ON THE POROUS VOLUME

The porous volume to be considered in the granitic rock corresponds to small cracks and fissures. The aqueous reacting solutions considered in the simulation (one kilogramme of water as reference) is located in a large volume of rock if the porosity is low (0.2 m^3 of rock for one liter of solution in a 0.5% porosity). This porous volume is increased by the dissolution of primary minerals from the rock, but decreased by the precipitation of secondary minerals: the volumic balances have been calculated for all the simulated sequences of alteration. The decrease of the porous volume due to an important alteration (at albite saturation point) was known (FRITZ et al., 1983) but this result has been precised here all along the sequences and for all conditions tested. The temperature increase favours the mass transfers between the altered rock and the secondary mineral phase, and these transfers tend systematically to close the fissure net where they occur, if the solutions reach the clay + calcite stability field, which is highly probable in the given field conditions.

2.1 VOLUMIC BALANCES ALONG THE ALTERATION SEQUENCES

The quantities of minerals altered or produced are calculated with reference to one liter of solution (in fact one kg of H_2O). The total mass transfers due to all the calculated reactions correspond to a volume change of the solid phase. The calculations show that two stages appear in all the simulations (Tables 7 to 12):

- In the initial dissolution stage, the total volume of dissolved minerals V_D is superior to the total volume of precipitated minerals V_P, the difference decreasing progressively as the reactions progress. In this part of the sequence, the amounts of mass transfers are low and the "created volumes" are very low (less than 1 mm^3) compared to the solution volume

($1l = 10^6$ mm^3). The secondary minerals are here goethite or pyrite, kaolinite mostly, while the saturation state of quartz and microcline are reached (also biotite in very low redox environments at 60°C).

- Later on, when both calcite and the clay phase co-precipitate, the volumic balance show an excess of volume for the solid phase. The porous volume is decreasing and the volume difference (V_P-V_D) becomes less and less negligible in this second part of the sequence, where the mass transfers are much more important, even without considering cumulative effects.

The major problem that remains for using the results of simulated dissolution sequences, based on a pure thermodynamic approach, is then, to know or to decide where do the solution go in the sequence, in a given system: the whole sequence is possible but will not be completed in all cases. This is a problem of reaction kinetics and time of interaction, which are not included in the modelling. However, the two major stages mentioned above correspond to two types of alterations in the nature. The first one, with light mass transfer per liter of solution, corresponds mostly to weathering processes or hydrothermal alteration in active geothermal areas: the drainage is high in the profiles or in the large cracks and fissures and the residence time of a given solution in a given rock system is short. Tropical alteration phenomena have been described by these processes (FRITZ, 1975), that may "wash" a rock from quite all its elements except iron and aluminium remaining as oxides (iron crusts, bauxites, laterites formation). These alterations are characteristic of largely open systems. The second type of transformations are specific of weathering in restricted environment or alteration occuring deeper in the sediments or rocks, where the porosity and the fluid velocities decrease. These conditions are encoutered here in crystalline rocks with very low porosities (less than1%) and water velocities (0.1 to 1 m/year). The rock/solution ratio is very high (more than 500 in weight for 0.5% of saturated porosity), the reactive surfaces also, and the system is much more closed. For all these reasons, it seems reasonable to consider that in the predicted sequences the solution will reach the saturation state of clay minerals and calcite, and therefore the corresponding processes will diminish the porosity progressively. It is <u>impossible to say now precisely</u> where the equilibrium point will be, or what the steady state of the system will be as a function of time within the (clay + calcite) stage. However, the calculated volume evolution shows that, if these minerals are produced, they close progressively the porous volume and the excess of volume due to precipitated minerals is stabilized with respect to the volume of altered minerals. For mean reducing conditions ($pO_2 = 10^{-45}$):

- <u>at 25°C</u> the excess of volume (V_P-V_D/V_D in %) is stabilized around 12-15% all along calcite + clay production (Table 7),

- at $60^{o}C$ the effect of calcite precipitation is initially important, but the excess of volume is also stabilized around 12 to 20% when the clay is formed (Table 8),

- at $100^{o}C$ the effect of calcite precipitation is still more important and the excess of volume is also important when clays form (up to 40%, Table 9). Under reducing conditions (pO_2 = 10^{-60}) the consequences are similar at 25°C (Table 10; goethite appears only later in the sequence) but still more important at 60 and 100°C (Tables 11 and 12; pyrite is produced instead of goethite).

2.2 CUMULATIVE EFFECTS

The decrease of porous volumes is always very small compared to the volume of the reacting solution (less than 1 cm^3 versus 1 000 cm^3). This is important for two reasons. First, the reactions will not be limited by volumic effect. Secondly, in a completely closed system, this means that even if the alteration goes on and reach the overall saturation state (all reactants stable) the total mass transfer will be quite negligible. The alteration will highly transform the chemistry of the solution, but the transformations will be quite undetectable in the total rock: one kilogram of water contained in about 540 kg of granite (porosity 0.5%; density 2.7) will induce a total mass transfer of about 1 g of inorganic matter!

This means that only repeated alteration can produce important mass transfers in a rock. This general phenomena was discussed for hydrothermal alterations and diagenetic transformations by FRITZ (1981) and FRITZ et al. (1984). If the system is not completely closed (water velocity is low but not zero), it is important to know if repeated alteration of one given rock unit will always give a descrease of porosity as obtained for one interaction. For this reason, a test of cumulative effects on volumes has been made by repeating the simulation (at 25°C only) using a solution obtained at a later stage of one sequence as initial solution for a new simulation. This test tries to follow what happen to a solution migrating in the granite from an altered area to a non or less altered zone. This was repeated two times (Tables 13 and 14). The following sequences are not much changed. The initial step of dissolution is cut away and the volumic effect is immediately stabilized with a decrease of the porous volume and an excess of volume in the reaction, higher than in the initial sequence (20 to 25% instead of 12 to 15%; Tables 13 and 14). This is very important: if one considers rock units for water-rock interactions, the solution will move from one unit to another and the alteration continue in a kind of steady-state for volumic effect characteristic of the second stage of alteration with clay and calcite production.

Table 7. Evolution of the porous volume due to dissolution and precipitation of minerals at 25°C (initial Eh = +120 mV).

Volume V_D of minerals dissolved ($mm^3/kg\ H_2O$)	Volume V_P of minerals precipitated ($mm^3/kg\ H_2O$)	Difference $100(\frac{V_P-V_D}{V_D})$ (%)	Evolution of the porosity (tendency)	Geochemical events
$1.08\ 10^{-6}$	0	-100	Increase	
$0.43\ 10^{-3}$	$0.024\ 10^{-3}$	- 94.4	Increase	Goethite precipitates
1.76	1.08	- 38.6	Increase	Kaolinite precipitates
2.22	1.58	- 28.8	Increase	Calcite precipitates
4.78	4.60	- 3.8	Increase	Microcline becomes stable
5.88	5.17	- 12.0	Increase	2:1 clay precipitates
13.6	13.5	- 0.7	~Stable	Kaolinite is redissolved
20.0	21.0	+ 5.0	Decrease	
26.9	29.0	+ 7.8	Decrease	
40.5	43.4	+ 7.0	Decrease	Goethite is redissolved
57.3	64.9	+ 13.3	Decrease	
86.6	97.1	+ 12.1	Decrease	
115.4	132.3	+ 14.6	Decrease	
352.2	391.7	+ 11.2	Decrease	Tremolite and albite become stable

Table 8. Evolution of the porous volume due to dissolution and precipitation of minerals at 60°C (initial Eh = +2 mV).

Volume V_D of minerals dissolved ($mm^3/kg\ H_2O$)	Volume V_P of minerals precipitated ($mm^3/kg\ H_2O$)	Difference $100(\frac{V_P-V_D}{V_D})$ (%)	Evolution of the porosity (tendency)	Geochemical events
0.011	7.553	>100	Decrease	
0.014	7.556	>100	Decrease	Goethite precipitates
5.87	11.99	>100	Decrease	Kaolinite precipitates
29.58	36.50	+ 23.4	Decrease	Quartz becomes stable
56.49	66.98	+ 18.6	Decrease	Microcline becomes stable
64.90	76.25	+ 17.5	Decrease	Tremolite becomes stable
144.4	170.6	+ 18.1	Decrease	2:1 clay precipitates
240.8	334.4	+ 12.4	Decrease	Illite precipitates
296.5	333.5	+ 12.5	Decrease	Kaolinite is redissolved

Table 9. Evolution of the porous volume due to dissolution and precipitation of minerals at 100°C (initial Eh = -155 mV).

Volume V_D of minerals dissolved ($mm^3/kg\ H_2O$)	Volume V_P of minerals precipitated ($mm^3/kg\ H_2O$)	Difference $100(\frac{V_P-V_D}{V_D})$ (%)	Evolution of the porosity (tendency)	Geochemical events
0.002	18.53	>100		
0.638	18.65	>100		Goethite precipitates
27.9	38.18	+ 36.7	Decrease	Kaolinite precipitates
29.6	39.79	+ 34.4	Decrease	Quartz becomes stable
59.1	66.28	+ 12.2	Decrease	Mg-chlorite precipitates
77.3	83.10	+ 7.5	Decrease	Tremolite becomes stable
192.6	201.00	+ 4.3	Decrease	Microcline becomes stable
234.4	252.43	+ 7.7	Decrease	2:1 clay precipitates
259.0	282.34	+ 9.0	Decrease	
				Mg-chlorite is redissolved

Table 10. Evolution of the porous volume due to dissolution and precipitation of minerals at 25°C (initial Eh = -95 mV).

Volume V_D of minerals dissolved ($mm^3/kg\ H_2O$)	Volume V_P of minerals precipitated ($mm^3/kg\ H_2O$)	Difference $100(\frac{V_P-V_D}{V_D})$ (%)	Evolution of the porosity (tendency)	Geochemical events
$0.16\ 10^{-3}$	0	-100	Increase	
$0.44\ 10^{-3}$	0	-100	Increase	Congruent dissolution
$1.05\ 10^{-3}$	$0.34\ 10^{-3}$	- 67.6	Increase	Kaolinite precipitates
$2.56\ 10^{-3}$	$1.18\ 10^{-3}$	- 53.9	Increase	
1.76	1.08	- 38.6	Increase	Goethite precipitates
2.22	1.58	- 28.8	Increase	Calcite precipitates
4.88	4.72	- 3.2	Increase	Microcline becomes stable
6.03	5.32	- 11.7	Increase	2:1 clay precipitates
13.60	13.60	0	Stable	Kaolinite is redissolved
19.60	20.70	+ 5.6	Decrease	

Table 11. Evolution of the porous volume due to dissolution and precipitation of minerals at 60°C (initial Eh = -260 mV).

Volume V_D of minerals dissolved ($mm^3/kg\ H_2O$)	Volume V_P of minerals precipitated ($mm^3/kg\ H_2O$)	Difference $100(\frac{V_P-V_D}{V_D})$ (%)	Evolution of the porosity (tendency)	Geochemical events
0.014	7.559	>100	Decrease	Goethite precipitates Kaolinite precipitates
5.88	13.26	>100	Decrease	Quartz becomes stable
16.41	27.24	+ 65.99	Decrease	
25.06	38.81	+ 54.49	Decrease	
25.93	39.98	+ 54.18	Decrease	Biotite becomes stable
26.80	40.90	+ 52.26	Decrease	Microline beomes stable
43.71	60.93	+ 39.39	Decrease	Chlorite precipitates
44.96	62.31	+ 38.59	Decrease	Tremolite becomes stable
46.93	64.47	+ 37.37	Decrease	
69.32	87.99	+ 26.93	Decrease	

Table 12. Evolution of the porous volume due to dissolution and precipitation of minerals at 100°C (initial Eh = -440 mV).

Volume V_D of minerals dissolved ($mm^3/kg\ H_2O$)	Volume V_P of minerals precipitated ($mm^3/kg\ H_2O$)	Difference $100(\frac{V_P-V_D}{V_D})$ (%)	Evolution of the porosity (tendency)	Geochemical events
ε	18.53		Decrease	Pyrite Precipitates
0.349	18.62	>100	Decrease	
0.638	18.69	>100	Decrease	Kaolinite precipitates
4.44	21.68	>100	Decrease	
17.42	31.73	+ 82.15	Decrease	
23.21	36.19	+ 55.92	Decrease	
28.10	39.64	+ 41.00	Decrease	Quartz becomes stable
37.24	48.54	+ 30.00	Decrease	

Table 13. Evolution of the porous volume due to dissolution and precipitation of minerals at 25°C (initial Eh = 110 mV). Second step. The solution obtained in the previous step is used as initial solution.

Volume V_D of minerals dissolved (mm^3/kg H_2O)	Volume V_P of minerals precipitated (mm^3/kg H_2O)	Difference $100(\frac{V_P-V_D}{V_D})$ (%)	Evolution of the porosity (tendency)	Geochemical events
0	0	-	-	2:1 clay initially stable
0.18	0.13	-27.78	Increase	Calcite precipitates
7.2	9.2	+27.5	Decrease	
22.0	27.7	+25.9	Decrease	
32.1	40.1	+24.9	Decrease	
40.4	50.3	+24.5	Decrease	
44.5	55.3	+24.3	Decrease	
47.9	59.4	+24.0	Decrease	
50.8	63.1	+24.2	Decrease	
52.9	65.6	+23.6	Decrease	

Table 14. Evolution of the porous volume due to dissolution and precipitation of minerals at 25°C (initial Eh = 108 mV). Third step. The solution obtained in the previous step is used as initial solution.

Volume V_D of minerals dissolved (mm^3/kg H_2O)	Volume V_P of minerals precipitated (mm^3/kg H_2O)	Difference $100(\frac{V_P-V_D}{V_D})$ (%)	Evolution of the porosity (tendency)	Geochemical events
0	0	-	-	2:1 clay initially stable
11.82	14.44	+22.16	Decrease	
19.76	24.23	+22.62	Decrease	
38.50	47.22	+22.65	Decrease	
49.77	60.69	+21.94	Decrease	
56.32	68.47	+21.57	Decrease	
70.01	84.63	+20.88	Decrease	

2.3 KINETIC CONSIDERATIONS

Recent works on the calculation of mass transfers among minerals and aqueous solutions as functin of time (HELGESON and MURPHY, 1983) gave a very helpful first approach of a thermodynamic and kinetic modelling of quartz, microcline and albite dissolution. These calculations show that early stages of the alteration need only few years to be reached, while the kaolinite-clay boundary (kaolinite to muscovite in this case, for microcline alteration) will need about one to two centuries. This simulated sequence, obtained at 25°C and 1 bar, with an initial dilute solution (pH = 4, due to a little excess of HCl) took into account of a total surface area of $10^{4.6}$ cm^2/kg H_2O. This number can be compared to an estimated surface area in the Swedish granite of 10^5 cm^2/kg H_2O, for a low porosity (0.5%) and a mean fissure width of 0.1 mm (100 microns). From this work of HELGESON and Murphy, we may consider that 100 to 200 years, can be sufficient for the solution to reach the clay stability field by alteration of quartz and felspars. If we extrapolate this result to our problem in the granite, we can expect that the presence of additional more soluble constituents (anorthite, biotite and tremolite) will of course modify the complex kinetic interactions pointed out by the authors, but will probably not slow down the whole process. So we can use that time as an indication to try to calibrate the simulated alteration sequence versus time. The increase of temperature as it favours thermodynamically the mass transfers, will also favour the chemical reactions for kinetic reasons, as pointed out by HELGESON and MURPHY.

If we consider the groundwater flow calculated and modelled by CARLSSON and WINBERG (1983) we may try to combine results of thermodynamic, kinetic and hydrological modellings. For this calculation, the porosity of the granite due to fissures and small cracks will again be fixed at 0.5% (1l of solution in 0.2 m^3 of rock). The average velocities of the water in such a rock is generally very low and ranges between 0.2 and 0.5 m/year (CARLSSON and WINBERG). If these velocities are not disturbed around the repository, the migration of the solution will be 20 to 50 meters per century. These distances are smaller than the distances of thermal influences near the repository (TARANDI, 1983) for the same period of time and the solutions will have enough time to complete the expected reactions. In a very simple scheme, the following characteristics have been combined:

- water velocity: 0.2 to 0.5 m/year (20 to 50 m/year)
- size of a rock unit parallel to the water flow: 20 to 50 m
- time of reaction in one unit: 100 years
- decrease of porous volume per unit of time: $\Delta V/V = 2.10^{-5}$ to 2.10^{-4} (20 to 200 mm^3 of porosity lost per 1 000 cm^3 for one century).

The size of this rock unit crossed by the water in one century is smaller than the distance of influence of the repository and may really exist in the field. The cumulative effect of volume decrease on the porosity, can be approached by the following relation

$$p = p^o \left(1 - \frac{\Delta V}{V}\right)^n ; \; p^o = \text{initial porosity}; \; p = \text{final porosity}$$

where n represents the number of cumulative reactions, if one supposes in a first approximation, that the relative volume change $\Delta V/V$ remains constant.

The results of these calculations (Table 15) show that the loss of porosity can be between 2 and 20% for 100,000 years. For longer reaction times (10^6 to 10^7 y) a drastic decrease can be expected, but in this case, the effect on water velocity must be dramatic and the reaction rates will be changed when the system will tend to be more and more closed. This calculation must be carried on more precisely.

Table 15. Decrease of porosity versus time, for successive alterations in rock units (residence time equal to 100 years in each unit).

Total time considered (years)	Number of successive reactions n	Porosity ratio $\frac{p}{p^o} = (1 \frac{\Delta V}{V})^n$	
		$\frac{\Delta V}{V} = 2.10^{-5}$	$\frac{\Delta V}{V} = 2.10^{-4}$
5,000	50	0.999	0.990
50,000	500	0.990	0.904
100,000	1,000	0.980	0.819
350,000	3,500	0.932	0.500
1,000,000	10,000	0.819	0.135
3,500,000	35,000	0.500	0.0009
10,000,000	100,000	0.135	0.0000

3 SIMULATION OF INTERACTIONS BETWEEN CLAY SOLID SOLUTIONS AND AQUEOUS SOLUTIONS

The interactions between clay minerals and aqueous solutions is thermodynamically very complicated: clay minerals are non-stoechiometric minerals which present large variations of chemical composition, due to different possibilities for cation substitution (octahedral, tetrahedral and interlayer sites). They can be introduced in chemical modelling by using multicomponent solid solutions. This has been made for the computer codes DISSOL and THERMAL used for the calculations already described, and permit to predict the production of kaolinites and smectites at 25°C and K-smectites + chlorites at 60 and 100°C. If one considers more precisely the behaviour of clays submitted to the heat flux near the repository, the risk of smectite alteration, and the possible transformation into illite-type clays becomes very important (ANDERSON, 1983). Na-bentonites used in the repository are chosen for their swelling properties, and an illitization would largely alter these properties. The simulation of water-clay interaction has been conducted and the results allow to point out as one key-factor, the clay/water ratio.

3.1 SIMULATED TRANSFORMATION OF CLAYS WITH LOW CLAY/WATER RATIOS

3.1.1 Clays produced in the granitic rock

Clays produced by alteration of the granite represent never more than one gram per liter of solution (Clay/water less than 0.001). With these conditions we found that 2:1 clays formed at 25°C (Table 3) fixed very little amount of potassium (4% of CEC) and no sodium in the interlayer sites. At 60 and 100°C the major difference in the composition of the clays was the increase of potassium uptake (respectively 25 and 87% of the CEC), while the tetrahedral and octahedral substitutions did not show important variations. In addition to that transformation of the smectite by

Ca-K exchange, a chlorite phase was produced at 60 and 100°C (Mg or Mg-Fe^{II} chlorites, depending on the redox potential). This is a general result obtained previously for other granitic rocks or also for sandstones between surface temperatures and 150°C (FRITZ, 1981).

3.1.2 Na-bentonites in equilibrium with an aqueous solution

The Na-bentonites composition considered here is derived from the Wyoming Montmorillonite (Clay Spur) described by KITTRICK (1971) and TARDY and FRITZ (1981):

$$(Si_{3.94}Al_{0.06})_T(Al_{1.52}Fe^{III}_{0.19}Mg_{0.22})_O\ O_{10}(OH)_2(Na_{0.27}Ca_{0.1}K_{0.02})_I$$

This smectite, with a very low tetrahedral charge (0.06) and an octahedral charge (0.43) cannot be directly simulated by the dissolution models. Two complementary computer codes have been developed only for this purpose (CISSFIT: Clay Ideal Solid Solution Fitting, and SOLSAT: Solid solution Saturation). These tools calculate the composition of a solution in equilibrium with a given clay, and the reverse, at different temperatures. For this Na-bentonite, the equilibrium condition, even at low temperature, needs more silica in the solution than generally encountered in the dilute well waters: 0.6 to 0.8 mmoles/l instead of 0.15 to 0.3. If the well waters are not dilute, as it is often in deep swedish granites (CARLSSON et al., 1983; ALLARD et al., 1983), the equilibrium with the aqueous phase is also not possible, more tetrahedral substitution is favoured, particularly if the pH is high (8 to 9). High salinities produce the same effect on clay stability as a temperature increase: the illites end-members become more important in the solid solution. This happens if the clay/water ratio is low, because the clay transformation does not modify too much the aqueous phase and can be completed. Na-bentonites, therefore seem to be unstable in well waters from the swedish granite. Theoretically, the temperature increase and possible high salinities will favour an illitization as observed by PUSH (1983) for clays submitted to a maximum of 100°C in natural environments.

3.2 SIMULATED TRANSFORMATION OF CLAYS WITH HIGH CLAY/WATER RATIOS

The Na-bentonites will be used in the repository. This filling material, muds or wet clays will only contain a minimum of water and the clay/water ratio will be as high as 1:1 in weight. In these conditions, for the same initial wetting water, the evolution can be very different. Initially, the thermodynamic state is the same: the bentonite is not stable. However, the consequent irreversible evolution of a very small part of the clay phase will produce silica and consume potassium and aluminium (if available) from the solution. If kaolinite and goethite are initially associated with the bentonite, they are destroyed. Nevertheless, the composition of the aqueous phase varies rapidly (increase of silica, decrease of potassium and aluminium) and this will tend to stabilize again the remaining bentonites. The simulation of this interaction showed that the "self-buffering" of the clay was so high that the change in the total composition of the bentonite was negligible between 10 to 100°C. This situation can be expected in closed cannisters and in the closed area around. The Na-bentonite will tend to transform into illite, but the amount of initial clay is high enough to act as a buffer.

CONCLUSIONS

The results of simulated granite alterations allow to point out the following conclusions:

(1) The alteration of the granitic rock is favoured by the temperature increase due to the active repository (up to 100°C).

(2) The porosity of the rock due to small fissures, is very low, the reactive surfaces for water-rock interactions are therefore very large while the water velocity is very low: these conditions favour an important chemical interaction and clays stability field can be reached. For this reason the alteration will produce a decrease of the porosity.

(3) With higher temperatures, the calcite deposit plays an important role in the porosity decrease.

(4) By combining the results of thermodynamic calculations, with results obtained recently with a kinetic approach of mineral dissolutions, and taking into account the known and calculated water flow in the swedish granites, a first attempt to calibrate the modelling in time scale has been made. The decrease of porosity can be estimated roughly between 2 and 20% for 100.000 years.

(5) The Na-bentonites considered in the repository environment seem to be unstable with respect to the chemistry of the well waters and should be transformed into illites, particularly when the temperature will increase. However, without being able to discuss the kinetics of this reaction, the modelling showed that high clay/water ratios will limit the evolution by "self-buffering" of the clay:

- one particle of bentonite floating in the Stripa well water will be transformed into illite if time is sufficient,

- one drop of Stripa well water within a cm^3 of bentonite will be highly transformed but will only alter few particles of clay and this will be of no consequence for the total clay.

This means that the behaviour of clays will be probably very different within the rock around the repository (illitization in slightly open system with low clay/water ratios) and within the repository itself (clay buffer in closed system for a long time, with high clay/water ratios). This chemical buffering effect is a positive point for the use of these clays, already discussed (PUSH, 1983b) on a more physical point of view.

REFERENCES

ANDERSON D M (1983)
Smectite alteration. Proceedings of a colloquium at State University of N Y at Buffalo, May 26-27 1982. SKBF KBS TR 83-03, 40 p.

ALLARD B, LARSON S Å, TULLBORG E-L, WIKBERG P (1983)
Chemistry of deep groundwaters from granitic bedrock. SKBF KBS TR 83-59.

CARLSSON L and WINBERG A (1983)
Model calculations of the groundwater flow at Finnsjön, Gideå and Kamlunge. SKBF KBS TR 83-45, 208 p.

CARLSSON L, ANDREWS J, FONTES J C, MICHELOT J L and NORDSTROM K (1983)
Geochemical and isotope characterization of the Stripa groundwaters - Progress Report. STRIPA PROJECT 83-01, Internal Report, 131 p.

FRITZ B (1975)
Etude thermodynamique et modélisation des réactions entre minéraux et solutions. Application à la géochimie des altérations et des eaux continentales. Thèse Doct Ing, Sci Géol, Mém 41, Strasbourg, 152 p.

FRITZ B (1981)
Etude thermodynamique et modélisation des réactions hydrothermales et diagénétiques. Thèse Sci, Strasbourg, et Sci Géol, Mém 65, 197 p.

FRITZ B, DUPLAY J and TARDY Y (1983)
Geochemical simulation of granitic rocks submitted to temperature variations: water-rock interactions. SKBF KBS contract report, July 1983, 43 p.

FRITZ B, CASSAN J P, CLAUER N and TARDY Y (1984)
Interstitial fluid circulations and diagenetic transformations in sedimentary basins: a geochemical modelling approach. Coll Intern, Thermal Phenomena in sedimentary basins, Bordeaux 6-10 June 1983, Technip Ed, (to be pub).

HELGESON H C and MURPHY W M (1983)
Calculation of Mass transfer among minerals and aqueous solutions as a function of time and surface area in Geochemical processes. I Computational approach. Math Geol, vol 15, n°1, pp 109-130.

HULTBERG B, LARSON S Å and TULLBORG E-L
Chemical and Isotopic compositions of ground waters from Finnsjön, Kråkemåla and Sternö, Sweden (preprint).

KBS II, GEOLOGY (1978)
Handling of Spent Nuclear Fuel and final storage of vitrified high level Reprocessing waste, 81 p.

KITTRICK J A (1971)
Stability of montmorillonite
Belle Fourche and Clay Spur montmorillonites. Proc Soil Sci Am, 35, pp 815-820.

MICHARD G (1979)
Géothermomètres chimiques. Bull Bur Rech gèol min, sér II, sect III, 2, p 183-189.

PUSH R (1983)
Stability of deep-sited smectite minerals in crystalline rock - chemical aspects. SKBF KBS TR 83-16, 68 p.

PUSH R (1983b)
Use of clays as buffers in radioactive repositories. KBS TR 83-46, 79.

TARANDI T (1983)
Calculated temperature field in and around a repository for spent nuclear fuel. SKBF KBS TR 83-22, 30 p.

TARDY Y and FRITZ B (1981)
An ideal solid solution model for calculating solubility of clay minerals. Clay Min, 16, pp 361-373.

WIKBERG P, GRENTHE I and AXELSEN K (1983)
Redox conditions in ground waters from Svartboberget, Gideå, Fjällveden and Kamlunge. SKBF KBS TR 83-40, 27 p.

List of KBS's Technical Reports

1977–78
TR 121
KBS Technical Reports 1 – 120.
Summaries. Stockholm, May 1979.

1979
TR 79–28
The KBS Annual Report 1979.
KBS Technical Reports 79-01 – 79-27.
Summaries. Stockholm, March 1980.

1980
TR 80–26
The KBS Annual Report 1980.
KBS Technical Reports 80-01 – 80-25.
Summaries. Stockholm, March 1981.

1981
TR 81–17
The KBS Annual Report 1981.
KBS Technical Reports 81-01 – 81-16.
Summaries. Stockholm, April 1982.

1982
TR 82–28
The KBS Annual Report 1982.
KBS Technical Reports 82-01 – 82-27.

1983
TR 83–77
The KBS Annual Report 1983.
KBS Technical Reports 83-01–83-76
Summaries. Stockholm, June 1984.

1984
TR 84–01
Radionuclide transport in a single fissure
A laboratory study of Am, Np and Tc
Trygve E Eriksen
Royal Institute of Technology
Stockholm, Sweden 1984-01-20

TR 84-02
Radiolysis of concrete
Hilbert Christensen
Studsvik Energiteknik AB,
Nyköping, Sweden
Erling Bjergbakke
Risö National Laboratory,
Roskilde, Denmark 1984-03-16

TR 84-03
Effect of β-radiolysis on the products from α-radiolysis of ground water
Hilbert Christensen
Studsvik Energiteknik AB,
Nyköping, Sweden
Erling Bjergbakke
Risö National Laboratory
Roskilde, Denmark
1984-07-10

TR 84—04
Analysis of some laboratory tracer runs in natural fissures
Luis Moreno
Ivars Neretnieks
The Royal Institute of Technology
Department of Chemical Engineering
Trygve Eriksen
The Royal Institute of Technology
Department of Nuclear Chemistry
Stockholm, Sweden 1984-03-15

TR 84—05
Diffusion in clay—Experimental techniques and theoretical models
Trygve Eriksen
Royal Institute of Technology, Stockholm
Arvid Jacobsson
University of Luleå, Luleå
Sweden 1984-06-28

TR 84—06
Uranium series disequilibrium studies of drillcore Km3 from the Kamlunge test-site, northern Sweden
John AT Smellie
Swedish Geological
Luleå, Sweden 1984-03-30

TR 84—07
Study of strontium and cesium migration in fractured crystalline rock
Erik Gustafsson
Carl-Erik Klockars
Swedish Geological Co
Uppsala, Sweden 1984-09-28

TR 84—08
Fracture fillings in the gabbro massif of Taavinunnanen, northern Sweden
Sven Åke Larson
Geological Survey of Sweden
Eva-Lena Tullborg
Swedish Geological Company
Göteborg August 1984

TR 84—09
Comparative study of geological, hydrological and geophysical borehole investigations
Kurt-Åke Magnusson
Oscar Duran
Swedish Geological Company
Uppsala September 1984