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Water Rock Interaction [WRI 14]**Risk evaluation of uranium mining: a new kinetic approach**Alexandro Scislewski^{a*}, Pierpaolo Zuddas^b^a*Brazilian Nuclear Energy Commission (CNEN), Avenida Santana, 680, Centro, Caetité-Bahia, 46400-000, Brazil*^b*Université Pierre et Marie Curie, Paris-Sorbonne, ISTEP place Jussieu, Tour 56-55, case 116, F75252 Paris Cédex 05 France***Abstract**

Release of uranium and associated heavy metals is the main environmental concern regarding exploitation and processing of U-ore. Increasing uranium mining activities potentially increase the risks linked to radiation exposure. As a tool to evaluate these risks, a geochemical inverse modeling approach was developed to estimate the water-mineral interaction in the presence of uranium. Our methodology is based on the estimation of dissolution rate and reactive surface area of the different minerals participating in the reaction by reconstructing the chemical evolution of the interacting fluids. We found that the reactive surface area of parent-rock minerals changes over several orders of magnitude during the investigated reaction time. We propose that the formation of coatings on dissolving mineral surfaces significantly reduces reactivity. Our results show that negatively charged uranium complexes decrease when alkalinity and rock buffer capacity is similarly lower, indicating that the dissolved carbonate is an important parameter impacting uranium mobility.

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1. Introduction

It is well known that uranium extraction operations can increase risks linked to radiation exposure. The release of uranium and associated heavy metals is the main environmental concern regarding exploitation and processing of U-ore. A background evaluation of harmful elements is important in order to prevent and/or quantify future water contamination resulting from possible migration of toxic metals coming from ore and waste water interaction. Modeling of water rock interaction is particularly pertinent to understand the phenomena controlling the transport and fate of pollutants in groundwater and surface water systems as well as carbon dioxide sequestration [1, 2]. However, the estimation of the reactive surface area during water-rock interaction is further complicated

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by the fact that precipitation of newly formed mineral phases may coat the dissolving mineral surface, thereby modifying the theoretical estimations [3, 4]. Moreover, it is generally considered that the total available surface area is between one and three orders of magnitude larger than the actual reactive surface area [4] and can vary by several orders of magnitude during the overall reaction process [2]. The aim of this study is to investigate the possibility of reconstructing the effective reactive surface area of the mineral phases dissolved during the water rock interaction using the chemical composition of the interacting fluids and involving the presence of uranium.

2. Experimental Methods

Fresh rock was obtained from a research watershed in Caetité (Brazil). This metasomatic albitite [5] is constituted by more than 70% of albite, with segregation or enriched zones of mafic minerals. The modal composition of the selected albitite rock sample is: albite (75%), microcline (10%), quartz (5%), biotite (5%), calcite (3%), and accessory minerals (garnet, epidote, magnetite, titanite and uraninite <2%). The rock sample was processed and sieved into 0.35-0.80 mm grain size fractions, from which 444.4 grams were separated and introduced into the glass column reactor. The temperature was kept constant at $22^{\circ} \pm 1^{\circ}\text{C}$. The input solution consisted of deionised water saturated with a 5% CO_2 – 95% air mixture (which stabilized the pH close to 4.6) introduced into the reactor by a micro pump and periodically sampled.

3. Results

We found that pH constantly decreased from an initial value of 8 to a final value of 6.5. Since the input fluid had a constant pH value of 4.6, the rock capacity to neutralize the fluid acidity was potentially active during the time of investigation. Alkalinity decreased as a function of time, confirming the decline in the rock capacity to neutralize the acidity of the starting fluid. Similarly, sodium decreased by 2 orders of magnitude during the investigated reaction time while potassium, decreased as a function of time by a factor of 2-3 as did calcium, magnesium, and aluminum. Uranium concentration slightly increased in the first 2 days, later on, assuming a general decreasing trend until the end of the investigated time. Since albite is the main mineral composing the rock containing sodium, and represents 75% of the total rock, dissolved sodium is thus primarily related to albite dissolution, while potassium is related to microcline dissolution. Calcium and magnesium in the output fluids come mainly from calcite and biotite dissolution, respectively. Uraninite is the main mineral composing the rock that contains uranium, thus dissolved uranium is related to uraninite dissolution.

We estimated the output fluid saturation state using the geochemical code PHREEQCi [6] with the wateq4f.dat thermodynamic database [7], assuming atmospheric oxygen partial pressure. We found that output fluids were oversaturated with respect to quartz and kaolinite, while they were constantly undersaturated with respect to calcite and the other main parent rock minerals. Uranium speciation calculations in the output fluids were undertaken using the same database but adapted with thermodynamic data for uranophane solid phase [8]. Scanning Electron Microscope (SEM) measurements carried out at the end of the experiment revealed the presence of newly formed minerals coating the surface of the parent rock minerals. We detected secondary iron hydroxides and phyllosilicate-like minerals, in agreement with the modelling of the solution saturation state.

4. Estimation of the reactive surface area

Our system can be described by a series of mass balance equations for the relevant mineral phases in relation to their dissolution reaction rates. If all reactions are described with kinetic rate laws, the system can be solved in time-mode using absolute reaction rates (experimentally determined). The reaction rate per unit of surface area (R_i , usually in $\text{mol cm}^{-2}\text{s}^{-1}$) is obtained from the surface area (S_i , in cm^2) of an i th mineral phase and the i th mineral absolute reaction rate (\bar{R}_i , in mol s^{-1}). As mineral-water interactions occur primarily at the mineral surface, the overall reaction rates are directly related to the surface area involved. The dissolving species in our system are: Ca^+ , Mg^{2+} , Na^+ , K^+ , H^+ , $\text{SiO}_{2(\text{aq})}$, Al^{3+} (or $\text{Al}(\text{OH})_4^-$), H_2CO_3 , HCO_3^- , CO_3^{2-} , H^+ and U^{+6} . Since output fluids are saturated with respect to quartz and kaolinite, silica and aluminum concentrations can be assumed to be controlled by these two equilibria. We therefore can consider that Ca^+ , Mg^{2+} , Na^+ , K^+ , HCO_3^- , H^+ and U^{+6} participate in dissolution reactions and are related to the dissolution of calcite, biotite, albite, microcline and uraninite, respectively. Thus, a system containing N_{tot} species and N_r reactions can be described by [9]:

$$I \frac{dn}{dt} = v R \quad (1)$$

where I = identity matrix (dimensions $N_{tot} \times N_{tot}$); n = vector of solute concentration (length N_{tot}); v = stoichiometric reaction matrix (dimensions $N_{tot} \times N_r$); t = time; and R = reaction rate vector (length N_r). The evolution of the fluid compositional trend can be reconstructed as a function of the fractional overall progress variable (ζ) through a sequence of discrete points, instead of using time mode [9]. Since the vector of solute concentration is known in the compositional space $0 \leq \zeta \leq 1$, the system is now solved for R :

$$I \frac{dn}{dt} = v R \rightarrow I \frac{dn}{d\zeta} = v R_\zeta \quad (2)$$

The single mineral absolute dissolution rate for silicates and calcite dissolution rate, \bar{R}_i , were estimated following the expression described by [1,2,9,10]. We found that the absolute dissolution rates of albite, microcline, biotite, and calcite remain constant during the time of investigation in the range of pH between 6 and 7.5. As expected, we also found that the calcite dissolution rate is orders of magnitude higher than silicates. The surface areas of the mineral phases are obtained at each discrete value of ζ after introducing the experimental reaction rates (or mineral absolute reaction rate, \bar{R}_i):

$$R_{\zeta i} = S_i \bar{R}_i \frac{d\zeta}{dt} \quad (3)$$

We found that the evolution of the reactive surface area is not monotonous. Three different stages were observed: a first characterized by one order of magnitude increase, a second stage of significant decrease and a last of significant increment. The initial increase of the mineral's reactive surface area is associated with the predominance of mineral dissolution. On the other hand, the decrease in the mineral reactive surface areas (particularly between 10-20 days) can be explained by the presence of newly formed minerals, specifically phyllosilicate-like minerals, iron hydroxides and quartz. This alteration is also observed in uraninite and occurs simultaneously with the stage on which the output fluid becomes saturated with respect to kaolinite thus, indicating that uraninite dissolution is also affected by the formation of neogenic phases.

The results of this study show that the mineral reactive surface area changes significantly during water-rock interaction, indicating that in contrast to the current assumptions in water-mineral reactivity modeling, this parameter can't be assumed to remain constant.

5. Risk evaluation for uranium

In oxidized surface and groundwaters, uranium is transported as highly soluble uranyl ion (UO_2^{+2}) and its complexes, the most important part of which are the carbonate complexes [11]. Formation of U carbonate complexes is important because it increases the uranium minerals solubility and facilitates the U(IV) oxidation, limiting the extent of uranium adsorption onto particles, and increasing its mobility [11]. We observed that output fluids of the albitite experiment were constantly saturated with respect to uranophane. Our study indicates that the most important uranium complex is $\text{UO}_2(\text{CO}_3)_2^{-2}$, followed by the $\text{UO}_2(\text{CO}_3)_3^{-4}$ in the first 10-12 days, while later, the ion pair (UO_2CO_3) became more abundant until the end of the investigated time. The negatively charged complexes decrease with the decreasing of alkalinity and the albitite buffer capacity to neutralize the acidic fluid. Our results are in agreement (type and complex abundance) with other studies [12] confirming that U carbonate ion complexation play an important role in the distribution of uranium in waters where the radionuclide concentrations are more elevated, becoming an important parameter that impacts uranium mobility.

6. Conclusion

The results of our study indicate that albitite-fluid interaction can be modeled to estimate the reactive surface area of the dissolving parent minerals. The amount of reactive surface area available to react depends not only on the parent mineral intrinsic properties but also on the precipitation and eventual dissolution of newly formed minerals. We propose that despite the decrease of rock buffer capacity and uranium release, the contaminant mobility may increase because ion pair complex increase. Nevertheless, risk assessment models should take into account reactive surface areas and secondary mineral precipitation since they also determine the U ion complex formation, which in turn, controls uranium mobility in natural systems.

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