

# Stability of an analcime-rich rock under acidic sulphate conditions

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The Abinky sedimentary formation is composed of massive analcimolites (i.e., a rock composed of analcime (over 70 wt%) and ferrous chlorite) that underlies the Tchirézrine 2 formation, known for hosting the Imouraren uranium (U) deposit (Niger). Tchirézrine 2 is mainly composed of sandstones which can contain analcime cement (>25 wt.%) as well as some sandstone analcimolitic levels. A potential project is under consideration by Orano to recover U from the Imouraren deposit by using a method based on an acidic leaching using H<sub>2</sub>SO<sub>4</sub> (In Situ Recovery<sup>[1]</sup>) of the sandstone aquifer. Consequently, study the stability of analcime-rich rocks under acidic sulfate conditions is the first step to understand and predict the mobility of water and solutes in these different geological formations submitted to such acidic gradients.

Analcime (NaAlSi<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O) belongs to the zeolite group: a hydrated tectosilicate family presenting isomorphic substitutions of silicon by aluminum leading to a negative charge in the crystalline edifice. Such charge unbalance is compensated by hydrated Na<sup>+</sup> atoms in the structure, thus enabling cationic exchange properties. In addition to the high analcime content, the Abinky formation shows an uncommon petrographic organization of analcime with (i) different spherules with an analcime cortex and a chlorite core varying according to the depth (size, organization, color, shape ...) and (ii) automorphic crystals set in a chlorite cement. This study aims to understand the main reactions responsible of the proton consumption by analcime-rich blocks in acidic sulphate conditions. Previous studies performed with Abinky samples using powders (i.e., with particles having a ~ micron size fraction) in contact with HCl and H<sub>2</sub>SO<sub>4</sub> solutions showed that H<sup>+</sup>-for Na<sup>+</sup> exchange was the main reaction of the H<sup>+</sup> consumption for pH ranging from 3.6 to 6, with amount of exchanged Na<sup>+</sup> by H<sup>+</sup> up to 30 meq/100g for rocks characterized by 85 wt.% analcime. For experiments performed at the lowest pH (i.e., pH~3.6) the maximum amount of H<sup>+</sup> consumed by the rock dissolution was assessed to be equal to ~ 1.5×10<sup>-5</sup> H<sup>+</sup>/g, corresponding to ~ 0.13 wt.% of the powder dissolved (based on the total silicon content in the sample studied).

Then, to understand dissolution mechanisms at lower pH (i.e., pH<3.2) by using the initial organization of the analcime-rich rocks, blocks of these rocks were immersed in H<sub>2</sub>SO<sub>4</sub> solutions (with initial pH from 2 to 4). Porosity distribution of the blocks before and after immersion in these acid solutions has been followed by autoradiography with samples impregnated by a <sup>14</sup>C-PMMA resin<sup>[2]</sup>, this method allowing to probe pores until nanometer sizes. The results show that the total porosity of the whole block before acidification can vary from 15% to 35%, and is correlated to the analcime and chlorite proportions, with the higher the analcime content is, the less porous the sample is. After acidification, results obtained by scanning electron microscope coupled with energy dispersal probe show localized dissolution of analcime as well as precipitation of neoformed phases (e.g., Si-amorphs and barite). Evolution of porosity distribution after acidification will be also discussed during this presentation.

## References :

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- [2] Prêt D, Sardini P., Beaufort D, Zellagui R, Sammartino S. (2004) Porosity distribution in a clay gouge by image processing of <sup>14</sup>C-PolyMethylMethAcrylate (<sup>14</sup>C-PMMA) autoradiographs: Case study of the fault of St. Julien (Basin of Lode`ve, France). *Applied Clay Science* **27**, 107-118

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