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► To cite this version:

Sylvain Grangeon, Christophe Tournassat, Catherine Lerouge, Eric Giffaut, Thorsten Schäfer. Prediction of nickel mobility in a clayey formation requires accurate knowledge of the mineralogical assemblage. International meeting "Clays in Natural and Engineered Barriers for Radioactive Waste Confinement", Oct 2012, Montpellier, France. hal-00703575

HAL Id: hal-00703575

<https://brgm.hal.science/hal-00703575>

Submitted on 3 Jun 2012

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Prediction of nickel mobility in a clayey formation requires accurate knowledge of the mineralogical assemblage

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Introduction

In the perspective of nuclear waste storage, ^{63}Ni is one of the radio-elements of primary concern. Modeling of its retention in clay formations is usually performed using modeling approaches which consider that only phyllosilicates participate to retention. However, isotopic exchange with stable nickel contained in phases (i.e. minerals and organic matter) from the clay formation may play a role. Thus, a sound understanding and prediction of Ni retention also requires detailed knowledge of Ni distribution amongst the different phases. Importance of such knowledge is reinforced by the fact that the distribution of stable Ni between solution and some reactive phases could be considered as representative of ^{63}Ni distribution after long-term interaction. The present study aimed at elucidating the relative contributions of fast reversible (e.g. sorption on phyllosilicates) and slowly reversible/irreversible (e.g. isotopic exchange) processes to Ni retention capacities of the Callovian-Oxfordian clay formation from Bure. To achieve this goal, we combined (i) short and long-term (up to 180 days) ^{63}Ni batch sorption experiments to determine the contribution of irreversible to total sorption and (ii) chemical and physical methods to determine Ni-bearing phases that may contribute to irreversible sorption through isotopic exchange.

Results and discussion

Short-term (24 hours) batch experiments led to ^{63}Ni Kd of $\sim 100 \text{ L kg}^{-1}$, that can be successfully predicted using a blind modeling approach by taking into account competition with stable Ni and Zn naturally present in the solution. However, ^{63}Ni Kd increased with time up to $\sim 600 \text{ L kg}^{-1}$ after 6 months reaction time, with a fraction of irreversible sorption also increasing with time (Fig. 1). This result cannot be explained by reversible sorption on phyllosilicates only: an additional slowly reversible or irreversible retention mechanism must be invoked. This mechanism could be linked to Ni incorporation in a preexisting phase or to a (co-)precipitation process. Ni is naturally present in the rock ($\sim 30 \text{ ppm}$) and its solubility in the experiment synthetic pore-water is far greater than the added ^{63}Ni concentration ($\sim 0.6 \mu\text{mol/L}$ vs. 1.5 nmol/L). This range of concentration is also in agreement with the value determined in pore-water extracted on site ($\sim 0.5 \mu\text{mol/L}$). It is thus necessary to understand natural Ni chemical behavior to interpret ^{63}Ni Kd experiment on the complex COx phase assemblage.

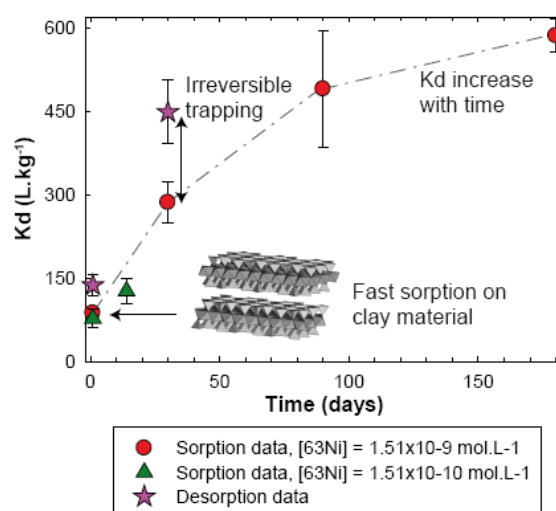


Figure 1 : Evolution of ^{63}Ni Kd with time in sorption and desorption batch experiments.

Determination of Ni-bearing phases was performed using a top-down approach. In a first step, statistical treatment of data from bulk rock chemical composition of EST205 borehole (~410 to ~510 m depth – Gaucher et al., 2004) revealed that Ni was anti-correlated to Ca, thus excluding calcite from main Ni-bearing phases. Then, sequential extraction (Tessier et al., 1978) on a clayey sample (K119) was performed and demonstrated that the main Ni reservoir was the detrital fraction and that carbonates and organic matter contain respectively ~10 ppm and ~250 ppm Ni. This latter information was confirmed using microprobe and synchrotron μ -XRF. The third step consisted in separating K119 sample in different granulometric fractions, using elutriation, and identifying minerals present in the different granulometric fractions by XRD. This combination of methods revealed that Ni was enriched in the smallest size fraction ($< 3.2 \mu\text{m}$), that consisted mainly of calcite, feldspars, phyllosilicates and pyrite, thus excluding quartz and dolomite from main Ni bearing phases. Finally, microprobe experiments revealed that the main Ni-bearing phases are chlorite (~300 ppm) and pyrite (~400 ppm), feldspars being minor contributors. Interestingly, analysis of the aqueous solution from batch experiments revealed that Ca and stable Ni (i.e. naturally released from the solid during equilibration) are linked to the $[\text{Ca}]/[\text{Ni}]$ ratio in calcites through the partition coefficient defined by Lakshtanov and Stipp (2007). Thus, although calcite is only a minor stable Ni reservoir, it may control natural Ni aqueous concentration, and may thus be the major phase that controls ^{63}Ni Kd irreversible trapping. This exemplifies the need to focus on most reactive rather than most enriched phases when trying to determine solid/liquid equilibria. The effect of irreversible trapping on Ni mobility was explored through predictive reactive transport modeling study according to different Ni retention scenarios.

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