

Plutonium redox reactions with iron oxides under anoxic conditions

R. KIRSCH^{1,2*}, D. FELLHAUER³, M. ALTMAIER⁴,
A. ROSSBERG¹, TH. FANGHÄNEL³, L. CHARLET²
AND A.C. SCHEINOST^{1*}

¹Inst. of Radiochemistry, HZDR, 013 14 Dresden, Germany
AND ROBL (BM20) at ESRF, BP220, 38043 Grenoble
(*correspondence: kirsch@esrf.fr, scheinost@esrf.fr)

²ISTerre, UJF/CNRS, BP 53, 38041 Grenoble, France

³EC-JRC-ITU, P.O. Box 2340, 76125 Karlsruhe, Germany

⁴KIT-INE, P.O. Box 3640, 76021 Karlsruhe, Germany

The environmental fate of plutonium, the major transuranium actinide in nuclear waste, is largely impacted by its sorption onto and redox reactions with iron oxide minerals [1, 2] that form as corrosion products of steel in the 'near field' and occur widely in sediments. To obtain information on oxid-ation state and local structure, we reacted ²⁴²Pu as electro-lytically prepared Pu (V) or Pu (III) (1×10⁻⁵ M) under anoxic conditions in carbonate free 0.1 M NaCl with hematite, goethite, maghemite and magnetite. Pu-L_{III}-edge XAFS spectra were collected after 40 d and 6 months of reaction.

Results and Discussion

After reaction of either Pu (III) or Pu (V) with hematite (> 99.9 % of added Pu is sorbed on α -Fe₂O₃), Pu is mainly present as Pu (IV), with up to 30 % Pu (V). Also after reaction with goethite (γ -FeOOH) both Pu (IV) (55 %) and Pu (V) (45 %) are present. For both minerals, EXAFS spectra show no strong Fe-backscattering from the substrate and also give no evidence for the formation of a solid PuO₂ phase. In contrast, EXAFS spectra of Pu reacted with maghemite (γ -Fe₂O₃) and magnetite (Fe₃O₄) are characterized by strong iron backscattering, indicating the formation of inner-sphere surface complexes. With maghemite, oxidation state mixtures of Pu (III) and Pu (IV) or Pu (IV) and Pu (V) were found while with magnetite, Pu (III) was the predominant oxidation state [3]. However, in one case and probably due to an increased Pu / magnetite surface area ratio, formation of PuO₂ after reaction of Pu (V) with magnetite was observed. These results highlight the importance of plutonium surface complexation, in addition to solid PuO₂ precipitation, in controlling environmental Pu concentrations. Further, under reducing conditions where Fe (II)-bearing oxides such as magnetite exist, it is necessary to consider trivalent in addition to tetravalent plutonium species and PuO₂ (am, hyd) for risk assessment.

[1] Novikov *et al.* (2006) *Science* **314**, 638–641. [2] Powell *et al.* (2005) *Environ. Sci. Technol.* **39**, 2107–2114. [3] Kirsch *et al.* (2011) submitted to *Environ. Sci. Technol.*

Monitoring CO₂-H₂O interactions using $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ at the CO2CRC Otway Project CO₂ storage pilot

D. KIRSTE^{1,2}, C. BOREHAM^{1,3}, L. STALKER^{1,4}
AND J. UNDERSCHULTZ^{1,4}

¹Cooperative Research Centre for Greenhouse Gas Technologies,

²Dept. of Earth Sciences, Simon Fraser University, Burnaby, BC V5A 1S6, Canada (dkirste@sfu.ca)

³Geoscience Australia, GPO Box 378, Canberra, ACT 2601, Australia (chris.boreham@ga.gov.au)

⁴Division of Petroleum Resources, CSIRO, Kensington, WA 6151, Australia (linda.stalker@csiro.au, james.underschultz@csiro.au)

The CO2CRC Otway Project is an extensively monitored demonstration site for the storage of CO₂ in a depleted gas field. Geochemical monitoring was carried out through the collection of high quality aqueous and supercritical fluid samples via a novel U-tube bottom hole sampling assembly. Several sampling zones within the depleted field were accessed using 3 separate U-tube lines, one completed in the methane-rich gas zone (U1) and two in the water leg at ~2 m (U2) and ~7 m (U3) below the initial gas-water contact. This configuration allowed for monitoring of the filling of the gas field by the injected CO₂. Injection of CO₂ began in late March, 2008 with breakthrough occurring between 101 and 121 days later and the transition to full self-lifting of U3 by day 303. Reservoir fluids were sampled for stable isotopic composition measurements of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the dissolved and immiscible phase CO₂ and the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water. The U-tube assembly enabled sampling of fluids at reservoir pressure but cooling during sample lift meant that the subsurface temperatures were not maintained. The $\delta^{13}\text{C}$ of the pre-breakthrough exsolved CO₂ and the gas phase CO₂ showed a fractionation consistent with that expected between CO₂ (g) and CO₂ (aq). As the injected CO₂ concentration increased the $\delta^{13}\text{C}$ shifted from that of the indigenous CO₂ to that of the injected. However, the $\delta^{13}\text{C}$ of the HCO₃⁻ showed a fractionation typical of a Rayleigh-type distillation and the fractionation factor reflected surface temperature conditions. The $\delta^{18}\text{O}$ of the water remained constant throughout the period for U2 and U3 until just prior to self-lift when there was an decrease. U3 showed considerable variability in the produced fluid immiscible/aqueous phase ratio near the transition and this is reflected in the oxygen isotopic of the aqueous and gas phase. Interestingly the $\delta^{18}\text{O}$ values showed no surface temperature fractionation like that seen for the $\delta^{13}\text{C}$.