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Iron content and reducing capacity of granites and bentonite

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IRON CONTENT AND REDUCING CAPACITY OF GRANITES AND BENTONITE

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SUMMARY

The iron contents in various granites and in bentonite have been determined. For granites, the content is usually in the range 1-9% (weight) and 2.5-3% for bentonite. Most of the iron is divalent in the granites (70-90%); in bentonite the divalent fraction is 25-50%. A large part of the divalent iron in the granites appears to be accessible for the reduction of dissolved oxygen in an aqueous system.

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1. INTRODUCTION

The redox conditions in the rock/groundwater system would have a large influence on the sorption and migration of redox sensitive radionuclides in connection with underground storage of spent nuclear fuel or high-level waste.

The redox potential (Eh) in a system in equilibrium with air would roughly be given by (1)

$$Eh = 0.8-0.06pH\pm 0.1 \ (V)$$

The concentration of divalent iron is high and the oxygen pressure is extremely low in most deep groundwaters in crystalline rocks, with a total Fe(II)-concentration in the water usually in the range 1-7 mg/l. The corresponding redox potential would be in the range (1)

$$Eh = 0.24-0.06pH\pm 0.06 \ (V)$$

The oxidation states in aerated and Fe(II)-buffered systems of some of the important long-lived radionuclides in spent nuclear fuel and high-level waste are given in Table 1.

Table 1. Oxidation states of redox sensitive radionuclides in groundwater environments.

Element	Reducing environment, Fe(II)	Oxidizing environment, O_2
Tc	IV	VII
U	IV[a]	VI
Np	IV	V
Pu	III+IV	IV+V

[a] Also V and VI at high total carbonate concentrations.

The oxidation state is of particular importance for technetium, uranium and neptunium, since the mobility is much higher for these elements in their high oxidation states.

A production of oxidizing agents due to radiolysis in the water, or even an intrusion of oxygenated waters, can not be excluded in a deep underground waste repository, and a local quantitative oxidation of Fe(II) to Fe(III) can change the conditions in the repository from reducing to oxidizing. The following questions are of importance:

- o What potential reducing agents, e.g. Fe(II)-minerals, are present in the rock and back-fill (bentonite)?
- o What is the availability of these agents? Would the Fe(II) present in the solid phase act as a redox buffering agent?

The purpose of the present study has been

- o determination of the amount of leachable iron, total divalent iron and total divalent + trivalent iron in granites and bentonite,
- o studies of the rate of reduction of oxygen dissolved in water in contact with granites.

The solid materials used in this study are given in Table 2.

Table 2. Solid Fe(II)-containing materials.

Material	Origin, type	Ref.
Granite	Stripa	2
Granite	Finnsjön	2
Granite	Studsvik	3
Bentonite	MX-80	4
Bentonite[a]	MX-80	4

[a] Heated to 425-500 °C for the removal of organic compounds.

At a later stage of the project the reduction of trace concentrations of redox sensitive elements by Fe(II)-minerals in granite will be demonstrated.

2. IRON CONTENT OF GRANITE AND BENTONITE

The following analyses of iron were performed (5-7):

- total iron; Fe(tot)
- divalent iron; Fe(II)
- leachable iron, acetic acid; Fe-HAc; this would represent the biologically available acid soluble iron
- leachable iron, dithionite; Fe-DT; this would represent the leachable "free" iron.

All samples were crushed prior to the analyses. Either the size fraction 0.09-0.25 mm or non-sieved samples were used for the analyses.

2.1 TOTAL IRON

A crushed sample (0.2 g) was wetted with HCl, dissolved in hot HF and evaporated to dryness. The residue was dissolved in HCl (10%). The iron concentration was determined by atomic absorption spectrometry.

2.2 DIVALENT IRON

2.2.1 Cerium sulfate titration

A crushed sample (0.5 g) was dissolved in a H_2SO_4(50%)-HF-mixture and treated with a H_2SO_4(50%)-boric acid solution. Ferroin-indicator was added, and the Fe(II)-content was determined from titration with Ce(IV)-sulfate.

2.2.2 Phosphate-dichromate titration

A crushed sample (0.2 g) was dissolved in a H_2SO_4(50%)-HF-mixture and treated with a boric acid solution. Phosphoric acid was added and the Fe(II)-content was determined from titration with potassium dichromate.

2.3 LEACHABLE IRON

2.3.1 Acetic acid

A crushed sample (2.5 g) was leached with acetic acid (25%) for 24 h. The iron content of the leachate was determined by atomic absorption spectrometry.

2.3.2 Dithionite

A crushed sample (0.5 g) was leached with a Na-citrate-$NaHCO_3$-Na-dithionite solution for 15 min. The iron content of the leachate was determined by atomic absorption spectrometry.

The leaching procedures give some general indications of the amount of iron that is easily leached or available for chemical reactions with components in the water, but no specific information on the chemical state of this iron. However, this leachable iron is not likely to come from iron silicate phases. The leachable quantities are not further discussed.

3. REDUCTION OF OXYGEN

The capacity for reduction of oxygen dissolved in water by the action of divalent iron in granites was determined in the following way:

A 160 ml thermostated (25 °C) titration vessel was equipped with electrodes for pH-, Eh- and O_2-measurements (O_2-electrode: EIL Dissolved Oxygen Probe Model No 8012, Electronic Instruments Limited, Chertsey, Surrey, England) and completely filled with air-saturated distilled water. A known amount of crushed granite (0.05-1 g, particle size 0.090-0.125 mm) was added to the vessel which was thoroughly closed. The pH- and Eh-values as well as the O_2-concentration were registered as a function of time. The O_2-consumption of the O_2-electrode in the absence of any reducing agents was determined in separate measurements.

4. RESULTS AND CONCLUSIONS

The iron determinations of the various materials are given in Table 3. (Two or three analyses were made from different batches except for some of the leaching studies).

Table 3. Iron content of the studied materials.

Material	Fe(tot),%	Fe(II),%	Fe-HAc,%	Fe-DT,%
Granite, Stripa	1.0-1.2	0.69-1.1	0.14	0.090 (0.03)[a]
Granite,Finnsjön	4.0-5.0	2.7-4.1	0.25	0.12 (0.03)[a]
Granite,Studsvik	7.5-9.0	5.2-9.4	0.33	0.12 (0.04)[a]
Bentonite, MX-80	2.5-3.0	0.64-1.5	0.019-0.024	0.11-0.19(0.12)[a]
Bentonite, MX-80 heated	3.0	0.36		

[a] Material that has been leached with HAc prior to the dithionite leaching.

Some data for similar materials reported in other investigations are given in Table 4.

Table 4. Iron content in some granites and bentonite.

Material	Fe(tot),%	Fe(II),%	Ref.
Granite, Stripa	0.94	0.64	8
Granite, Finnsjön	3.6	2.6	8
Granite, Studsvik	1.6	1.3	8
Granite, Svartboberget	7.5-11.0	7.0-10.2	8
Granite, Fjällveden	3.1	2.8	8
Granite, Gideå	0.86-4.1	0.51-3.3	8
Bentonite, MX-80	2.55-2.77	0.69	4
Bentonite, MX-80, heated	2.55-2.72	0.12	4

The reduction of the O_2-concentration vs time for Finnsjön granite and Stripa granite is given in Fig. 1. As a comparison the oxygen reduction by iron powder is also given in the figure.

The total amount of iron and the consumption of oxygen are given in Table 5.

Table 5. Oxygen reduction in water by granite.

Solid	Weight g	Total Fe(II) moles	O_2-consumption[a] moles	Time[b] h
Granite, Finnsjön	0.0510	3.8×10^{-5}	3.6×10^{-5}	477
	0.1014	7.4×10^{-5}	3.2×10^{-5}	784
Granite, Stripa	0.8195	16.1×10^{-5}	3.2×10^{-5}	286

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[a] Corrected for the consumption of the electrode

[b] The experiment was stopped when less than 0.1 mg/l O_2 remained in the aqueous phase.

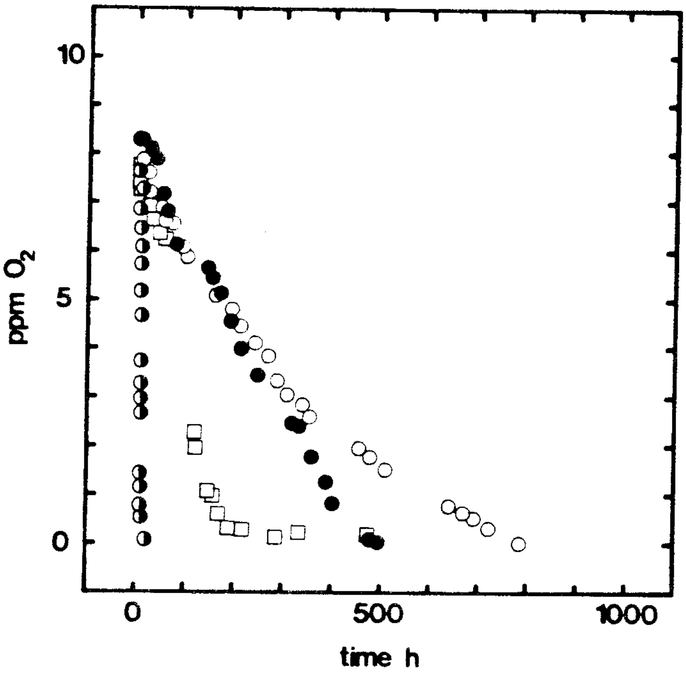

Figure 1. Remaining O_2-concentration vs time. ◑ Fe-powder, ○ Finnsjön (0.0510), ● Finnsjön (0.1014), □ Stripa.

The following preliminary conclusions can be drawn:

- The iron contents in the studied granites is in the range 1-9% (weight); most of the iron is divalent, usually 70-90%. The data from this study are confirmed by other independent measurements on similar granites.
- The iron contents in bentonite, MX-80, is in the range 2.5-3% (weight); 25-50% of this iron is divalent (depending on the pretreatment?). In bentonite that has been heated for the removal of organics the fraction of divalent iron is reduced to 5-10%.
- A large part of the divalent iron in the granites, which was more than one order of magnitude higher than the leachable iron fraction, is accessible for the reduction of oxygen (diffusion controlled) under the present conditons (fine-grained material); in fact the observed oxygen consumption appears to be larger than the corresponding total Fe(II)-content. Possibly the oxygen reduction takes place within the mineral grains.

Although freshly distilled water and freshly crushed rock from homogeneous larger rock samples, previously not exposed to water, were used a biological activity contributing to the oxygen consumption can not a priori be ruled out. However, this possible oxygen consumption would at least to some extent be included in the correction for the oxygen consumption of the electrode itself. This was measured in the presence of an iron-free geologic material (0.1-1 g of quarts or Al_2O_3 in distilled air-saturated water) in the same way as the measurements in the granite systems. If the oxygen consumption would be due to organic material present in the granite itself similar reducing effects would also be expected under natural conditions.

Present experiments are performed under UV-irradiation to eliminate any effects due to biologic activity.

The preliminary nature of this study should be emphasized. Experiments with larger particle fractions and with other O_2/Fe(II)-ratios in the system are in progress, as well as efforts to reduce actinides (U, Np) and technetium in similar model experiments. Conclusions concerning kinetics, reaction sites, the role of leachable fractions, Eh- and pH-effects, etc. will appear in subsequent reports.

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