

Fracture Sealing by Mineral Precipitation in a Deep Geological Nuclear Waste Repository

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INTRODUCTION.

The safe management of nuclear waste is one of the main scientific and technical concerns at a global scale. Nuclear waste displays a high level of activity for around 100000 y, which implies that a final storage must be found. With this purpose, many countries are planning to build a deep geological repository for the final storage of spent nuclear fuel.

One of the most advanced nuclear waste management programmes in the world is being carried out by the Swedish Nuclear Waste Agency (SKB). The Swedish repository system consists of copper canisters, with a cast iron insert containing spent nuclear fuel, which are surrounded by bentonite clay and deposited at approximately 500 m depth in saturated, granitic rock. Two sites in Sweden are being characterised as possible candidates for hosting the proposed repository: Forsmark and Laxemar.

For the deep repository to be considered safe, the risks for man or for the environment have to be eliminated or, at least, minimized. One of the main risks for the long-term safety of the repository is the creation of preferential flow-paths during underground opening for repository construction because these flow paths would increase the risk of radionuclide transport towards the biosphere.

During the deep repository excavation and construction stage, the rock and groundwaters at repository depth will be exposed to open atmospheric conditions, their temperature will increase (up to 100°C in the rock surrounding the bentonite) throughout the years due to the thermal impact of the residual radioactivity of nuclear waste and they will possibly mix with

dilute infiltration waters and deep saline groundwaters. As a consequence of all these processes, the saturation state of the groundwaters at repository depth with respect to several mineral phases may change and mineral precipitation reactions may take place. This implication is important because mineral precipitation may lead to the sealing of the fractures created by the repository construction, shortcutting or at least minimizing the paths for preferential flow towards the biosphere.

The aim of this study is to contribute to the understanding of the potential for mineral precipitation reactions to occur at the planned repository depth in the two Swedish candidate areas (Forsmark and Laxemar) by means of geochemical modelling.

METHODOLOGY.

For modelling purposes, five groundwater compositions were selected as hydrogeochemically

representative of the main water types at the planned repository depth; three for Forsmark and two for Laxemar. In addition, a deep saline groundwater and a shallow infiltration groundwater have been added for each site in order to be able to perform the mixing calculations (Table 1).

Five modelling cases have been considered, corresponding to the scenarios described above: (1) present conditions (2) variation of temperature at depth to 50 and 100°C, (3) opening to atmospheric conditions, (4) mixing with shallow infiltration groundwater, and (5) mixing with deep saline groundwater. The geochemical calculations have been done using the PHREEQC computer code (Parkhurst and Appelo, 1999) version 2.12.5.669 released on November 16 of 2005 and using the inbuilt thermodynamic database WATEQ4F.dat (Ball and Nordstrom, 2001). For the precipitation of amorphous iron oxyhydroxides, a value of logK of -5 has been used.

| Site | Sample | pH | pe | HCO ₃ | Na | Ca | Cl | SO ₄ | Fe |
|---|--------|------|-------|------------------|------|-------|-------|-----------------|---------------|
| Representative groundwaters from repository depth | | | | | | | | | |
| Forsmark | 8016 | 8.40 | -2.50 | 126 | 2040 | 934 | 5410 | 498 | 1.85 |
| Forsmark | 12343 | 8.30 | -4.55 | 17.1 | 1770 | 1840 | 5960 | 31.1 | 0.76 |
| Forsmark | 12818 | 8.10 | -4.55 | 6.98 | 1900 | 2740 | 7460 | 101 | <i>b.d.l.</i> |
| Laxemar | 10091 | 7.60 | -4.72 | 189 | 791 | 234 | 1390 | 127 | 0.44 |
| Laxemar | 15008 | 7.42 | -3.71 | 14.1 | 2080 | 1540 | 5890 | 425 | 0.56 |
| Groundwaters selected for mixing cases | | | | | | | | | |
| Dilute Forsmark | 8335 | 7.91 | 4.00 | 466 | 274 | 41.1 | 181 | 85.1 | <i>b.d.l.</i> |
| Saline Forsmark | 8843 | 8.04 | -4.42 | 7.36 | 2780 | 5740 | 14400 | 103 | 0.29 |
| Dilute Laxemar | 10231 | 8.17 | 4.00 | 265 | 110 | 11.2 | 23 | 35.8 | 0.08 |
| Saline Laxemar | 2731 | 7.90 | -5.25 | 9 | 8030 | 18600 | 45500 | 832 | 0.41 |

All the analytical values expressed in mg L⁻¹ / *b.d.l.*: below detection limit

Table 1. Hydrochemical characterisation of the groundwater samples chosen for modelling purposes as representative from the repository depth in Forsmark and Laxemar. The composition of the corresponding dilute and saline groundwaters, used for the modelling cases focused on groundwater mixing, is also displayed.

palabras clave: almacenamiento de residuos nucleares, sellado de fracturas, calcita, oxihidroxidos de hierro

key words: nuclear waste disposal, fracture sealing, calcite, ferric oxyhydroxides

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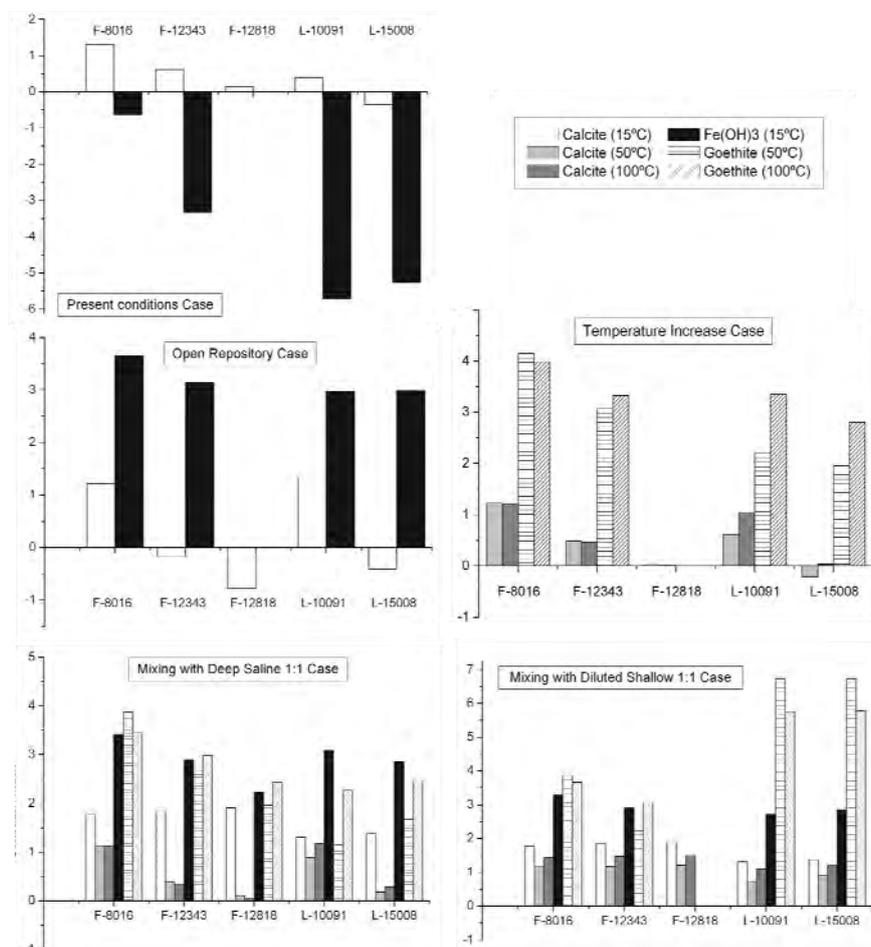


fig 1. Summary of results from the saturation indices calculations carried out for Forsmark (samples beginning with F) and Laxemar (beginning with L) in the different modelling cases.

Within the range of conditions assessed in this study, the main mineral phases able to precipitate are calcite (CaCO_3) and ferric oxyhydroxides. In the simulations carried out at 15°C, only amorphous iron oxyhydroxides (generically represented as $\text{Fe(OH)}_{3(a)}$) have been allowed to precipitate. For simplification, goethite has been the only iron oxyhydroxide allowed to precipitate in the simulations carried out at 50°C and 100°C, although hematite precipitation is also possible at 100°C under the simulated conditions (Cornell and Schwertmann, 2003, and references therein). Precipitation reactions have been considered to be in equilibrium.

RESULTS AND DISCUSSION.

The speciation-solubility calculations for the ambient conditions (Figure 1) indicate that the groundwaters are generally close to equilibrium with

respect to calcite (except the sample 8016 from Forsmark, which is oversaturated) and subsaturated with respect to amorphous iron hydroxides

As displayed in Figure 1, most of the studied groundwaters or the mixtures of different groundwaters are close to equilibrium or even oversaturated with respect to calcite and ferric oxyhydroxides. Therefore, the occurrence of mineral precipitation reactions is thermodynamically feasible in most of the studied cases. Moreover, most of the groundwater compositions do not exhibit any capacity to dissolve calcite or ferric oxyhydroxides and, in the scarce cases of subsaturation with respect to those phases, the effect is very small.

The largest amounts of precipitated minerals are obtained for the mixtures of groundwaters from the repository depth with shallow infiltration waters.

The main mineral phase potentially responsible for the fracture sealing is generally calcite (Figure 1). The estimated amounts of mineral precipitated are expected to be generally between one and three orders of magnitude larger than the amounts of precipitated ferric phases (calculations not shown). As a general trend, the largest amounts of precipitated ferric phases are predicted to take place in the scenarios of open repository conditions (i.e. equilibrium with atmospheric partial pressures of $\text{O}_2(\text{g})$). This can be attributed to the setting of oxidising redox conditions in which Fe(II) transforms into Fe(III) and precipitates. In contrast, under the reducing conditions present in closed repository conditions are assumed (p_e values < -2.5) the predicted precipitation of ferric oxyhydroxides is smaller, increasing slightly if the temperature at repository depth is increased, which increases the oversaturation with respect to more crystalline and insoluble ferric phases (mainly goethite or hematite).

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