Alunite (KAl$_3$(SO$_4$)$_2$(OH)$_6$) dissolution kinetics at acidic pH

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INTRODUCTION

Sulphate minerals are among the most abundant minerals in mine wastes, where they control the mobility of potentially toxic elements such as Al (Jambor *et al.*, 2000). High concentrations of Al can have severe effects on ecosystems and humans and, for example, Al intake has been implicated in neurological pathology (e.g., Alzheimer's disease; Flaten, 2001).

The dissolution of aluminium sulphates result in the release of their constituent Al. Compared to common Fe-bearing sulphates such as jarosite [KFe$_3$(SO$_4$)$_2$(OH)$_6$] and schwertmannite [Fe$_8$O$_8$(OH)$_6$SO$_4$] much less is known about the reactivity of Al-sulphates in mine wastes and, particularly, about one of the most important and ubiquitous aluminium sulphates in mine environments (Nordstrom, 2011): Alunite (KAl$_3$(SO$_4$)$_2$(OH)$_6$). For instance, alunite dissolution rates and their controlling factors under conditions similar to the ones found in mining environments have, to the best of our knowledge, not been assessed in any previous work.

In order to contribute to bridge this knowledge gap, batch dissolution experiments have been carried out to shed light on the dissolution rate of potassium alunite under different pH conditions and to ascertain if the release rates of its ionic components (Al, SO$_4^{2-}$ and K) is only dependent on the mineral stoichiometry.

MATERIALS AND METHODS

The experiments have been done using pure K-Alunite synthesised according to a modification of the method by Lager *et al.* (2001). The pure mineralogy and geochemistry of the starting alunite was confirmed by X-Ray Diffraction and by chemical analyses of the leachate obtained by acid digestion using aqua regia. The shape, size and surface of the alunite grains before and after the experiments have been examined by Scanning Electron Microscopy (SEM).

The batch dissolution experiments have been carried out in the Wolfson Laboratory of Environmental Geochemistry (University College of London). In these batch experiments, 100 mg of synthetic pure alunite were placed in glass beakers, stirred to 400 rpm and kept in contact with 200 mL of different types of solutions (pH 3 and 4 H$_2$SO$_4$ and pH 5.5 MES-buffered) and under controlled temperature conditions (20ºC) for around 2 weeks. These conditions are intended to be similar to the ones found in environments affected by acid drainage after contact with sulphide minerals.

During the experiments, 6 ml aliquots were removed at regular intervals, filtered using 0.22 μm filters and acidified to 1% HNO$_3$ for ICP analyses of the dissolved concentrations of Al, S and K, used to monitor the progress of the dissolution process and to obtain the dissolution rates. Solution pH and temperature were also monitored during the experiments. All the experiments were run at least in triplicate. The error associated with the dissolution rates, calculated by the Gaussian error propagation method is around 20 %.

Since the starting solutions already contain sulphate ions and Al may partially o totally precipitate in the experiments at pH 5.5, the dissolution rates will be assessed based on K concentrations. For the experiments at pH 3 and 4, sulphate concentrations will be estimated as the difference between the concentration in the initial solution and the one in each one of the sampled leachates during the dissolution experiments. For the experiments using MES-buffered solutions, sulphate concentrations could not be monitored due to the relatively larger values already present in the initial solution.

Dissolution rates are presented as molar amounts per unit of time and normalized to the initial surface area of the synthetic alunite (0.74 m^2/g), which was determined by the BET-method using 5-point N$_2$ adsorption isotherms.

RESULTS AND DISCUSSION

An example of the main solution results obtained is shown in Fig. 1a and b. The dissolved concentrations of Al, S and K generally evolved according to a linear trend (Fig. 1a), allowing obtaining the elemental release rates.

As displayed in Fig 1b, the obtained alunite dissolution rates, based on the evolution of dissolved K concentrations, were very similar for the three different pH conditions explored in the experiments. The average dissolution rate value is around 3.3·10^{-11} mol/m^{2}s. This value is between the dissolution rates reported for for K-jarosite, isostructural with alunite, by Welch *et al.* (2008) and Elwood-Madden *et al.* (2012) using a similar methodology.

Although a very slight increase in the dissolution rate with increasing pH is apparent in the plot displayed in Fig. 1b, such dependence is most probably negligible, especially taking into account experimental and analytical errors. Therefore, pH does not seem to play a significant role on the alunite dissolution kinetics within this pH range.

Alunite dissolution has proved to be an incongruent process, as already reported for jarosite by Welch *et al.* (2008).
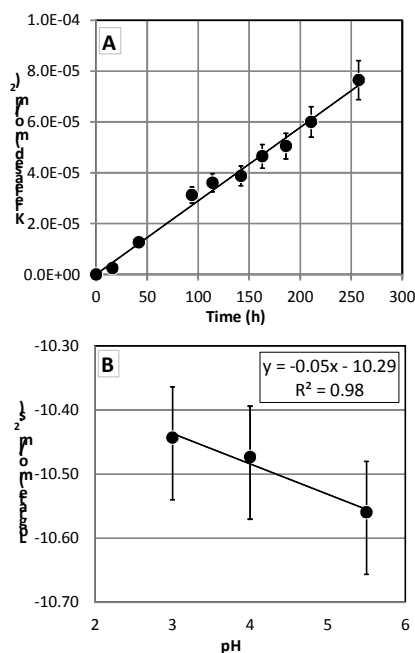
fig 1. A: Evolution of released K (normalized to the surface area) during a representative dissolution experiment (at pH 3 in H_2SO_4 solution), showing the clear linear evolution throughout the whole experiment; B: Variation of alunite dissolution rates (average values, in logarithmic units and expressed in $mol/m^2 \cdot s$) vs. pH in the studied range. The error bars represent the global experimental error (20%).

fig 2. SEM images showing a general view of the alunite samples before (A) and after the dissolution experiment at pH 3 (B), as a representative example of the general features observed.

In the experiments at pH 3, the stoichiometric molar ratios Al/SO_4 and K/SO_4 are usually below 0.7 and 0.4, respectively (Fig. 1b), lower than the corresponding ratios in K-alunite (1.5 and 0.5, respectively). The same ratios in the experiments at pH 4 are around 1.1 and 0.6, respectively, which indicates that Al is depleted and K slightly enriched compared to the stoichiometry in the solid phase. Al depletion in solution is particularly clear for the experiments done at pH 5.5, where its concentrations were always below the quantification limit. For these experiments, the stoichiometric ratios with respect to sulphate ions could not be evaluated due to the large dissolved sulphur concentrations in the MES-buffered solutions. Finally, the molar stoichiometric K/Al ratios are generally between 0.4 and 0.6 both in the experiments at pH 3 and 4. These values are well above the ratio in pure K-alunite (0.33).

All these data point towards the formation of secondary phases of aluminium during K-alunite dissolution, either as new particles or on the surface of the dissolving mineral grains. Moreover, they suggest that such precipitation processes are different for different pH conditions.

The study of the grain surfaces before and after the dissolution experiments by SEM (Fig. 2) does not allow observing any new precipitate or coating on the surface of the reacted alunite compared to the pristine sample. In fact, the distribution of grain sizes, shapes and other surface features are almost indistinguishable between both types of samples. Thus, other mineralogical techniques (e.g. high-resolution transmission electron microscopy, micro X-ray diffraction, X-ray photoelectron spectroscopy) should be used to fully understand the nature of the secondary mineral phases formed during alunite dissolution.

In any case, the formation of secondary precipitates does not seem to passivate the surface of dissolving alunite. This can be inferred from the existence of a linear increase of released K concentrations throughout the experiments, without any decrease in the slope of their variation vs. time (Fig. 1a).

CONCLUSIONS

Alunite dissolution kinetics in the pH range between 3 and 5.5 and at 20ºC has been examined by means of stirred batch dissolution experiments. The obtained dissolution rates are in the range of the rates proposed by other authors in earlier works for jarosite and are almost independent of pH.

The dissolution of alunite seems to be an incongruent process, with Al being clearly depleted in solution compared to the composition of the solid phase as a result of the formation of Al-secondary phases. The nature and textural features of such phases could not be characterized by SEM and will require more detailed techniques in the future.

However, these secondary phases do not passivate or inhibit alunite dissolution under the studied conditions.

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