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Thermodynamic Model of Uranium and Arsenic Accumulation in Saline Lakes

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1 Introduction

The attractiveness of Shaaazgai-Nuur Soda Lake (pH 9.2 - 9.4) as an alternative metal source is explained by the high concentration of dissolved uranium (~1 mg/l) due to the location of water drainage territory within the Tsagan-Shibetinskaya uranium-ore zone [Isupov et al., hereinafter]. Alkaline soda waters favor accumulation of uranium as uranyl-carbonate species, but uranium is accumulated in the Shaaazgai-Nuur bottom sediments too. The total U concentration in bottom sediments is up to 10.4×10^{-2} g per kg of sediment, which is higher than the bulk concentration in water by two orders of magnitude. According to sequential extraction procedure, the most significant uranium solid species are ion-exchangeable and sorbed by iron (hydr)oxides. Besides uranium, the lake water contains rather high concentrations of B, Li and Sr. Noteworthy is the concentration of As as high as 250 µg/l. The concentration of uranium correlates positively with HCO₃⁻, As, B and Si. The purpose of this work was to simulate by means of thermodynamic calculations the main uranium and arsenic species in solutions and bottom sediments of Shaaazgay-Nuur lake, and to offer a possible way of As removal as an undesirable impurity in commercial products.

2 Results and discussion

Thermodynamic modeling at 25°C and 1 bar total pressure was performed with the "HCh" code using a free energy minimization algorithm and the UNITERM

Table 1. Logarithm of surface complexation constants on the surface of calcite (>CaOH) and goethite (>FeOH).

Adsorption reaction equations	log K
$>\text{FeOH} + \text{H}^+ = >\text{FeOH}_2^+$	7.29
$>\text{FeOH} = >\text{FeO}^- + \text{H}^+$	-8.93
$>\text{FeOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = >\text{FeOHUO}_3 + 2\text{H}^+$	-3.05
$>\text{FeOH} + \text{UO}_2^{2+} = >\text{FeOHUO}_2^{2+}$	6.63
$>\text{FeOH} + \text{AsO}_4^{3-} + 3\text{H}^+ = >\text{FeH}_3\text{AsO}_4^0 + \text{H}_2\text{O}$	30.94
$>\text{FeOH} + \text{AsO}_4^{3-} + 2\text{H}^+ = >\text{FeH}_2\text{AsO}_4^- + \text{H}_2\text{O}$	26.75
$>\text{FeOH} + \text{AsO}_4^{3-} + \text{H}^+ = >\text{FeHAsO}_4^{2-} + \text{H}_2\text{O}$	20.16
$>\text{CaOH} + \text{HCO}_3^- = >\text{CaCO}_3^- + \text{H}_2\text{O}$	6.77
$>\text{CaOH} + \text{HCO}_3^- + \text{H}^+ = >\text{CaHCO}_3 + \text{H}_2\text{O}$	-1.7
$>\text{CaOH} = >\text{CaO}^- + \text{H}^+$	-12.0
$>\text{CaOH} + \text{H}^+ = >\text{CaOH}_2^+$	11.85
$>\text{CaOH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 = >\text{CaOHUO}_2\text{CO}_3 + 2\text{H}^+$	-1.03
$>\text{CaCO}_3^- + \text{UO}_2^{2+} + \text{HCO}_3^- = >\text{CaCO}_3\text{UO}_2\text{CO}_3^- + \text{H}^+$	6.0
$>\text{CaCO}_3^- + \text{H}_2\text{AsO}_4^- = >\text{CaHAsO}_4^- + \text{H}^+ + \text{CO}_3^{2-}$	-8.79
$>\text{CaCO}_3^- + \text{CaHAsO}_4^0 = >\text{CaAsO}_4\text{Ca}^0 + \text{H}^+ + \text{CO}_3^{2-}$	-9.07

Note: Sign ">" means the surface sites

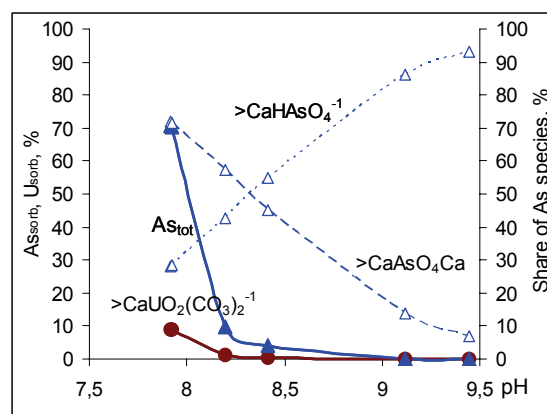


Fig. 1. Dependence of total adsorbed U and As on pH (1 g/L of calcite) as well as the adsorbed species of arsenic

database [Shvarov, 2008]. We modeled the heterophase 20-components system H-O-Na-K-Ca-Mg-Cl-C-S-Al-Si-Sr-U-As-Ba-Cu-Mn-Fe-Pb-Zn; the dissolved and adsorbed U-

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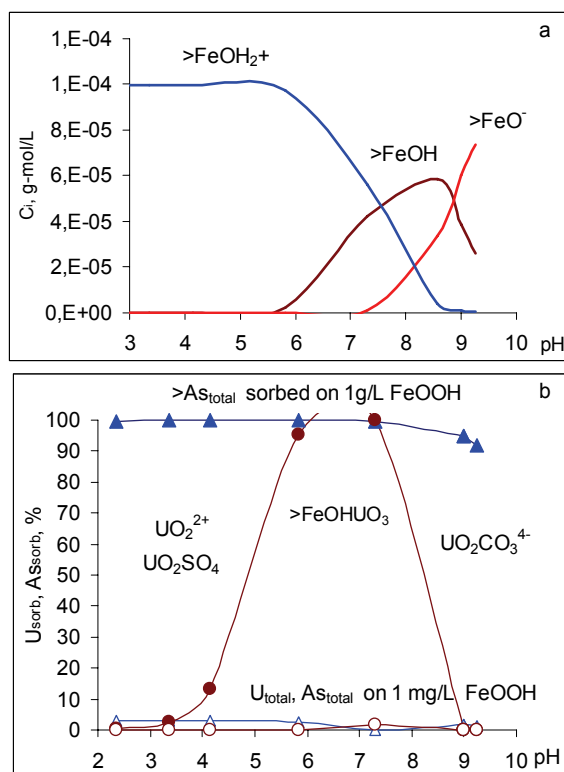


Fig. 2 Variation of the sorption sites on goethite surface with pH (a) and As and U sorption variation with pH onto 1 mg/L FeOOH (empty symbol) compared to the sorption on 1 mg/L of goethite (solid symbol) together with the predominance of the different uranium species in solution and on the surface according to the "HCh" code

species as it's solid phases were incorporated into the model using data borrowed from the literature elsewhere. The results of calculations show that water in Shaazgai-Nuur Soda Lake is supersaturated with respect to CaCO_3 , MgCO_3 and SrCO_3 (70 mg/L of carbonates would precipitate), to FeOOH (0.04 mg), Quartz (2.21 mg) and Montmorillonite (0.43 mg). It is available prerequisites of an effective sorption barrier formation composed of clay and carbonate minerals with goethite. Therewith the water is undersaturated markedly with respect to any uranium minerals, e.g. CaUO_4 , $\text{b-UO}_2(\text{OH})_2$ or Uranophane $\text{Ca}[\text{UO}_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}]$. Main uranium soluble species is $\text{UO}_2(\text{CO}_3)_3^{4-}$ (pH 9.4, Eh 180 mV). Calculations have shown that this kind of solutions are aggressive in relation to U-containing rocks and minerals and are capable to leach up to ~3 g/l of U. Moreover, the schemes of industrial uranium extraction are based on the interaction of enriched materials with (bi)carbonate solutions of alkali metals. $\text{NaAsUO}_6 \cdot 3\text{H}_2\text{O}$ could precipitates during the evaporation of salt solutions.

The adsorption of U and As was simulated on the surface of CaCO_3 as prevailing phase and on the FeOOH surface with maximum adsorption capacity (Table 1). The plot in

Fig 1 shows the distribution of adsorbed UO_2^{2+} and AsO_4^{3-} on 1 g of calcite versus pH as well as the adsorbed species of arsenic. As a whole, the results of these calculations predict insignificant adsorption at pH 9.4 and only with pH lowering arsenic is adsorbed as a variety of As species ($>\text{CaAsO}_4\text{Ca}$ in near neutral solutions and $>\text{CaHAsO}_4^-$ in alkaline ones).

The plot in Fig 2^a shows the distribution of goethite surface sites versus pH. The surface is charged negatively at pH above 8. While it should assist cations adsorption, the formation of stable UO_2^{2+} carbonate complexes is responsible for the uranium solubilization as $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ species. Fig. 2^b illustrates the distribution of adsorbed UO_2^{2+} and AsO_4^{3-} on 1 g and 1 mg of FeOOH versus pH as well as the uranium species in solution and on the surface ($>\text{FeOHUO}_3$). The main As adsorbed species are $>\text{FeHAsO}_4^-$ and $>\text{FeAsO}_4^{2-}$. The most special feature is that As could be captured by goethite surface both in acid and alkaline solutions in case of AsO_4^{3-} / $>\text{FeOH}$ ratio is low. To achieve the best separation from dissolved uranium the use of coagulation is reasonable.

2 Conclusions

The present work suggests that authigenic calcite and goethite can not adsorb a significant quantity of U and As in alkaline solutions during the bottom sediments formation. It is likely that the high empirical distribution coefficient K_d 138 L/kg is characteristic only for the "bottom sediment - pore waters" system with low W/R ratio. There is the possibility of uranium and arsenic partitioning in acidified or alkaline solutions when a sufficient quantity of FeOOH is added. During the evaporation of Shaazgai-Nuur Soda Lake salt solutions some uranium (hydr)oxides $\text{UO}_2(\text{OH})_2$ - $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ could precipitate, as well as $\text{NaAsUO}_6 \cdot 3\text{H}_2\text{O}$.

Key words: saline lakes, uranium, arsenic, sorption, thermodynamic model, calcite, goethite.

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