Migration of cement pore fluids from a radioactive waste repository: experimental studies of chlorite dissolution rates

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Current concepts of the geological disposal of low- and intermediate-level radioactive wastes in the UK envisage the construction of a mined facility in fractured basement rock at a depth of up to one kilometre (Nirex, 1989). The intermediate-level radioactive waste will be encapsulated in a cementitious wasteform and sealed in steel drums or concrete boxes, the whole to be contained in a vault backfilled with cementitious grout. Nirex are currently investigating the possible location of such a facility in low-grade metamorphic rocks, the 'Borrowdale Volcanic Group' (BVG) near Sellafield, Cumbria. After closure, the vaults will saturate with groundwater and become part of a modified regional groundwater flow system. Groundwater equilibrated with cement will, at some stage, migrate by advection and dispersion from the repository into the surrounding rock. Reactions with the host rock will occur in advance of radionuclides migrating from the repository. Consequently, it is desirable to have some understanding of these reactions and the rate at which they occur. As Fe-rich chlorite will be important in the BVG lithologies as a source of Mg and reduced Fe, dissolution rate experiments were conducted on this mineral to provide kinetic information that can be used in computer modelling studies of fluid/rock reactions in the vicinity of the proposed repository.

Eight experiments were conducted under conditions of 0.1 MPa (atmospheric) pressure and temperatures of 25 and 70°C, to cover the likely range of temperatures encountered at the Sellafield site. The experiments were of approximately 8 weeks duration, and performed in mixed-flow reactors. 5 g of a well-characterised Fe-rich chlorite sample (of composition $Mg_{5.36},Al_{2.61},Fe_{3.93})[(Si_{5.55},Al_{2.45})O_{20}](OH)_8$, a nitrogen adsorption surface area of 0.8925 $m^2 g^{-1}$, and stripped of fines) was used in each experiment. The fluids used consisted of simple NaCl/NaOH pH buffers, chosen to avoid potential complexation that might have been expected if organic- or other inorganic-based buffers were used. Fluid samples were continuously extracted during each experiment (in order to monitor how the dissolution rates varied with time) and analysed for pH, major anions and cations.

Average dissolution rates were calculated from the fluid analyses of samples taken after the experiments had stabilised. Where possible, dissolution rates were calculated based upon release rates of more than one element, however this was not always possible as concentrations of certain analytes were often below analytical detection limits.

The dissolution rates at 25 and 70°C are summarised in Figures 1 and 2. Three observations can be made from these; that non-stoichiometric dissolution became more important with increasing pH, that the dissolution rate increased with increasing pH, and that the dissolution rate increased with temperature. The apparent non-stoichiometric dissolution could result from either; precipitation after dissolution (though no secondary phases were observed), or preferential dissolution of one part of the chlorite structure relative to the other.

At 25°C under alkaline conditions, the average rate constant was 7.9×10^{-16} $mol.m^{-2}.s^{-1}$ (at pH = 0) and increased with increasing pH proportional to approximately $a_{H^+}^{-0.3}$. At pH = 13 such a dissolution rate would equate to 7.9×10^{-12} $mol.m^{-2}.s^{-1}$, i.e. 20 times less than that of albite or quartz (Knauss and Wolery, 1986, 1988).

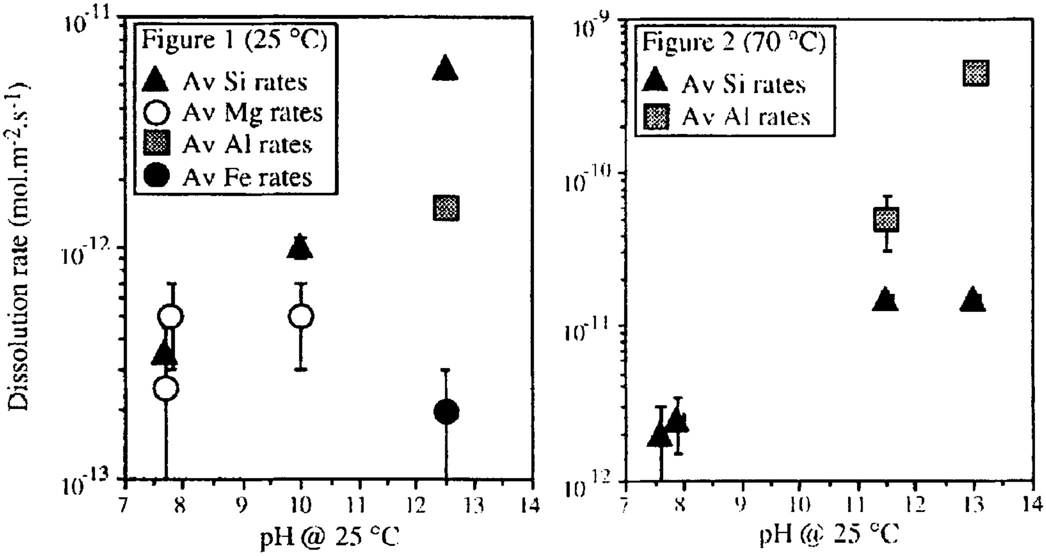

FIG. 1.

At 70°C the observed preferential release of Al relative to Si was the opposite to that observed at 25°C. This could be important if due to a change in Al speciation (and hence reaction mechanism), though it would be desirable to have further (i.e. more than one) data points at 25°C to confirm the observation. For alkaline conditions, the rate constant based upon Si appeared to be independent of pH, being 1.5×10^{-11} mol m^{-2} s^{-1}. However, the rate constant based on Al was determined to be 6.3×10^{-19} mol m^{-2} s^{-1} (at pH = 0), and increased with pH proportional to approximately $a_{H^+}^{-0.7}$. For data based upon Si at pH 13 the dissolution rate of the chlorite was thus 3000 times slower than quartz, 60 times slower than albite, but 3 times faster than that of muscovite (Knauss and Wolery, 1989).

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