

Reactive transport around Bangombé uranium deposit, Gabon

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The Bangombé uranium deposit is located about 20 km south of the Oklo mining district, and is considered to be a nuclear reactor which underwent fission 1.8 Ga ago. It is located about 12 m from the surface and has not been mined. These features make it the object of an intensive study on the behaviour of radionuclides in meteoric oxydized environment.

This article describes a reactive transport model of the immediate surroundings of the Bangombé deposit. Such a model can help in the understanding of factors affecting the dissolution of uraninite in a near-surface environment, and to predict the future behaviour of the system.

Hydrogeochemical setting

The geology of the Bangombé area is made up of subhorizontal strata belonging to the early Francevillian formations (2 Ga): the upper part of the FA sandstones and the lowermost meters of the FB pelites (Gauthier-Lafaye, 1986). The uraninite deposit is a 0.1 m thick lens body located at the boundary between these two formations. A lateritic soil covers the previously mentioned rocks.

The hydrogeology of the Bangombé area is detailed in Gurban *et al.* (1996). The deposit is located at the edge of the Litani river valley, at the foot of the Comilog plateau. The climate is equatorial and the average rainfall is about 1m/y. Most of the rain circulates through the soil, and only a fraction (about 0.01 m/y) infiltrates into the aquifer. In addition to infiltration, a regional flow of 0.3 m/a, recharged into the plateau, circulates horizontally, mainly through the sandstones. The maximum residence time of water in the aquifer is about 2,000 y.

Major, trace elements and isotopic data have been obtained from water samples from boreholes (labelled BAX from here on) in several campaigns from 1993 to 96 (Lédoux and Made, 1997). Groundwater reaching the reactor could possibly be the result of the mixing of a deep reduced water (BAX01), and an oxydizing surficial water (BAX07).

The result of this mixing (BAX05) is undersaturated in uraninite upstream from the reactor. The whole set of analyses appear to be buffered by the Fe^{2+} - $\text{Fe}(\text{OH})_3$ equilibrium.

Initial and boundary conditions

A 2D section of 10×8 m around the reactor was selected for modelling. The uppermost metres of laterite and weathered rock were not considered in the calculations to save computing time. The initial mineral composition of each lithology is as follows: 1) sandstones = quartz, illite; 2) reactor = illite, uraninite; pelites = illite, chlorite, quartz; weathered rock = illite, kaolinite, quartz. Porosity was assumed to be 0.01 in all cases.

The water infiltrating from the upper boundary was assumed to be very similar to that of BAX07, i.e. diluted, acidic and oxydizing ($[\text{solute}] = 10^{-6}$ M, $[\text{U}] = 5 \times 10^{-10}$ M, $\text{pH} = 4.5$, $\text{Eh} = 0.46$ V, $\text{pCO}_2 = 2.5$). The water infiltrating from the left hand boundary was assumed to be similar to that sampled in BAX05, upstream from the modeled area: it is slightly ionized, slightly acidic and less oxydizing ($[\text{solute}] \cong 10^{-4}$ M, $[\text{U}] = 2 \times 10^{-8}$ M, $\text{pH} = 6.2$, $\text{Eh} = 0.16$ V).

Geochemical model

In order to describe the solutions behaviour we considered the following aqueous primary species: Mg^{2+} , K^+ , Fe^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{SiO}_2(\text{aq})$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, HCO_3^- , SO_4^{2-} , H^+ , e^- ; and 15 additional aqueous complexes. From the mineralogical composition of the rocks the following minerals have been included in the model: daphnite-14a, illite ($\text{Si}_{3.14}\text{Al}_{0.86}$) ($\text{Al}_{1.66}\text{Mg}_{0.26}\text{Fe}_{0.09}^{\text{II}}\text{Fe}_{0.07}^{\text{III}}$) $\text{O}_{10}(\text{OH})_2\text{K}_{0.97}$, kaolinite, chalcedony, $\text{Fe}(\text{OH})_3$, pyrite, quartz, uraninite, and coffinite. Equilibrium constants were from EQ3NR and NEA datafiles, except for illite (Gurban *et al.*, 1996). In addition, the uranium sorbing capacity of the rocks was included through the following species: $\text{AlO} > \text{UO}_2^+$, $\text{AlO} > \text{UOOH}$, $\text{SiO} > \text{UO}_2^+$, $\text{SiO} > \text{UOOH}$, $\text{FeO} > \text{UO}_2^+$

and $\text{FeO} > \text{UOOH}$, with equilibrium constants experimentally obtained by Del Nero (1997). Mineral-water interaction was calculated using the kinetic laws. The dissolution rate equation included a first order saturation-dependent term. The precipitation law was assumed to be the reverse of dissolution. The rate constants were taken from experiments reported in the literature. Uncertainties in the rate constant were included in the reactive surface area (areas ranging within two orders of magnitude were checked).

Reactive transport model

We used the code RETRASO that couples solute transport and chemical reactions (Saaltink *et al.*, 1997). It can handle complexation, adsorption and precipitation /dissolution of minerals. The latter reaction can be assumed to be in equilibrium or kinetically controlled. The model code uses a one-dimensional or two-dimensional finite element discretization and a Direct Substitution Approach (DSA) for coupling solute transport and chemical equations.

Results and discussion

The infiltration from the upper boundary of the acidic and oxidizing water causes the dissolution of illite. The results after 10,000 years show that illite transformed into kaolinite, amorphous $\text{Fe}(\text{OH})_3$ and chalcidony in the weathered zone, in agreement with the field observations. These reactions partially buffer the pH and Eh of the water infiltrating through the upper boundary. Dissolution of chlorite in the upper part of the pelites also contributes to this effect. As a consequence the pH-Eh of the pore water remains close to the Fe^{2+} - $\text{Fe}(\text{OH})_3$ equilibrium, in accordance with the measurements performed in the boreholes.

The water flowing in from the left side of the model was supersaturated with respect to the rock forming silicates. This is probably due to the increase of pH caused by the dissolution of dolomite present interbedded in the pelites in the plateau recharge area. However, a supersaturation threshold prevented the silicate minerals from precipitating.

The aqueous solutions infiltrating from both the upper and lateral boundaries were subsaturated in uraninite. Then, the uraninite from the reactor was

dissolved generating a plume of uranium downstream

Since the $^{235}\text{U}/^{238}\text{U}$ ratio of the reactor is lower (0.00630) than the regional ratio (0.007250), the uranium plume shows a depletion in the $^{235}\text{U}/^{238}\text{U}$ ratio. This fact is clearly shown by the analyses of water samples from the boreholes downstream the reactor (Gurban *et al.*, 1996). The uranium concentration and the $^{235}\text{U}/^{238}\text{U}$ values predicted by the model were higher and lower, respectively, than those analysed in the boreholes downstream from the reactor.

With the assumed flow pattern, the pore water in contact with uraninite reached equilibrium for a large range of tested reactive surface areas. This is in agreement with the analyses of samples from the borehole intersecting the reactor. An analysis of sensitivity to several uncertain parameters reveals that the uranium concentration of the plume is not significantly affected by the kinetic behaviour of silicates and oxides. The uranium content in the plume is decreased by a factor lower than five, by sorption on aluminosilicate surfaces, and by a hypothetical precipitation of coffinite. Sorption on an $\text{Fe}(\text{OH})_3$ surface has not been modelled yet. A larger depletion of uranium in the plume can be caused by dilution and changes in the detailed flow regime due to fractures. This can explain the uranium content and the $^{235}\text{U}/^{238}\text{U}$ ratio of the waters from boreholes downstream from the reactor.

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