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**Geochemical modelling of the
evolution of a granite-concrete-water
system around a repository for spent
nuclear fuel**

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GEOCHEMICAL MODELLING OF THE EVOLUTION OF A
GRANITE-CONCRETE-WATER SYSTEM AROUND A
REPOSITORY FOR SPENT NUCLEAR FUEL

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

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SUMMARY

The interactions between a granitic rock and concrete due to the natural solutions circulating around a repository for spent nuclear fuel has been simulated considering the dissolution of Ca(OH)_2 as the major source of alkalinity due to the concrete. This study follows a previous one (SKB-Technical Report 84-10 by Fritz, Kam and Tardy, 1984) considering the same interaction without concrete at 25, 60 and 100°C. The temperature range has been extended to 150° C for both hypothesis (with or without Ca(OH)_2).

The results of the modelling are considered as following :

- evolution of the water chemistry due to detected possible chemical reactions. (major chemical species, activities, pH, Eh, pCO_2 ...)
- minerals produced and dissolved.

The calculations give mass transfers and volumic consequences (opening or closing tendencies).

The conclusions of this yearly report are mainly the following :

- (1) the extent of the temperature range for the storage (up to 150°C) does not change the tendencies previously detected (Fritz et al., 1984) in the same conditions without any particular alkaline effect due to concrete dissolution, the reactions occurring tend to decrease the porosity of the rock by a sealing effect due to calcite precipitation and clays formation.
- (2) The effect of an alkaline concrete dissolution is clearly important, pH may reach very high values in closed system (very low pCO_2), and the volumic consequence is found in favour of an opening of the porosity, at the stage of saturation of the portlandite.

This is probably an important point considering the security of natural barrieres around such a repository.

INTRODUCTION

This study was conducted as a complementary study to a previous one (FRITZ, KAM and TARDY, 1984, SKB-KBS TR 84-10) by (1) extending the temperature range from 100 to 150°C and (2) by introducing in the reacting rock phase the mineral Ca(OH)_2 , portlandite, as representative of the soluble part of a concrete.

The questions were, concerning the rock-water interactions around a repository for spent nuclear fuel :

- are previous conclusions still valuable at 150°C as shown between 25 and 100°C ?
- are previous conclusions modified if the rock phase contains an alkaline soluble mineral from a concrete ?

These questions arise as a result of SKB studies of the so called WP-cave concept. In order to remain in continuity with the previous mentioned study, the conditions for rock and solutions were considered here in complete consistency with the previous ones, except for the temperature and the added alkaline phase.

Conclusions given here, will therefore be complementary. Possible reactions are detected on thermodynamic assumptions and the consequent mass transfers represent in fact the maximum of potential evolution of the system, when it tends to return to the minimum of energy after the disturbance due to the nuclear waste storage.

1 INITIAL CONDITIONS FOR THE SIMULATIONS

1.1 The initial aqueous solution at different temperatures

The calculations have been made at 25, 100 and 150°C. This means that the natural solution in contact with the rock (about 10°C in in situ conditions) is supposed to be preheated before reacting with that rock. This corresponds exactly to what will happen in a repository where the thermal effect is responsible for the geochemical evolution of the rock-water system.

This first stage of heating is simulated using the computer code THERMAL (FRITZ, 1981) with three steps (25-100-150°C). This is of course a simplified approach of the natural system where the heating will go progressively and the consequent reactions will also begin progressively and not only at three given temperatures.

The initial composition of the solution (at 10°C) is the same as in the previous study (FRITZ et al., 1984) called F1, a dilute well water from FINNSJON ("mean drilled well", HULTBERG et al.). This water was chosen in order to give an estimation of the maximum of mass transfer, or "alteration risk", for the rock surrounding the storage. The calculated chemical composition of that solution considered as an initial reacting solution in the modelling at 25, 100 and 150°C is given in table 1. The initial amounts of dissolved trace elements considered here (Al, Fe) are given by the saturation limits of kaolinite for aluminium, and goethite (FeOOH) or pyrite FeS₂ for iron, depending on redox conditions. In situ conditions for solutions at depth in swedish granites (WIKBERG et al., 1983) are represented by reduced conditions (log pO₂ = -44.5), but without an active reducer in the system :

- Eh = +137 mV at 25°C
- Eh = -157 mV at 100°C
- Eh = -365 mV at 150°C

The major evolution of the solution between 10 and 150°C is related to the formation of a calcite deposit (decrease of Ca and alkalinity). This mineral formation will, of course, be taken into account in the total mass transfers calculation (heating + alteration at a given tem -

Table 1 - Chemical composition of the solutions F1 used for the simulations of the alteration of granite at 25°C, 100°C and 150°C.

Temperature	10°C	25°C	100°C	150°C
pH	7.400	7.319	6.836	6.752
Eh (mV)	+200.000	+136.913	-156.963	-364.603
Log pCO ₂	-2.238	-2.031	-1.147	-0.911
Na (10 ⁻⁰⁶ moles /l)	634.422	644.657	644.645	643.061
K -----	190.435	190.430	190.430	190.430
Ca -----	1524.400	1524.400	1052.000	818.940
Mg -----	188.796	188.800	188.800	188.800
Al -----	0.001	0.001	0.001	0.001
Fe -----	10 ⁻⁰⁵	10 ⁻⁰⁵	0.006	0.255
Si -----	184.738	184.740	184.740	184.740
SO ₄ -----	175.500	175.500	175.500	175.500
Cl -----	566.486	566.490	566.490	566.490
Alkalinity (10 ⁻⁰⁶ eq/l)	3344.000	3344.000	2399.200	1932.000
Total Charge (mg/Kg H ₂ O)	365.000	365.000	318.000	295.000
Calcite deposit (10 ⁻⁰⁶ moles / l)	0.000	0.000	502.000	705.000

Table 2 - Chemical composition of the solution V1 used for the simulations of the alteration of granite at 150°C.

Temperature	10°C	150°C
pH	9.310	7.127
Eh (mV)	-560.000	-618.239
Log pCO ₂	-6.103	-3.614
Na (10 ⁻⁰⁶ moles /l)	12048.200	12048.000
K -----	30.690	30.690
Ca -----	4291.420	4241.352
Mg -----	7.815	7.815
Al -----	0.300	0.300
Fe -----	0.013	0.004
Si -----	216.360	216.360
SO ₄ -----	1061.770	916.180
NO ₃ -----	112.889	112.890
F -----	242.105	151.111
Cl -----	18104.400	20004.800
Alkalinity (10 ⁻⁰⁶ eq/l)	139.000	95.555
Total Charge (mg/Kg H ₂ O)	1230.000	1103.000

perature). The carbon dioxide pressure was not fixed in the simulation, as it is commonly done for the simulation of near surface weathering processes or for reactions in soils : the rock-water system surrounding the storage is supposed to be closed to atmosphere and to any CO₂ gas input : the values given for logfCO₂ in table 1 and following is only calculated from the alkalinity and pH data within the aqueous speciation calculation and represents the theoretical equilibrium CO₂ partial pressure for the system.

The coupled modelling for water circulation, thermal effect and water - rock interaction has only recently be considered for very simple chemical systems, (COUDRAIN-RIBSTEIN, 1988) and will need an introduction of kinetic laws for all reactions. This is still on development in the laboratory.

A second type of solution has been tested in this study. It is a more concentrated solution from STRIPA, the V1 solution (see previous report, FRITZ et al., 1983). This has been done for estimating the effect of a more important salinity on the predicted alteration sequences. As this report is more focused on the 150°C temperature range, the tests with V1 were only conducted at that temperature (Table 2).

1.2 The mineral reacting assemblage

The mineral assemblage chosen for the calculations (FRITZ et al., 1984) fits the chemical composition of the granodiorite from FINNSJON Lake (KBS-1 report 78-II, Geology, see bore hole (1)) with quartz, Na-, K- and Ca- Feldspars, ferrous mica (Annite) and one Mg-Amphibole. The composition of that rock is given in Table 2.

In addition to the granite, the concrete is supposed now to react with the same solution. We only considered that reaction as a source of alkalinity, using the mineral portlandite (Ca(OH)₂). The relative influences of respectively concrete and granite dissolutions in a given volume of solution are very difficult to measure or estimate. The concrete-water and granite-water interactions will generally be successive with unequal reacting times and under different physical conditions (interaction surfaces, fractures or porosity, etc...) and obviously very different kinetic laws. For that reason we decided to simply "add" to the granite a given proportion of portlandite : 1.0 moles of Ca(OH)₂ (2.0 éq. of alkalinity) the reference granite units which corresponds to 2.2 éq. of alkalinity. With these hypothesis, the system will reach the saturation (and stability) of the portlandite. Again, the modelling with these simple hypothesis gives a prediction of the maximum of mass transfer (and risk).

At 150°C, one test was also made with a concrete/granite ratio ten times higher (10.0 moles of Ca(OH)₂ the granite unit).

1.3 The simulation parameters

Both programs THERMAL (heating of the initial solution) and DISSOL (water-rock interaction at constant temperature) have been used with the CLOSED SYSTEM option. This option means that reactant and product minerals and the aqueous solution are considered as a closed system for mass balance equations. As a consequence any early precipitated mineral in a given calculated sequence may be redissolved if unstable again in a late stage of the reaction. This option seems more reasonable for simulating interactions in deep aquifers (low porosity, low water flux through the rock) when the thermal disturbance ($\Delta T > 0$) is followed by a long-term granite-(concrete)-water interaction.

The initial reactant assemblage (Table 3) is dissolved in the solution. Any reacting mineral disappears from that "dissolved rock" as soon as its saturation state is reached in the solution.

These minerals have also not been allowed to precipitate even if this may appear possible thermodynamically for quartz, K-Feldspar and tremolite. This choice, based on a first kinetic approximation may however be discussed for quartz, for example, at 150°C.

The secondary minerals are produced at equilibrium with the solution:

- pure minerals as goethite, pyrite, kaolinite, calcite, ... ;
- a binary solid solution for chlorite (clinochlore - daphnite) ;
- a multicomponent solid solution for a 2 : 1 clay phase ;

As in the previous report (SKB-TR-84-10) the simulation does not include kinetic laws for the chemical reactions involved. The reactant minerals, if initially unstable with respect to the solution are dissolved irreversibly. The consequent mass transfers are calculated supposing that the aqueous ions speciation and the precipitation of secondary phases are constrained by thermodynamic equilibrium conditions.

Table 3 - Mineralogical composition of the granite used in the simulation (Granodiorite of FINNSJON Lake).

Minerals	Formula	% molar
Quartz	SiO ₂	64.40
K-Feldspar	KAlSi ₃ O ₈	7.90
Albite	NaAlSi ₃ O ₈	12.50
Anorthite	CaAl ₂ Si ₂ O ₈	10.00
Annite	Si ₃ AlFe ^{II} ₃ O ₁₀ (OH) ₂	3.70
Tremolite	Si ₈ Mg ₅ Ca ₂ O ₂₂ (OH) ₂	1.50

2. SIMULATED MINERALOGICAL SEQUENCE AT 150°C WITHOUT CONCRETE IN CONTACT WITH THE GRANITE AND THE SOLUTION F1

This computer run is a simple extension of the previous study done at 25, 60 and 100°C (FRITZ et al., 1984) in order to verify if the geochemical evolution tendencies predicted up to 100°C are confirmed, or not, at 150°C.

2.1 Stability sequence for primary minerals

The primary minerals are saturated in the following order (table 4, figure 1A) :

- Tremolite
- Quartz
- K-Feldspar
- Na-Feldspar

while anorthite and annite do not reach their stability field.

This sequence is in perfect continuity with what was predicted from 25 to 100°C. With the temperature increase, quartz and alkaline Feldspars are progressively destabilized among the primary minerals, while the Mg-bearing mineral, tremolite appears more stable.

2.2 Stability sequence for secondary minerals

For secondary minerals also, the results at 150°C just confirm tendencies described for lower temperatures (table 4, figure 1)

- calcite precipitation all along the sequence ;
- initial precipitation of goethite ;
- early formation of a chlorite phase, later in competition with a transitory kaolinite phase and a 2 : 1 clay phase.

From 25 to 100 and finally 150°C one observes that chlorite is appearing more and more earlier in the sequence and is formed even in competition with other clay phases and a zeolite (laumontite). At this temperature, the two clay-phases seem to select respectively magnesium in a chlorite-type chlorite and iron as ferrous iron in a ferrous mica type 2 : 1 clay (Table 5, first line).

Table 4 - Sequence of events in the simulated dissolution of granite at 150°C
(initial Eh = -365 mV, Log pO₂ = -44.642, Log pCO₂ = -0.911)

Log ξ	Mineralogical events	pH	Log pCO ₂	Eh(mV)
	Calcite initially stable	6.750	-0.911	-364.603
-8.680	Goethite precipitates	6.752	-0.911	-364.588
-6.126	Chlorite precipitates	6.755	-0.911	-364.836
-6.048	Goethite has been redissolved	6.751	-0.912	-364.447
-5.442	2:1 Clay precipitates	6.723	-0.885	-362.051
-5.441	Kaolinite precipitates	6.722	-0.884	-361.967
-4.821	Tremolite becomes stable	6.808	-0.964	-369.155
-4.801	Quartz becomes stable	6.814	-0.969	-369.636
-4.524	K-Feldspar becomes stable	6.937	-1.082	-379.971
-4.431	Laumontite becomes stable	6.992	-1.136	-384.534
-3.463	Kaolinite has been redissolved	7.949	-1.710	-464.640
-3.365	Albite becomes stable	8.181	-1.897	-484.032

Table 5 - Chemical composition of the total 2:1 Clay produced by a simulated alteration of only the granite, the granite with 1.0 Ca(OH)₂ and the granite with 10.0 Ca(OH)₂ in solution F1 at saturation point of Albite (150°C).

Temperature	Clay formula		
	Tetrahedra	Octahedra	Interlayer
150°C	Si _{3.087} Al _{0.913}	Al _{0.566} Fe _{2.139} Mg _{0.011} O ₁₀ (OH) ₂	K _{0.795} Na _{0.114} Ca _{0.002}
	and Chlorite (Clinochlore) : Al ₂ Mg ₅ Si ₃ O ₁₀ (OH) ₈		
150°C with 100 Ca(OH) ₂	Si ₃ Al	Fe _{2.930} Mg _{0.070} O ₁₀ (OH) ₂	K _{0.950} Na _{0.035} Mg _{0.007}
150°C with 1000 Ca(OH) ₂	Si ₃ Al	Fe _{2.936} Mg _{0.064} O ₁₀ (OH) ₂	K _{0.950} Na _{0.033} Ca _{0.002}

Table 6 - Evolution of the porous volume due to dissolution and precipitation of minerals at 150°C .

Log ξ	Mineralogical events	Volume V _D of minerals dissolved	Volume V _p of minerals precipitated	Difference V _p - V _D 100($\frac{V_p - V_D}{V_D}$)
		(mm ³ /kg H ₂ O)	(mm ³ /kg H ₂ O)	(%)
	Calcite initially stable	0.000	26.000	>100
-8.680	Goethite precipitates	0.012	26.050	>100
-6.126	Chlorite precipitates	4.161	26.760	>100
-6.048	Goethite has been redissolved	5.423	27.490	>100
-5.442	2:1 Clay precipitates	20.540	32.698	+59.19
-5.441	Kaolinite precipitates	21.270	33.000	+55.15
-4.821	Tremolite becomes stable	84.300	81.550	- 3.26
-4.801	Quartz becomes stable	88.070	84.350	- 4.22
-4.524	K-Feldspar becomes stable	140.100	135.500	- 3.28
-4.431	Laumontite becomes stable	160.200	157.200	- 1.87
-3.463	Kaolinite has been redissolved	1030.000	1240.000	+20.39
-3.365	Albite becomes stable	1280.000	1530.000	+19.53

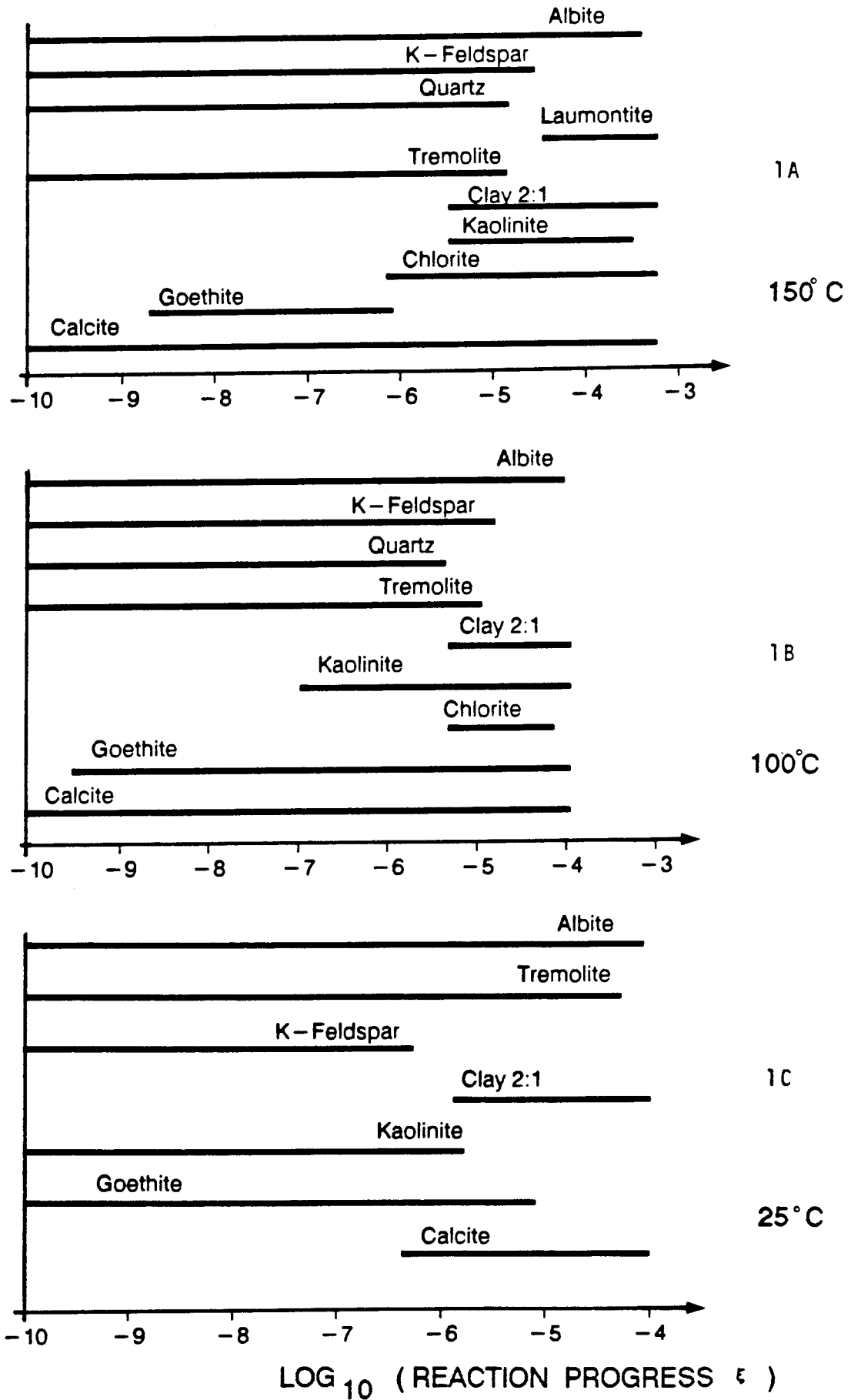


Figure 1. Mineralogical sequences as simulated along the dissolution path of the granite in solution F1 (after FRITZ et al. 1983 at 25°C and 100°C, this study at 150°C).

2.3 Chemical composition of the clay phases

Three different clay phases are formed in this simulation, a kaolinite, a chlorite and a 2:1 clay.

The kaolinite has a constant composition $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ as it was not considered as a possible solid solution (no Al^{3+} - Fe^{3+} substitution expected in a reduced environment).

The chlorite phase is considered as resulting from a binary solid solution between clinocllore ($\text{AlMg}_5\text{Si}_3\text{O}_{10}(\text{OH})_8$) and daphnite ($\text{Al}_2\text{Fe}^{\text{II}}_5\text{Si}_3\text{O}_{10}(\text{OH})_8$).

The 2:1 clay is a multicomponent solid solution between 20 end-members with three levels for substitutions :

- in tetrahedral sites : Si-Al
- in octahedral sites : Al- Fe^{II} - Fe^{III} -Mg
- in interlayer sites : K-Na-Ca-Mg

These phases are, of course, competing for the some chemical elements. In this sequence they remain produced together until the late stage of reaction, when kaolinite is no more formed (table 4, fig.1). The solid solution effect is not really acting for the chlorite, which tends to join the pure clinocllore end-member, the ferrous iron being precipitated by a ferrous mica-type clay (table 5).

The system tends to produced phases which are, so to say "purified", with Fe^{2+} in one phase and Mg^{2+} in the other.

2.4 Volumic balance along the alteration sequence

The calculation of the volumes of dissolved and precipitated minerals allows to estimate the respective increase or decrease of the porosity of the rock when these mass transfer occur. The volumic balance at each step of the calculation is given in table 6. Initially positive it corresponds to an excess of precipitated minerals due to an initial calcite precipitation during the heating of the water. Then the mass transfer becomes quite equilibrated with a light tendency to increase the porosity before reaching again the field of porosity decrease at the "end" of the sequence (near albite saturation) when the mass transfer becomes also significant with respect to the volume of the reacting solution :

- dissolution or precipitation of about 1 cm^3 per liter of solution.

One may notice, however, that for the total sequence these volumic effects for either dissolution or precipitation do not exceed 0.1 % of the porosity containing the solution. The volumic balance remains even largely smaller. Only cumulative effects on long term reaction with circulating solutions would really significantly alter the porosity as previously shown with equivalent numbers (FRITZ et al., 1984).

3. SIMULATED MINERALOGICAL SEQUENCE AT 150°C WITHOUT CONCRETE IN CONTACT WITH THE GRANITE AND THE SOLUTION V1

The calculation is done with the V1 Stripa solution described above (Table 2) in order to take into account the effect of an initial higher dissolved salt content :

- TDS is 1,23 g/l for V1, with Na, Ca, Cl as major ions ;
- TDS is 0,37 g/l for F1, with Ca, Na, HCO₃ as major ions.

3.1 Stability sequence for primary minerals

The primary minerals reach successively their saturation state, except annite :

- tremolite very early in the sequence (Table 7, figure 2) ;
- then quartz and K-Feldspar ;
- albite ;
- even anorthite saturation is obtained here because of particular pH-pCO₂ conditions (high pH, low pCO₂).

3.2 Stability sequence for secondary minerals

The V1 solution is more saline, contains less bicarbonate and corresponds to a more reducing environment. This induces differences in the secondary phases :

- the calcite is not initially produced and appears only at the very end of the alteration sequence (Fig. 2) ;
- fluorite and pyrite are precipitated from the beginning ;
- chlorite is formed, like with F1, but will be replaced progressively by a 2 : 1 clay phase associated with the zeolite (laumontite). The 2 : 1 clay phase is also here a ferrous mica (Table 8).

Table 7 - Sequence of events in simulated dissolution of granite at 150°C in water V1. (initial Eh = -618 mV, Log pO₂ = -55.225, Log pCO₂ = -3.614).

Log ξ	Mineralogical events	pH	Log pCO ₂	Eh(mV)
	Fluorite + Pyrite initially stable	7.127	-3.614	-618.239
-6.826	Tremolite becomes stable	7.147	-3.634	-619.684
-6.327	Chlorite precipitates	7.168	-3.654	-621.615
-5.898	2:1 Clay precipitates	7.191	-3.617	-623.555
-5.679	Pyrite has been redissolved	7.129	-3.617	-618.203
-5.477	Laumontite precipitates	7.134	-3.622	-618.203
-4.817	Fluorite has been redissolved	7.066	-3.543	-612.782
-4.521	Quartz becomes stable	7.016	-3.481	-608.488
-4.273	Chlorite has been redissolved	7.031	-3.470	-609.833
-3.637	K-Feldspar becomes stable	7.147	-3.373	-619.626
-3.150	Albite becomes stable	8.267	-3.939	-713.676
-3.041	Calcite precipitates	8.279	-4.215	-714.747
-3.026	Anorthite becomes stable	8.289	-4.318	-715.554

Table 8 - Chemical composition of the total 2:1 Clay produced by a simulated alteration of only the granite and the granite with 1.0 Ca(OH)₂ in solution V1 at saturation point of Albite (150°C).

Temperature	Clay formula		
	Tetrahedra	Octahedra	Interlayer
150°C	Si _{3.015} Al _{0.985}	Al _{0.293} Fe _{2.555} Mg _{0.003} O ₁₀ (OH) ₂	K _{0.914} Na _{0.069} Ca _{0.001}
150°C with 100 Ca(OH) ₂	Si ₃ Al	Fe _{2.981} Mg _{0.004} O ₁₀ (OH) ₂	K _{0.669} Na _{0.312} Ca _{0.002}

Table 9 - Evolution of the porous volume due to dissolution and precipitation of minerals at 150°C in water V1.

Log ξ	Mineralogical events	Volume V _D of minerals dissolved	Volume V _P of minerals precipitated	Difference V _P - V _D
		(mm ³ /kg H ₂ O)	(mm ³ /kg H ₂ O)	100($\frac{V_P - V_D}{V_D}$) (%)
	Fluorite + Pyrite stable	0.000	0.055	>100
-6.826	Tremolite becomes stable	0.829	0.086	-89.59
-6.327	Chlorite precipitates	2.484	0.172	-93.07
-5.898	2:1 Clay precipitates	6.577	0.599	-90.89
-5.679	Pyrite has been redissolved	10.986	1.225	-88.84
-5.477	Laumontite precipitates	17.239	2.252	-86.93
-4.817	Fluorite has been redissolved	79.775	73.073	- 8.40
-4.521	Quartz becomes stable	154.000	153.268	- 0.47
-4.273	Chlorite has been redissolved	160.400	161.151	+ 0.65
-3.637	K-Feldspar becomes stable	903.414	1137.413	+25.90
-3.150	Albite becomes stable	2255.000	2874.073	+27.45
-3.041	Calcite precipitates	2573.900	3252.800	+26.38
-3.026	Anorthite becomes stable	2623.570	3305.517	+25.99

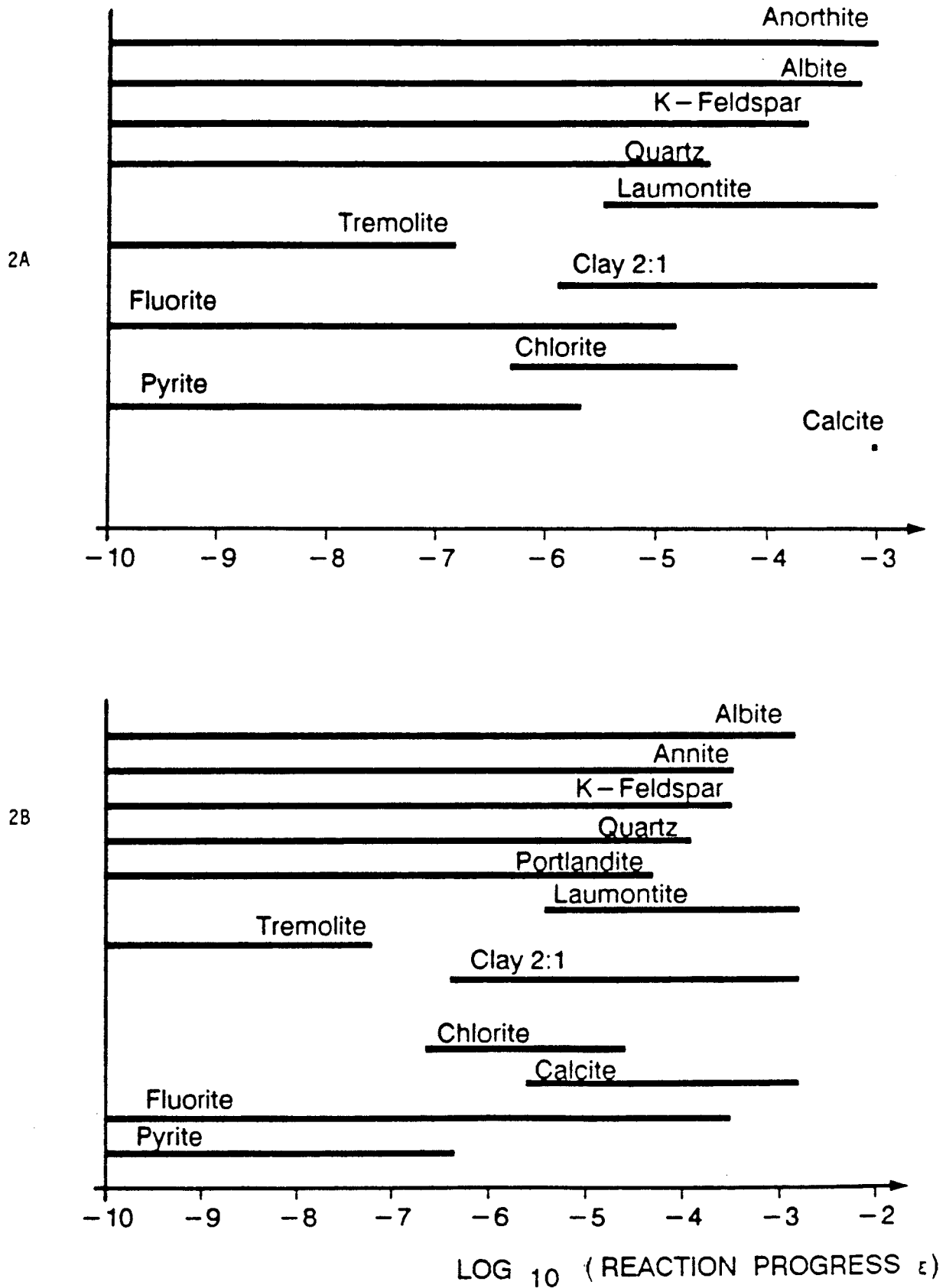


Figure 2. Mineralogical sequences as simulated along the dissolution path of the granite in solution VI at 150°C. 2A : without portlandite. 2B : with 1 Mole of portlandite per unit of granite.

3.3 Volumic balances

The volumic balances calculated at each step of this process (Table 9) shows clearly an initial stage of alteration with a clear tendency to increase the porosity. However, when the interaction is completed, after K-Feldspar and Na-Feldspar saturations, the volumic balance is stabilized around a 25% of excess of the volume of precipitated minerals over the volume of the dissolved minerals.

These calculations at 150°C for the granite-solution interaction allow to extend the conclusions given for the same interaction between 25 and 100°C : the system disturbed by the heating due to the nuclear waste storage is obviously destabilized, and the primary minerals from the rock are partially dissolved producing secondary minerals. If the alteration sequence is completed (Feldspars saturation reached) it tends to decrease the porosity of the rock by an excess of volume of the precipitated minerals.

4. SIMULATED MINERALOGICAL SEQUENCE FOR THE GRANITE-CONCRETE-SOLUTION F1 SYSTEM AT 25, 100 AND 150°C

The influence of a possible concrete dissolution in the water reacting with the heated granite has been conducted at 25, 100 and 150°C. The results of all calculations will not be all detailed here, but the major results are summarized in tables and figures. The discussion will essentially point out the differences with previous granite-water interaction modelling in order to underscore the particular influence of an alkaline input in the system, from the concrete.

4.1 Option (1) : granite - Ca(OH)₂ (1 mole/granite unit) - solution F1.

The sequence of events and the evolution of the porous volume are given successively in tables 10 and 11 (at 25°C), 12 and 13 (at 100°C), 14 and 15 (at 150°C). The comparison with the same sequences without concrete, shows that the possible alteration is considerably enhanced. The alkaline effect is clear, the pH variation leads to very high values at the "end" of each sequence, when both albite and portlandite are stable :

- pH = 12,9 at 25°C (Table 10)
- pH = 10,4 at 100°C (Table 12)
- pH = 9,6 at 150°C (Table 14)

These very alkaline conditions, together with calcite precipitation, are only possible because the CO₂ partial pressure is strongly depleted. This corresponds to an extension of what has been observed and discussed by FRITZ et al. (1987) and CLAUER et al. (1988, in press) for in situ conditions in STRIPA waters : very low pCO₂, high pH and calcite equilibrium in the fractures of the granite.

The portlandite is acting here as a strong base increasing the alteration of the granite : the mass transfers are increased all along the sequence. However, considering the volumes of dissolved rock and secondary formed minerals, the results are apparently not as much different as expected. One observes clearly that the porosity tends to decrease as long as portlandite is not saturated (Tables 11, 13, 15). This is due to the formation of calcite, clay minerals and laumontite. At 25°C only, this tendency does not appear immediately at the begin-

Table 10 - Sequence of events in simulated dissolution of granite at 25°C with 1.0 Ca(OH)₂ (initial Eh = +137 mV, Log pO₂ = -44.588, Log pCO₂ = -2.031).

Log ξ	Mineralogical events	pH	Log pCO ₂	Eh(mV)
	Quartz initially stable	7.319	-2.031	+136.913
-13.543	Goethite precipitates	7.319	-2.031	+136.899
-10.017	Kaolinite precipitates	7.319	-2.031	+136.897
-6.548	Calcite precipitates	7.436	-2.139	+129.995
-6.265	K-Feldspar becomes stable	7.449	-2.158	+129.224
-5.955	2:1 Clay precipitates	7.477	-2.199	+127.553
-5.938	Kaolinite has been redissolved	7.482	-2.206	+127.064
-5.325	Goethite has been redissolved	7.692	-2.512	+114.356
-4.976	Tremolite becomes stable	8.203	-3.256	+ 84.174
-4.741	Laumontite precipitates	9.236	-4.893	+ 23.010
-4.649	Goethite precipitates	10.328	-7.048	- 41.552
-3.722	Portlandite becomes stable	12.419	-12.870	-165.258
-1.897	Albite becomes stable	12.919	-11.546	-194.974

Table 11 - Evolution of the porous volume due to dissolution and precipitation of minerals at 25°C with 1.0 Ca(OH)₂.

Log ξ	Mineralogical events	Volume V _D of minerals dissolved (mm ³ /kg H ₂ O)	Volume V _p of minerals precipitated (mm ³ /kg H ₂ O)	Difference V _p - V _D 100($\frac{V_p - V_D}{V_D}$) (%)
	Quartz initially stable	0.000	0.000	—
-13.543	Goethite precipitates	0.00001	0.000	—
-10.017	Kaolinite precipitates	0.0007	0.0002	-96.88
-6.548	Calcite precipitates	2.097	0.687	-67.25
-6.265	K-Feldspar becomes stable	4.039	3.455	-14.46
-5.955	2:1 Clay precipitates	7.724	9.166	+18.66
-5.938	Kaolinite has been redissolved	8.815	10.195	+15.65
-5.325	Goethite has been redissolved	32.605	46.394	+42.29
-4.976	Tremolite becomes stable	70.827	104.390	+47.39
-4.741	Laumontite precipitates	117.380	167.420	+42.63
-4.649	Goethite precipitates	143.630	205.510	+43.08
-3.722	Portlandite becomes stable	1168.300	839.080	-28.18
-1.897	Albite becomes stable	36508.000	42942.000	+17.62

Table 12 - Sequence of events in simulated dissolution of granite at 100°C with 1.0 Ca(OH)₂ (initial Eh = -157 mV, Log pO₂ = -44.444, Log pCO₂ = -1.147).

Log ξ	Mineralogical events	pH	Log pCO ₂	Eh(mV)
	Calcite initially stable	6.836	-1.147	-156.963
-10.503	Goethite precipitates	6.836	-1.147	-156.947
-6.836	Kaolinite precipitates	6.841	-1.154	-157.260
-5.708	Chlorite precipitates	6.912	-1.253	-162.539
-5.283	Quartz becomes stable	6.998	-1.392	-168.865
-5.096	Tremolite becomes stable	7.113	-1.570	-177.362
-4.961	K-Feldspar becomes stable	7.298	-1.848	-190.981
-4.888	Laumontite precipitates	7.489	-2.135	-205.003
-4.760	Kaolinite has been redissolved	7.811	-2.600	-228.976
-3.974	Portlandite becomes stable	10.322	-8.893	-413.870
-2.883	2:1 Clay precipitates	10.351	-6.710	-416.031
-2.882	Chlorite has been redissolved	10.350	-6.689	-415.891
-2.494	Albite becomes stable	10.404	-6.004	-419.862

Table 13 - Evolution of the porous volume due to dissolution and precipitation of minerals at 100°C with 1.0 Ca(OH)₂.

Log ξ	Mineralogical events	Volume V _D of minerals dissolved (mm ³ /kg H ₂ O)	Volume V _P of minerals precipitated (mm ³ /kg H ₂ O)	Difference V _P - V _D 100($\frac{V_P - V_D}{V_D}$) (%)
	Calcite initially stable	0.000	18.500	>100
-10.503	Goethite precipitates	0.0003	18.539	>100
-6.836	Kaolinite precipitates	1.292	19.431	>100
-5.708	Chlorite precipitates	17.344	35.933	>100
-5.283	Quartz becomes stable	46.222	63.702	+32.82
-5.096	Tremolite becomes stable	66.974	88.442	+32.06
-4.961	K-Feldspar becomes stable	87.436	114.237	+30.65
-4.888	Laumontite precipitates	99.728	131.330	+31.69
-4.760	Kaolinite has been redissolved	127.135	185.915	+46.23
-3.974	Portlandite becomes stable	671.252	601.422	-10.40
-2.883	2:1 Clay precipitates	4063.230	5025.660	+23.69
-2.882	Chlorite has been redissolved	4101.200	5059.500	+23.36
-2.494	Albite becomes stable	6471.960	7861.630	+21.47

Table 14 - Sequence of events in simulated dissolution of granite with 1.0 Ca(OH)₂ at 150°C (initial Eh = -365 mV, Log pO₂ = -44.642, Log pCO₂ = -0.915).

Log ξ	Mineralogical events	pH	Log pCO ₂	Eh(mV)
	Calcite initially stable	6.752	-0.915	-364.603
-8.733	Goethite precipitates	6.752	-0.915	-364.571
-6.159	Chlorite precipitates	6.767	-0.941	-365.888
-6.039	Goethite has been redissolved	6.767	-0.944	-365.860
-5.479	2:1 Clay precipitates	6.778	-0.987	-366.796
-5.375	Kaolinite precipitates	6.789	-1.012	-367.723
-4.975	Tremolite becomes stable	7.020	-1.375	-387.014
-4.910	Laumontite precipitates	7.462	-1.529	-395.023
-4.909	Kaolinite has been redissolved	7.118	-1.657	-395.156
-4.273	Chlorite has been redissolved	9.159	-6.724	-565.977
-4.119	Portlandite becomes stable	9.359	-7.263	-582.626
-3.880	Quartz becomes stable	9.235	-6.978	-572.251
-3.670	K-Feldspar becomes stable	9.251	-6.919	-573.578
-3.039	Albite becomes stable	9.412	-4.912	-587.078
-2.891	Anorthite becomes stable	9.558	-6.861	-599.333

Table 15 - Evolution of the porous volume due to dissolution and precipitation of minerals at 150°C with 1.0 Ca(OH)₂.

Log ξ	Mineralogical events	Volume V _D of minerals dissolved (mm ³ / Kg H ₂ O)	Volume V _p of minerals precipitated (mm ³ / Kg H ₂ O)	Difference V _p - V _D 100($\frac{V_p - V_D}{V_D}$) (%)
	Calcite initially stable	0.000	26.000	>100
-8.733	Goethite precipitates	0.011	26.060	>100
-6.159	Chlorite precipitates	6.144	30.000	>100
-6.039	Goethite has been redissolved	6.144	30.000	>100
-5.479	2:1 Clay precipitates	30.030	48.520	+61.57
-5.375	Kaolinite precipitates	37.920	54.330	+43.27
-4.975	Tremolite becomes stable	94.440	111.900	+18.49
-4.910	Laumontite precipitates	108.900	126.400	+16.07
-4.909	Kaolinite has been redissolved	119.823	156.480	+ 5.58
-4.273	Chlorite has been redissolved	456.940	358.833	-21.47
-4.119	Portlandite becomes stable	646.804	469.824	-27.38
-3.880	Quartz becomes stable	933.800	765.920	-17.98
-3.670	K-Feldspar becomes stable	1236.000	1163.500	- 5.86
-3.039	Albite becomes stable	3216.600	3798.000	+18.10
-2.891	Anorthite becomes stable	3807.090	4607.120	+21.05

ning of the sequence, while calcite is not initially stable and produced. However, at the three tested temperatures, the volumic balances show a stage of reopening (increase of favority) around the saturation state with respect to portlandite. This disappears again after, when the system reaches the albite stability field at the very end of the alteration.

This result seems important, if one considers that the portlandite can be considered as a more easily dissolved phase (in terms of kinetics) than the constituents of a granitic rock. Therefore the probability seems higher to reach the portlandite saturation state and not the albite stability. Then, one must conclude qualitatively that there is a new risk with this alkaline effect : possible mass transfers are clearly enhanced together with a possible tendency to increase the porosity.

It must be noticed that the alkaline effect on mass transfer, pH increase, pCO_2 decrease is maximum at 25°C (Table 10, figure 3). This could mean that the effect of concrete-water interaction has to be expected as important even during the early storage, when temperature will begin to increase. During that stage, the granitic-water system is at the reverse probably less active for kinetic reasons.

Table 16 - Chemical composition of the total 2:1 Clay produced by a simulated alteration of the granite with 1.0 Ca(OH)₂ in solution F1 at saturation point of Albite.

Temperature	Clay formula		
	Tetrahedra	Octahedra	Interlayer
25°C	Si ₃ Al	Al _{1.883} Fe _{0.042} Mg _{0.075} O ₁₀ (OH) ₂	K _{0.47} Na _{0.223} Ca _{0.153} Mg _{0.038}
100°C	Si ₃ Al	Al _{1.450} Fe _{0.514} Mg _{0.036} O ₁₀ (OH) ₂	K _{0.943} Na _{0.041} Ca _{0.001} Mg _{0.045}
150°C	Si ₃ Al	Fe _{2.930} Mg _{0.070} O ₁₀ (OH) ₂	K _{0.95} Na _{0.035} Mg _{0.007}

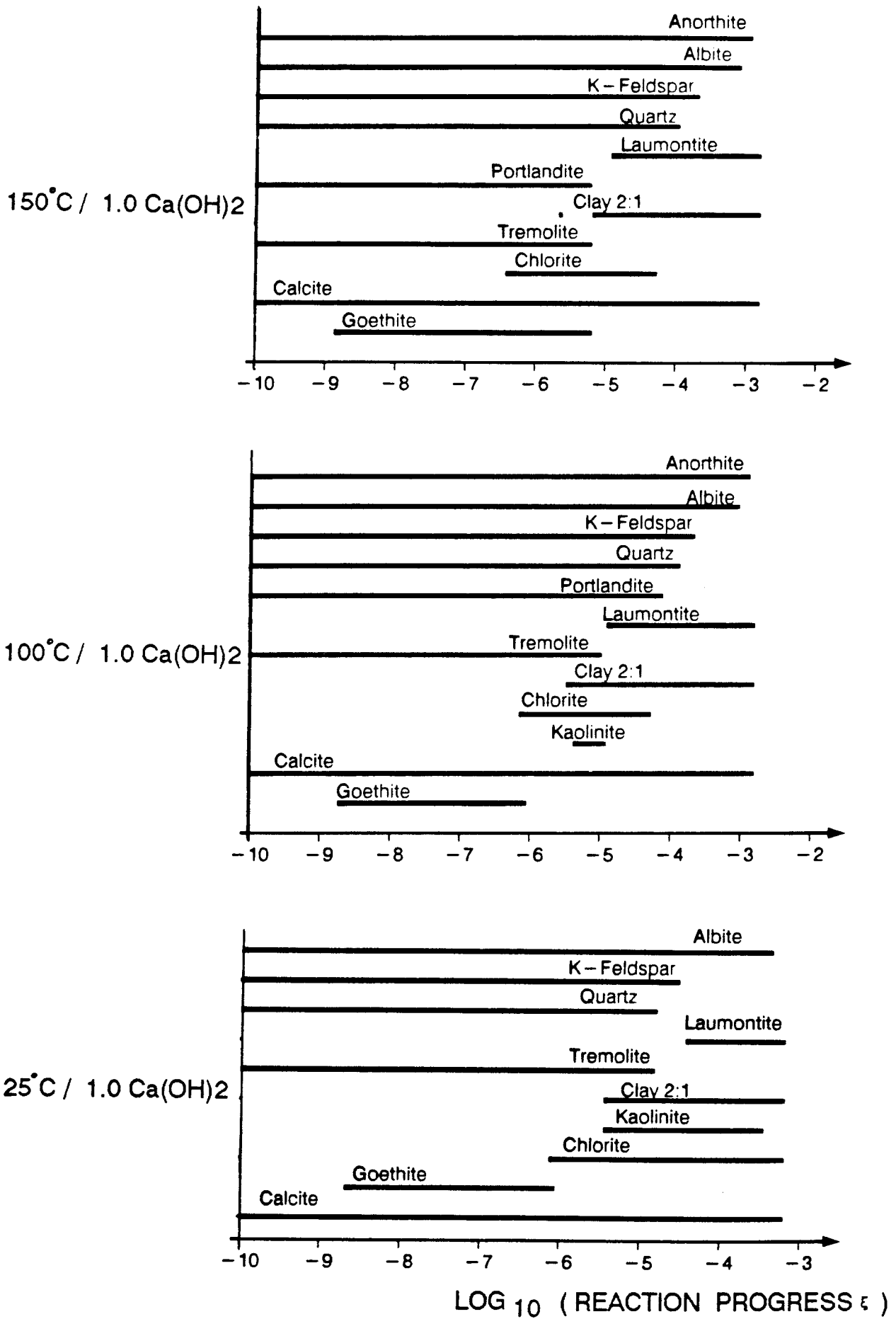


Figure 3. Mineralogical sequences as simulated along the dissolution path of the granite+concrete assemblage in solution F1 at 25, 100 and 150°C (1 Mole of portlandite per unit of granite).

4.2 Option (2) : granite + Ca(OH)₂ (10 moles/unit of granite) + solution F1 at 150°C

This test was made for increasing the alkaline effect considering a solution reacting more efficiently with the concrete than with the granite. This may be due to kinetic effects or to physical properties of the system : the solution may leach the concrete at the contact of the granite before circulating into the granite near the repository.

The results of this test are given in tables 17 and 18 and on figure 4C. The sequences for successive minerals stability is only slightly altered :

- tremolite and portlandite are saturated earlier ;
- after an early portlandite saturation the alkaline input in this system is of course stopped and the following part of the sequence is only due to granite dissolution at pH conditions similar to those from the previous simulation.

However, these results show clearly again that there is a tendency to open the system (porosity increase) near the saturation point of portlandite. This tendency only disappears very late in the sequence when the plagioclases are stabilized (albite + anorthite). Consequently, one must remember as an important result that the earlier the solution will be equilibrated with portlandite (Ca(OH)₂, the earlier the rock-water concrete interaction will tend to open the fractures, and the longer this risky stage of the process will last.

It is also interesting to notice that the difference obtained here by increasing only the relative rate of dissolution of Ca(OH)₂ versus granite does not correspond to a major change in the mass balances and volumic balances : the total amount of mass transfer is even smaller.

4.3 Option (3) : granite + Ca(OH)₂ (1 mole per unit of granite) + solution V1 at 150°C

This test corresponds to the test done in paragraph 3 also at 150°C but without concrete for taking into account a different and greater salinity in the initial solution (V1, STRIPA, see table 2). The major results are given in tables 19 and 20 and on figure 2. They confirm the effect of the concrete dissolution detected for the more dilute solution F1 at the same temperature (respectively tables 7 and 19/ 9 and 20). Here the portlandite will be saturated in the sequence (it was not with F1). The pH will reach higher values (about + 1 unit ; 9.38 at albite saturation) and the corresponding mass transfer is increased from 50 to 60 %. The volumic balance remains longer and more negative (increase of porosity) as long as the portlandite stability field is not reached and even after like previously discussed. The tendency is only reversed, here also, at the end of the reacting sequence when annite and albite become stable in the solution.

Table 17 - Sequence of events in simulated dissolution of granite with 10.0 Ca(OH)₂ at 150°C (initial Eh = -364 mV, Log pO₂ = -44.642, Log pCO₂ = -0.923).

Log ξ	Mineralogical events	pH	Log pCO ₂	Eh(mV)
	Calcite initially stable	6.752	-0.923	-364.603
-8.858	Goethite precipitates	6.752	-0.923	-364.589
-6.418	Chlorite precipitates	6.832	-1.056	-371.297
-5.846	Tremolite becomes stable	7.121	-1.585	-395.534
-5.669	2:1 Clay precipitates	7.879	-3.084	-459.197
-5.622	2:1 Clay has been redissolved	8.297	-4.166	-494.381
-5.197	Portlandite becomes stable	9.391	-7.200	-586.203
-5.189	2:1 Clay precipitates	9.389	-7.199	-586.131
-5.174	Goethite has been redissolved	9.389	-7.198	-586.023
-4.930	Laumontite precipitates	9.352	-7.136	-582.938
-4.268	Chlorite has been redissolved	9.261	-6.906	-574.965
-3.959	Quartz becomes stable	9.112	-6.563	-562.386
-3.688	K-Feldspar becomes stable	9.132	-6.483	-564.044
-3.088	Albite becomes stable	9.285	-4.446	-576.914
-2.936	Anorthite becomes stable	9.434	-6.470	-589.363

Table 18 - Evolution of the porous volume due to dissolution and precipitation of minerals at 150°C with 10.0 Ca(OH)₂.

Log ξ	Mineralogical events	Volume V _D of minerals dissolved (mm ³ /kg H ₂ O)	Volume V _P of minerals precipitated (mm ³ /kg H ₂ O)	Difference V _P - V _D 100($\frac{V_P - V_D}{V_D}$) (%)
	Calcite initially stable	0.000	26.000	>100
-8.858	Goethite precipitates	0.053	26.120	>100
-6.418	Chlorite precipitates	14.749	44.635	>100
-5.846	Tremolite becomes stable	55.070	100.163	+81.88
-5.669	2:1 Clay precipitates	82.458	137.331	+66.55
-5.622	2:1 Clay has been redissolved	91.889	141.670	+54.17
-5.197	Portlandite becomes stable	243.424	144.017	-40.83
-5.189	2:1 Clay precipitates	244.003	144.043	-40.96
-5.174	Goethite has been redissolved	244.003	144.043	-40.96
-4.930	Laumontite precipitates	273.086	149.505	-45.25
-4.268	Chlorite has been redissolved	497.373	403.298	-18.91
-3.959	Quartz becomes stable	777.000	663.700	-14.58
-3.688	K-Feldspar becomes stable	1127.400	1159.000	+ 2.81
-3.088	Albite becomes stable	2859.250	3451.060	+20.70
-2.936	Anorthite becomes stable	3398.540	4183.300	+23.09

Table 19 - Sequence of events in simulated dissolution of granite at 150°C in water V1 with 1.0 Ca(OH)₂.
(initial Eh = -617 mV, Log pO₂ = -55.225, Log pCO₂ = -3.614).

Log ξ	Mineralogical events	pH	Log pCO ₂	Eh(mV)
	Fluorite + Pyrite initially stable	7.127	-3.614	-618.239
-7.215	Tremolite becomes stable	7.176	-3.662	-622.281
-6.645	Chlorite precipitates	7.293	-3.777	-632.126
-6.399	2:1 Clay precipitates	7.389	-3.870	-640.151
-6.353	Pyrite has been redissolved	7.396	-3.878	-640.976
-5.610	Calcite precipitates	8.019	-4.519	-693.245
-5.420	Laumontite precipitates	8.190	-4.870	-707.572
-4.585	Chlorite has been redissolved	9.028	-6.633	-777.806
-4.308	Portlandite becomes stable	9.284	-7.209	-799.291
-3.917	Quartz becomes stable	9.116	-6.850	-785.225
-3.503	Microcline becomes stable	9.194	-6.858	-791.905
-3.500	Fluorite has been redissolved	9.197	-6.860	-792.000
-3.479	Annite becomes stable	9.203	-6.866	-792.555
-2.848	Albite becomes stable	9.378	-5.152	-807.169

Table 20 - Evolution of the porous volume due to dissolution and precipitation of minerals at 150°C in water V1 with 1.0 Ca(OH)₂.

Log ξ	Mineralogical events	Volume V _D of minerals dissolved (mm ³ /kg H ₂ O)	Volume V _P of minerals precipitated (mm ³ /kg H ₂ O)	Difference V _P - V _D 100($\frac{V_P - V_D}{V_D}$) (%)
	Fluorite + Pyrite stable	0.367	0.059	<100
-7.215	Tremolite becomes stable	0.534	0.065	-87.85
-6.645	Chlorite precipitates	1.936	0.112	-94.23
-6.399	2:1 Clay precipitates	3.373	0.325	-90.35
-6.353	Pyrite has been redissolved	3.886	0.472	-87.78
-5.610	Calcite precipitates	20.756	1.858	-91.05
-5.420	Laumontite precipitates	32.165	3.143	-90.23
-4.585	Chlorite has been redissolved	219.635	112.031	-48.99
-4.308	Portlandite becomes stable	415.695	229.020	-44.91
-3.917	Quartz becomes stable	785.636	614.020	-21.84
-3.503	Microcline becomes stable	1516.600	1601.100	+ 5.56
-3.500	Fluorite has been redissolved	1530.000	1631.025	+ 6.61
-3.479	Annite becomes stable	1551.500	1671.457	+ 7.73
-2.848	Albite becomes stable	4010.400	5096.580	+27.08

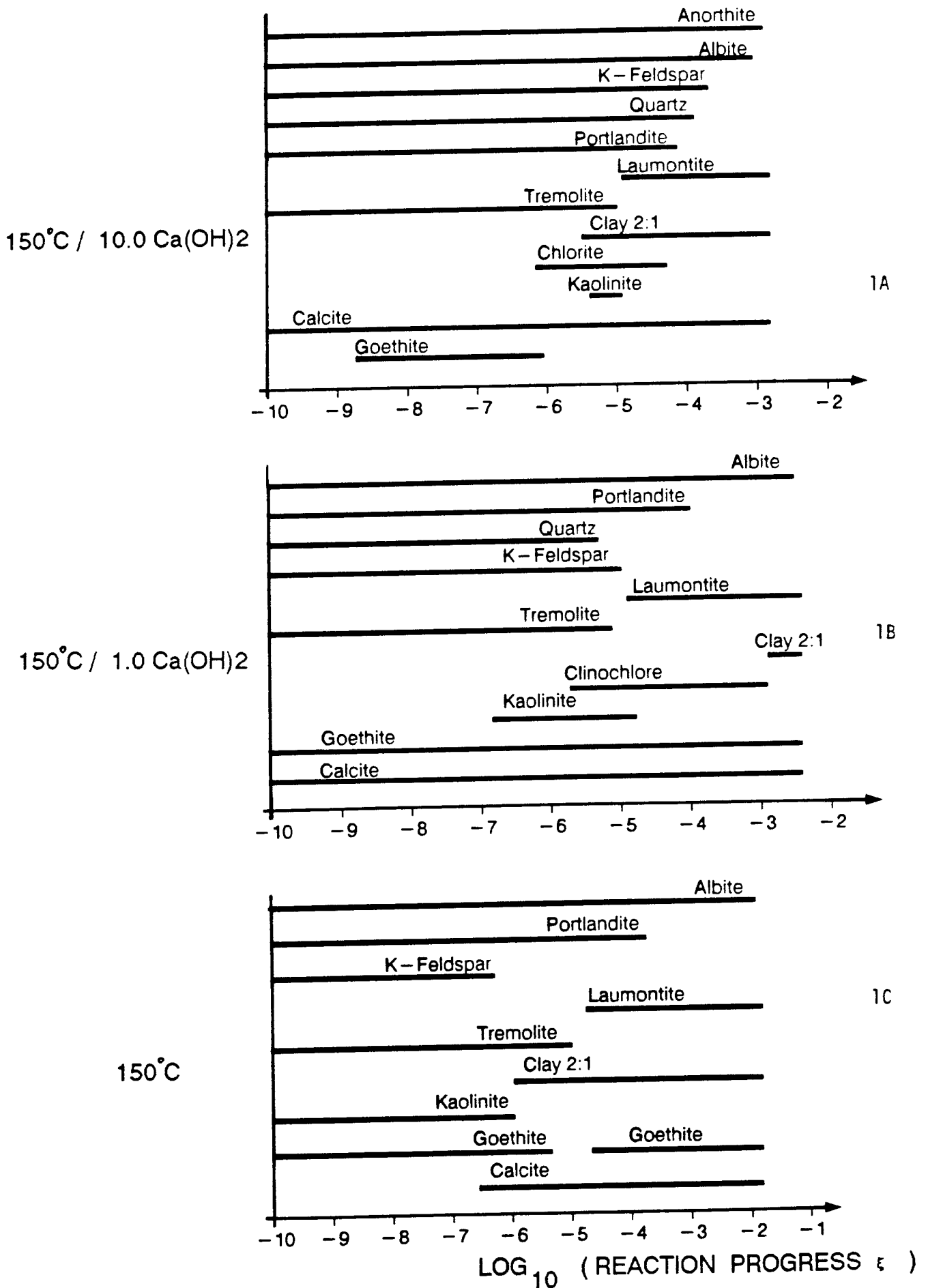


Figure 4. Mineralogical sequences as simulated along the dissolution path of the granite+ concrete assemblage in solution F1 at 150°C.
1A :10 moles of Ca(OH)₂ - 1B : 1 mole of Ca(OH)₂ - 1C : no Ca(OH)₂

CONCLUSIONS

Regarding the questions asked for this study, the major conclusions concern (1) the extension of the temperature range from 100 to 150°C and its consequence on the previous prediction for mineral assemblage and (2) the effect of alkaline input due to the granite-concrete contact near the repository and its consequence on the possible mass transfers and the porosity of the rock.

The extent of the temperature range for the storage (100 to 150°C) does not change the tendencies previously detected for the evolution of a granite-solution system submitted to the thermal effect of the heat producing nuclear waste repository. Particularly, the detected possible rock alteration and secondary minerals production lead to a decrease of the porosity by a sealing effect due to calcite and clays precipitation in the fractures and fissures where the solution reacts with the granite. However this will not seal the system very rapidly because the actual volumic effect is very low for one given volume of solution. Only a cumulative effect over a long period of time will quantitatively reduce the porous volume as described by FRITZ et al. (1985), while considering a rock with a low porosity reacting with water in a slightly open system. KAM (1986), predicted in these conditions, a possible reduction of about 20% of the porosity after 100.000 years at 100°C. This estimation remains valid at 150°C.

The important effect of an alkaline input in the solutions because of a concrete-solution interaction is clearly demonstrated, at all temperatures tested from 25 to 150°C :

- (1) The pH of the solution may reach very high values, while the CO₂ partial pressure is reduced to very low values and the calcite still remains precipitated.
- (2) The sequence of saturation for reacting primary minerals and for secondary produced minerals are not dramatically changed, qualitatively, except the formation of a secondary zeolite (laumontite), but this is also due to the temperature increase from 100 to 150°C. However, the possible alteration is considerably enhanced by the alkaline effect of portlandite dissolution.

Mass transfer are increased significantly and the volumic balances show a systematic stage of reopening of the rock porosity around the simulated step of the sequence where the portlandite becomes stable with respect to the solution. This tendency is reversed at the end of the alteration sequence but does exist. Even if the calculation made here is based on a very simple approximation on the actual granite / concrete alteration ratio, the importance of this result has not to be underestimated because the concrete phase must be considered as a more easily dissolved phase than the granite itself. Therefore one must consider that the alkaline effect of the concrete on the granite-water interaction leads to a potential risk for the nuclear waste storage if the natural granitic barriers may be weakened on a long term time scale.

The complementary tests made using a more saline solution (V1) do not lead to different conclusions. The "reopening window" in the alteration sequence may even be larger if the solution is more saline.

A further discussion of that problem would need now a more precise discussion on how the respective concrete-solution and solution granite interaction are acting in space and time.

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Karsten Pedersen

University of Göteborg

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January 1988

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Flow and solute transport in a single fracture. A two-dimensional statistical model

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April 1987

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Stefan Sehlstedt

Swedish Geological Co, Luleå

February 1988

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Description of geological data in SKBs data-base GEOTAB

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Swedish Geological Co, Luleå
April 1988

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Herbert Henkel
Swedish Geological Survey, Uppsala
October 1987

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Field test in the Stripa mine. Final report.**

Lars Birgersson, Ivars Neretnieks
Royal Institute of Technology, Stockholm
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G P Marsh, K J Taylor, Z Sooi
Materials Development Division
Harwell Laboratory
February 1988

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Version 1.0**

Roger Thunvik¹, Carol Braester²
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April 1988

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**Groundwater numerical modelling of the Fjällveden study site – Evaluation of parameter variations
A hydrocoin study – Level 3, case 5A**

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October 1987

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Near-distance seismological monitoring of the Lansjärv neotectonic fault region

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Seismological Department, Uppsala University,
Uppsala
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Validation of the rock mechanics HNFEMP code against Colorado school of mines block test data

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University of Luleå, Luleå
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Karstein Monsen
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A preliminary study**

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First evaluation of preinvestigations 1986-87
and target area characterization**

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Roy Stanfors
Peter Wikberg
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March 1988