

Experimental study and modelling of the interaction between U(VI) and the surface of iron(II)-rich olivine

F. Z. El Aamrani
J. de Pablo

Chemical Engineering Department, UPC, 08028 Barcelona, Spain

L. Duro
J. Bruno

QuantiSci S.L, Parc Tecnològic del Vallès, 08290 Cerdanyola del Vallès, Spain

Iron(II)-rich olivine has been proposed as an additive to the buffer material placed in high level radioactive waste final repository [1] due, both to its reducing capacity given by its content in iron(II) as well as to its ability to sorb heavy metals and radionuclides. Preliminary results have shown a good sorption capacity of the olivine [2,3].

In this work, a systematic study of the uranium (VI) sorption onto the olivine has been undertaken as a function of pH and the olivine mass.

Experimental part

The sorption of uranium (VI) onto olivine has been studied by means of batch tests performed at 25°C in air. Preliminary experiments indicated that the system needed a maximum of 6 hours to reach equilibrium. Stopped glass tubes containing variable weights of solid in contact with 0.20 dm³ of NaCl 0.02 mol dm⁻³ have been shaken during 6 h in a continuous rotary mixer. The solid particle size has been the same for all the experimental tests: 120-160 microns, for which the B.E.T. surface area was determined to be of 0.173 m² g⁻¹. The following range of experimental conditions has been used in the present work: initial uranium concentration between 210⁻⁷ and 810⁻⁵ mol dm⁻³; initial pH of the solutions between 3 and 10 and solid weight to volume ration between 2.5 and 250 g dm⁻³.

Results and analysis of the data

The results obtained are shown in Fig. 1 in terms of sorption percentage versus pH. It can be observed that the maximum of the sorption edge is located at pH around 6.5.

These results have been modeled by using both, traditional isotherms as well as surface complexation approaches.

According to the Langmuir approach, the sorption equilibrium of a sorbate A onto a surface S can be

expressed by the following reaction: $S + A \rightleftharpoons SA$, which is defined in terms of an adsorption constant, $K_{ads} = \frac{[SA]}{[S][A]}$

The expression of the Langmuir isotherm is given by the following equation:

$$\Gamma = \Gamma_{max} \frac{K_{ads}[A]}{1 + K_{ads}[A]} \quad (1)$$

where Γ stands for the density of occupied surface sites and Γ_{max} is the maximum density of surface sites. In table I, parameters obtained from the application of equation (1) to the experimental data are collected. From Table 1, we can observe the dependence of the value of K_{ads} with pH.

The value of γ_{max} obtained varies between 1.0310⁻⁵ and 2.0910⁻⁶ moles of sites per g of solid. Most oxides and silicates present a density of coordination sites ranging from 1 to 10 sites per nm² [4]. In the case of olivine, by taking into account its specific surface area (0.173 m² × g⁻¹), this corresponds to a value ranging from 2.9 × 10⁻⁷ to 2.9 × 10⁻⁶ moles of coordination sites per gram.

As a second approach we have applied a non-electrostatic surface complexation model to the data. The model has been further simplified by assuming a unique type of surface sites available for the surface coordination of U(VI) species. The surface acidity of

TABLE I. K_{ads} values as a function of pH

[U] ₀ (mole dm ⁻³)	pH	Γ_{max} (mole/g)	log K_{ads}
8.72 × 10 ⁻⁷	4	2.09 × 10 ⁻⁶	7.36
9.02 × 10 ⁻⁷	6.2	6.07 × 10 ⁻⁶	6.68
1.59 × 10 ⁻⁶	7.2	1.03 × 10 ⁻⁵	6.12
7.15 × 10 ⁻⁷	7.3	6.56 × 10 ⁻⁶	6.36
7.60 × 10 ⁻⁷	7.4	7.24 × 10 ⁻⁶	6.29
6.51 × 10 ⁻⁷	8.5	8.54 × 10 ⁻⁶	5.51

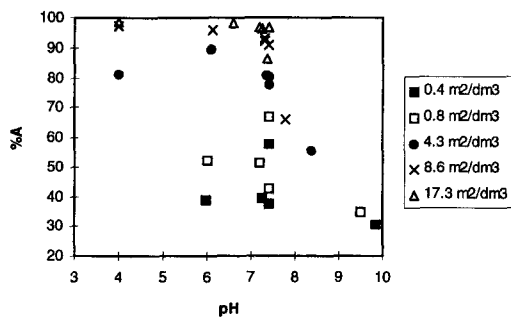
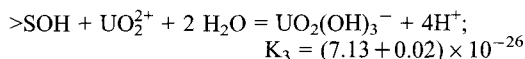
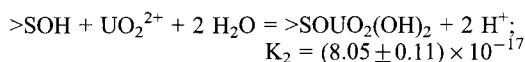
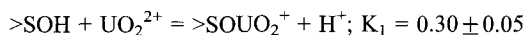


FIG. 1. Sorption percentage versus pH at different SA/V.

the olivine surface functional groups has been taken in analogy with data for other minerals according to Sverjenski and Sahai (1995) [5].

The analyses indicated that the set of equilibrium processes better describing the system involved the formation of three different surface species:



where >SOH stands for the surface groups on the olivine surface.

The comparison between the experimental data and the calculations is shown in Fig. 2.

The agreement between the data and the model is fairly good, indicating that the surface of uranium onto the olivine surface can be explained by using the set of surface species proposed above.

Acknowledgements

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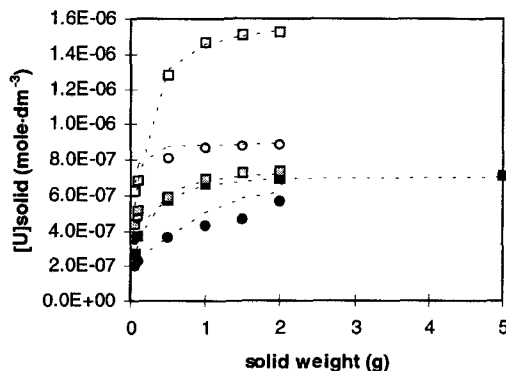


FIG. 2. Comparison between the measured and the calculated uranium sorbed onto the olivine surface by applying the non-electrostatic surface complexation model described in the text. Symbols stand for experimental data and dashed lines for model results.

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