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AUI GEOLOGIE

Preliminary data regarding the tailing pond of Suha Valley – Tarnița, Suceava County (Romania)

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Abstract

The tailings pond of Suha Valley consists of the waste material generated by the now-abandoned ore-processing plant of Tarnița. In terms of mineralogy, primary minerals (quartz, galena, sericite, subordinate barite and sphalerite) and secondary minerals (probably sulfates and Fe oxy-hydroxides) have been identified. Over 70% of the solid material falls within the fine and very fine fractions (less than 0.25 mm). Soluble fractions can exceed 58%, increasing with the amount of secondary minerals; the pH values are extremely low (2.17–3.51). The abundance of toxic metals emphasizes two sequences, as follows: (1) Zn > Cu > Pb > As (specific to samples with a high content of secondary minerals); (2) Cu > Pb > Zn > As (specific to samples with a low content of secondary minerals).
The physical and chemical parameters of the waste deposit indicate a high risk of environmental contamination, amplified by their susceptibility to airborne, hydromechanical and hydrochemical transport.

Keywords: tailings ponds, mineralogy, grain-size, soluble fraction, toxic metals.

Introduction

Mining has a significant impact upon the environment, either through its destructive effect upon the immediate landscape, or through the significant amount of waste resulting from this industrial activity. Once extracted through surface or underground works, ore is processed both mechanically (milling) and chemically (chemical treatment with cyanides, sulfuric acid etc.) so as to remove as much of the valuable metals as possible. The waste from the ore processing consists most frequently of a liquid or a slurry (tailing) which is deposited in a so-called tailings pond/dam or tailings storage facility (Chunhacherdchai et al., 2011); this type of mining waste is constantly leached or

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removed by means of airborne transport, through which significant amounts of potentially toxic metals are carried (Dinelli et al., 2001; Ferreira da Silva et al., 2006; Mlayah et al., 2009). The effects of toxic metals and acids being released into the environment persist for a long time, and they lead to instability of both the physical and the chemical parameters of the environment (Pirrie et al., 2002; Ávila et al., 2005).

Throughout the second half of the 20th century, the Polymetallic Belt of Cu-rich volcano-sedimentary mineralizations, developed along the Eastern Carpathians (Romania) (Mârza, 1982; Berbeleac, 1988, Balintoni, 1997), was the object of an intense, mainly underground, exploitation. The mining works were mainly concentrated in the following three metallogenic districts (from NNW to SSE): (1) Borșa – Vișeu District; (2) Fundu Moldovei – Leșu Ursului District; and (3) Bălan – Fagu Cetății District (Berbeleac, 1988; Stumbea, 2007). Ore-processing plants mostly operated in two of these three mine districts (districts 2 and 3), leaving behind numerous tailings ponds.

The present study focuses on the tailings pond located on the Suha River (Fig. 1b), in an attempt to make a preliminary description of the sludge pile resulted from the extraction activity of the Tarnița ore-processing plant. Geologically, the mineralizations processed by the Tarnița plant belong to the Fundu Moldovei – Leșu Ursului metallogenic District, more precisely to the metallogenic field of Leșu Ursului.

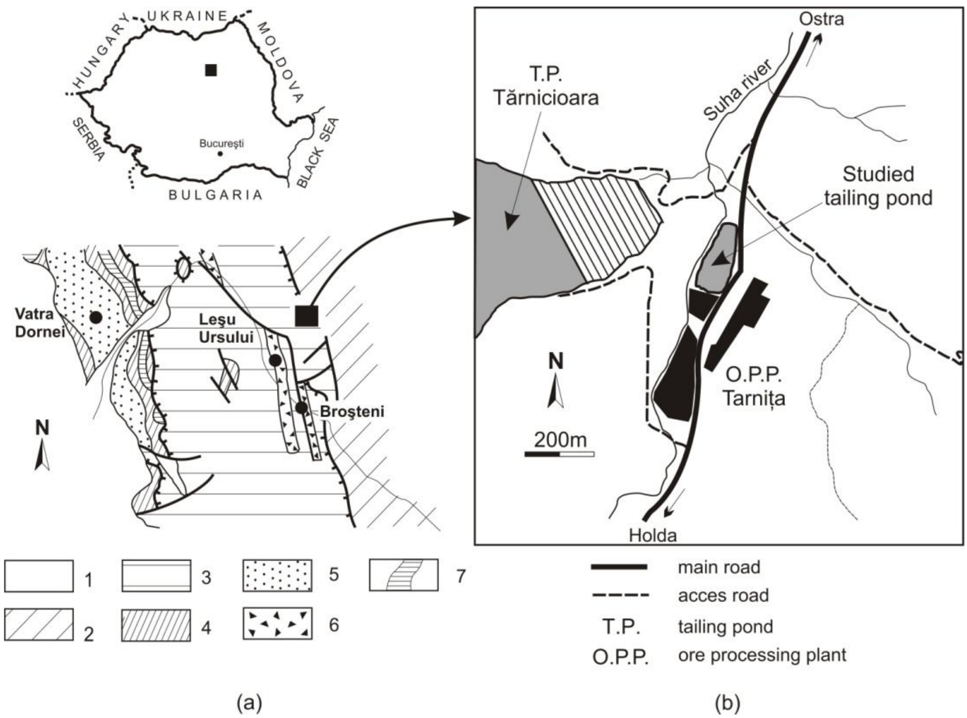

Fig. 1 Geological setting of the Leșu Ursului metallogenic Field (modified from Berbeleac, 1988) (a) and the location of the tailings pond from the Suha Valley (b). 1-post-mid-Cretaceous sedimentary cover; 2-flysh nappes; 3-Bucovinian nappe; 4-sub-Bucovinian nappe; 5-infra-Bucovinian nappes; 6-Cu, Zn, Pb-rich pyrite ores; 7-Mn-Fe-barite ores.

Geological setting

The Leșu Ursului metallogenic field is located approximately in the middle of the 200 km-long Polymetallic Belt of the Eastern Carpathians. The Cu-rich volcano-sedimentary ore deposits of the metallogenic belt are hosted by a geological megastructure involving a succession of overthrust nappes, as follows: flysh nappes, Bucovinian, sub-Bucovinian, and infra-Bucovinian nappes (Fig. 1a); the whole complex of nappes is locally covered by post-mid-Cretaceous sedimentary formations.

The polymetallic ore appears as layered sulfide mineralizations, genetically related to a bimodal magmatism and associated to the meta-volcanic and meta-sedimentary rocks of the Tulgheș Group (Tg) (Lithogroup – Balintoni, 1997); the Tulgheș Group is a low-grade metamorphic unit that underwent important polymetamorphic changes during the Caledonian and Variscan metamorphic events. In the metallogenic field of Leșu Ursului, as well as along the entire belt, the sulfide mineralizations are spatially related to the Tg_3 unit, which is roughly equivalent to the Leșu Ursului lithozone of Balintoni (1997). Despite quantitative differences related to depth, the mineralizations of Leșu Ursului are of the fine-grained pollymetallic type, and they consist of pyrite, chalcopyrite, sphalerite, galena, and barite; low amounts of arsenopyrite, pyrrhotite, tetrahedrite and bournonite occur as well (Berbeleac, 1998; Stumbea, 2007).

Mine tailings of Suha Valley

The mine tailings deposit under study is located on the right bank of the Suha River, about 6 km south-west from the Ostra village; it is bordered in the east by the Holda – Frasin road (Fig. 1b). The tailings pond has an elongated shape and a NNE-SSW orientation; its length is of roughly 200 m, and the maximum width is of 90 m. The solid material deposited on site represents the residue derived from the abandoned ore-processing plant of Tarnița. The sludge cuttings appear as 3–4 m high piles of a sandy-like material of grayish color, deposited onto the quasi-horizontal surface of the dried tailings pond (Fig. 2); the maximum depth of the waste deposit can be estimated at over 10–12 m.

(a)

(b)

Fig. 2 The tailings pond from Suha Valley, near the Holda-Frasin road; (a) general view; (b) detail.

In the southern part of the tailings pond, the remnants of two 50 m long, 8–10 m wide and 1–1.5 m deep settling pits can be seen; one of them is filled with a dark-brown liquid, most probably resulted from the accumulation of water during rainy periods. Here and there, in the lower parts of the waste deposit, shallow pools of dark-brown water can be observed (Fig. 2b); these areas seem to develop, due to the evaporation processes, toward white and sometimes greenish surfaces consisting of salt crusts (most probably Fe, Al, Mg and/or Cu sulfates) (Figs. 2a,b). The salt crusts are sometimes up to 1 cm thick and they are very brittle. On the flanks of the tailing pond, ravines up to 40–50 cm deep can be observed; they are caused by rapid water flow during intense rainfall events. In the riverbed of the Suha River, which flows on the western side of the tailings pond, pebbles, cobbles and boulders coated with a brown-reddish film (probably Fe^{3+} oxy-hydroxides) have been observed.

Samples and analytical techniques

The present study is based on the description and the analysis of 20 samples, collected using a plastic paddle. From the areas where salt crusts have developed onto the surface of the waste deposit, separate sample of crust aggregates and regular waste material were also collected.

For this preliminary approach, the mineralogical composition of each sample was described with the help of a Stereo Optika SZM2 stereo microscope, with a magnification of up to 45×; in order to obtain more accurate images of mineral grains, some samples were rinsed with distilled water prior to microscopical examination.

All samples were dried in an oven, at a temperature of 50°C, after which the following four grain-size intervals were determined: > 1 mm, 1–0.25 mm, 0.25–0.063 mm, < 0.063 mm. In order to determine the pH, the samples were placed in a beaker and distilled water was added (1:1 solid/liquid ratio); after having been stirred with a glass rod, the samples were left to settle for 10 minutes, then the pH was determined using a MeterLab PHM 250 Ion Analyzer – Corning 555.

In order to determine the soluble fraction, the samples (10–15 g) were soaked in 80 mL of distilled water, at room temperature, for 1.5 h, and shaken intermittently. After the sample preparation, the amount of soluble fraction was determined by adapting the gravimetric method for total filterable solids.

Chemical analyses of major elements (Si, Al, Fe, Mg, Mn) and some toxic elements (Cu, Pb, Zn, As) were performed with an X-ray Fluorescence Spectrometer – EDXRF Epsylon 5.

Results and discussion

The waste samples collected from the tailings pond generally exhibit a grey color and a sandy appearance; some clay-like samples have been collected as well. The analysis of the samples by means of a stereo microscope revealed a quite simple mineralogy, consisting mostly of the primary minerals from the sulfide-bearing metamorphic rocks of the Tulgheș Group (Tg_3), namely: quartz (Plate I, Figs. 1, 2, 3), galena – frequently displaying a cubic habit (Plate I, Figs. 1, 2, 4) and sericite (Plate I, Figs. 1, 2, 3); rare needle-like barite and very rare sphalerite have been identified as well (Plate I, Fig. 5). On the other hand, the microscopical examination of the unrinsed samples revealed the presence of some whitish minerals, associated in crusts and aggregates of either tabular (Plate I, Figs. 6, 7) or needle-like (Plate I, Fig. 8) grains. Most frequently, they cover the grains of primary minerals, especially quartz and galena; they result from the weathering of waste material from the tailings pond, and are, therefore, considered secondary minerals. As long as these aggregates are absent from the rinsed samples, it can be concluded that they belong to a highly soluble group of minerals, most likely secondary salts and sulfates, as described in similar occurrences (e.g. Stillings, 2003; Lottermoser and Ashley, 2005).

Although the conclusions reached based on granulometric analyses are usually enhanced by the study of certain textural features (e.g. the morphology of the mineral grains), these parameters have no meaning in the particular case of the samples collected from tailings ponds. Consequently, the granulometric analyses were limited to the assessment of the granulometric classes (Tab. 1) and the grain-size distribution (Fig. 3).

Table 1 General granulometric data (wt%) regarding the waste of the tailings pond

	>1.0 mm	1.0–0.25 mm	0.25–0.063 mm	<0.063 mm
Minimum	0.00	0.72	14.82	6.14
Maximum	27.13	39.55	67.95	40.44
Average	10.05	20.23	43.81	25.91

The granulometric analyses are based on the particle-size classes used in the study of unconsolided sedimentary deposits; in this respect, the mineral grains were included in the following four grain size classes: similar to very coarse sand (>1.0 mm); similar to coarse and medium sand (1.0–0.25 mm); similar to fine and very fine sand (0.25–0.063 mm); and similar to the silt and clay fraction (< 0.063 mm). The results in Table 1 show that the largest fraction of the tailings (an average of about 70%) consists of fine and very fine mineral grains (a grain size similar to that of fine sand, silt and clay). Most of the cumulative curves of the grain-size distribution are similar to those in Figure 3b, revealing a poorly-sorted material (Anfuso et al., 1999; Mycielska-Dowgiałło and Ludwikowska-Kędzia, 2011), which is justified by the procedure of random discharge of the slurry into the tailings pond. Nevertheless, two samples exhibited the features of a well-sorted material (Fig. 3a), suggesting that the waste materials accumulated as a result of either airborne or hydromechanical transport on the surface of the tailings pond.

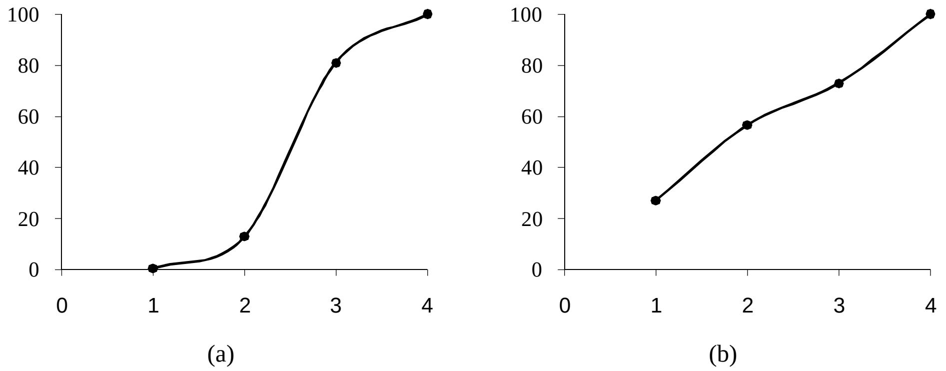

Fig. 3 Examples of grain-size distribution (cumulative curves): samples 411 (a) and 413 (b).

The quantitative determination of the soluble fraction emphasizes a wide content range, from 3.12 to 58.72 wt%. The highest values are specific to waste samples collected from the tailing areas where whitish, greenish and rarely ochre crusts have been identified on the surface of the sludge. The macroscopical and microscopical observations made during the present study, as well as the conclusions of previous scientific works (e.g. Moncur et al., 2005; Gunsinger et al., 2006; Graupner et al., 2007), lead to the assumption that the crusts developed on the surface of the tailings pond are composed of highly soluble Al, Fe, Mg (Cu, Mn)-rich hydrated sulfates.

Previous studies carried out on similar tailings waste (e.g. Romero et al., 2007; Hayes et al., 2009) revealed that the concentration of the soluble fraction is controlled by a complex series of reactions, such as oxidation – precipitation – dissolution; moreover, the concentration of each dissolved constituent is a function of the pH. As a result, both the pH and the chemical composition of the tailings from Suha Valley have been determined.

A synthesis of the pH values is presented in Table 2, which includes minimum, maximum and average values, placed in relation to the sample type, namely samples containing high amounts of either white or greenish efflorescent aggregates (probably sulfates), and samples showing no visible trace of sulfates. As expected based on previously published data (e. g. Bhattacharya et al. 2006; Conesa et al., 2008), the values in Table 2 emphasize the high acidity of the tailings from Suha Valley; it also seems that the pH values are quite low, regardless of the amount of sulfates identified in each sample.

Table 2 General pH values (wt%) specific to the waste of the tailings pond

Sample type	pH		
	Minimum	Maximum	Average
White efflorescent aggregates	2.38	3.51	2.82
Greenish efflorescent aggregates	2.17	2.99	2.72
Total efflorescent aggregates	2.17	3.51	2.77
No efflorescent aggregates	2.22	3.03	2.58

Table 3 presents the content ranges and the averages of some major elements and toxic elements determined through XRF spectrometry. In terms of major elements, rather significant variations of Al, Fe^{3+} and Mg could be noticed in either samples with efflorescent aggregates or samples where sulfates were not visible; this geochemical behavior can be attributed to the fact that the three elements enter the structure of both primary and secondary minerals (sulfates) occurring in the tailings. The average values of the major elements specific to the two categories of samples do not indicate any obvious differences.

Table 3 General chemical data specific to the waste of the tailings pond

	Al	Fe^{3+}	Mn	Mg	Cu	Zn	Pb	As
	(wt%)	(wt%)	(wt%)	(wt%)	(ppm)	(ppm)	(ppm)	(ppm)
Samples with high content of efflorescent aggregates								
Minimum	1.41	8.45	0.01	0.11	403.62	177.63	111.80	85.00
Maximum	9.38	21.93	0.18	1.49	6576.12	19083.75	5238.51	1725.96
Average	3.75	17.95	0.07	0.61	1974.00	5377.71	1257.78	393.79
Samples with low content of efflorescent aggregates								
Min.	1.54	11.04	0.01	0.09	322.91	108.58	303.86	118.86
Max.	9.92	22.15	0.05	0.82	4312.18	2460.74	6612.72	2188.34
Avg.	4.11	18.27	0.02	0.36	1664.66	791.16	1301.66	453.60

Regarding the behavior of toxic elements, the sulfate-rich samples seem to concentrate Zn, as indicated by its much higher amount (an average of 5377.71 ppm), compared to the average of 791.16 ppm determined for the samples with a low content of secondary minerals. Cu, Pb and As display quite similar amounts, with a moderately higher Cu average and a lower average for Pb and Zn, determined in samples containing more efflorescent aggregates. The higher amount of Cu could be explained by its preferential absorption by the alleged secondary minerals (Fe oxy-hydroxides and sulfates) (Sherriff et al., 2011). However, in terms of the abundance of toxic metals, the following two sequences can be identified:

Samples with high sulfate content:	Zn > Cu > Pb > As
Samples with low sulfate content:	Cu > Pb > Zn > As

The observations carried out on the Suha riverbed revealed an intense brown-reddish coloration of the scattered pebbles, cobbles and boulders; the explanation for this appearance is assumed to lie in the coating of these rock fragments with Fe oxy-hydroxides, a frequent phenomenon in areas with intensive mining works, where acid mine drainage usually occurs (Montero et al., 2005; Huminicki and Rimstidt, 2009). Although the coloration can be observed up to 6–7 km downstream of the Suha River, the pH of the water, determined based on 10 samples, revealed a neutral acidity (pH = 7.68–8.44).

Conclusions

The preliminary data collected on the waste of the Suha Valley (Tarniţa) tailings pond have led to certain conclusions regarding the main risk factors for the environment.

The location of the tailings pond in a wide, open valley, highly exposed to the wind, increases the risk of airborne transportation of waste. The transport of solid material by air is likely to occur due to: (a) the alleged high speed of the drying process affecting the exposed surface of the waste deposit; (b) the large mass of fine and very fine particles (over 70% of the waste). The assumption of an airborne transport is also supported by: (a) the shape of some grain-size cumulative curves; (b) the development of up to 1 cm-thick crusts of largely brittle efflorescent aggregates with low specific weight, onto the cvasi-horizontal surfaces of the tailings pond.

The precipitation regime with heavy rainfall, specific to mountainous regions, increases the risk of removal of toxic metal-bearing waste from the surface of the tailings pond. The removal involves the transport of waste as either suspensions or soluble fractions. This hypothesis is supported by: (a) the ravines caused by the water flow during the heavy rains, identified on the flanks of the tailings pond; (b) the grain-size of the solid waste, largely smaller than that of coarse sands; (c) the highly soluble efflorescent sulfates developed onto the tailings pond; (d) the brown-reddish coating displayed by the rock fragments and boulders scattered on the Suha riverbed; (e) the two settling pits from the southern part of the tailings pond, which, during the periods of heavy rainfall, develop the risk of discharging large amounts of acid, toxic elements-rich leachates into the Suha River.

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CAPTION OF PLATE

Plate I

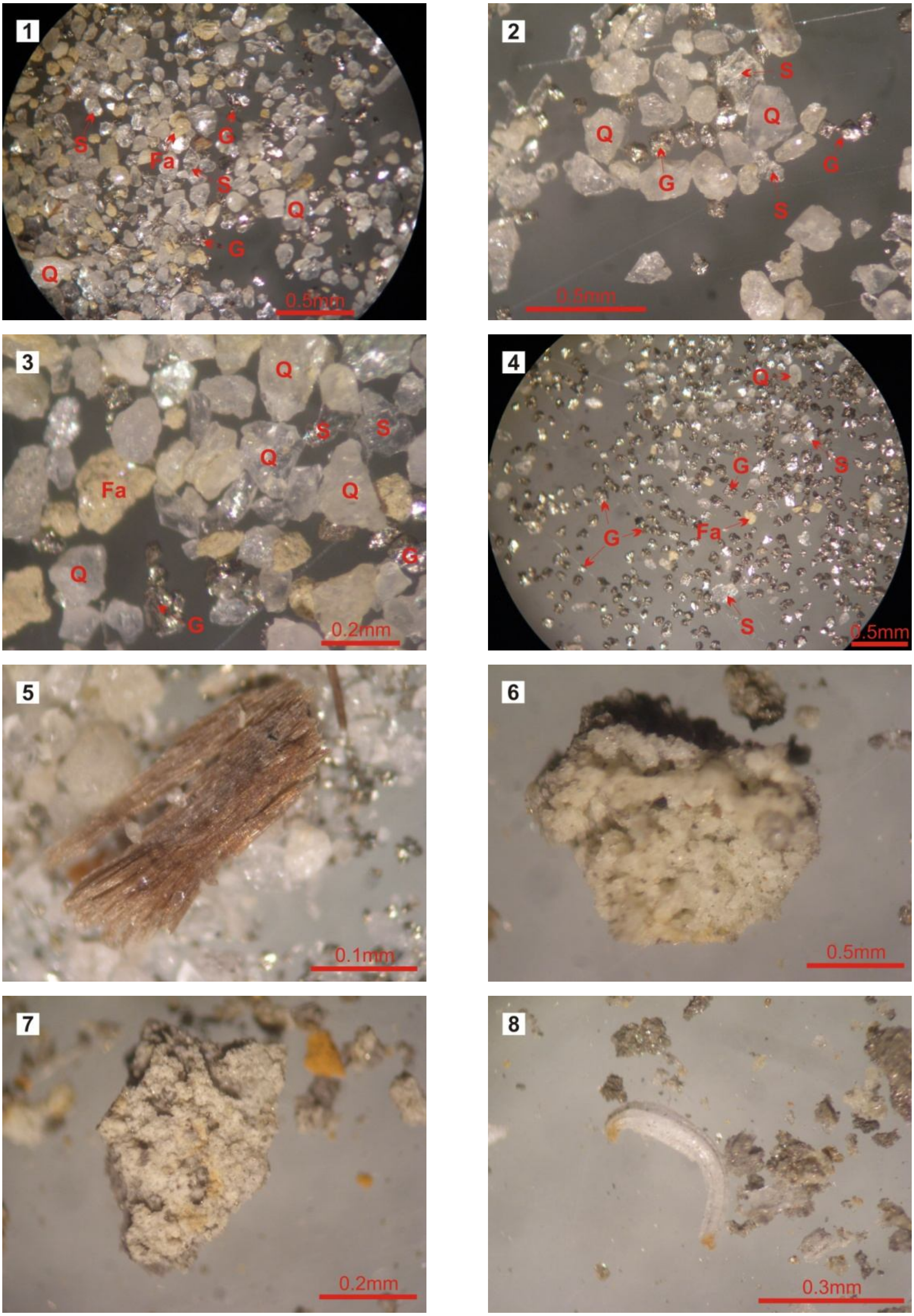
1-4. Polymineral solid product. Q-quartz; G-galena; S-sericite; Fa-altered feldspar (chemical attack) (rinsed samples).

5. Barite (rinsed samples).

6-7. Sulfates crusts; mineral aggregate with tabular habit (unrinsed samples).

8. Needle like sulfates (unrinsed samples).

Plate I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