

Risk assessment analysis of Kadji-Sai uranium tailings site, Kyrgyzstan

ZH. KULENBEKOV* AND BRODER J. MERKEL

TU Bergakademie Freiberg, Gustav Zeuner Str. 12, 09596, Germany (*correspondence: kulenbekov@gmail.com)

Sediment samples and coal ashes from Kadji-Sai uranium tailing site, Kyrgyzstan (a former coal and uranium mine) taken at depth of 0.1-0.2, 1, and 2 meters were investigated with gamma spectrometry and electron microscopy coupled with Energy-Dispersive X-ray Fluorescence Spectroscopy (SEM/EDX). Gamma spectroscopy showed significant elevated activities for uranium, radium, and lead-210 (Table 1).

Sampling points	Depths (m)	^{238}U kBq kg $^{-1}$	^{226}Ra kBq kg $^{-1}$	^{210}Pb kBq kg $^{-1}$
Catchment pool	0.1-0.2	0.43 to 1.2	0.10 to 0.07	0.11 to 0.07
Uranium tailing dump	1.0	6.8	31.2	23.9
Uranium tailing dump	2.0	7.2	26.6	24.2

Table 1: Gamma activity at shallow depths of the Kadji-Sai uranium tailing site

These results reveals that the uranium extraction technique was rather inefficient leaving about between 20 and 30% of the uranium in the tailings and that no sufficient cover of the tailings is in place. SEM/EDX was used to study the chemical forms and morphology of the coal ash and sediments particles. The precise knowledge of the elemental composition of radioactive wastes occurring in the tailings is important for future remediation and migration of radioactive elements and stability of secondary minerals being formed in the dump piles.

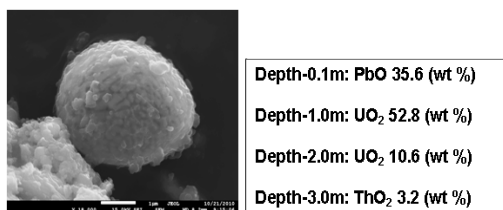


Figure 1: SEM image and EDX data of coal ash from different depths

Consistent treatment of entropy, enthalpy and volume effects of multi-dentate adsorption reactions

D.A. KULIK¹* AND J. LÜTZENKIRCHEN²

¹Paul Scherrer Institut, 5232 Villigen PSI, Switzerland (*correspondence: dmitrii.kulik@psi.ch)

²KIT INE, Postfach 3640, 76021 Karlsruhe, Germany (johannes.luetzenkirchen@kit.edu)

Evidence for aqueous ions binding to several oxygen atoms on mineral-water interfaces (MWI) has raised interest in multi-dentate surface complexation models [1, 2]. We investigated [3] how (fitted) intrinsic equilibrium constants K_M^\ominus for a δ -dentate M adsorption reaction depend on the choice of concentration scale for $\equiv\text{M}$, e.g. molarity ($^{\text{I}}$); relative surface fraction ($^{\circ}$); molecular surface density ($^{\text{e}}$, in mol·m $^{-2}$); or relative surface density Γ/Γ_0 ($^{\text{o}}$, where $\Gamma_0 = 2 \cdot 10^{-5}$ mol·m $^{-2}$ [4]). We have shown that, for $\delta \geq 2$, only K_M^{e} and K_M^{o} are density-invariant, and only K_M^{o} is independent of the real site density Γ_C . This makes the ($^{\text{o}}$) scale the best choice for defining the standard state of a surface species.

In this contribution, our approach is extended to T and P corrections of K_M^{e} defined by the partial molal entropy $\Delta_r S$, enthalpy $\Delta_r H$, isobaric heat capacity ($\Delta_r C_p$), and volume $\Delta_r V$ effects (at $T_r = 298$ K) of the M adsorption reaction. These effects can be predicted, or fitted from K_M^{o} values known for several temperatures. For the same experimental data set, fitted $\Delta_r S$ values depend on the chosen concentration scale for K_M^{e} ; the bias can reach 275 J·K $^{-1}$ ·mol $^{-1}$ for tetradentate cations on rutile surface. General conversions such as

$$\Delta_r S_{M,298}^{\text{I}} - \Delta_r S_{M,298}^{\text{o}} = -R(\delta - 1) \ln[\equiv]_{\text{TOT}} \quad (1)$$

$$\Delta_r S_{M,298}^{\text{e}} - \Delta_r S_{M,298}^{\text{o}} = -R(\delta - 1) \ln \Gamma_0 \quad (2)$$

($[\equiv]_{\text{TOT}}$ is the total molarity of sites \equiv at site density $\Gamma_{C_0} = \Gamma_0$) depend on δ and on the chosen value of Γ_{C_0} (1) or Γ_0 (2).

Upon adsorption of aqueous M, several H₂O molecules must be liberated from its solvation shell and from the MWI. Thus, a standard-state density Γ_0 should lead to ‘standard’ $\Delta_r S_{M,298}^{\text{e}}$ and $\Delta_r V_{M,298}^{\text{e}}$ effects consistent with known entropies and volumes of hydration of aqueous cations (cf. [5]). We find that Γ_0 cannot be chosen arbitrarily; setting it close to the density of H₂O molecules in the surface monolayer ($2 \cdot 10^{-5} \pm 1 \cdot 10^{-5}$ mol·m $^{-2}$ [6]) leads to entropy and volume effects related to $^{\text{o}}K_M^\ominus$ that are compatible with the available data on partial dehydration of aqueous ions and surfaces upon adsorption. In turn, this provides a constructive basis for future discussions aimed at reaching the ultimate thermodynamic convention on standard states of any-dentate surface complexes on MWIs.

[1] Zhang *et al.* (2004) *Langmuir* **20**, 4954–4969. [2] Ridley *et al.* (2009) *GCA* **73**, 1841–1856. [3] Kulik, Lützenkirchen, Payne (2010) *GCA* **74**(12S1) A544. [4] Kulik (2006) *Interf. Sci. Technol.* **11**, 171–250. [5] Marcus (1997) *Ion properties*. [6] Tamura *et al.* (1999) *JCIS* **209**, 225–231.