

Synthetic faujasite based on coal by-products for the treatment of acid mine drainage (AMD)

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Introduction

Acid mine drainage (AMD) has long been a significant environmental problem associated to mining operations at the Parys Mountain copper-lead-zinc deposit of Anglesey (North Wales), a volcanogenic massive sulphide district of major metallogenic importance. AMD is a natural occurrence resulting from the microbial oxidation of sulphide minerals, especially pyrite (FeS_2), pyrite in presence of water and air, which produces polluted waters strongly acidic containing high concentrations of Fe, sulphate and toxic metals. The treatment of AMD has traditionally been conducted by neutralization with lime or similar materials. However, liming is often temporary and produces secondary wastes, such as metal hydroxide sludges and gypsum, which are highly regulated and have costly disposal requirements [1]. Several methods for AMD treatment have been developed, although adsorption being the preferred method for heavy metal removal due to its effectiveness. AMD remediation can be very costly and difficult, due to the high costs of activated carbon production and regeneration for water treatment. Therefore, alternative low-cost liming materials are constantly sought. Such adsorbents should be readily available, economically viable and easily regenerated. The aim of this study is to investigate the efficiency of synthetic faujasite obtained from coal by-products as adsorbent in removing heavy metals from AMD generated at the Parys Mountain copper-lead-zinc deposit.

Experimental procedures

Sampling of AMD was carried out in three major locations of the abandoned copper-lead-zinc deposit at Parys Mountain, accompanied by on-site analyses of pH and electrical conductivity (EC). X-ray diffraction patterns of the as-synthesized faujasite were recorded with a Philips PW1710 diffractometer operating in Bragg-Brentano geometry with Cu-K α radiation (40 kV and 40 mA) and secondary monochromation. A ZEISS EVO50 scanning electron microscope, equipped with an energy dispersive (EDX) analyser, was used for microstructural characterization. Synthetic faujasite was used as sorbent in laboratory batch experiments carried out at room temperature to investigate its efficiency in removing heavy metals from AMD. Metal concentrations were determined using a Spectro Ciros ICP-AE Spectrometer.

Results

Fig. 1 illustrates the XRD patterns and SEM images of the as-synthesized faujasite obtained from fly ash and natural clinker via alkaline fusion with NaOH followed by hydrothermal treatment at 60°C for 92 h (using fly ash) and 100°C for 24 h (using natural clinker). The XRD patterns are characterized by the disappearance of the characteristic peaks of the raw materials. The activation of fly ash produced faujasite as the single mineral crystalline phase (Fig. 1a); whereas faujasite along with hydroxysodalite crystallized when natural clinker was used as starting material (Fig. 1b). SEM images reveal that faujasite crystallized with a typical octahedral morphology and hydroxysodalite develops aggregates of bladed crystals.

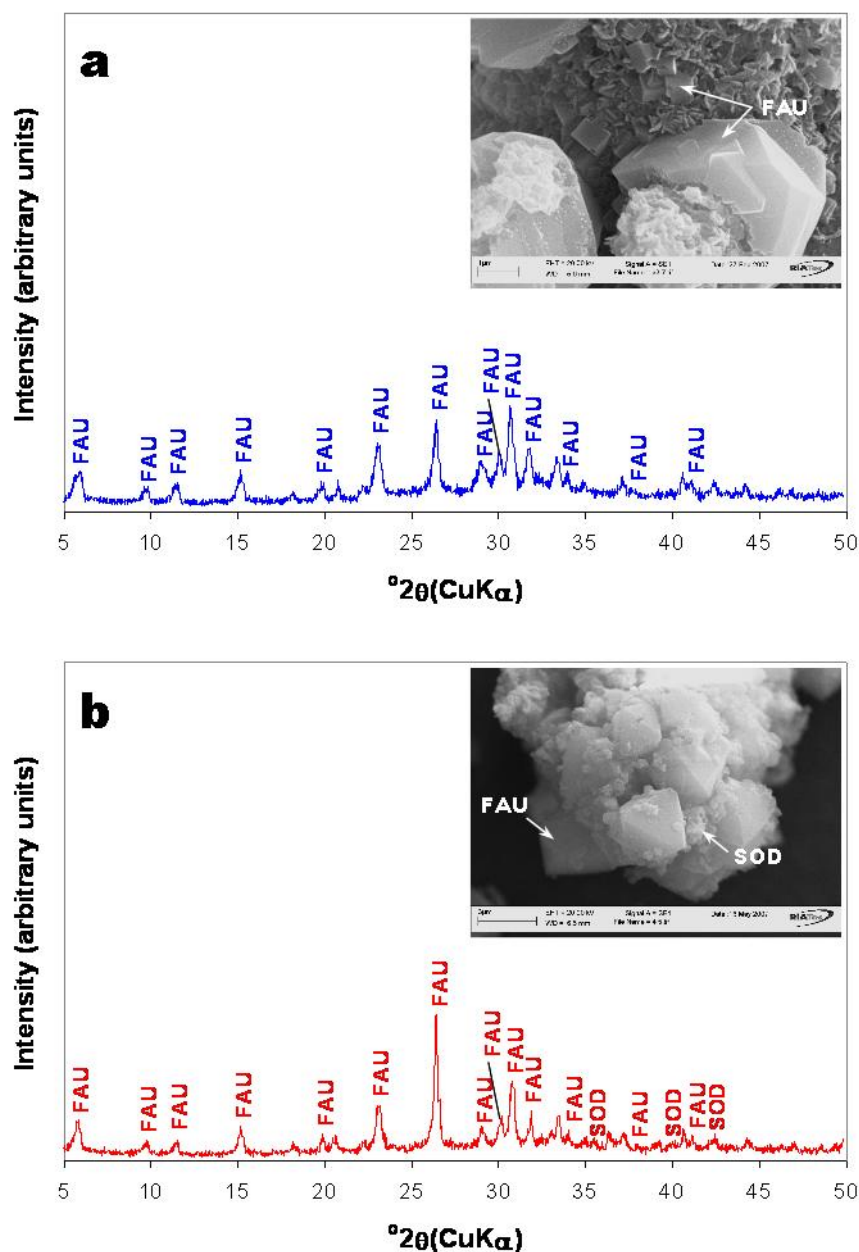


Fig. 1. XRD patterns and SEM images of the sorbents used to clean-up AMD: (a) fly ash-based faujasite and (b) natural clinker-based faujasite. FAU, faujasite; SOD, hydroxysodalite-like structure.

The pH and EC trends for the neutralization reactions between the investigated sorbents and the AMD are shown in Fig. 2. The starting pH (1.96) changed during a monitoring time of 24 h to 4.42 (fly ash-based faujasite) and 4.29 (natural clinker-based faujasite), although for the monitoring time natural clinker-based faujasite generally produced slight pH values than those obtained with the addition of fly ash-based faujasite, with a similar behaviour observed in the EC trends. The removal of heavy metals from AMD using the as-synthesized faujasite is illustrated in Fig. 3, indicating that this zeolite, in spite of the starting material during the synthesis process, showed a similar efficiency in heavy metal removal. However, the natural clinker-based faujasite produced the lowest residual concentrations of all metal ions, except Cu and Zn. The main mechanism for metal uptake is precipitation and not sorption and the increase in pH with the addition of the sorbents decreases the metal concentrations probably due to precipitation on the surface of the sorbents [2]. Therefore, to investigate the effect of sorbent dose, natural clinker-based faujasite was selected to develop an additional batch reaction test (results not shown), taking into account that this sorbent produced the highest pH value (9.43) between several tested materials after a contact time of 24 h. pH is strongly affected by the sorbent material rather than the AMD composition and particularly with a higher sorbent dose.

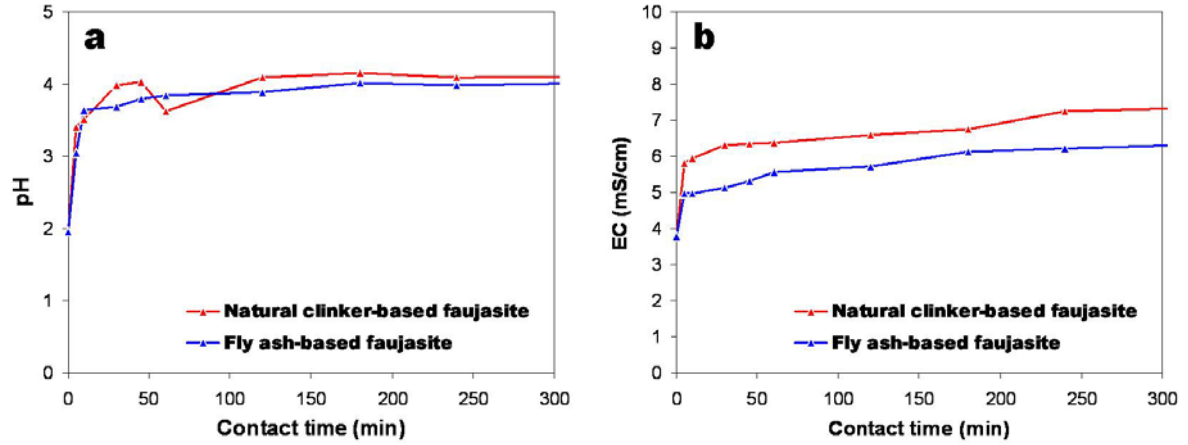


Fig. 2. pH (a) and EC (b) variation as a function of time during the adsorption batch experiments with starting pH of 1.96 and EC of 3.77 mS/cm, sorbent dose of 0.25 g and volume of AMD of 20 ml.

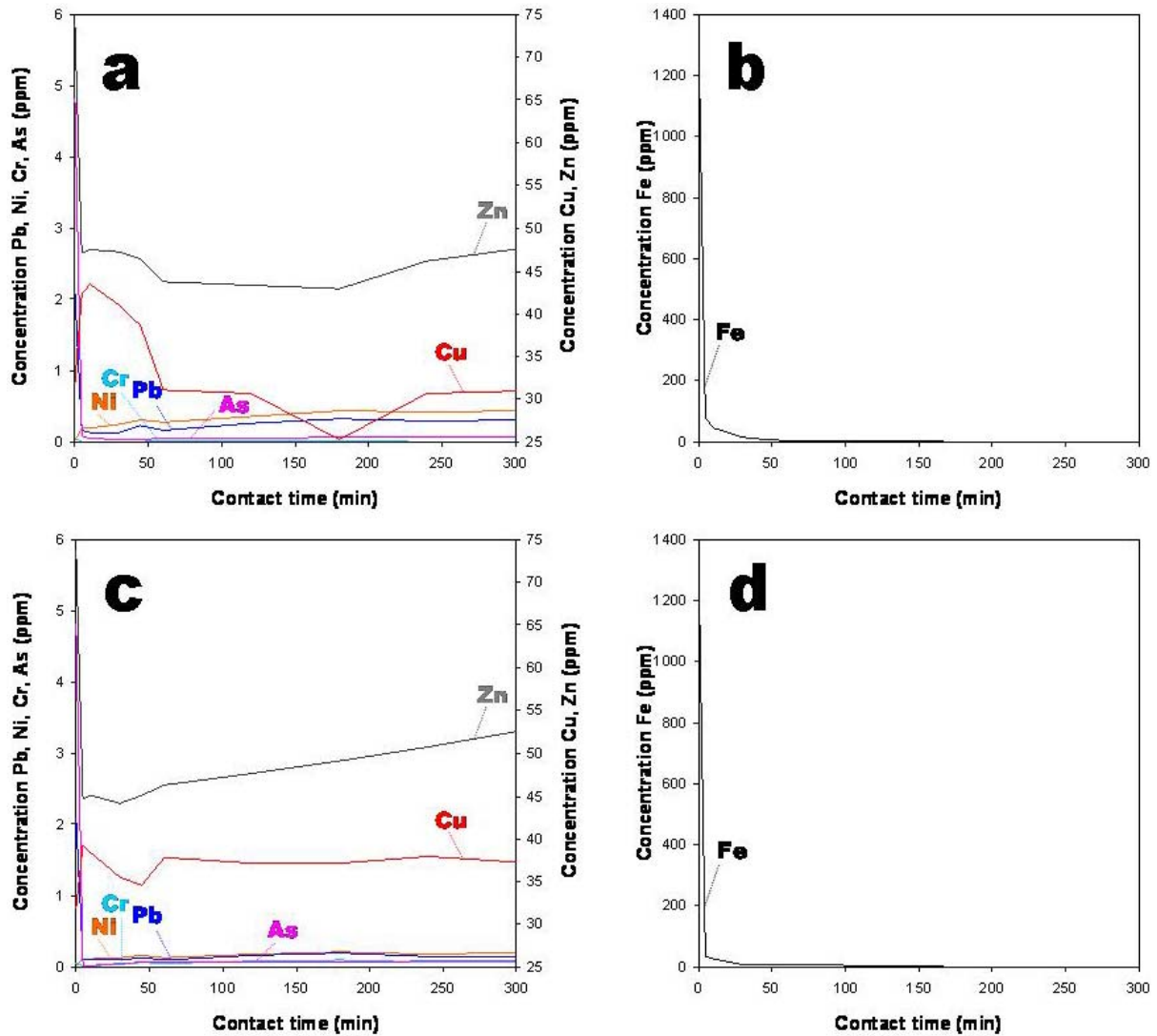


Fig. 3. Heavy metal concentration variation as a function of time during the adsorption batch experiments with starting pH of 1.96 and EC of 3.77 mS/cm and sorbent:AMD mixture of 0.25 g / 20 ml; (a-b) fly ash-based faujasite; (c-d) natural clinker-based faujasite.

The relationship between pH and the dissolved metal content in AMD can be summarized using 'Ficklin' diagrams [3], which have been applied in the initial prediction of the potential impact from mining sulphide-bearing mineral deposits, enabling an assessment of correlations between particular mineral-deposit types and the observed metal, metalloid, pH and sulphate chemistry in the drainage [2]. However, Ríos et al. [4] used the Ficklin diagrams to make a relationship between the metal concentration in treated AMDs and that corresponding to natural AMD associated to different mineral assemblages and geological conditions as suggested by Bowell and Parshley [2]. Fig. 4 indicates that a faujasite:AMD mixture of 0.25 g / 20 ml produced leachates characterized by moderate acid values of pH and extreme to high metal concentrations, which are equivalent to AMDs associated with pyrite-sphalerite-galena-chalcopryrite in carbonate-poor rocks. In addition, the use of a higher sorbent dose (1 g / 20 ml) in the treatment of AMD promoted the increase of the pH and the reduction of metal concentration, with near neutral pH values and low to high metal concentrations, which are corresponding to AMDs associated with pyrite-poor sphalerite-galena veins and replacements in carbonate rocks or with pyrite-poor gold-telluride veins and breccias with carbonates.

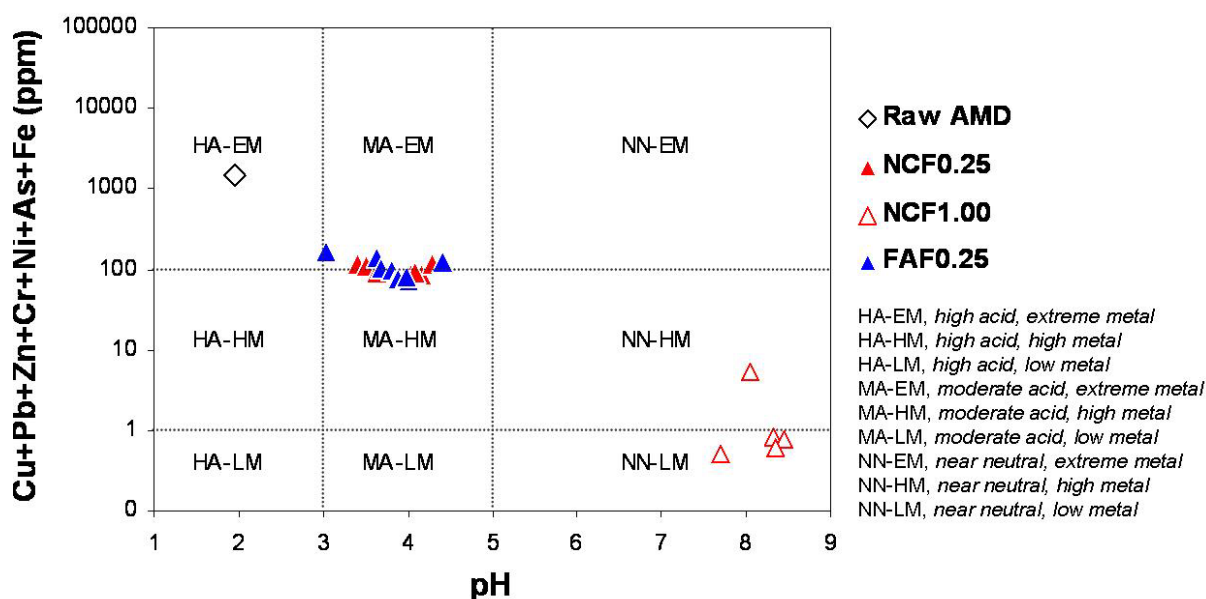


Fig. 4. Ficklin diagram showing the sum of aqueous base metal concentrations in AMD treated with different sorbents. FAF0.25, fly ash-based faujasite:AMD mixture of 0.25 g / 20 ml; NCF0.25 and NCF1.00, natural clinker-based faujasite:AMD mixture of 0.25 g / 20 ml for and 1 g / 20 ml, respectively. An open rhomb indicates the starting heavy metal concentration and pH of the raw AMD.

Conclusions

Results reveal that the efficiency of the as-synthesized faujasite in removing heavy metals from AMD depends on the sorbent material and applied dose. Selectivity of faujasite for metal removal was in decreasing order: Fe>As>Pb>Zn>Cu>Ni>Cr. In addition to cation exchange reactions, precipitation of hydroxide species (mainly of Fe) also played an important role in the co-precipitation and adsorption, and thus immobilization of metals in the batch experiments carried out [4]. The sorption study suggests that natural clinker-based faujasite represents a beneficial product as ion exchanger in removing acidity and heavy metals, which can be considered in future applications for the treatment of AMDs.

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