Splittings, satellites and fine structure in the soft X-ray spectroscopy of the actinides

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Despite the limitations imposed by their sometimes high levels of radioactivity, there has recently been remarkable progress in the soft X-ray spectroscopy of the actinides, particularly that of Plutonium (Pu) and Uranium (U). For example, synchrotron-radiation-based X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) played important roles in the progress of the understanding of Pu electronic structure, [1-5] leaving only the last issue of electron correlation before a complete understanding is achieved. [6] Two examples of the manifestations of the large spin-orbit splitting in the 5f states are (1) the large disparity in the 4d branching ratios of Pu and U (Fig 1.), and (2) the presence of the pre-peak structure in U and its absence in Pu. Even more recently, we have begun experiments upon the important nuclear fuel system UO_2, [7-9] which also exhibits strong electron correlation. [7] Our new measurements using Resonant Inverse Photoelectron Spectroscopy (RIPES) and X-ray Emission Spectroscopy (XES) [10] indicate new satellite structure, to complement that already observed in XPS [9] and XAS. [7, 8]

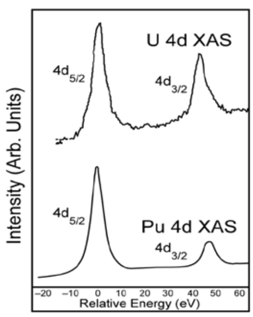

Figure 1 Comparison of the 4d XAS in elemental U and elemental Pu. From Ref 5.

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Plugging of porous media and rock fractures using ureolysis-driven calcite precipitation

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Ureolysis-driven calcite precipitation has shown great potential in a wide range of applications, including solid-phase capture, concrete crack remediation, soil stabilisation and carbon sequestration. Here, this process is investigated as a means of reducing the primary porosity and/or secondary fracture porosity of host rocks surrounding nuclear waste repositories in order to control or prevent radionuclide transport. Several studies have used simple sand column experiments to determine the best approach to plug pore spaces between grains; however, a field deployable approach that ensures a homogenous and stable seal has not yet emerged. Furthermore, there is no study that assessed the potential of this method to seal rock fractures. This is important as the hydraulic regime in fractures is very different compared to grain porosity.

Here, flow-through experiments in various media (sand columns, fractured / non-fractured rock cores) were carried out to examine the potential of ureolysis–driven calcite precipitation to seal primary and secondary porosity effectively and homogenously. The 'plugging efficiency' was examined as a function of varying injection strategies, flow rate, urea and Ca^{2+} concentration and the addition of a grout (e.g. silica nanoparticles). The temporal change in porosity was monitored by the decrease in hydraulic conductivity, and the local spatial distribution of the calcite fill was quantified using scanning electron microscopy.

Results from sand column / sandstone rock core experiments show that under continuous flow conditions, a gradient in calcite fill developed along the flow path of the column / core. In contrast, static conditions (i.e. no flow) permitted the reaction to occur homogenously throughout the column / core resulting in a stable plug. Note that under both static and continuous flow conditions, new bacteria needed to be injected every 1-2 days due to embedment of the bacteria within the forming precipitates. Initial results from fractured rock core experiments indicate that bacteria less likely 'attach' to fracture surfaces, which significantly lowers rates of ureolysis and calcite precipitation within the fracture. The use of a saline fixative and varying flow rates will be tested to increase the reaction yield.