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Mineral precipitates from mine water as adsorbents -Part I- Site-specific characterization of natural deposits

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Abstract
Secondary minerals, and mixtures of Fe-Al compounds such as oxohydroxy and hydroxosulfates can be naturally generated from mine water in response to oxidation /bio-oxidation, mixing, evaporation and neutralization processes. Deposits observed in significant quantities, with very high iron content, from the mining perimeters of Certej-Coranda, Rosia Montana, and Boita Hateg 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 preliminary evaluation of the adsorption capacity for As(III) was performed for the original material and for products obtained after calcination. Depending on calcination temperature, adsorption capacity decreases, and a leveling effect can be observed, most probably due to pore sinterizing and transformation to hematite, irrespective of the initial mineral.

***Keywords:** mine water, schwertmannite, arsenic adsorption*

INTRODUCTION

Secondary minerals, such as Goethite, Ferrihydrite and Schwertmannite, all being Fe(III) precipitates, can be formed by chemical and biochemical precipitation of weathered species existing in mine water, depending on various conditions, including acidity and pH [1].

Iron is present in AMD in both, ferrous and ferric forms. While ferric iron precipitates at pH 3-4, ferrous iron does not precipitate at pH lower than 6.

The oxidation of Fe^{2+} (naturally or induced with hydrogen peroxide) followed by Fe^{3+} hydrolysis will produce schwertmannite as the dominant Fe-phase precipitated in acid mine water (AMD) over the pH range 2.5 - 4.5 and for sulphate levels 1000 to 3000 mg/L.

Chemical formula of natural schwertmannite was suggested to be $Fe_8O_8(OH)_{(8-2x)}(SO_4)_x{\bullet}nH_2O$ where $1 \leq x \leq 1.75$ and Fe/S molar ratio is in the interval 8 – 4.57, the sulfate content is variable and some of the sulphates may be present not as the structural but as the adsorbed form [2-4]. Occurrence of natural schwertmannite having $1.74 \leq x \leq 1.86$ and Fe/S molar ratio in a tighter interval 4.59 – 4.30 was reported [4, 5]. Schwertmannite will be converted to ferric hydroxide $Fe(OH)_3$ in water with higher acid binding capacity [6].

Schwertmannite is metastable with respect to goethite FeOOH and will re-dissolve and precipitate as goethite over varying timescales through reaction (1). Some field relation was observed between the two minerals: schwertmannite is always in contact with flowing acid mine water, while goethite is formed if has no direct contact with AMD, by-redissolving schwertmannite and re-precipitation, being generally found above the waste-rock water table [7].

$$Fe_8O_8(OH)_{(8-2x)}(SO_4)_x\,(s) + (2x)\,H_2O\,(l) \rightarrow 8FeOOH\,(s) + (2x)H^+\,(aq) + xSO_4^{2-}\,(aq) \quad (1)$$

Schwertmannite is known as an As absorbent, but it can be a sink for other species such as uranium 0and also Pb, Zn, Mn [7]. Goethite α-FeO(OH) and hematite α-Fe_2O_3 also have absorption capacity [8]. Arsenate, chromate and molybdate are retained by a mechanism of surface complexes between the oxyanions and the iron surface reactive groups, but also by exchange with sulfate groups in the case of schwertmannite. At high arsenate loading, adsorption is associated with the sulphate release from the schwertmannite structure [9].

Adsorption capacity of secondary minerals is important for the retention of harmful species in natural environments, but also can qualify these minerals as adsorption products in some applications, e.g. passive barriers [10] (further processing could be needed).

Our research was focused on the assessment of the chemical properties and adsorption capacity of minerals sampled from some Romanian AMD flows, where were observed as accumulated naturally abundant precipitates.

EXPERIMENTAL PART

Iron rich precipitates were sampled from central Romanian mining area, from Rosia Montana Orlea Orizont714, Certej P1 Coranda-Galerie and Boita Hateg Orizont120 and stored in HDPE bags. These samples are referred further as *Orlea714, P1C* and *BH120*.

The first two mineral materials are produced by acid mine water flows, pH = 2.2-2.5, and the third by a circum-neutral mine water (pH = 5.0-7.0) [11-13].

Mineral samples were conditioned in the laboratory by removing vegetal debris and analyzed for elemental composition by X-ray fluorescence, metals and sulphur (Rigaku CG X-ray Spectrofluorimeter) [14]. After calcination (800ºC) a second elemental analysis was performed.

Thermal gravimetric (TG) and differential thermal analysis (DTA) were conducted on a Netzsch STA 409 thermal analyzer (air, linear heating rate 10°C/min).

The adsorption capacity was studied in batch experiments on 1 g dry matter (d.m.)L^{-1} as mineral adsorbent suspensions for an initial concentration of 72.69 mg/L As(III) in distilled water, at neutral pH, contact time 180 min, temperature 24±1ºC, orbital shacking, 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 PinaAcle 900T atomic absorption spectrometer.

RESULTS AND DISCUSSION

Elemental analysis results

All three precipitates have, as common characteristic, a very high iron content, about 500 g/kg d.m., Table 1.

Table 1. Analysis of secondary minerals**,** mg/kg d.m.

Parameter	Orlea714	P1C	BH120	**Parameter**	Orlea714	P1C	BH120
As	1865	2960	28.8	Se	<2	<2	<2
Ba	<30	<30	<30	Zn	35.7	15000	50210
Cd	<5	<5	34.4	Fe	407340	554000	428240
Cr	178	287	282	Mn	-	856	5666
Cu	27.1	<10	<10	Al	1306	1620	14731
Hg	<2	<2	<2	Ca	1060	5590	*14121*
Mo	<2	<2	<2	Mg	2405	5050	4062
Ni	<10	<10	<10	Si	2179	14000	26325
Pb	<5	<5	<5	S	48750	17433	8544
Sb	<5	<5	<5				

BH120 precipitate is characterized by a very low arsenic content, which is about 10 times lower compared to Orlea714 or P1C samples, so it could have a greater acceptability as adsorbent product. The mineral 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. Analyzing the results processed in 0, 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 $Fe_8O_8(OH)_{(8-2x)}(SO_4)_x$ giving a brut formula $Fe_8O_8(OH)_6(SO_4)$, Table 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 oxohydroxides. However, also the P1C sample could have a relevant schwertmannite content.

Table 2. Analysis of secondary minerals samples - Fe/S ratio

Parameter	Mineral source		
	Orlea714	P1-C	BH120
Fe (gram-atom/kg d.m.)	7.28	9.9	7.64
S (gram-atom/kg d.m.)	1.52	0.55	0.27
Fe/S ratio (gram-atom/ gram-atom)	4.77	18.2	28.7

Thermal behavior of the precipitates and of the calcined products

TG Analysis

With the goal to further study the adsorption capacity of calcined products, the mineral samples were subjected to a thermal analysis.

Natural precipitate from Rosia Montana 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 (Fig. 1). This thermal behavior can be explained by the characteristic two-step decomposition of ferric hydroxosulfates, first at 560-580°C with water loss, producing Fe_2SO_4 and the second step being represented by the transformation to hematite, an endothermic reaction above 580°C with release of SO_3. For pure $Fe(OH)SO_4$ the mass loss is of 7% for the first decomposition step and 45.5% for the second one [15]. Natural precipitate Orlea 714 shows a thermal decomposition similar to the schwertmannite obtained by Macingova [4] by using H_2O_2 and real acid mine water, Table 1. Other authors consider that characteristic for schwertmannite is the direct thermal release of SO_3 and $Fe_2(SO_4)_3$ is not formed [16].

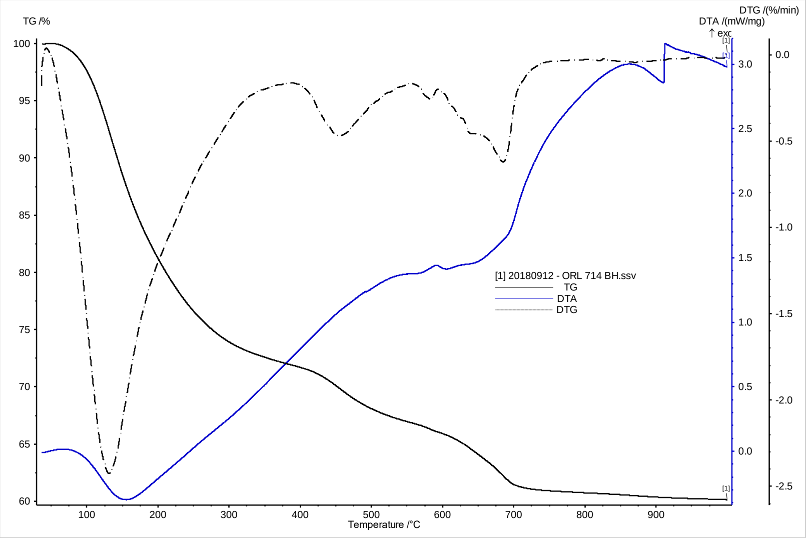

Fig. 1. TG, DTG, DTA curves for Rosia Montana, Orlea 714 mineral sample

The P1C precipitate has a somewhat similar TG curve (Fig. 2), 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 Hateg is rather goethite $Fe_2O_3 \cdot H_2O$, with a more modest mass loss than Orlea714 (Fig. 3), explainable also by the formation conditions, the mine water having in this case a circum-neutral character.

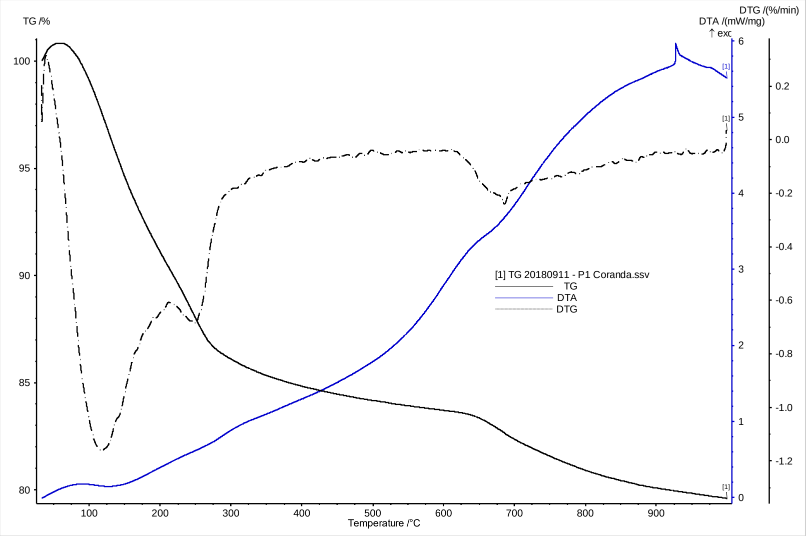

Fig. 2. TG, DTG, DTA curves for Certej P1Coranda mineral sample

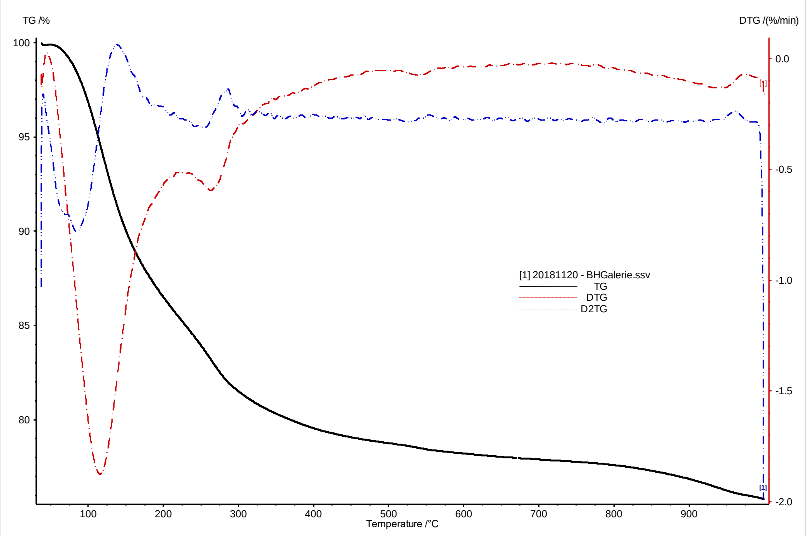

Fig. 3. TG, DTG, D2TG curves for Boita Hateg Orizont 120 mineral sample

Calcined products

Mass loss values for the mineral bulk samples calcined at 300°C and 800°C (10°/min, 1h) are presented in Table 3.

Table 3. Mass loss during calcination of minerals samples

Calcination temperature	Mass loss		
	Orlea714	P1C	BH120
300ºC	23.4%	12.1%	16.7%
800ºC	36.7%	16.3%	20.0%

The most significant Sulfur mass content variation by calcination at 800°C was observed for Orlea714 sample (-84%) as shown in 0. Sulfur mass variation for P1C has an intermediate value, while for BH120 it is negligible. These can be explained for the Orlea714 and P1C by a high iron sulfate content. Most probably the sulfur is present in the Boita Hateg sample as gypsum and magnesium sulfate, this mine water having important concentration of Ca^{2+} and Mg^{2+}. Magnesium and especially calcium sulfates are known to decompose at high temperatures, above 1000°C.

Iron content was found to increase in the calcination residue, as expected due to the mass loss, *e.g.* from 407 g/kg d.m. to 624 g/kg d.m. in the case of Orlea714 sample, respectively from 554 g/kg d.m to 626 g/kg d.m. for P1C.

Table 4. Sulfur loss for the mineral samples after calcination at 800ºC

Parameter	Measure unit	Orlea714	P1C	BH120
S, after calcination	mg/kg d.m.	7788	6919	8430
S, initial content	mg/kg d.m.	48750	17433	8544
Variation	%	-84%	-60%	<2%

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, Table 5. It is interesting to observe that Orlea714 and P1C already had a relevant initial arsenic content of 1.87 g/kg d.m. and 2.96 g/kg d.m. respectively, sorbed from the mine water, these mineral being effective trace metals sinks as observed by some researchers [7, 17, 18].

Table 5. As(III) adsorption capacity of the mineral samples

Mineral ID	pH	Mineral dosage, g/L	$C_{0,}$ mg/L As	Sorbed quantity, mg As/g
Orlea714	6.91	1.0	72.7	57.3
P1C	7.56	1.0	72.7	42.1
BH120	7.60	1.0	72.7	39.5

For the calcined products, at a temperature of 300ºC, 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 Hateg natural precipitate gallery (Table 6).

Table 6. As(III) adsorption capacity for calcined products

Mineral	Calcination temperature, ºC	Sorbed quantity, mg As/g
ORL714	300	40.8
	800	8.4
P1C	300	38.1
	800	7.4
BH120	300	46.4
	800	7.7

Mineral dosage: 1 g/L, initial As(III) C_o = 72.7 mg/L

Porous hematite prepared from the calcination of goethite concentrate was found to have a good adsorption capacity for As(III) by Yang et al. [19], e.g. up to 14.46 mg/L, depending on equilibrium concentration (<12 mg/L, informative).

In the case of calcination at a temperature of 800°C, an effect of a significant decrease of the adsorption capacity (about seven times for ORL714) was observed. In addition, the adsorption capacity values became similar, close to a median value of 7.8 mg/g with a standard deviation of

0.51 mg/g as informative figure. The levelling effect of calcination may be explained due to the formation in all cases of a product containing mainly hematite.

The decrease of the absorption capacity for the case of calcination would be a consequence of some transformations during calcination that are to be expected according to some researchers. Goethite (α-FeOOH) present in mineral samples or derived from schwertmannite will be transformed in hematite (α-Fe_2O_3) by direct dehydration without an intermediate phase, *slit-shaped micropores* being formed [20]. By increasing the calcination temperature to 800°C, the sinterization of hematite pores and the crystal growth will occur, but also the disappearance of pores [21] and this could cause the decrease of the adsorption capacity as observed in this work. Especially for the case of schwertmannite type ORL714 sample, the mechanism of mineral structural sulfate exchange with the anions in solution (arsenite) obviously cannot work anymore due to sulfate loss after calcination.

CONCLUSIONS

A comparative study on the elemental composition, thermal behavior and adsorption capacity for As(III) was done for secondary minerals which are naturally formed by precipitation from three mine water flows.

Precipitate from Rosia Montana - Orlea 714 is most probably of schwertmannite type $Fe_8O_8(OH)_6(SO_4)\bullet nH_2O$. Mineral from Certej P1-Coranda has an intermediary composition and it would contain goethite and some schwertmannite. Boita Hateg Orizont 120 sample contain most probably mainly goethite.

The three precipitates have the capacity to adsorb arsenite and the adsorption capacity is the highest for the sample of schwertmannite type, Orlea714.

If the minerals were processed by calcination, the As(III) adsorption capacity generally decreased, a smaller variation occurring up to 300°C, but for higher calcination temperature, 800°C, above the hydroxosulfates point of decomposition, the adsorption capacity dropped significantly, most probably due to pore structure alteration (sinterization) and loss of sulfate capacity exchange for arsenite in the solution. Calcination at 800°C, also leveled the adsorption capacity, probably due to formation of hematite as the final product for the three mineral samples.

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