Modelling of radium-barium sulphate co-precipitation in the near field of a HLNW repository

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The solubility limit of radium is one of the main uncertainties remaining in the safety assessment of high-level nuclear waste repositories. Previous evaluations have commonly considered $RaSO_4$ as the solubility limiting phase, although observations in Nature indicate that this phase never occurs. Since the pionnering laboratory work of Germann (1921) and Doerner and Hoskins (1925), which showed a readily incorporation of radium into the barium sulphate (barite) lattice, most studies have concluded that the fate of radium in waters is intimately linked to barite precipitation. Both radium and barium are present in spent nuclear fuel,. Most of the barium will be created during fuel irradiation, but some will also be generated shortly after the fuel is discharged from the reactor through decay of the short-lived isotopes of caesium, namely ^{134}Cs and ^{137}Cs. About 5 kg of Ba are estimated for each waste canister (SKB, 2006). On the other hand, radium is progressively generated by U-Th isotope decay chain, and maximum Ra inventory is going to be produced from the spent fuel after 100,000 years. The coexistence of both, Ba and Ra, in the fuel makes feasible the formation of $(Ba,Ra)SO_4$ solid solution, and, therefore, there is a great potential for reducing the calculated releases of ^{226}Ra if co-precipitation effects are considered. These solid solution would occur at the interface between canister and clay-based barrier when, as a consequence of failure of canister integrity, a sulphate-rich water from the barrier leaches Ba and Ra from the spent fuel. In this conceptual model, the supply of sulphate is a key parameter to ensure $(Ba,Ra)SO_4$ formation. Calcium sulphate is a common accessory mineral in many bentonite rocks used in the barriers, although it can be easily leached by inflowing groundwaters, especially in ice-melting water intrusion.

In this study, we have calculated the effect of solid solution formation on the radium solubility limit in wide ranges of radium, barium and sulphate concentrations. The results obtained show that radium solubility limit can be reduced up to 4-5 orders of magnitude, mainly in those cases in which initial barium concentration is higher.

References

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Single particle sampling and analysis

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The ability to sample and analyse individual particles is paramount for the determination of their sources, their distribution and to understand their interaction with the environment. Electromagnetic and thermophoretic sampler have been designed for collecting the ultrafine fraction (< 0.5PM) directly onto TEM grids. The results from numerical modelling of the deposition patterns and the sampling efficiency compared well with the experimentally determined performance of the samplers. Particle counts and chemical analysis (SEM, TEM) of individual particles sampled on a TEM grid can, therefore, easily be translated into quantitative information about the sampled aerosol.

Different sources of ultrafine particles have been studied using the new collectors. Particle emission from railway traffic and welding workplaces have been investigated by conventional EDS-based single particle analysis. Synchrotron based scanning transmission X-ray microscopy (STXM) and carbon(1s) near edge xray adsorption fine structure (NEXAFS) spectroscopy have been used to analyse soot particles produced by diesel engines and wood fires. First results show clear differences in the chemical structure of the particles from the two sources. NEXAFS may, therfore, be used as tool for the source apportionment of soot particles, but also to follow their evolution with time.