

## Dissolution rate of bunsenite (NiO) in acid solution to 130°C

A. BELLEFLEUR<sup>1</sup>, M. BACHET<sup>1</sup>, P. BENEZETH<sup>2</sup> AND  
J. SCHOTT<sup>2</sup>

<sup>1</sup>EDF R&D, Site des Renardières, Avenue des Renardières,  
Ecuelles 77818 Moret Sur Loing Cedex  
(alexandre.bellefleur@edf.fr ; martin.bachet@edf.fr)

<sup>2</sup>GET, 14 Avenue Edouard Belin, 31400 Toulouse  
(benzeth@get.obs-mip.fr ; jacques.schott@get.obs-  
mip.fr)

Rates of proton-promoted dissolution of bunsenite (NiO) were measured from 50 to 130°C in hydrochloric acid solutions (pH 3 and 4.5) in a titanium mixed flow reactor. Measurements were also realized at 25°C with the stationary pH method [1] to confirm data from literature [2]. Pure bunsenite powder (Alfa Aesar Puratronic, Lot n°23430) was used for dissolution rate measurements, after being calcinated for 2\*20 h at 1000°C in air. To avoid plug up of the outlet filter by fine particles, the powder was not directly introduced in the titanium reactor but in a specifically designed cell with walls made of a porous membrane. Measured bunsenite dissolution rate at 25°C are  $2.4 \pm 0.3 \cdot 10^{-10}$  and  $7.5 \pm 0.6 \cdot 10^{-11}$  mol.m<sup>-2</sup>.s<sup>-1</sup> at pH 3 and 4.5, respectively. Apparent activation energies for dissolution rate (25-130°C) are equal to  $59.7 \pm 5.3$  kJ.mol<sup>-1</sup> and  $32.9 \pm 2.4$  kJmol<sup>-1</sup> at pH 3 and 4.5, respectively. Bunsenite proton-promoted dissolution rate can be expressed as  $R_H = k_H \{>NiOH_2^+\}^n$  where,  $k_H$ ,  $\{>NiOH_2^+\}$  and  $n$  stand for the dissolution rate constant, the concentration of protonated surface sites and the order of reaction with respect to adsorbed protons, respectively [3]. A two pK, one site surface speciation model which assumes a constant capacitance of the electric double layer was used to calculate  $\{>NiOH_2^+\}$  as a function of pH and temperature. The variation of the apparent activation energy with pH can be explained by the contribution of the enthalpy of protonation of surface sites to the dissolution reaction ([4], [5]). However, the variation in dissolution rate observed between pH 3 and 4.5 is not compatible with the surface protonation constant of  $10^{8.17}$  from [2], suggesting a lower constant for the powder studied here. Therefore, more work on surface properties of NiO is foreseen.

[1] Westrich H. *et al* (1992) *Am. J. Sci.* **293**, 869. [2] Ludwig C. and Casey W. (1996) *J. Colloid Interface Sci.* **178**, 176-185. [3] Furrer G. and Stumm (1986) *Geochim. Cosmochim. Acta* **50**, 1847. [4] Schott J. *et al* (2009) *Rev. Mineral. Geochem.* **70**, 207. [5] Casey W.H. and Sposito G. (1992) *Geochim. Cosmochim. Acta* **56**, 3825.

## Experimental studies on cesium retardation on Brazilian crystalline rocks: Petrography, porosity and distribution coefficients

J.B. BELLINE<sup>1\*</sup>, M. SIITARI-KAUPPI<sup>2</sup>, M. KELOKASKI<sup>2</sup>,  
P. SARDINI<sup>3</sup>, M.E.B. GOMES<sup>4</sup> AND M.L.L. FORMOSO<sup>1</sup>

<sup>1</sup>Post-Graduate Program in Geosciences. IG/UFRGS. Brazil.  
(\*correspondence: jean.belline@ufrgs.br)

<sup>2</sup>Laboratory of Radiochemistry. Univ. of Helsinki. Finland

<sup>3</sup>Laboratory HydrASA. Univ. of Poitiers. France

<sup>4</sup>Dep. of Mineralogy and Petrology.IG/UFRGS.Brazil

Cesium is an important radionuclide in the waste from the nuclear power plant [1,2]. The diffusion and sorption of cesium into rock is important to the safety of the radiowaste disposal. The mechanisms of sorption onto the minerals are important mechanisms to predict migration rates in the host rocks [3, 4]. The low porosity of granites is considered to prevent the radionuclides migration from repository site to the biosphere. This work discusses <sup>134</sup>Cs diffusion in three brazilian granites of São Sepé Complex Granitic, Rio Grande do Sul, Brazil, in the laboratory conditions. One sample comes from an outcrop and the two others (fresh and altered) are borecores from Camaquã mine. The porosities and densities of the each sample were measured by a water saturation method (pycnometry and water immersion techniques [5]). The porosity was measured also by C-14-PMMA autoradiographic method [6, 7]. Batch experiments and in diffusion test were made on crushed rock samples with several size fractions and blocks having volumes of about 8cm<sup>3</sup>, respectively, to obtain the distribution coefficients ( $K_d$  values) of cesium-134 and diffusion paths from <sup>134</sup>Cs autoradiographs.

[1] Milnes (1985). "Geology Radwaste". [2] Cornell.(1993) *J. of Rad. Nuc. Chem.* **171(2)**, 483-500.[3] . Tsukamoto and Ohe (1991) *Chem.Geol.***90**, 31-44. [4] Langmuir (1997) *Aqueous Environmental Geochemistry*. [5] Melnyk and Skeet.(1986) *Can. L. Earth Sci.* **23** 1068-1074.[6] Hellmuth and Siitari-Kauppi. (1990) *STUK-B-VALO.* **63**. [7] Siitari-kauppi.(2002) *Thesis*. Univ. of Helsinki. Finland..