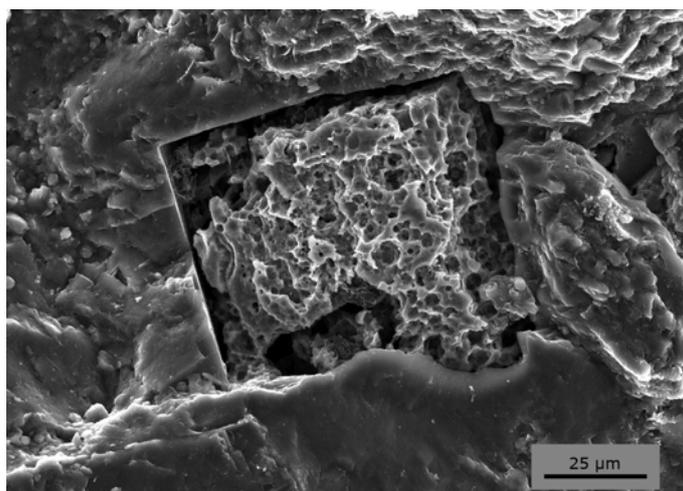


**Environmental mineralogical and geochemical studies
on the Bányabérc waste dump in the Gyöngyösroszsi mining area,
Hungary**

Theses of the PhD dissertation

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INTRODUCTION

Mining is a necessity of human activity, since products of traditional and modern technology (vehicles, computers, telephones etc.) belong to our everyday lives. The list of goods the manufacture of which relies on the production of ores and other raw materials would run very long. During ore mining and processing large quantities of waste is produced as well. For instance, today's North America produces solid mine waste ten times as much as household garbage (JAMIESON 2011). Nowadays in many countries the treatment of mine wastes is strictly regulated by a legislative framework incorporating results of scientific research as well. Mine wastes cause problems not only because of large quantities but also because they may contain minerals that are reactive in surface environments. The induced processes and reactions are the subjects of environmental mineralogy and geochemistry. Wastes of sulphide ores are of outstanding concern due to their high acid production and heavy metal pollution potentials. The storage and environmental safety of mine wastes raise many questions. It is not by chance only that the treatment of mine wastes is in the focus of the attention of many professions. The European Parliament and the Council has issued their relevant directive (2006/21/EK) in 2006.

The timeliness of the topic is also shown by a recent issue of the *Elements* magazine (December 2011; HUDSON-EDWARDS *et al.* 2011) dealing with mine wastes. The monograph of LOTTERMOSER (2010) on mine wastes is already at the third edition in a mere nine years. There is a huge number of researchers working on the weathering processes and products of waste dumps. When one is to describe environmental geochemical processes, it has to be kept in mind that the key role is played the solid phases and that any sort of risk assessment is incomplete without their explicit evaluation. Thus, the starting point of every remediation procedure should be the precise analysis of the mineral constituents; without this information the assessment of the realistic environmental hazards and the prediction of future processes are laden with rather high uncertainties.

Secondary sulphate minerals play a distinguished role in the evolution of sulphide ore waste dumps. Certain secondary sulphates tend to extract acidity and a part of the available metals from the surroundings, reducing the impact of wastes on the environment, surface waters and biota. These sulphates, however, have various stabilities. Many of them will become unstable upon relatively slight changes in physical-chemical conditions (e.g. pH, temperature, humidity). The breakdown or transformation of such phases may trigger additional acid production or a discharge of heavy metals. Thus, without an awareness of these sulphates, the environmental risks of a waste dump may be underestimated. Other sulphate minerals, on the other hand, are stable in a wide range of environmental conditions. If the acidity and the stored metal content of these mineral phases are added to the risks, the predicted environmental hazard of the waste dumps may be significantly overestimated. Thus, remediation plans relying on total chemistry without an assessment of environmental mineralogy may either be insufficient or excessive for the actual problem.

Remediation projects in Hungary are mostly executed based on the knowledge of the chemical components of the waste and the measures taken are planned accordingly. Therefore the mine waste-related environmental pollution and its prevention raise important environmental mineralogical questions.

The environmental pollution related to the ore mining activity and its aftermath in the Gyöngyösoroszi–Mátraszentimre region is the best known and most thoroughly investigated environmental problem in Hungary. A number of environmental impact studies have been prepared about the area. These studies were written from predominantly chemical, geochemical (*e.g.* HORVATH & GRUIZ 1996, FÜGEDI 2006) or biological (*e.g.* HORVATH & GRUIZ 1996, TAMÁS & KOVÁCS 2005, FEIGL *et al.* 2010) viewpoints, concentrating on contaminants (heavy metals and metalloids), on the area of contamination and on potential sources of contamination. Though the title of the PhD dissertation of MÁDAI (2007) suggests an environmental mineralogical study, the analysis of solids is subordinate and his conclusions are drawn concerning mainly general environmental geochemistry.

The present dissertation focuses on the mineralogical and connected geochemical aspects of the formation of secondary sulphates on an acidic waste dump. Emphasis was laid on mineralogical characterisation and geochemical conclusions were drawn in view of the mineralogical results.

Three major groups of secondary minerals have been recognised and characterised in detail: jarosites, iron oxyhydroxides and iron oxyhydroxide sulphates, and water-soluble sulphates. The identification of the mineral phases provides information about pH conditions as well as metal and sulphate concentrations in their environments of formation. I hope that through the detailed description of processes occurring in the Bányabérc waste dump I will contribute to the future prediction of the phenomena related to similar dumps.

AIMS

In the frame of a large-scale remediation programme, the complete relocation of mining wastes or the environmental isolation of waste dumps have been planned and partly carried out in the Gyöngyösoroszi mining area. In this programme, the relocation of mining waste from the Bányabérc waste dump started in 2006. The material of the approximately 40-year-old waste dump, estimated to have a volume of 26,000 m³ (CSÖVÁRI 2004), was relocated to the Száraz-völgy tailing dump in an attempted full-scale remediation of the dump site. The planning of the remediation was typically based on incomplete chemical analyses of surface samples.

The aim of this study is to provide a general overview of the processes occurring in a sulphide ore waste dump by means of mineralogical investigations. The identification and characterisation of minerals allowed the disclosure of potential hazards caused by the further weathering of these minerals. My unconcealed goal was to set an example by performing a detailed mineralogical study, emphasising the importance of such hazards and encouraging

the undertaking of similar investigations. After the remediation of the dump site, the material will no longer be available for study, therefore this work also serves “archiving” purposes.

I wish to emphasise, through the presentation of the results of my mineralogical investigations, that secondary minerals carry truly fascinating and indispensable information about transformation processes in the waste dump. It has to be explicitly mentioned that the identification and precise characterisation of the minerals in this study are occasionally beyond routine tasks of mineralogy. Some of the difficulties lie in small grain sizes, in the sensitivity of certain phases to atmospheric humidity, low abundance, poor crystallinity, water solubility *etc.* As a result, the identification of mineral phases as well as the understanding of their roles in environmental processes is sometimes indeed challenging.

The new results allow outlining the general patterns in the processes and contribute new knowledge that helps, through deciphering the current state of a waste dump, to foresee environmental geochemical processes with better reliability.

ANALYTICAL METHODS

The analytical methods used in this study may be divided into several groups. To assemble a representative sample set, field *sampling* had to be done carefully, so that the conclusions drawn in view of later results would be characteristic for the waste dump as a whole. The vertical section of the waste dump opened up by remediation activities provided a unique opportunity to collect samples along a full profile of the dump. Samples were collected from various depths below the original surface. The selection of sampling points was guided by the macroscopic appearance of the material. Sampling was performed in wet as well as after extended dry periods of weather.

Collected samples were sorted according to their macroscopic appearance. After a closer inspection under a *stereomicroscope*, samples were prepared for further analysis. A subset of the samples was *grain size separated* to enrich jarosite (1–5 µm typical grain size). Wet sieving with deionised water and settling of the finest fraction was done to separate seven grain size fractions (>500 µm, 500–250 µm, 250–125 µm, 125–63 µm, 63–32 µm, 32–2 µm and <2 µm). The mineral composition of every size fraction and the bulk samples were analysed using *X-ray powder diffraction* (86 measurements).

Traditional optical microscopy (using stereomicroscope, and *transmitted and reflected light polarised microscopes*) was followed by morphological observations on *ca.* 100 individually prepared single grains in a *scanning electron microscope* (SEM). The same grain mounts were subjected to semi-quantitative *local chemical analyses* (SEM-EDX) after grinding and polishing. Later the same measurement points were analysed by *Raman spectroscopy*. In addition to grain mounts, secondary crusts formed on rock fragments were studied in thin sections. Ore mounts (10 pcs) were prepared preserving the characteristic secondary sulphate and iron oxyhydroxide coatings. Raman spectroscopic and SEM-EDX

analyses were also carried out on the ore mounts. A total of 398 SEM-EDX point analyses and 416 Raman point spectra were recorded and evaluated.

Selected grain size separated fractions were subjected to a sequential extraction procedure to measure main and trace elements (ICP-AES and ICP-MS, respectively) released in the extraction steps. The water soluble main and trace element composition of a number of $<2 \mu\text{m}$ size fractions was also measured after leaching with a diluted nitric acid solution of pH 2.

THESES

- 1.** Through the study of the Bányabérc waste dump it was possible to investigate a several decades old natural laboratory. The conclusions drawn from the new results, compared to findings of previous investigations done on materials sampled mostly from the exposed dump surfaces, offer a significantly more reliable basis for the prediction of processes taking place in this and similar waste dumps. It has also been demonstrated that small-scale investigations of mineral phase compositions provide indispensable information on waste evolution processes.
- 2.** Jarosite found abundantly in the waste dump has been newly established to have compositions mostly in the jarosite–hydroniumjarosite solid solution series. This is of crucial importance since hydronium-substituted jarosite has a decreased stability compared to the pure-K end member. The small grain size of jarosite-group phases also plays a role in their increased reactivity.
- 3.** The formation of hydroniumjarosite has been shown. Since potassium is abundantly available in the dump, the presence of hydroniumjarosite suggests intensive oxidation processes.
- 4.** Plumbojarosite has been shown to occur as outer rings around anglesite and galena. Though an anglesite crust increases the stability of galena, during extended periods of time galena is consumed by intense oxidization processes. Plumbojarosite, which may release Pb from its structure above a pH of 4–5 through dissolution, has been invariably found around anglesite.
- 5.** Using Raman spectroscopy and SEM-EDX, the reddish-brownish crusts covering rock fragments, in cases resembling dried gels, have been found to consist of schwertmannite and poorly crystalline goethite. This is the first evidence of schwertmannite from the territory of Hungary, as well as the first Raman spectrum of a natural schwertmannite published in the literature.
- 6.** On the basis of Raman spectroscopic phase identification combined with SEM-EDX chemical data, schwertmannite from Bányabérc has a minimum calculated Fe/S atomic ratio of 4.2, in contrast with previously published values of 4.6 (BIGHAM *et al.* 1990, 1996) and 4.3 (YU *et al.* 1999), possibly explained by the high sulphate concentrations in the dump.

7. The transformation of schwertmannite to goethite has been found not to occur along straight fronts. The initial appearance of goethite in brown crusts is scattered, point-like. As a result of advanced transformation processes, parts of the crusts may become dominated by goethite, apparently preferentially near pores. All goethite samples showed detectable sulphate contents.

8. Heavy metals have been identified in water-soluble sulphates. Since these sulphates are ephemeral (they only exist in solid form until the next rainfall), their heavy metal content is easily released into the environment.

9. After three years of storage, control measurements on sample stability have shown mineralogical changes among the water-soluble sulphates. The observed changes support the view that the determined mineralogical composition of water-soluble sulphates is no more than a “snapshot” of conditions. Since these sulphates crystallize from the pore fluids, their chemical composition provide indirect evidence on pore fluid compositions as well.

10. A major difference between water-soluble sulphates precipitated on the waste dump and those crystallized in the finest-grained fraction after wet sieving is that pure iron sulphates were only identified in the latter. In water-soluble sulphates from the waste dump, iron was present in the form of substitution in halotrichite group minerals, in epsomite and alunogen. The transformation processes observed on water-soluble sulphate samples suggest oxidation, neutralization (rhomboclase to coquimbite), hydration (rhomboclase to coquimbite) and in certain cases dehydration (halotrichite group to copiapite, or epsomite to hexahydrate to pentahydrate transformations). New phases formed during storage in the laboratory prove that the analysis of samples immediately after collection is highly important.

11. Using a sequential extraction procedure, it was demonstrated that though the mining waste contained high concentrations of toxic elements, only a part of them were in mobilizable form. Based on the dissolution experiments, the sequence of decreasing total concentrations of the investigated elements in the mining waste has been established as follows: Fe > S > Al > Ca > Zn > Pb > As > Sb > V > Cu > Tl > Cd. The succession changes if element mobilizability is considered: Ca > Cd > Zn > As > Cu > S > Fe > Pb > Tl > V > Al > Sb. Realistically, the latter sequence is thought to give a more reliable view on element behaviour. These results confirm that in questions of waste hazard assessment and bioavailability of elements it is inadequate to only measure total concentrations; instead, an analysis by sequential extraction is necessary.

12. The main source of arsenic in the Bányabérc waste dump has been shown, by parallel SEM-EDX and Raman spectroscopic analyses, to be arsenian pyrite.

13. The large quantities of pyrite still found in the waste indicates that acid production has not ceased even after half a century of weathering, and doubtless continues after the complete relocation of the dump. The iron content of sphalerite also augments acid production.

14. The low-pH stability of jarosite has been confirmed by identifying large quantities of jarosite as well as by results of the sequential extraction analysis, implying that incorporated toxic elements are stable in jarosite in the Bányabérc waste dump. In view of the results, it is evident that the dynamics of the environmental risks posed by a waste dump need to be assessed, whereas a static analysis restricted to pyrite and total chemical composition is insufficient.

CONCLUSIONS

Results have highlighted that the water–mineral interactions take place in microenvironments and that only the fine-scale studies of the mineralogical composition provide us accurate information about these processes. During the weathering of the sulphides present in the waste dump, large amounts of Zn, Cd, As, Cu, Fe and Pb are released. The relatively large quantities of pyrite in the material suggest that acidity is still actively generated.

Jarosites are important secondary sulphates in the waste material. Their abundance indicates that oxidation processes are active after 50 years of exposure. The weathering of disseminated as well as locally massive pyrite produces large quantities of minerals belonging to the jarosite–hydronium jarosite solid-solution series. The foreseeable environmental chemical evolution of the waste dump predicts a decrease of the amount of pyrite and thus an increase of the pH in the coming decades. Jarosites, though stable in acidic conditions, may become instable with rising pH and toxic elements (Pb, As) may be released from its structure.

Reddish crusts covering the surfaces of rock fragments consist of schwertmannite and goethite, and rarely of a jarosite–goethite mixture, also indicating acidic, sulphate-rich environments. Protons are released during the schwertmannite to goethite transformation, further decreasing pH. The initial appearance of goethite in brown crusts is scattered, point-like. As a result of advanced transformation processes, parts of the crusts may become dominated by goethite, apparently preferentially near pores. All goethite samples showed detectable sulphate contents.

Water-soluble sulphates identified in the waste dump represent an important source of contamination, since significant heavy metal contents have been detected in them and the existence of these sulphates is ephemeral. Their compositions indirectly provide a snapshot of pore fluid compositions. The characterisation of water-soluble sulphates gives information only about a transient state; this has also been shown by changes in phase compositions seen in control measurements carried out after three years of storage.

The results of the sequential extraction procedure have shown that it is inadequate to measure total element concentrations only if risk assessment and the bioavailability of toxic

elements are in question. Sequential extraction should be the preferred method to give a realistic account of the mobility of the elements in waste dumps. For a successful treatment during remediation the knowledge of the mobility of elements is of outmost importance.

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