

Is basaluminite a mineral?

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INTRODUCTION

Basaluminite is a poorly crystalline aluminum sulphate oxyhydroxide that precipitates in acid mine drainage waters and acid sulphate soils when pH increases above 4.5 approximately. The pH increase can be due to mixing with natural waters or to the addition of an alkaline reagent, a method commonly used in remediation treatments. Basaluminite is a scavenger of elements such as Se, As, P, Mo and rare earth elements (REEs) and acts as a vector for their transport in the environment. The retention of these elements has important environmental and economic impact due to their toxicity and to the potential extraction of REEs for technological applications. Despite the long history of basaluminite, initially described as a mineral in the late 40s, little is known about its stability and its eventual transformation in other less metastable phases.

Literature reports on the structure of basaluminite are confusing. Earlier studies described broad diffraction peaks such as those expected in nanocrystalline phases. Farkas and Pertlik (1997) gave unit cell parameters and atomic positions of basaluminite and felsöbanyáite, establishing that the first is just a nanocrystalline version of the second. This fact is confusing for two reasons: (i) the basaluminite formed in AMD is typically very disordered, and the occurrence of single crystals has never been reported; and (ii) felsöbanyáite is a rare mineral, never reported in AMD. As indicated by Carrero et al. (2017b), the similarity between the structures of basaluminite and felsöbanyáite could be due to a simple fortuitous coincidence. These authors confirmed the Al-octahedral framework of the structure with sulphate coordinated as outer-sphere ligands. Regarding its stability, some experiments showed that the mineral partially or totally recrystallizes with temperature forming alunite, depending on the conditions (Adams and Rawajfih, 1977; Prietzel and Hirsch, 1998).

The objective of the present work is to study the stability of basaluminite during ageing. Since basaluminite is a mineral that precipitates in acidic and rich sulphate

waters, the second objective is to understand the role of pH and aqueous sulphate in its stability.

AGEING EXPERIMENT

Twelve suspensions of 5 mg of synthetic basaluminite in 50 mL of a 0.01 M NaNO_3 background solution were equilibrated for 48 hours. Then, increasing amounts of NH_4OH 0.5 M were added to each solution to adjust the pH to values ranging from 4.95 to 9.22. OH^- consumption occurred mainly during the first 19 days, and the solution pH continued to decrease for 81 days (Fig. 1A). At the end of the experiment, the pH values ranged between 4.61 and 6.46. The solution pH decreased 0.5 pH units for the suspension with the lowest amount of NH_4OH added and 3.0 pH units for the solution with the highest amount of NH_4OH added. No NH_4OH was added to the first suspension, and after the ageing time, the pH decreased only 0.34 units.

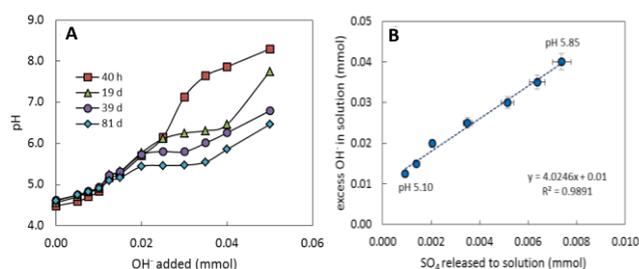


Fig. 1. (A) Evolution of pH for the suspensions with different initial pH values. (B) Correlation between the OH^- excess and sulphate concentration for the suspensions with higher pH values. The OH^- excess is calculated as the difference between the added NH_4OH and the OH^- invested in the rising pH.

At the end of the experiment, the aqueous aluminium and sulphate concentrations did not correlate with pH. At lower pH values (4.61-5.10) the amount of sulphate remained almost constant, whereas the aluminium concentration in the solution decreased slightly. For pH values higher than 5.10, the aluminium concentration in solution was below the detection limit (0.001 mM), but the sulphate concentration increased constantly. At the pH range 5.10 to 5.85, a linear correlation between

sulphate release and $[\text{OH}^-]$ excess was observed ($R^2=0.989$) with a molar ratio $\text{OH}^-:\text{SO}_4$ of 4.0 (Fig. 1B).

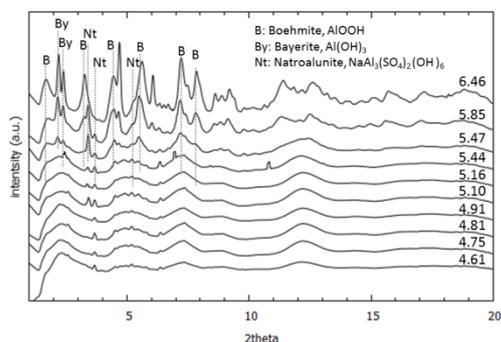


Fig. 2. Structure factors for solid samples equilibrated and aged during 81 days. 2θ was converted from Q values using X-ray wavelength $\lambda=0.181 \text{ \AA}$.

The structure factors of the samples at lower pH values exhibit typical broad oscillations characteristic of amorphous or poorly crystalline materials. New broad peaks appear in the patterns of the solids formed at pH values higher than 5.47, clearly defined from pH 5.85. These peaks correspond to boehmite with two possible peaks belonging to bayerite and a possibly few peaks attributed to natroalunite ($\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$) (Fig. 2).

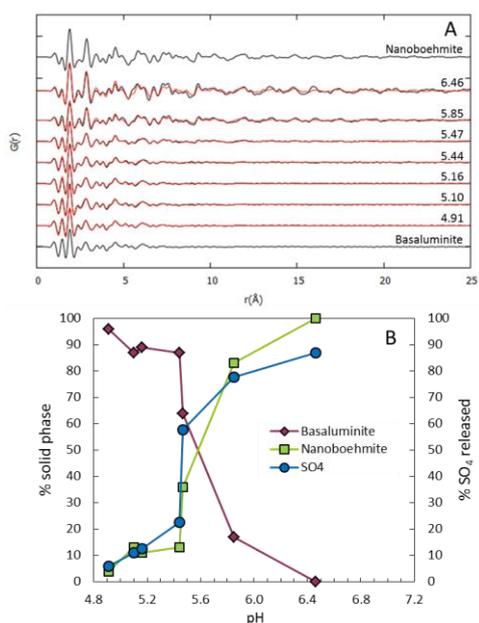
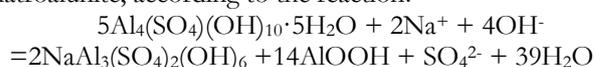


Fig. 3. (A) Experimental PDFs (black) and LCF fits of the PDFs (red) using pure basaluminite and nanoboehmite as end members for the fits of solids from the slow ageing experiments. (B) Percentages of the end members, basaluminite (rhomboids) and nanoboehmite (squares) calculated from the LCF fitting for experiments without. Percentage of released sulphate calculated from aqueous chemistry (circles).

Concomitantly, the pair distribution functions (PDFs) of these solids reflected an increase in the crystallinity at higher pH values (Fig. 3A). At lower pH values, the PDFs are very similar to the PDF of synthetic basaluminite, whereas at higher pH values, a transition to a nanoboehmite-like local structure is observed. From these observations, a transformation of basaluminite to nanoboehmite with time can be inferred. This

transformation was more evident when a higher amount of OH^- was added into the solution. Since the PDF spectrum at the lowest pH is very similar to basaluminite and at the highest pH to synthetic nanoboehmite, linear combination fits (LCF) of the experimental PDFs were performed using these two synthetic solids as end members (Fig. 3A). The results of the fitting show a clear decrease in the proportion of basaluminite along with an increase in nanoboehmite as NH_4OH was added and the final pH value was higher (Fig. 3B). When it could be measured, this behaviour with pH is also consistent with the transfer of sulphate from the solid to the aqueous phase (Fig. 3B). The increase in nanoboehmite in the solid phase was consistent with the amount of sulphate released from basaluminite. The molar ratio between the SO_4 released and OH^- consumed was 4. This result can be explained by a sequence of chemical reactions involving the dissolution of basaluminite and the formation of nanoboehmite and natroalunite, according to the reaction:



CONCLUSIONS

In contact with water, basaluminite dissolves incongruently, precipitating amorphous Al-hydroxide and releasing sulphate to the solution. This process and the recrystallization of amorphous Al-hydroxide into nanoboehmite were enhanced with increasing pH. However, for high sulfate concentrations, such as those found in acid mine waters, the transformation to nanoboehmite was partially inhibited. The ageing processes highlighted here point to a potential pathway for the release of trace elements upon neutralization of acid mine drainage. Furthermore, PDF analyses of basaluminite show a high similarity with the local structure of a synthetic amorphous Al-hydroxide. Therefore, basaluminite can be considered an amorphous precipitate, which questions its currently accepted classification as a mineral.

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