MINERAL PRECIPITATES FROM MINE WATER AS ADSORBENTS – SITE SPECIFIC CHARACTERIZATION OF SOME NATURAL DEPOSITS

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Introduction
Secondary minerals, mixtures of Fe-Al compounds such as oxhydroxyls and hydroxosulfates can be naturally generated from mine water in response to processes such as oxidation/hio-oxidation, mixing, evaporation and neutralization. Deposits observed in significant quantities, with a very high iron content, from the mining perimeters of Certej-Coranda, Rosia Montana and Boita Hatag were sampled and characterized. Schwertmannite and Goethite can function as adsorbents after drying or further processing. In both cases, the chemical analysis of the product is important in order to promote it to potential users. A comparative study on the elemental composition, thermal behaviour and adsorption capacity for As(III) was done for secondary minerals which are naturally formed by precipitation from three mine water flows.

Materials and methods
Iron rich precipitates were sampled from central Romanian mining area, from Rosia Montana Orlea Orizont714, Certej P1 Coranda-Galerie and Boita Hatag Orizont120. These samples are referred further as Orlea714, P1C and BH120. Mineral samples were conditioned in the lab by removing vegetal debris and analysed for elemental composition by X-ray fluorescence, metals and sulphur (SR-EN-15309:2008, Regaku CG X-ray Spectrophotometer). After calcination (300°C, 800°C), a second elemental analysis was performed. Thermal gravimetric (TG) and differential thermal analysis (DTA) were conducted on a Netsch STA 404 thermal analyser (air, linear heating rate 10°C/min).

The adsorption capacity was studied in batch experiments on 1 g d.s. 1 g mineral adsorbent suspensions for an initial concentration of 72.7 mg/l As(III) in distilled water, at neutral pH, contact time 180 min, temperature 24±1°C, orbital shaking, 175 rpm. Minerals were conditioned by drying and sieving (0.75 mm, passed). After the contact time, the samples were filtered through 0.45 μm membrane filters and the concentration of arsenic was determined using a Perkin Elmer PnaAct 900T atomic absorption spectrometer.

Results and Conclusions
Elemental analysis
All three precipitates have, as common characteristic, a very high iron content, about 500 g/kg d.s. BH120 precipitate is characterized by a very low arsenic content (28.8 mg kg d.s.), which is about 100 times lower compared to Orlea714 (1865 mg kg d.s.) or P1C samples (2960 mg kg d.s.), so it could have a greater acceptability as adsorbent product.

Iron rich precipitates from Rosia Montana Orlea 714 has the highest sulfur (sulfate) content, probably due to the presence of hydroxosulfates, including schwertmannite.

The ratio Fe/S gram-atom / gram-atom is very different among the three minerals. Only the natural precipitate taken from the Rosia Montana Orlea 714 Gallery would be mainly schwertmannite, the (Fe/S) ratio being 4.77 gram-atom / gram-atom which corresponds to x = 0.97 for the formula FeO(OH)(OH)(SO4)2 giving a brut formula FeO(OH)(SO4)2.

The other two precipitates have a [Fe/S] ratio outside the range identified in the literature for schwertmannite. 8.0±4.7 gram-atom / gram-atom and contain mainly oxhydroxides. However, also the P1C sample could have a relevant schwertmannite content.

Thermal behaviour of the precipitates and of the calcined products
Natural precipitate Orlea714 shows a thermal decomposition with adsorbed and structural water loss occurring above 100°C and two transformations at approx. 580°C and 680°C respectively, with total mass loss due to thermal decomposition of about 38% up to 700°C. This thermal behaviour can be explained by the characteristic two-step decomposition of ferric hydroxosulfates, first at 560-580°C with water loss, producing Fe2(SO4)3 and the second step being represented by the transformation to hematite, an endothermic reaction above 580°C with release of SO3.

The P1C precipitate has a somewhat similar TG curve, but with a higher final residual mass, about 80% of the initial and no observable decomposition at 500°C. The natural precipitate taken from Boita Hatag is rather goethite FeO(OH), with a more modest mass loss than Orlea714, explainable also by the formation conditions, the mine water having in this case a circum-neutral character.

Adsorption capacity for As(III)
Among the products considered, the mineral with the highest As(III) adsorption capacity was the schwertmannite type precipitate from Orizont 714 Orlea Gallery, followed by the natural precipitate obtained from P1-Coranda Gallery. It is interesting to observe that Orlea714 and P1C already had a relevant initial arsenic content of 1.87 g/kg d.s. and 2.36 g/kg d.s. respectively, sorbed from the mine water, these minerals being effective trace metals sinks as was also observed by some researchers.

For the calcined products, at a temperature of 300°C, the adsorption capacity of the initially Goethite or Schwertmannite containing minerals is preserved after calcination, with a certain decrease for the Orlea714 precipitate and with a certain increase in the case of Boita Hatag natural precipitate gallery.

In the case of calcination at a temperature of 800°C, an effect of a significant decrease of the adsorption capacity (about 7 times for ORL714) was observed. Also, the adsorption capacity values became similar, close to a median value of 7.8 mg/kg with a standard deviation of 0.51 mg/kg as informative figure. The levelling effect of calcination may be explained due to the formation in all cases of a product containing mainly hematite. Goethite (α-FeO(OH)) by direct dehydration without an intermediate phase, slit-shaped micropores being formed. By increasing the calcination temperature to 800°C, the crystallization of hematite pores and the crystal growth will occur, but also the disappearance of pores and this could cause the decrease of the adsorption capacity as observed in this work.

• The three naturally formed precipitates have the capacity to adsorb arsenite and the adsorption capacity is the highest for the sample of schwertmannite type, Orlea714.
• Depending on calcination temperature, adsorption capacity decreasing and a leveling effect can be observed, most probably due to pore shrinking and transformation to hematite, irrespective to the initial mineral.

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