Automated Mineral Analysis to Characterize Metalliferous Mine Waste

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Abstract. The objective of this study was to investigate the applicability of automated QEMSCAN® mineral analysis combined with bulk geochemical analysis to evaluate the environmental risk of non-acid producing mine waste present at the historic Albertsgrube Pb-Zn mine site, Hastenrath, North Rhine-Westphalia, Germany. Geochemical analyses revealed elevated average abundances of As, Cd, Cu, Mn, Pb, Sb and Zn and near neutral to slightly alkaline paste pH values. Mineralogical analyses using the QEMSCAN® revealed diverse monomer and polymineralic particles across all samples, with grain sizes ranging from a few µm up to 2000 µm. Calcite and dolomite (up to 78 %), smithsonite (up to 24 %) and Ca sulphate (up to 11.5 %) are present mainly as coarse-grained particles. By contrast, significant amounts of quartz, muscovite/illite, sphalerite (up to 10.8 %), galena (up to 1 %), pyrite (up to 3.4 %) and cerussite/anglesite (up to 4.3 %) are present as fine-grained (<500 µm) particles. QEMSCAN® analysis also identified disseminated sauconite, coronadite/chalcophanite, chalcopyrite, jarosite, apatite, rutile, K-feldspar, biotite, Fe (hydr) oxides/CO₂ and unknown Zn Pb(Fe) and Zn Pb Ca (Fe Ti) phases. Many of the metal-bearing sulphide grains occur as separate particles with exposed surface areas and thus, may be matter of environmental concern because such mineralogical hosts will continue to release metals and metalloids (As, Cd, Sb, Zn) at near neutral pH into ground and surface waters. QEMSCAN® mineral analysis allows acquisition of fully quantitative data on the mineralogical composition, textural characteristics and grain size estimation of mine waste material and permits the recognition of mine waste as “high-risk” material that would have otherwise been classified by traditional geochemical tests as benign.

1. Introduction

In Europe, there is a large number of abandoned historic metal mine sites, which have not been subject to any risk assessment and rehabilitation activities after mine closure. Un-rehabilitated relics of metal mine sites (e.g. waste dumps) represent major threats to local (and regional) environment and accordingly to human health. Weathering of well-exposed waste material and subsequent oxidation of e.g. sulphide minerals, for example, may produce acid mine waters, resulting in elevated mobility and contamination by certain elements (e.g. heavy metals; [1, 2, 3]). Within recent years, increasing concerns regarding the environmental threats arising from metalliferous mine waste material have led to greater efforts to develop and improve methods to monitor and assess the risk potential of abandoned mine sites. However, today’s mine waste characterisation exclusively relies on geochemical static tests to classify materials based on their propensity to generate acid mine drainage. Unfortunately, such risk assessment
does not consider mineralogical properties of wastes nor the fact that environmentally significant elements such as Cd and Zn may be mobile at near-neutral to alkaline pH values, leading to neutral metalliferous drainage. The objective of this study is to investigate the applicability of automated QEMSCAN® mineral analysis combined with bulk geochemical analysis to evaluate the environmental risk of non-acid producing mine waste present at the historic Albertsgrube Pb-Zn mine site, Hastenrath-Stolberg, North Rhine-Westphalia, Germany and to evaluate the potential of this technique for environmental risk assessment of mine waste.

2. Description of the Albertsgrube area
2.1. Geography and Mining History of the Albertsgrube
The historic Albertsgrube Pb-Zn mine site and associated waste dump are located ca. 4 km E of Stolberg, North Rhine-Westphalia, Germany at latitude 50°47’ N, longitude 6°16’ E and at an altitude of ca. 250 m (Figure 1). The climate is temperate with a mean annual rainfall of 740 mm and mild mean temperatures ranging from min. 3°C (in January) to 18.5°C (in July). The mine site is partially surrounded by woodland, however, most of the area is used for agriculture (pasture and crop plantation) and lime-stone mining.

The Stolberg region comprises historically significant metal mineralisation types (e.g. Pb, Zn, Cu ore) and particularly during the 16th and the 19th century, the region has been exploited for their Pb and Zn sulphide ore [4]. Due to possessing a Pb smelter as well as an important metal-manufacturing industry, Stolberg is a significant industrial region until today. Pb-Zn mining activity in the Albertsgrube is reported to have taken place between the early 18th to the early 20th century.

2.2. Site description of the Albertsgrube
The Albertsgrube is hosted in Lower Paleozoic/Upper Devonian sedimentary rocks: (i) black slates and associated tonalite and tonalite porphyry intrusions and (ii) nodular limestone, marly shales and black shales [5]. The vein-type Pb-Zn ore deposit of the Albertsgrube is suggested to represent a low-temperature, carbonate-hosted Mississippi-Valley-type mineralisation and consists mainly of hydrothermal galena and sphalerite as well as supergene cerussite and smithsonite [5]. The tailing disposal system of the Albertsgrube consists of ca. 4500 m² large mine dump that is erodible, largely unvegetated and that contains ca. 100.000 m³ of unconsolidated, oxidising, generally sulphidic waste, with particle sizes ranging from clay to sand. A currently performed characterisation of the heavy metal input in this area reveals elevated contents of Pb, Zn, Cu, Tl and Cd, [4].

![Figure 1. A) Map of the Stolberg area and location of case study site Albertsgrube. B) Photograph of the waste dump of the Albertsgrube](image-url)
3. Sampling and methodology
During two field campaigns in spring 2016, a total of 21 samples from representative surficial levels of the mine waste dump at the Albertsgrube were collected for pH, bulk element and QEMSCAN® mineral analysis.

Sixteen pulp samples from representative surficial waste dump material were dried at room temperature and digested with HF-HNO₃-HClO₄ acid solution. The residue was subsequently topped up with a dilute HCl acid solution and the sample material was analysed for its total element contents (48 elements) using an inductively coupled plasma-atomic emission spectrometry (ICP-AES) at the Australian Laboratory Services (ALS, Ireland). Five samples of representative surficial waste dump material were analysed using a QEMSCAN® 4300 automated mineral/phase analysis system at the Camborne School of Mines, University of Exeter, UK in order to evaluate the modal mineralogy and textural details and with particular interest in the siting of Zn, Pb, As, Cd and Sb. The analyses were operated using an accelerating voltage of 25kV and beam current of 5nA. The applied QEMSCAN® software’s were iMeasure for the data acquisition and iDiscover for the spectral interpretation and data processing [6].

4. Results and Discussions
Geochemical analyses of sixteen bulk samples (Figure 2) demonstrated elevated average abundances of As (127 ppm), Cd (397 ppm), Cu (151 ppm), Mn (3641 ppm), Pb (>1 wt%), Sb (61 ppm) and Zn (>1 wt%) and near neutral to slightly alkaline paste pH values. Elevated concentrations of Cu, Cd, As, Sb and particularly of Pb (up to 13 wt%) and Zn (up to 6 wt%) are also reported from soils of other regions in the Stolberg area [4]. The sample P-20 has remarkably lower (> 0.5 times) Pb, Zn, As, Cd, Cu, Mn, Ni and Sb abundances relative to the other samples, which may be attributed to its relatively distal location of the waste dump and therefore possibly lower metal-bearing sulphide concentrations. Mineralogical analyses on five representative samples, using the QEMSCAN® revealed diverse mono- and polymineralic particles across all samples, with grain sizes ranging from a few µm up to 2000 µm. Calcite and dolomite (up to 78 %), smithsonite (up to 24 %) and Ca sulphate (up to 11.5 %) are dominant minerals in the coarse-grained fraction. By contrast, significant amounts of quartz, muscovite/illite, sphalerite (up to 10.8 %), galena (up to 1 %), pyrite (up to 3.4 %) and cerussite/anglesite (up to 4.3 %) are present as fine-grained particles (<500 µm). QEMSCAN® analysis also identified accessory sauconite, coronadite/chalcophanite, chalcopyrite, jarosite, apatite, rutile, K-feldspar, biotite, Fe (hydr) oxides/CO₃ and unknown Zn Pb(Fe) and Zn Pb Ca(Fe Ti) phases. The mineralogical hosts of As, Cd and Sb could not be identified using QEMSCAN® analysis, yet it appears likely that these elements are included as trace elements in sulphides (e.g. sphalerite, galena; [7, 8]).

Figure 2. Abundances (in ppm) of specific metals in soil samples from the Albertsgrube waste dump
Many of the metal-bearing sulphide grains (Figure 3) occur as disseminated particles that are not or not fully enclosed by other phases. These metal-rich sulphides have particularly fine mineral grain sizes (<500 µm) and relatively large grain surfaces. The abundance of labile sulphide grains with relatively large reactive surface area is of environmental concern because such mineralogical hosts are likely to release toxic metals and metalloids (e.g. As, Cd, Sb, Zn) at near-neutral pH into ground and surface waters (e.g. during heavy rainfall; [9]). Another major environmental concern may arise from the metal-rich, fine grain fraction, since it is easily dispersed to the surrounding areas via wind erosion [10].

![Figure 3](image)

**Figure 3**: False colour imaging of the QEMSCAN® mineral analysis from samples A) AG-1, B) AG-2, C) AG-5, D) AG-7, E) AG-9.

In combination with bulk geochemical analysis, the QEMSCAN® mineral analysis proved to be a potential tool for the qualitative and quantitative mineralogical characterisation of mine wastes, their textures and grain sizes. It provided high-quality information on the mineralogical association and element deportment and classified mono- and poly-mineralogical particles at all scales. QEMSCAN®
analysis further allowed the recognition of mine waste as “high-risk” material that would have otherwise been classified by traditional geochemical tests as benign.

5. Conclusions
At the historic abandoned Pb-Zn mine Albertsgrube in North Rhine-Westphalia, mine waste dump contains fine- to coarse-grained mono- and polyminerallc waste material with very high (> 1 wt%) Pb and Zn concentrations and elevated abundances of Cd, As, Cu, Mn, Ni and Sb. QEMSCAN® analysis identified heavy-metal bearing sulphide grains with fully exposed surface areas particularly in the fine-grained waste matrix and allowed the classification of the Albertsgrube mine waste as potential “high-risk” material. QEMSCAN® analysis therefore provides a valuable tool for the qualitative and quantitative characterisation and risk assessment of mine waste.

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