

Research Article

An Integrated Process for Innovative Extraction of Metals from Kupferschiefer Mine Dumps, Germany

Andreas Kamradt^{1,*}, Gregor Borg¹, Juliane Schaefer², Stephanie Kruse³, Marco Fiedler¹, Phillip Romm⁴, Axel Schippers⁵, Ralf Gorny⁶, Michael du Bois⁷, Christin Bieligg⁷, Nadine Liebetrau⁷, Sylvie Nell⁴, Bernd Friedrich³, Henning Morgenroth², Hermann Wotruba⁴ and Charlotte Merkel³

DOI: 10.1002/cite.201200070

Dumps in the Central German Mansfeld mining district have been investigated by a multi-disciplinary research team to develop a holistic concept for the recovery of base and trace metals from low-grade Kupferschiefer ore. Geochemical and mineralogical data from representative sampling indicate that the low-grade Kupferschiefer dumps contain significant amounts of Cu (0.6 %) and Ag (up to 800 ppm), besides exploitable grades of Pb and Zn. Additionally to flotation and hydrometallurgy, first shake flask bioleaching experiments on otherwise untreated Kupferschiefer ore yield Cu recovery rates of up to 95 %. A total of 900 t Cu and 5 t Ag contained in black copper can thus be produced from the pilot dump of 100 000 m³ low-grade Kupferschiefer ore. Additionally, large volumes of limestone waste, separated from the dumps by sensor-based sorting, can be utilized as aggregate in the construction industry.

Keywords: Bioleaching, Copper sulfides, Flotation, Hydrometallurgical extraction, Sensor-based sorting, Vertical roller mill, Waste utilization

Received: May 08, 2012; *revised:* July 31, 2012; *accepted:* August 09, 2012

1 Preface

The past decade has seen an increased awareness of both political decision makers and industry alike of the significance of a reliable mineral resource supply. Specifically the so-called high-tech metals, e.g., copper, platinum, or rare earth elements, are necessary raw materials for numerous technical uses and solutions. The more complete utilization of previously mined ores is particularly the main aspect that has been the focus of the presented research project, namely to extract remaining metals from low-grade copper ores of the Kupferschiefer mining district of Mansfeld/Sangerhausen in Central Germany. The materials in question are ores and low-level mineralized rocks that have been mined and

brought to surface over the last 150 years. Thus one of the most significant cost factors, the mining costs, has already been incurred in the past and the material is now resting on surface with easy accessibility. However, the mineralized material, which consists predominantly of fine-grained, organic carbon-rich black shale with extremely fine-grained disseminated base metal sulfide mineralization, has proven to be extremely difficult to process. This is one of the main reasons for the material to still exist as mine dumps. Similar subeconomic low-grade ore and mineralized waste dumps of black shale-hosted copper ores can be found worldwide, e.g., the Polish Kupferschiefer district around Lubin, the African Copperbelt of Zambia and Zaire, and the deposits of Dzhezkazgan, Central Kazakhstan. The successful devel-

¹Andreas Kamradt (andreas.kamradt@geo.uni-halle.de), Prof. Dr. Gregor Borg, Marco Fiedler, Martin-Luther University Halle-Wittenberg, Institute for Geoscience and Geography, 06099 Halle (Saale), Germany; ²Juliane Schaefer, Dr.-Ing. Henning Morgenroth, UVR-FIA GmbH, Chemnitzer Straße 40, 09599 Freiberg, Germany; ³Stephanie Kruse, Prof. Dr.-Ing. Dr. h.c. Bernd Friedrich, Charlotte Merkel, RWTH Aachen University, Institute for Process Metallurgy and Metal Recycling, Intzestraße 3, 52056 Aachen, Germany; ⁴Phillip Romm, Sylvie Nell, Prof. Dr.-Ing. Hermann Wotruba, RWTH

Aachen University, Department of Mineral Processing, Lochnerstraße 4–20, 52064 Aachen, Germany; ⁵Prof. Dr. Axel Schippers, Geomicrobiology, Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany; ⁶Dr.-Ing. Ralf Gorny, CONMET GmbH, Jülicher Straße 336, 52070 Aachen, Germany; ⁷Dr. Michael du Bois, Christin Bieligg, Nadine Liebetrau, Neue Mansfelder Bergwerkschaft GmbH & Co. KG, An der Hütte 6, 06311 Helbra, Germany.

opment of a method – or rather a well-adjusted combination of several methods of mineral processing, metal extraction, and the complete utilization of the remaining non-metalliferous raw materials – thus holds a great potential to increase the raw material efficiency and to supply metals from an alternative source, both in Germany and elsewhere in the world.

2 Initial Approach

The mining of Kupferschiefer in the Mansfeld-Sangerhausen region over a timespan of nearly 800 years (1199 to 1990) left large volumes of dump material, which has recently been analyzed for the recovery of metals. Such a recovery requires a multi-disciplinary approach, which includes an input from various disciplines such as geology/mineralogy, mineral processing, metal extraction and marketing. The mining district has two main types of mine dumps: flat-shaped dumps of either low-grade ore or barren waste rocks and the widely visible conical dumps containing almost exclusively barren waste rock.

An initial geological/mineralogical assessment of the flat-shaped dumps was based on available historical documents. The representative sampling of the dump surface, trenches and drilling was necessary for a reliable data inventory, which characterizes the mineralogical and chemical composition of the low-grade ores. The results from these investigations are the base of the development of a suitable and improved processing technology. The processing has to involve sensor-aided sorting to separate waste from low-grade ore material, thus avoiding unnecessary treatment costs, e.g. from crushing. This separation process needs to be followed by ultra-fine grinding, froth flotation, and hydrometallurgical treatment. The combination of the consecutive steps takes into account the results of the mineralogical and geochemical analysis of the particularly complex low-grade ore.

As a geological characteristic, the black shale of the Kupferschiefer has a relatively high content of organic carbon of up to 15% organic matter (kerogen type II). The use of this energy resource has also to be taken into account. The use (preferentially in the construction industry) of material, which does not contain

base or precious metals but occurs as barren waste in several processing steps, completes the proposed integrated process.

3 Selection and Sampling of Kupferschiefer Mine Dumps

Nine Kupferschiefer dumps in the Mansfeld mining district dating back to between the 1870s and 1940s, were made accessible for research purposes by an agreement with the Society for Custody and Utilization of Disused Mining Operations (GVV mbH). Surficial geochemical screening and mapping were followed by more detailed investigations of the lithological composition, mineralogy and geochemistry as well as mineral processing techniques on material from two mine dumps in the study area (see Fig. 1).

The Theodorschacht (Shaft “Theodor”) dump south of Hettstedt is one of the oldest dumps in the Mansfeld mining district. The dumping of waste ceased in 1898 and has left a dump with a base area of 250 m by 235 m, with a height of 20 m (tonnage: 683 000 m³) [1, 2]. A separately dumped portion of low-grade Kupferschiefer ore of 59 000 m³ has been newly explored and sampled in September 2010 by five 40 cm drill auger holes to obtain samples material at 1 m intervals.

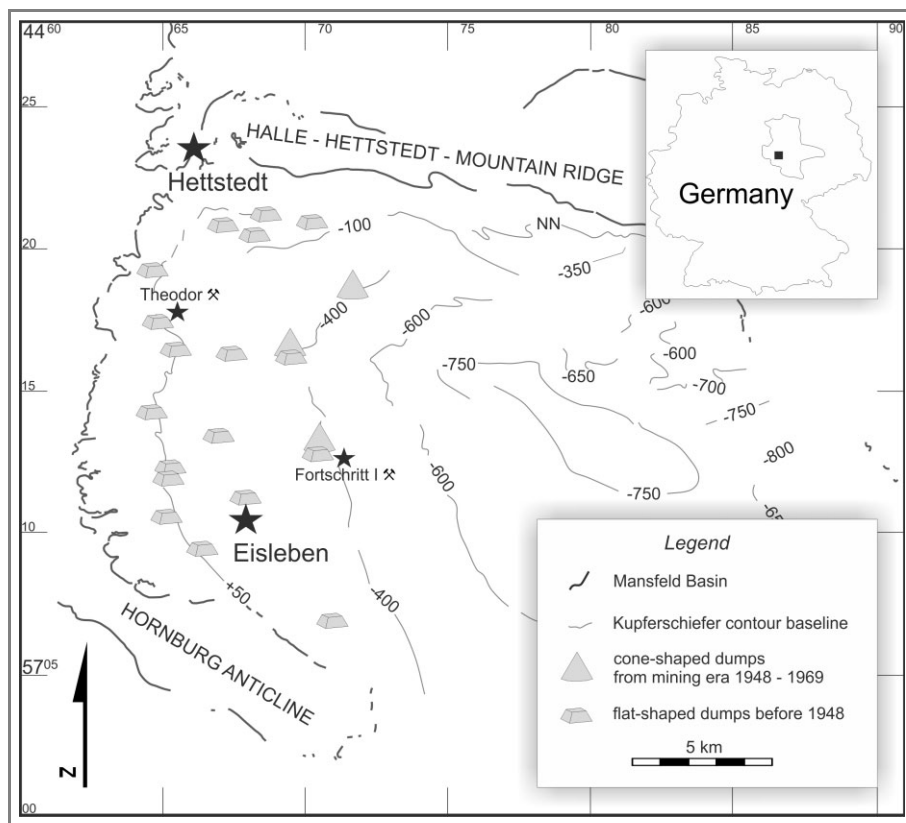


Figure 1. Map showing the location of flat-shaped and cone-shaped Kupferschiefer dumps and corresponding depth of mining in the Mansfeld mining district.

The dump complex of the Fortschrittshacht I (Shaft "Success 1") near Eisleben comprises an older, flat-shaped portion of low-grade ore, which is partially covered by a younger, 153 m high conical waste dump dating from the mining era of the 1950s to 1980s. The entire dump has a total volume of 6 million m³, but consists only of 100 000 m³ low-grade Kupferschiefer ore separately dumped in the flat-shaped portion [2]. The Fortschrittshacht I dump is one of the youngest dumps in the Mansfeld mining district. The shaft had been initially sunk in 1906–1909 for potash mining and the later production of Kupferschiefer ore started in 1923, which left waste and low-grade ore as flat-shaped dumps until 1950 [2]. A part of the low-grade Kupferschiefer ore-bearing flat-shaped dump was investigated in greater detail and had the status of a test dump during the project. Thus, the geochemical and mineralogical investigations were mainly carried out on Fortschrittshacht I dump material that was also primarily used for the mineral processing studies. Additionally, the flat-shaped dump portion has been intersected recently by auger drilling to access and sample an entire vertical dump profile in two bore-holes.

4 Revision of Postulated Contents and Concentrations of the Mining Dumps

For a reliable estimation of the geochemical characteristics of highly heterogeneous material from Kupferschiefer ore dumps a representative sampling method is quite important. For this purpose, so-called bulk samples of 40 to 60 kg were taken. The fine-sized material (<6.3 cm) was sieved, whereas the remaining material was manually separated as hand specimens. After determination of the host rock, i.e., shale, limestone, sandstone, all hand specimens were separately analyzed. The analyses of all sub-samples, i.e., sieved fractions as well as hand specimen, of one bulk sample were used to calculate the mass-balanced average concentration of the whole bulk sample. So far, approximately 600 sub-samples have been analyzed by XRF and 150 sub-samples have been analyzed by ICP-AES, ICP-MS as well as by fire assay followed by ICP-MS.

The results demonstrate the highly variable metal content of the stockpiled low-grade ore. The Cu content fluctuates from virtually barren samples to single samples with up to 12% Cu, which is higher than the previously reported concentration range of the high-grade ore [3]. This demonstrates that published concentration ranges are an unsuitable base for a serious validation of the economic value of the dump material. However, based on 21 bulk samples, consisting of numerous sub-samples, it was possible

to set the following limits of the average base metal content of the Fortschritt I test dump: 0.5–0.6% Cu, 0.56–0.6% Pb, 0.69–0.75% Zn. The majority (>70%) of the base metal content is contained in coarse-sized particles (>1.6 cm), which is a precondition for the successful application of automated sensor-based sorting techniques (see below). The mineralized hand specimen consists predominately of shale (approx. 80 wt%) and subordinate of limestone (approx. 18%), whereas the occurrence of other host rocks is negligible (<2%).

It is well known that the Kupferschiefer shows elevated to anomalously high concentrations of several minor and trace elements and some of these elements have also been industrially recovered. In order to evaluate the importance as potential by-products the concentrations of these elements were determined. Unfortunately, only ranges of concentrations of these elements have been reported in previous publications and in the case of precious metals, only maximum values are known [3]. In Fig. 2, the concentrations of selected trace elements in the low-grade ores and related averages are compared with previously reported values of these elements from high-grade ores [3]. Although the values of the low-grade ores are generally lower, some Mo concentrations from the analyzed low-grade ores exceed the range of concentration of the high-grade ores, which again shows the limited significance of the published concentration ranges.

As a consequence, it is more important to evaluate if these elements are contained in the ore minerals, i.e., within the sulfides, or not. Surprisingly, this approach has not been chosen for material from the former mining districts

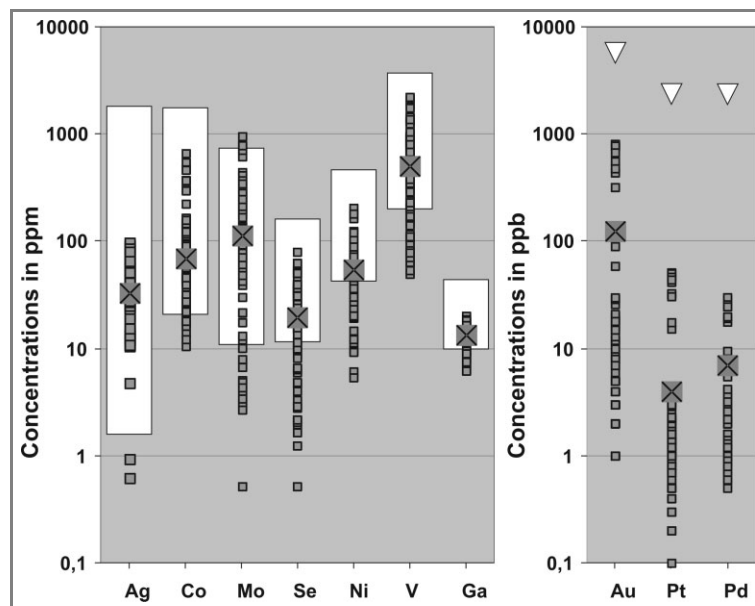


Figure 2. Showing concentrations of analyzed low-grade Kupferschiefer ores (small squares) and related averages (squares with crosses) in comparison to previously reported values for high-grade ores in [3]: Ranges of concentration (white-filled rectangles) or maximum values (triangle), respectively. See text for further explanations.

of Mansfeld and Sangerhausen. The reasons for this might be seen in the pyrometallurgical process of historical beneficiation, i.e., the lack of separation between ore and gangue minerals prior to smelting. In order to present the affinities of some selected elements, the elements will be subdivided into the following groups: 1) related to copper sulfides, 2) related to other sulfides, 3) related to organic carbon and aluminosilicates, 4) precious metals:

- 1) Only Ag and (less pronounced) Co show a positive linear correlation with Cu, which shows that both elements are predominately incorporated into the Cu sulfides, which are – in order of decreasing importance – bornite (Cu_5FeS_4), chalcopyrite (CuFeS_2), and chalcocite (Cu_2S), which is in good agreement with previously reported results of the Polish and German deposits [4, 5]. As a consequence, only Ag and Co will be enriched by a separation between Cu sulfides and gangue minerals as well as remaining sulfides.
- 2) The remaining sulfides predominately consist of galena (PbS), sphalerite (ZnS), and pyrite (FeS_2). Especial the latter can contain significant amounts of Co, Ni, Mo, and Se. Consequently, these elements will be enriched during an unselective sulfide flotation between sulfides and gangue minerals. However, it should be noted that Se and Ni can be partly related to the organic carbon content. Ni porphyrins have been found in significant amounts in low-grade mineralized Kupferschiefer of the Lower Rhine Basin [6], whereas the content of such organometallic compounds in the Cu-mineralized Polish Kupferschiefer is variable [4, 6–9].
- 3) It is well established that V is closely related to the organic carbon content of the Kupferschiefer and other black shales. At least in parts this element can be bound to vanadyl porphyrins [6, 7, 10, 11], although it is not possible to preclude that it was also incorporated into aluminosilicates (clay minerals like illite) during diagenesis (i.e. lithification) of the host rock [11]. The organic carbon compounds as well as the aluminosilicates are gangue minerals of the host rock. Consequently, enrichment by adequate sulfide flotation cannot be expected for V, because it is not incorporated in the sulfides. Thus relatively high contents of organic carbon (7.63% TOC) and V (854 ppm) of a sulfide concentrate of the active Polish Kupferschiefer mine at Lubin with a combined base metal content of approx. 22% [12] show that this concentrate still contains a significant amount of gangue minerals and this can be interpreted as a kind of contamination.
- 4) The analyzed samples generally contain only background values of Au (< 5 ppb) and PGE (< 4 ppb), with few samples containing between 20 and 90 ppb Au. However, initial analyses of the sieved fractions revealed significantly higher Au and – to a lesser extent – Pt and Pd concentrations. The nine sieved fractions between 1.6 cm and the clay fraction (< 63 μm) all contain between 300 to 800 ppb Au (17–51 ppb Pt, 9–30 ppb Pd), whereas sie-

ved fractions larger than 1.6 cm feature low concentrations like those reported above. These new results document local but apparently highly irregular precious metal mineralization in the dump material. The Au-bearing sampling sites at the active Polish Kupferschiefer mines [4, 13, 14] as well as those of the former deposit of Sangerhausen [15] occur in rocks that have undergone secondary oxidation (Rote Fäule) or are situated in the direct vicinity to the redox front. Thus the erratic nature of Au-bearing dump material might be seen as a further indication of the epigenetic nature of the mineralization [16]. Although it was not possible to identify the individual precious metal bearing minerals, the striking similarities to the Polish deposit suggest that the high Au values might be related to natural alloys [4, 13, 14]. Nonetheless, the overall low precious metal concentrations, their erratic distribution, and the unknown mineralogy preclude the possibility to design a systematic beneficiation process that exclusively aims for the precious metals.

5 Process Development and Optimization

In this project a selective processing sequence has been developed (Fig. 3), which is discussed extensively in the following sections.

5.1 Sensor-Based Sorting

Sensor-based sorting is an automated hand picking process, which is based on certain sorting criteria. Today fast computerized digital processing and high resolution scanners permit high throughputs and a processing of coarse particle sizes of up to 250 mm [17].

Fig. 4 shows the functional principle of sensor-based sorting and its main sub-processes. There are numerous sensor techniques, each of which detects a different feature and is suitable for a specific sorting task. For the Mansfeld Kupferschiefer dump material, sensors working in the NIR electromagnetic spectrum as well as CCD color cameras, XRF and XRT sensor have been tested and here, the latest test results of the CCD and XRF sorting tests are summarized. Optical sorting with CCD sensors is the one sensor-based sorting technique that is best comparable to the human eye. Color scanners detect minor differences in color, brightness, reflection, or transparency. Regarding the Kupferschiefer dump material from the Fortschrittschacht I, the sorting criteria for a distinction between copper-rich and copper-poor rocks is the green coating originating from surface oxidation of the copper sulfides.

The results of the optical sorting tests are summarized in Tab. 1. In a single sorting step the CCD sorting software is able to discharge 66% of predominantly barren waste rock with a loss of copper recovery of 25%. The overall copper grade of the 20 to 50 mm material portion can be upgraded

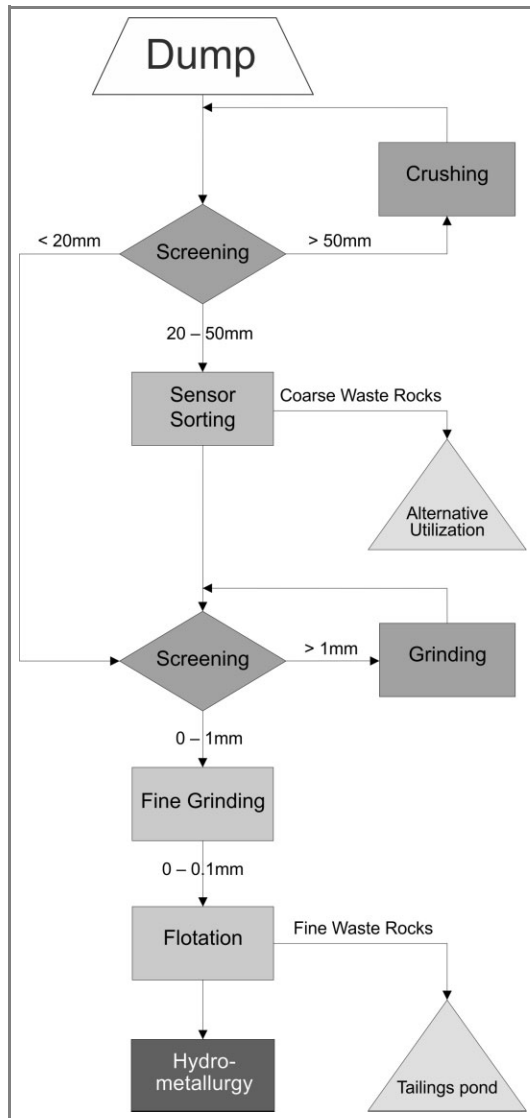


Figure 3. Generalized flow sheet of the possible utilization of low-grade Kupferschiefer ore and waste from the Mansfeld mining district shows the processing path from source to product. Process stages are described in detail in Section 5 and 6.

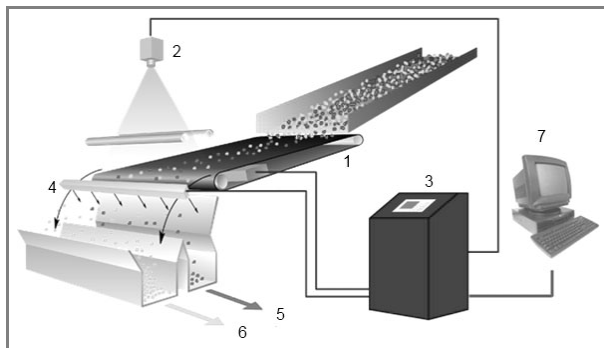


Figure 4. Functional principle of a sensor based sorter [18]. (1) Material conditioning, (2) scanner, (3) data processing unit, (4) mechanical sorting device, (5) rejected product, (6) accepted product, (7) control unit.

Table 1. Mass streams, Cu recovery and -grade by optical sorting.

| | Waste | Concentrate | Total |
|-----------------|-------|-------------|-------|
| Mass [%] | 66 | 34 | 100 |
| Cu recovery [%] | 24.71 | 75.29 | 100 |
| Cu grade [%] | 0.32 | 1.87 | 0.85 |

significantly from 0.85 % to 1.87 %; which more than doubles the metal grade.

The X-ray fluorescence (XRF) technique of pulverized rock samples is an established method of elemental composition analysis. Since 2011 Tomra Sorting Solutions, provider of sensor-based sorters, offers the first industrial XRF sorter called the TITECH x-tract for recycling applications. In 2011 the Department of Mineral Processing of the RWTH Aachen University ran a series of mineral application tests, including Kupferschiefer ore samples on such a machine. After a phase of initial calibration, the sorter was able to detect the copper grade of single rock particles with an accuracy of over 95 %, compared to stationary XRF analysis. The machine is not ready yet for medium-scale throughput test, but offers great near-future potential in the process of sensor-based sorting with the actual element grade as the sorting criteria.

5.2 Flotation

Until the end of mining of the Mansfeld Kupferschiefer ore in 1990, the ore was selectively mined and smelted directly to gain the copper [2]. Because of the very finely disseminated sulfide ore minerals, the mineral processing of the Mansfeld Kupferschiefer has been known as a challenge ever since. Mineral liberation analyses (MLA, including scanning electron microscopy with energy dispersive X-ray spectroscopy), as well as ore microscopic investigations reveal particle grain sizes of the copper sulfides in the range of 2 to 100 μm , mostly within the range of 10 to 40 μm . An aggravating factor in processing the Mansfeld Kupferschiefer ore is that gangue minerals basically consist of quartz (40 wt %), carbonates (20 %), clay minerals (30 %), and bituminous compounds (3 %).

Due to the finely intergrown nature of the ore and gangue minerals, a separation by density is not possible. Also direct leaching of the copper-bearing shale has proven to be difficult because of the partially high content of organic carbon particles (bitumen). Hence, flotation is the method of choice to produce a pre-concentrate for the subsequent metallurgical processes. However, the flotation process has to be optimized regarding known problems in the flotation of fines. First, the probabilities of the particle-bubble collision and -contact are lower than in the flotation of coarser-grained material. Additionally, entrainment can result from low inertia force and high specific surfaces entailing excessive adsorption of reagents [19]. Especially clay minerals

with their capability to intercalate ions make it difficult to sustain stable conditions (e.g. pH value) during flotation. Particularly the Kupferschiefer has the problem of unselective flotation (referring to gangue minerals) since hydrophobic bitumen particles adhere to gangue minerals due to physicochemical forces.

The flotation tests were carried out using material originating from the Fortschrittsschacht I dump, which was preselected in respect to the Cu grade. This material was sized up to 50 mm in diameter and had a copper-content of about 1%. In preparation of the flotation tests, the material was crushed by jaw crushers and subsequently grinded in a ball mill.

The flotation tests were carried out in a lab-scale flotation machine, type Denver (modified for adjustable air flow rate). The aim of the flotation tests was to gain a concentrate with a high copper content. The procedure to perform the flotation tests consists of suspending the material, adjusting pH value, adding dispersant, collector and frother and, after a certain time of conditioning, eventually starting the air inlet and froth skimming. In the end, the flotation products were dried, weighed, and finally prepared for chemical analyses. Initially, flotation tests were executed to scan numerous combinations of reagents and pH values. After the optimum was found (30% solid content; pH 10; 100 g t⁻¹ polyacrylate; 300 g t⁻¹ potassium amyl xanthate; 150 g t⁻¹ mix of alkyl polyglycol ether and alcohol), it was determined, which particle size of the material led to best flotation ratios. The tests showed that the best results were achieved with material grinded to just 100 μm. The flotation of material with further reduced particle sizes (75 and 25 μm, respectively) was less successful.

To adapt the flotation to the large fraction of finest particles in the material – 100 μm (Q20 = 55%), further tests for agglomeration flotation were carried out. Previous investigations showed promising results and indicated the advantage of the pH independence of this kind of flotation [20]. For agglomeration flotation, relatively high amounts of nonpolar oil (2–50 kg t⁻¹) were added to the flotation suspension [21].

The agglomeration flotation tests have shown an increase in copper recovery of about 20%, attended by a lower enrichment coefficient of 1.7. Considering the entailing higher costs, the results of the agglomeration flotation do not justify the addition of nonpolar oil to the flotation of Mansfeld Kupferschiefer.

Fig. 5 illustrates that a flotation time of about 25 min would be necessary to ensure a copper recovery of 80%. To avoid the dilution of the concentrate, the residence time during the rougher flotation should be 10 min and further flotation stages should follow. To float the Mansfeld Kupferschiefer, different paths can be taken to achieve the best possible results. On the one hand, the whole material could be introduced to the sulfide rougher flotation and the concentrates are cleaned in several following flotation stages (three stages in cleaner and scavenger flotation each). This would result in a relatively high bitumen content of about 18% in the copper concentrate. To avoid such a high bitumen content, the sulfide rougher flotation could be preceded by a separate bitumen flotation, thus reducing the bitumen in the copper concentrate to 8%.

So far, it has not been possible to produce a marketable copper concentrate, which meets the requirements of international operating copper mills. More efforts in a technical expedient and an economical way have to be made to gain the floatable copper sulfides. Therefore future investigations focus on the higher flotation selectivity as well as the separation of carbonaceous compounds. More efforts in a technical expedient and an economical way have to be made to gain the floatable copper sulfides. Therefore future investigations focus on the higher flotation selectivity as well as the separation of carbonaceous compounds.

5.3 Hydrometallurgical Treatment of Flotation Concentrate

Subsequent to the previously explained grinding and flotation steps the concentrate contains 2–10% Cu, 3–6% Zn,

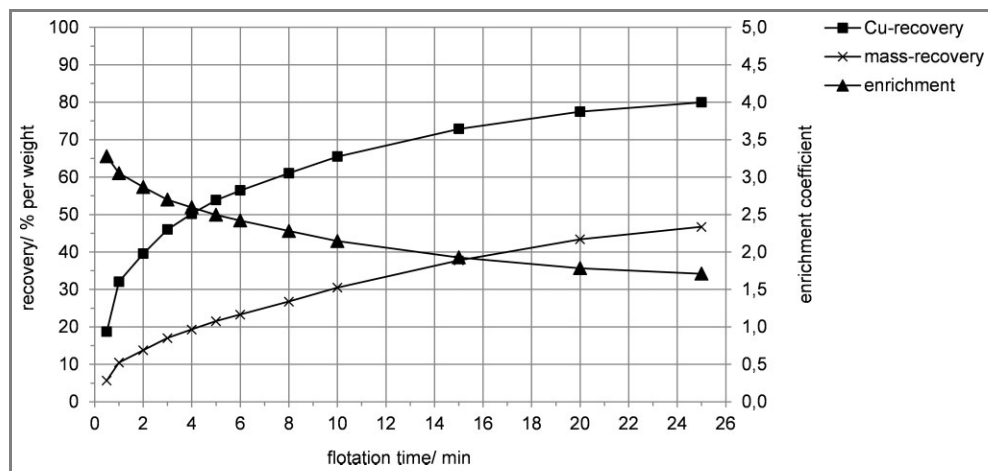


Figure 5. Kinetics of the sulfide rougher flotation of Mansfeld Kupferschiefer ore.

1–2% Pb and up to 800 ppm Ag. Aim of the following extraction steps is to gain intermediate products, which contain the metals mentioned above. As the content of valuable metals is lower than in conventional concentrates a simple and low cost extraction process is needed. Pyrometallurgical processes are generally characterized by high energy consumption unless the contained sulfur generates an autothermic process. However, this is not applicable due to the low sulfur content in the here applied ore. Compared to hydrometallurgical extraction steps, the selectivity is low in consequence of the high reaction rates [22].

Hydrometallurgical processes on the other hand are well suitable for materials containing only a small amount of valuable metals. The first step in hydrometallurgical processing is to dissolve the target metals by appropriate solvents. The dissolving of undesired metals should be avoided, since this would increase the chemical consumption and costs. In cases where valuable metals accrue as sulfides, a pyrometallurgical conditioning step like roasting might be recommendable. Test trials with the present Mansfeld Kupferschiefer ore have shown that an acidic solvent is needed for the leaching step; otherwise neither sulfides nor sulfates or oxides are dissolved in noteworthy amounts as can be seen in Fig. 6 [22, 23].

Sulfuric or hydrochloric acids are known to be most efficient for treating sulfide copper ores. H_2SO_4 , HCl, H_2O and NH_3 have been used as solvents during the experiments to leach Kupferschiefer ore containing 10% Cu. The extraction process has been carried out for 24 h at 50 °C. The used material had three modifications: the original Kupferschiefer ore and two which have been pretreated by roasting. Even though the roasted materials have achieved a higher yield of dissolved Cu, the use of unroasted material might

be preferred due to the energy amount spent for roasting processes, if it is not an autothermic process. However, the dissolution of silver only seems to be possible after roasting at 900 °C.

A promising alternative to reduce the costs for the leaching agent is a nitric acid solution (not represented in Fig. 6), which is a waste product in other industrial processes such as the etching of wafers. First experiments have shown that up to 80% of the contained Cu can be dissolved using this alternative leaching agent. However, these preliminary data have to be validated by subsequent experiments with varying parameters. The aim is to combine two waste streams, one being the mine dump material and the other being the waste nitric acid. This will allow a significant reduction of acid costs and – simultaneously – a more sustainable use of all raw materials involved in the process. After dissolving the elements, a second step in hydrometallurgical extraction is the precipitation as a metal or as marketable compound. To continue the concept of bringing together different waste streams, a cementation process should take place, which is robust, cost-saving, and can easily be established on a small scale [24]. Cementation is based on the different standard electrode potential of elements. Adding a less noble metal to a solution results in dissolving this metal and it precipitates a nobler one. Iron scrap or zinc dust can be used as precipitation agent for Cu. By adding a hyper stoichiometric amount of iron swarf to the hydrochloric acid solution, first results have given a decreasing of the dissolved Cu down to $<0.1 \text{ g L}^{-1}$. This cementation process has to be optimized in further experiments. However, the final treatment of the so produced iron containing solution has to be clarified as this is not a disposable product [25].

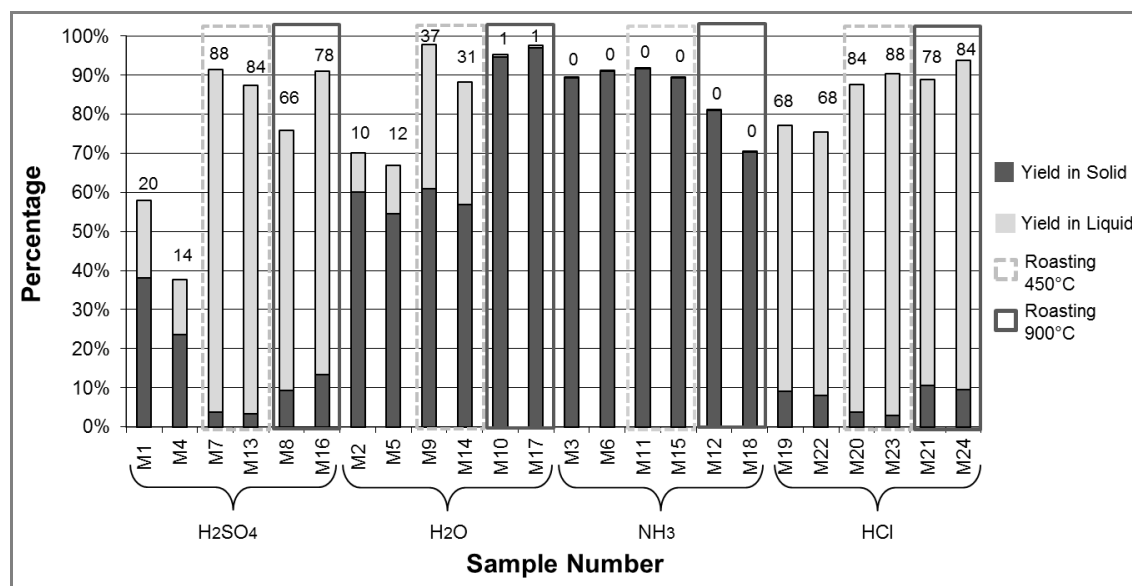


Figure 6. Mass balance of Cu in different solvents with varying pretreatment of the material.

6 Optimized Metal Recovery by Alternative Processing and Utilization of Kupferschiefer Dump Material

6.1 Metal Extraction by Bioleaching

Studies on the processing of low-grade Kupferschiefer dump material by bioleaching were already undertaken in the late 1970s by the German Federal Institute for Geosciences and Natural Resources (BGR) [29–31]. The investigations were implemented in laboratory and pilot scale with percolator experiments to simulate heap bioleaching as well as shake flasks experiments for tank leaching with maximum recovery of 80% Cu [29]. Further work regarding to bioleaching of Kupferschiefer material within the Bioshale project of the 6th European Union Framework Program on Research and Development led to recovery rates of up to 98% Cu by leaching of Polish Kupferschiefer middlings and concentrates in reactor tanks [32].

To examine the potential of bioleaching for the Mansfeld-type Kupferschiefer dump material and verify the previous results, three presorted samples consisting of Zechstein carbonates, Kupferschiefer shale and Weißliegend sandstone were provided for bioleaching tests at the German Federal Institute for Geosciences and Natural Resources (BGR). The samples were crushed, milled, analyzed mineralogical via X-ray diffraction and whole rock chemistry by XRF-analysis. The carbon and sulfur contents were determined by combustion infrared detection technique (LECO elemental analyzer).

Overall, all three samples were characterized by an elevated content of Cu (Zechstein carbonates = 1.74%; Kupferschiefer shale = 7.49% and Weißliegend sandstone = 4.69%) and a significant proportion of carbonate.

Ground samples were bioleached in three parallel experimental approaches as previously described [33, 34]. The bioleaching assays were inoculated with a pregrown mixed culture consisting of the acidophilic Fe(II)-, sulfur- and organic carbon-oxidizing bacteria *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Acidiphilium* spp. (strains Ram 8T and Ram 6F from the bacterial strain collection of the BGR). Each experimental assay was performed in a 500-mL Erlenmeyer flask by adding 2% ore in 200 mL mineral medium [35] and 50 mg L⁻¹ Fe(II). The tests were started by inoculation of the bacterial strains with incubation on orbital shakers in the dark at 30 °C. In one control assay, a mixture (2 vol. %) of thymol and methanol (1:9) was added to sterilize the solution; another assay ran blank without inoculation, both assays in order to evaluate chemical acid leaching for comparison. Evaporation losses were compensated by addition of deionized water. The pH values were intensely monitored during the first few days and adjusted with sterile 3M H₂SO₄ to pH 2.5.

The recovery of Cu and Zn in the inoculated bioleaching assays was significantly higher than that in both control assays for all three samples. The residue analysis of the bacterial strain inoculated assays yielded recovery rates of up to

95% and 85% for Cu and Zn, respectively. The recovery rates were even higher according to the analyses of the dissolved metals in the solution.

These first results on bioleaching of Mansfelder Kupferschiefer heap material open the door for an alternative processing of these low-grade ores, which occur as an abundant deposit in the area. Further work should address an optimization and a scale-up of bioleaching embedded in an integrated concept of an intelligent combination of ore processing technologies. The final goal is the industrial application of a new low-cost, low-energy processing technology for metal recovery from low-grade ores, especially Cu from Kupferschiefer.

6.2 Potential Utilization of the Barren Waste Fraction

Beside the extraction of metals from the Kupferschiefer dumps, it is also the aim of this project to investigate the physical properties of the barren waste fractions (limestone and sandstone/conglomerate), according to the statutory guidelines provided by the German Closed Substance Cycle and Waste Management Act [26].

The investigation has a two-fold approach. In a first approach has been tested the tailings for its potential technical and industrial use. As displayed in Fig. 3, the application of sensor-based sorting of the low-grade Kupferschiefer ore produces dry and large particles of mineral waste. The primary characteristics of the waste rocks, which have been dry-sorted and have a defined particle size of 20 to 50 mm, have a significant marketing potential for further utilization such as aggregate for road construction or as filling material in different technical applications.

The waste rocks were chemically analyzed according to the parameters of the German directive of *construction material regulations* in order to validate possible utilization options [27]. The results indicate that the metal content in the soluble fraction exceed the statutory limits for Pb, Cu, Cd, Zn and sulfate, respectively. Thus, the waste from mineral processing is a product with no options for utilization, according to the above mentioned regulations.

The second approach focuses on the predominant portion of the Mansfeld Kupferschiefer dumps consists of barren waste material, which are mainly Zechstein lime- and dolostones with minor volumes of anhydrite. Representative samples from the Theodorschacht dump near Klostermansfeld (Fig. 1) have been analyzed. The test results show that a utilization, according to the directive *construction material regulations* [27] is possible. The material can be recycled for technical construction and for the potential application in road construction, filling material, or frost protection layers. Further standardized tests will assess the mechanical and weathering resistance, compressibility, and environmental compatibility with respect to mineral recycling opportunities. These test results are currently still pending.

6.3 Alternative Grinding Techniques by Vertical Roller Mills

Vertical roller mills (VRM) are dry operating mills, traditionally used in the cement industry. Basically, the material to be comminuted is crushed and ground between the rotating grinding track and the stationary grinding rollers in an in-bed comminution. Depending on the mill size, it is possible to feed material with feed sizes up to 150 mm. It is possible to choose between different comminution principles, either a combination of compressive and shear stress or shear-free grinding with pure compressive comminution.

The freshly ground material is pneumatically transported by the air flow sucked through the mill up to an air classifier, where finished product is separated from the grits. The rejected grits – material coarser than product fineness – are fed back to the mill. If drying is required, the air flow is heated by a hot gas generator.

The standard aggregate for fine grinding in mineral applications down to flotation size ($< 100 \mu\text{m}$) is a ball mill. In cooperation with the Loesche GmbH, Düsseldorf, the possible advantages of a dry grinding with VRM have been tested in respect to conventional ball mill grinding.

The Bond Work Index for grinding the low-grade Kupferschiefer ore is 12.8 kWh t^{-1} . Therefore, a specific energy consumption to gain a product $< 100 \mu\text{m}$ by grinding in a ball mill of 13.1 kWh t^{-1} (wet operated mill) and 17.1 kWh t^{-1} (dry operated mill), respectively, would be necessary. However, the dry operating VRM consumes 7.2 kWh t^{-1} and produces a higher amount of finest particles compared to the ball mill product.

7 Market Potential and Sales Opportunities to the Smelting Industry

As a result of the multi-disciplinary study, the process flow sheet shown in Fig. 3 has been developed. Cu, Pb, Zn and Ag were identified as marketable metals. Certain concentration of minor metals as Mo (up to 930 ppm), Co (up to 640 ppm), Se (up to 77 ppm) and Ni (up to 198 ppm) may act as sweetener. Unfortunately, precious metals, rare earth elements or minor metals do not occur in the concentrates in sufficient concentration.

The value and operational balance of the marketable metals have been simulated in a computer program. The mass flow, recovery of the metals, and treatment costs are determined for each processing step. For the dump material, the intermediate products, concentrates and tailings, the metal contents, and their value at the London Metal Exchange are determined and compared with the production costs. Thus, the individual process steps are combined into an integrated processing model, which allows an evaluation of the expected profitability of the process.

The currently proposed integrated model for an integrated treatment process can be easily modified or extended to

other metals and process steps, so that process variations and improvements can be evaluated quickly.

Based on the available analytical results and in a best-case scenario, the $100\,000 \text{ m}^3$ of low-grade Kupferschiefer ore from the pilot dump at Fortschrittschacht I can be processed to produce estimated 900 t Cu and 5 t Ag, contained within in black copper, plus additional 600 t Zn and 500 t Pb concentrate. The black copper and the lead concentrate can be sold to European smelters. The zinc is marketed as finished good directly to the end consumers. The total recoverable value of the pilot dump can be estimated to be 10 Mio. €.

Abbreviations

| | |
|---------|--|
| CCD | charge-coupled device |
| ICP-AES | inductively coupled plasma atomic emission spectroscopy |
| ICP-MS | inductively coupled plasma mass spectroscopy |
| NIR | near-infrared |
| PGE | platinum group elements |
| SEM/EDX | scanning electron microscopy with energy dispersive X-ray spectroscopy |
| TOC | total organic carbon |
| XRF | X-ray fluorescence |
| XRT | X-ray transmission |

This study is supported by the funding priority r^2 “Innovative Technologies for Resource Efficiency – Resource-Intensive Production Processes“ of the German Federal Ministry for Education and Research (BMBF).

References

- [1] www.kupferspuren.eu
- [2] *Mansfeld – Die Geschichte des Berg- und Hüttenwesens*, Verein Mansfelder Berg- und Hüttenleute e.V., Lutherstadt Eisleben 1999.
- [3] J. Hammer, H. J. Rösler, S. Niese, *Z. Angew. Geol.* **1988**, *34*, 339–343.
- [4] S. Oszczepalski, *Miner. Deposita* **1999**, *34*, 599–613.
- [5] G. Knitzschke, *Freiberg. Forschungsh. C* **1966**, *207*, 1–147.
- [6] W. Püttman, W. J. J. Fremont, S. Speczik, *Ore Geol. Rev.* **1991**, *6*, 563–579.
- [7] Z. Sawlowicz, *Miner. Polon.* **1985**, *16*, 35–42.
- [8] F. Czechowski, in *Organic Matter and Mineralization: Thermal Alteration, Hydrocarbon Generation, and Role in Metallogenesis* (Eds: M. Glikson, M. Mastalerz), Kluwer Academic, London **2000**, 243–259.
- [9] A. Szubert, Z. Sadowski, C. P. Gros, J. M. Barbe, R. Guillard, *Miner. Eng.* **2006**, *19*, 1212–1215.
- [10] A. Bechtel, R. Gratzner, W. Püttmann, S. Oszczepalski, *Chem. Geol.* **2002**, *185*, 9–31.

- [11] G. N. Breit, R. B. Wanty, *Chem. Geol.* **1991**, *91*, 83–97.
- [12] J. Gouin, T. Augé, L. Bailly, P. D'Hugues, J.-R. Disnar, D. Kervis, in *Digging Deeper, Proc. of the Ninth Biennial SGA Meeting* (Eds: C. J. Andrew et al.), Vol. 1, Irish Association for Economic Geology, Dublin **2007**, 269–272.
- [13] J. Pieczonka, A. Piestrzynski, J. Mucha, A. Głuszek, M. Kotarba, D. Wieclaw, *Ann. Soc. Geol. Pol.* **2008**, *78*, 151–280.
- [14] A. Piestrzynski, J. Pieczonka, A. Gluszek, *Miner. Deposita* **2002**, *37*, 512–528.
- [15] S. Walther, G. Borg, B. C. Ehling, in *Smart science for exploration and mining* (Eds: P. J. Williams et al.), Vol. 2, The Society for Geology Applied to Mineral Deposits, Genf, **2009**, 502–504.
- [16] G. Borg, A. Piestrzynski, G. H. Bachmann, W. Püttmann, S. Walther, M. Fiedler, in *Geology and Genesis of Major Copper deposits and Districts of the World: A Tribute to Richard Sillitoe* (Eds: J. Hedenquist, M. Harris, F. Camus), Society of Economic Geologists, Littleton, CO **2012**, in print.
- [17] H. Wotruba, H. Harbeck, in *Ullmann's Encyclopedia of Industrial Chemistry: Sensor-Based Sorting*, Wiley-VCH, Weinheim **2010**.
- [18] H. Wotruba, in *Proc. of XXIII Int. Mineral Processing Congress* (Eds: G. Önal et al.), Promed Advertising Agency, Istanbul **2006**.
- [19] W. J. Trahar, L. J. Warren, *Int. J. Miner. Proc.* **1976**, *3* (2), 103–131.
- [20] H. Schubert, J. Schmidt, *Bergakademie* **1963**, *15* (12), 850–855.
- [21] J. Liu, T. Mak, Z. Zhou, Z. Xu, *Miner. Eng.* **2002**, *15* (9), 667–676.
- [22] F. Habashi, *Textbook of Hydrometallurgy*, 2nd ed., Métallurgie Extractive Québec, Québec City **1999**.
- [23] W. G. Davenport, M. King, M. Schlesinger, A. K. Biswas, *Extractive Metallurgy of Copper*, 4th ed., Elsevier Science, Oxford **2002**.
- [24] F. Pawlek, *Metallhüttenkunde*, de Gruyter, Berlin **1983**.
- [25] *Winnacker-Küchler: Chemische Technik. Prozesse und Produkte* (Eds: R. Dittmeyer et al.), Vol. 6, 5th ed., Wiley-VCH, Weinheim **2006**.
- [26] *Gesetz zur Vermeidung, Verwertung und Beseitigung von Abfällen* (BGBl. I Nr.66), German Federal Ministry of Justice, Bonn **1994**.
- [27] *Anforderungen an die stoffliche Verwertung von mineralischen Reststoffen/Abfällen*, 5h ed., Länderarbeitsgemeinschaft Abfall, Erich Schmidt-Verlag, Berlin **2003**.
- [28] DIN 38414-4, *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung: Schlamm und Sedimente (Gruppe S); Bestimmung der Eluierbarkeit mit Wasser (S 4)*, Beuth Verlag, Berlin **1984**.
- [29] K. Bosecker, *Bakterielle Laugung deutscher Kupferschiefervorkommen*, Final report, **1976**.
- [30] D. Neuschütz, U. Scheffler, K. Bosecker, *Bakterielle Laugung deutscher Kupferschiefervorkommen*, Final report, Krupp Forschungsinstitut, Essen **1976**.
- [31] K. Bosecker, *Bakterielle Laugung von Armerzen unter Einsatz von Submersverfahren*, Final report, **1981**.
- [32] <http://bioshale.brgm.fr/>
- [33] K. Bosecker, *Microbial Leaching*, in *Fundamentals of Biotechnology* (Eds: P. Präve, U. Faust, W. Sittig, A. Sukatsch), Verlag Chemie, Weinheim **1987**, 661–683.
- [34] A. Schippers, K. Bosecker, in *Methods in Biotechnology* (Ed: J. L. Barredo), Vol. 18, Humana Press, Totowa **2005**, 405–412.
- [35] W. W. Leathen, L. D. McIntyre, S. A. Braley, *Science* **1951**, *114*, 114–115.