

The application of nuclear microprobe analysis and secondary ion mass spectrometry to radioactive waste disposal studies

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Many plans for long-term disposal of low- and intermediate-level radioactive waste in the UK involve disposal in an underground repository. There will be three main barriers to the release of radionuclides to the biosphere: 1) the containers into which the waste will be sealed, 2) the backfill material (cement) used to fill the repository vault (the Near Field) and 3) the host rocks surrounding the repository itself (the Far Field). With time, groundwaters will penetrate the repository structure, leading to dissolution of the waste containers and the release of radionuclides into the groundwaters which will flow through the highly alkaline backfill into the surrounding rocks. The subsequent movement of these radionuclides through the geosphere will be significantly retarded by sorption onto minerals in the rocks along flowpaths. The quantification of this sorption is central to an assessment of the performance of a proposed radioactive waste repository.

This paper describes the application of advanced surface analytical techniques; Nuclear microprobe analysis and Secondary Ion Mass Spectrometry (SIMS) to the field of radioactive waste disposal.

The experimental approach used was to contact intact rock samples, in the form of polished thin sections, with solutions containing the radionuclides of interest for 1–6 months. By coupling α - and β -autoradiography with standard petrographic techniques such as optical microscopy and Electron Probe Microanalysis (EPMA), the distribution of radionuclides sorbed on a rock surface were mapped for subsequent analysis by the nuclear microprobe and SIMS.

Nuclear microprobe analysis was used for determining depth profiles and surface loadings of radionuclides on individual minerals in rocks because the technique is particularly suitable for measuring heavy elements deposited on or near the surfaces of lighter substrates. The nuclear

microprobe at AEA Harwell has been used previously to investigate the contamination of steels by thorium and plutonium. At AEA Harwell, a finely focused 2MeV $^4\text{He}^+$ beam produced by a 5MV Van de Graaff accelerator is targeted onto the sample. Some incident helium ions are scattered elastically by sample atoms and are detected at high angles; this is called Rutherford backscattering (RBS). Simultaneously, the helium ion beam interacts with atoms in the first 10–20 μm of the sample resulting in the production of X-rays with energies characteristic of the atoms excited by the beam. This technique is known as particle induced X-ray emission or PIXE. RBS spectra obtained contain information about the variations of elemental concentration with depth. The technique is particularly sensitive for the determination of high atomic mass elements such as actinides sorbed onto mineral surfaces in a rock, with recorded detection limits of $1\text{ng}/\text{cm}^2$ for uranium and plutonium by irradiating to a dose of $8\mu\text{C}$. Computer simulations of RBS spectra enable actinide depth profiles to be determined. Total loadings can be calculated from the depth profiles. PIXE is highly sensitive to low atomic weight rock-forming elements (particularly those with atomic numbers greater than neon). The elemental composition of the surface being analysed can be derived from X-ray spectra. PIXE and RBS spectra are recorded simultaneously.

SIMS combines high elemental sensitivity, good spatial and depth resolution, and the ability to discriminate between isotopes. At AEA Harwell, two SIMS instruments are used: a Cameca IMS 3F ion microscope and a VG Scientific gallium microprobe instrument based on a quadrupole mass spectrometer. The former is a high sensitivity, high mass resolution instrument while the latter offers a higher spatial resolution.

These instruments were used to provide qualitative data on the distribution of actinides sorbed onto a rock and penetration rates into minerals. The importance of microfissures in controlling the penetration of actinides into rocks was demonstrated by the technique.

Individually, nuclear microprobe analysis and SIMS are powerful techniques for locating and measuring radionuclides sorbed on rock surfaces. However, their complementary qualities provide added advantages when used in parallel. RBS quantifies actinide surface loadings with somewhat limited lateral and depth resolution but allied to SIMS, which has excellent spatial resolution, samples can be analysed both quantitatively and with high spatial resolution. The poor elemental selectivity of RBS for high atomic number elements is a disadvantage when competitive sorption of two or more actinides from a solution onto a rock is being studied but this problem can be circumvented by the parallel use of SIMS, which has excellent selectivity.

These techniques have been used to study the sorption of uranium and plutonium from solution onto polished thin sections of granite, diorite and sandstone. The results have identified the minerals which control sorption, namely phyllosilicates such as biotite for the granite, Fe-Ti oxides for the diorite and hematite and clay coatings for the sandstone. The results also give insights into the mechanisms of sorption that occur. For example, uranium and plutonium sorption onto diorite is pH dependent with greater sorption occurring under more alkaline conditions. The dominant sorbing phase is ilmenite in this rock. RBS and SIMS depth profiling show that the sorbed actinides are confined to ilmenite surfaces with little penetration into the lattice. These observations are consistent with a surface complexation mechanism in which positively-charged uranium or plutonium oxy-hydroxide species (predicted by speciation modelling) are sorbed onto negatively-charged (at alkaline pH's) metal oxide surfaces.