



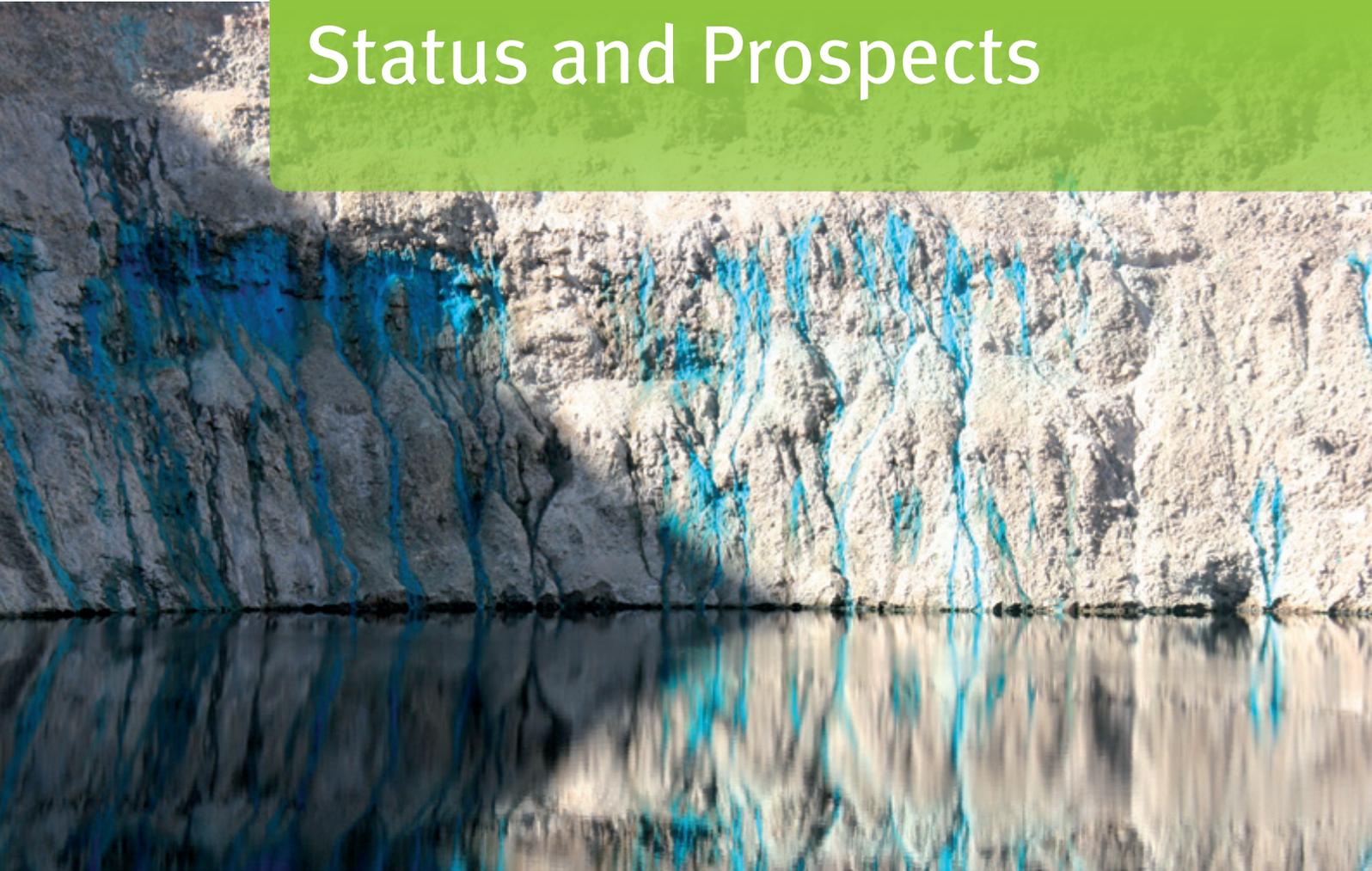
DECHEMA

Gesellschaft für Chemische Technik
und Biotechnologie e.V.

STATUS PAPER

Geobiotechnology

Status and Prospects



Foreword	4
1. Biomining – Mining with bacteria (Primary raw materials)	5
2. Mining heaps – Remediation or a depot for recyclable materials?	10
3. Metal-containing mining waters – Avoidance, waste or raw material?	15
4. Metal-containing residues from industry and the environment – biotechnological reprocessing	23
5. Geomicrobiology underground – opportunities for geobiotechnology	29
6. Training in biotechnology	34
7. Network structures at State, Federal and EU level	42
References	45
List of authors	49

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Non-renewable raw materials such as metals and fossil energy resources are needed increasingly due to the global growth of the population and the economy. It will not or only partially be possible to replace them in the foreseeable future by renewable raw materials. Due to its raw material situation, Germany is largely dependent upon imports of metals, selected chemical raw materials and rare earths, as well as energy commodities such as crude oil and coal. In Germany and Europe in general, a high degree of importance is therefore attached to raw material efficiency and the environmentally sound extraction and processing of local raw materials, as well as the recycling of raw materials. In this respect, geobiotechnology can make an important contribution.

The subject geobiotechnology deals primarily with the use of microbial processes in mining and the protection of the environment. Microorganisms control to a large extent the natural biogeochemical cycles. Thus, they play an important role in the formation and alteration of metal, oil, coal and phosphate deposits. The diverse interactions between microorganisms and raw materials in mining-specific ecosystems form the basis for the efficient extraction of resources using bio-mining techniques (bio-leaching, bio-organic extraction, bio-mineralisation) or „microbial enhanced oil and gas recovery“ (MEOR), as well as for remediation activities in mining areas (bioremediation). Microbial processes can also be used for raw material recycling. Furthermore, geobiotechnology deals with bio-geochemical processes in the deep, geological underground, which is used for the storage of raw materials and waste, or for geo-thermal purposes.

In 2011, the Temporary Working Group for Geobiotechnology was founded within the DECHEMA e.V. with the aim of pooling the activities of geobiotechnology within Germany (and Europe) and to provide an impetus for further developments. The German edition of the present status report was prepared in 2013 by the working group and summarizes the state of geobiotechnology with a main focus on Germany and makes recommendations for the needs of research in geobiotechnology.

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1 Biomining – Mining with bacteria (Primary raw materials)

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Introduction

For about 10,000 years, people have been extracting metals from mineral ores. The ores of the metals copper, nickel, cobalt, lead and zinc occur mainly as metal sulphides in nature. Under normal environmental conditions, metal sulphides are insoluble even in weak acids. Therefore, sulphide ores are mostly enriched using flotation processes to give concentrates, from which the crude metals are then smelted using pyrometallurgical techniques.

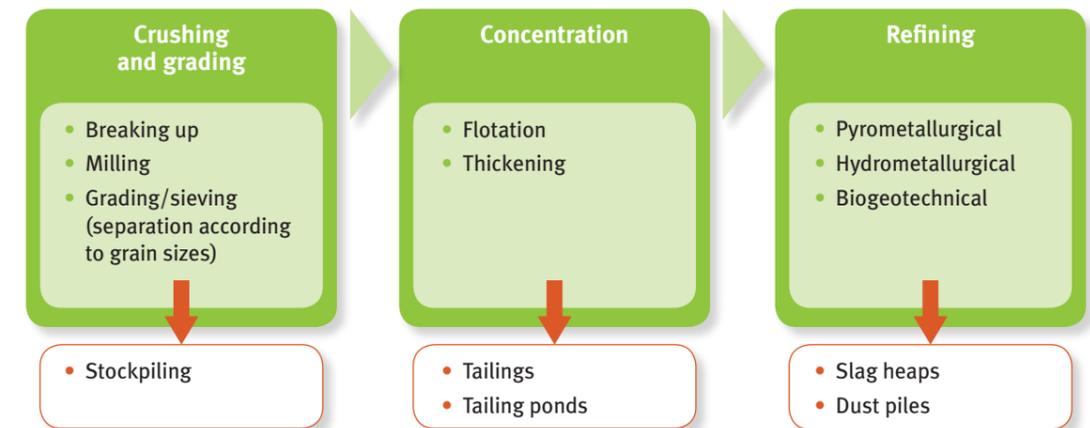


Fig. 1: Schematic diagram of ore preparation processes and incidental flow of by-products

An eco-friendly and economical alternative for low-sulphide ores, whose metal sulphides cannot be economically enriched by flotation, is to extract the metals using microorganisms. This procedure is called bio-mining. Bio-mining is a well-established biotechnology, which is used also throughout Europe.

The fact that bio-mining has spread worldwide in the last few years is due to several factors: Firstly, progress has been made in the construction of plants, in the development and operation of heap leaching processes, as well as their process design and implementation. On the other hand, the amount of knowledge on the microorganisms involved in these processes and the conditions under which they work best has grown to such an extent that bio-mining can now successfully compete with hydro-metallurgical chemical processes.

In bio-mining, the ores are “leached”. Bio-leaching is the biological conversion of an insoluble metallic compound into a water-soluble form. In the case of the bio-leaching of metal sulphides, these are oxidized in acidic solution by acidophilic aerobic Fe(II) and/or sulphur-compound oxidizing bacteria or archaea to metal ions and sulphate.

Important types of leaching bacteria are, for example, *Acidithiobacillus ferrooxidans* (previously *Thiobacillus ferrooxidans*) and *Leptospirillum ferrooxidans*. The oxidizing agent Fe(III) for metal sulphides originates from microbial iron (II) oxidation. In metal sulphide oxidation, sulphur compounds and elementary sulphur arise; they are transformed by microbial oxidation into sulphuric acid, thereby creating an acidic environment. During the bio-leaching process, depending upon the sulphide content of the ore, large quantities of iron sulphates, and dilute sulphuric acid may arise, which have to be precipitated out or neutralized as part of the required disposal. So far, it has not been possible to achieve adequate treatment of these residues technically.

Nowadays, the extraction of copper from low-grade ores mined is the most important industrial application of bio-mining, and a significant part of the global copper production already comes from the bio-leaching of mining heaps or stockpiles. Bio-mining is also used for the extraction of gold, cobalt, nickel, zinc and uranium.

Sulphide ores

The largest part of the global copper and molybdenum resources is bound in porphyry deposits; they can also be sources of gold, silver, tin, platinum, palladium and tungsten. This type of deposit is associated with subduction zones and volcanic archipelagos, so that the largest deposits are to be found in regions such as the Andes and the Rocky Mountains, or the Philippines and Papua New Guinea. Currently, 50-60% of the world production for copper

Types of Ore:

Primary ores Emerged during geological rock formation and have so far not undergone any conversion processes

Secondary ores: Are formed from primary ores by chemical weathering or metamorphosis

Refractory ores: Are extremely resistant and difficult to break down

Low-grade ores: Have a low metal content

Supergenic enrichment: Weathering processes cause minerals to go into solution, which can precipitate out again near the surface as metal salts

and 95% of that for molybdenum comes from this type of deposit. Main ore minerals are copper iron sulphides, such as chalcopyrites (Cu_3FeS_2), bornite (Cu_5FeS_4), but also enargite (Cu_3AsS_4). Molybdenum (as molybdenite, MoS_2) is – in addition to gold – an important coupling product. In areas close to the surface, supergenic enrichment occurs, which is characterised by the occurrence of simple copper sulphides (chalcocite-digenite (Cu_2S), covellite (CuS)). The ore content is relatively low (0.2-1.5 wt.-% copper), but thanks to the enormous volume the deposits are still very profitable to exploit. However, this results in huge amounts of tailings, which generally have the tendency to form acidic pit water (acid mine drainage).

In addition to the copper-porphyry deposits, sediment-bound poly-metal deposits represent the world's second most important copper source. In addition to copper, they contain a number of key co-products, especially silver, cobalt, lead, and zinc. Most important examples of this type of deposit are the Central African copper belt in Zambia and the Democratic Republic of the Congo, as well as the copper slate found in the Central European Permian basin, especially in Poland and Germany. The main minerals are copper sulphide (chalcocite) as well as copper-iron sulphides (bornite (Cu_5FeS_4), with some chalcopyrites). Also, cobalt, zinc and lead occur in sulphide deposits. The copper content of this type of deposit is mostly 1-2 wt.-%, with highly variable concentrations of coupling products.

Bio-leaching and bio-oxidation

There are basically two processes which can be differentiated: in the industrial process of bio-leaching, microorganisms are used to convert ores containing insoluble valuable metals into a soluble form. With organic oxidation, mostly gold can be released from refractory ores in the large bio-oxidation plant tanks for further processing steps.

In the industrial bio-leaching of sulphide-containing ores, three different processes are used:

- » heap or dump bioleaching of mostly low grade sulphide ores,
- » stirred-tank bioleaching of e.g. copper concentrates,
- » *in-situ* (or *in-place*) bio-leaching of e.g. uranium



Fig. 2: Chalcocite, Rob Lavinsky, iRocks.com – CC-BY-SA-3.0

The heap leaching or dump leaching of secondary copper ores such as chalcocite and covellite currently has the most significance in the bio-leaching of copper. Around 80% of bio-leached copper comes from projects with secondary copper ores.

In the case of *in-situ* bioleaching, instead of mining the ore it is extracted by leaching directly into the storage natural deposit. This method has been used for copper and zinc extraction on a pilot or demonstration scale in Germany (Rammelsberg), Ireland, Italy, Romania, Australia and South Africa. Uranium has been extracted industrially in Canada and at the Wismut site in Königsstein using *in-situ* leaching. In each case, blocks of ore were separated underground in the ore deposit and leached there. Direct *in-situ* leaching was carried out in Bulgaria, whereby the leaching liquid was pressed into the shale. In order to avoid both losses and problems with the environment, bottom sealing has to be introduced when using *in-situ* leaching in the mine. Another challenge is to stop the leaching processes after mine closure.

In bio-oxidation, one can differentiate between three processes:

- » bio-oxidation in dump leaching for low-grade, refractory gold ores,
- » bio-oxidation in stirred tank bioleaching of refractory gold ores with a higher gold content,
- » covering inert tailings with sulphide-containing gold concentrates and their subsequent leaching in ventilated tanks or ore heaps.

Strictly speaking, it is not actually possible to leach out gold organically, as it is already present in the metallic state – and is neither oxidised nor reduced in the process. However, the iron and possibly arsenical sulphide matrix is biologically oxidised – in which gold is either integrated into the crystal lattice or included as particles. By leaching out the oxidised mineral components, this allows access to the previously refractory gold.

Copper

According to research of the Federal Institute for Geosciences and Natural Resources (BGR), at least 8% of the primary production of copper in 2010 (total 2010: 15.7 million t) originates from bio-leaching of sulphurous copper ores. In this case, heap leaching processes are already included to a small extent whereby low-grade sulphide ores are directly bioleached after being mined without any further crushing (run-of-mine) (dump bioleaching, for example, in the United States). As there are no specific production numbers for the latter, there still exists an unknown but significant proportion of biologically leached copper. Overall, the share of bio-mined to primary mined copper is estimated at over 10 to 20%.

Nickel, cobalt and zinc

Compared to copper leaching, the bioleaching of other metals such as nickel, cobalt, and zinc so far represents the exception rather than the rule. An example of dump leaching of a polymetallic ore is the project Talvivaara in

Heap or Dump Bioleaching

The ores are stacked up and sprinkled with acidic drainage water. The microorganisms which occur naturally in this environment multiply and the leaching processes begin.

Tank Bioleaching

The material to undergo the leaching process is stirred with (sulphuric)



Fig. 3: Bioleaching in Chile

Finland: 50,000 t nickel, 90,000 t zinc, 15,000 t copper and 1,800 t cobalt per year will be obtained here at full production capacity by biological dump leaching from low-grade ores. Thus, dump leaching could be able to provide about 3% of the world's primary nickel supply.

In a tank bioleaching plant in Kasese, Uganda, 240 t pyrites concentrate are oxidised every day for the extraction of cobalt, copper, nickel and zinc; this produces about 1,100 tons of cobalt per year. This represents approximately 1.25% of the world production of cobalt, which amounted to about 88,000 tonnes in 2010.

Uranium

For the *in-situ* bioleaching of uranium ore, insoluble UO_2 is directly oxidised in the deposit to water-soluble uranyl ions (UO_2^{2+}) by means of microorganisms such as *Acidithiobacillus ferrooxidans*. Uranium(IV) is oxidised in this way to Uranium(VI), whereby Fe(III) is reduced to Fe(II) in a redox reaction. The oxidising agent Fe(III) for UO_2 is once again provided by a microbial iron(II) oxidation.

The worldwide capacity of around 30 active *in-situ* leaching projects for uranium is about 34,000 t uranium content, i.e. one-third of the global production capacity for uranium. The *in-situ* leaching of uranium is to be estimated with an output of 70-80% as very effective. Environmental problems can arise from *in-situ* leaching by uncontrolled

seepage of the solution. Another risk is that in the presence of suitable substrates for leaching microorganisms (FeS_2 , Fe(II)), even decades after the end of active production it is difficult to stop the leaching process, i.e. a further threat to groundwater and surface waters will exist for a longer period of time. Up until 1990, uranium was biologically produced in Germany by Wismut using both *in-situ* leaching (Königstein) as well as heap leaching (Ronneburg).

Autotrophic organisms are able to build up organic matter from inorganic materials (e.g. by photosynthesis). Heterotrophic organisms need organic matter.

Gold

Currently, at least 16 active gold projects utilise bio-oxidation to produce at least 90 tonnes of gold and 161 t silver according to the BGR. The proportion of gold mined in this way is thus about 3.5% of global gold production compared to total production, which amounted to around 2450 tons in 2010. By comparison: the 444 gold projects, in which hydro-metallurgical gold is extracted as a primary or secondary process, have a total gold production capacity of about 1950 t.

Silicate, carbonate and oxide ores

So far, there are only a few projects for the biotechnical preparation of carbonate, silicate and oxide-containing ores of an industrial scale. In the production of kaolin in Slovakia, iron is removed using heterotrophic microorganisms to improve the quality of the material. Further application potential lies, for example, with the extraction of aluminium and lithium from spodumene ($LiAl(Si_2O_6)$), cobalt and nickel from laterites or cobalt, nickel, copper, and manganese from polymetallic deep-sea nodules (manganese nodules). Significant nickel deposits of the laterite type are located mostly in subtropical and tropical regions. There are also deposits of nickel laterite containing 2% nickel to be found in the Saxon Granulite Mountains.

It has been demonstrated in the laboratory that the bioleaching of ores using heterotrophic bacteria and fungi is generally possible. These microorganisms require the addition of organic carbon (e.g. reprocessed waste from agriculture or the food industry or biomass (algae)). On the one hand, this makes the process control expensive, on the other hand, undesirable microorganisms can be disruptive, as these processes cannot be operated under

sterile conditions. A new perspective is offered by anaerobic bioleaching developed recently in the laboratory for the reprocessing of carbonate, silicate and oxide-containing ores (Ferredox process). This process uses *Acidithiobacillus ferrooxidans* under the exclusion of oxygen (anaerobic) to oxidise added sulphur, thereby reducing Fe(III) and bringing laterites into solution at the same time.

Outlook

The largest copper reserves are primary copper sulphides such as chalcopyrites ($CuFeS_2$). Their dissolution is so far limited using normal heap bioleaching with mesophilic bacteria that work at a moderate range of temperatures. Research is currently focusing, therefore, on the development of new bio-mining methods for primary copper sulphides. A high copper output could be achieved using bioleaching with thermophilic archaea (genera *Acidianus*, *Metallosphaera*, *Sulfolobus*) at approximately 65 °C. Both tank bioleaching and heap bioleaching are used at high temperatures on a pilot and/or demonstration scale, adding increased demands on material and process management. There are still some promising approaches in the laboratory stage for the electrochemically controlled tank bioleaching of chalcopyrites, with a very high output of copper.

On an industrial scale, bio-mining is so far only used in the processing of sulphide ores and uranium ore. Bio-technical laboratory procedures already exist for the digestion of silicate and oxide ores. The newly developed Ferredox process will probably enable the reprocessing of laterites and oxide ores, such as manganese nodules. In this way, an organic source of carbon such as glycerol or cheaper elementary sulphur is oxidised. At the same time, *Acidithiobacillus ferrooxidans* reduces Fe(III) bound in the mineral to soluble Fe(II) in acidic solution. There may still be other, possibly more powerful microorganisms in nature which can be used for anaerobic bioleaching. These have so far not been specifically sought after and cultured. The potential for anaerobic bioleaching still has to be developed.

It is currently not possible to estimate the extent to which bio-mining offers a perspective for the recovery of rare earths and other metals for use in electronic applications. There is a chance, however, that bio-mining will be used as a low-cost reprocessing treatment.

NEED FOR RESEARCH

- Upscaling of the most promising laboratory processes
 - New bio-mining processes for primary copper sulphides
 - Processes for the digestion of silicate and oxide-rich ores
- Assessment of the potential offered by anaerobic bioleaching
- Develop new biogeotechnological processes into marketable commodities
- Analyse the interface between processes in bioleaching and acid mine drainage / acid rock drainage

2 Mining heaps – Remediation or a depot for recyclable materials?

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Introduction

In the Harz Mountains, Mansfelder Land, Thuringia and in the Erzgebirge (Ore Mountains), mining and smelting slagheaps have developed over the centuries to dispose of tailings, inferior ore as well as processing and/or smelting residues such as slag, dust and sludge.



Fig. 4: Mining heaps in the Mansfelder Land

These heaps often pollute the environment through emissions of dust and leachates containing harmful substances. In particular, sulphide tailing heaps can release acidic waters by microbial and chemical weathering processes containing in part very high concentrations of metals (acid mine drainage). On the other hand, many, often large heaps still contain a considerable potential for recyclable materials. At the time they emerged, treatment technologies were not able to economically harvest metals such as lead, cobalt, lithium, molybdenum, nickel, silver, tungsten, zinc and tin, contained in complex ores and/or in low concentrations. In addition, they also contain metals such as gallium, germanium, indium and niobium. At the time, these were not required – however, today they are in strong demand in the electronics industry. Due to the limited source of supply, they are considered strategic raw materials. For example, indium and gallium were enriched in the slag during zinc and copper ore smelting, niobium and tantalum in tin ore smelting and tin in lead-zinc smelting. Today, copper shale heaps in the Mansfelder Land left over from the copper mining activities still contain considerable amounts of copper and other metals. There are often significant amounts of metals such as silver, lead, lithium, molybdenum, niobium, tungsten, zinc and tin left in the flushing heaps (tailings) that resulted from flotation processes. The metal content in mining residues in Germany is sometimes higher than in the primary mined ores worldwide. In the face of rising raw material demand and the shortage of strategic metals, there is a need to open up secondary sources of raw materials in Germany with intelligent combinations of classic and new processing technologies. Bio-mining can occupy a key position here as a favourable reprocessing technology.

Bio-geochemical processes in mining heaps

In mining areas, tailing and reprocessing residues were often stored unsecured in the form of heaps and tailing ponds. The coarse grain of the material allows the unobstructed access of air and precipitation. Under these conditions, sulphuric acid is formed from metal sulphides by oxidation with atmospheric oxygen – with the help of bacteria. Previously bound, insoluble heavy metals are thus solubilised. These acidic waters (acid mine drainage or acid rock drainage) contain heavy metals and can significantly endanger the environment, plant, animal and humans, and can also contaminate groundwater and surface water.

Microorganisms play a vital role in the emergence of heavy metal-containing acid water in mining slag heaps. Pyrite is converted by special bacteria in the presence of atmospheric oxygen to iron(III) and sulphuric acid. This process is called biological leaching. At neutral pH, such as is to be found in carbonate-buffered tailing materi-

als, pyrite is first chemically oxidized by atmospheric oxygen to iron(III), thiosulphate ($S_2O_3^{2-}$), polythionates (SnO_6^{2-}) and sulphuric acid. Thiosulphates and polythionates are oxidized by weak acidophilic bacteria which specialise in sulphur compounds (e.g. *Thiomonas intermedia*) to sulphuric acid. When the neutralisation potential of the tailing material is exhausted, the pH decreases to values below 4, and the solubility of iron increases by several decimal powers. The chemical oxidation rate of iron(II) at pH values below 4 is lower than at a neutral pH by several decimal powers. However, strongly acidophilic iron(II)-oxidising bacteria of the species *Leptospirillum ferrooxidans* and *Acidithiobacillus ferrooxidans* (formerly *Thiobacillus ferrooxidans*) can increase the iron(II)-oxidation rate by decimal powers and thus provide continuous amounts of iron(III), the oxidising agent of pyrites. Under acidic conditions, pyrite undergoes almost quantitatively microbial conversion to iron(III) compounds and sulphuric acid. A significant by-product is the chemically inert element sulphur, which is converted by strongly acidophilic sulphur-oxidising bacteria of the species *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* in the presence of atmospheric oxygen to sulphuric acid.

As considerable amounts of reaction energy are released during the complete oxidation of pyrites with -1546 kJ/mol, the end result is that slagheaps tend to heat-up. In pyrites-containing slagheaps of the uranium mines of Wismut GmbH in Thuringia, temperatures of up to 100°C have been measured, for example. At temperatures above 45°C, the listed bacterial species are no longer able to grow, and instead strongly acidic and thermophilic iron(II) and sulphur-oxidising archaea prevail, such as those of the species *Acidianus brierleyi*, or *Sulfolobus acidocaldarius*. Besides pyrites, residual amounts of e.g. galena (PbS) and sphalerite (ZnS) can also be found in mining heaps. In contrast to pyrites, these are not oxidised purely chemically to sulphate under acidic conditions, but mainly to the essentially chemically inert element sulphur. The further conversion to sulphate takes place biologically, as described above.

In addition to bacteria which oxidise metal sulphides, the presence of bacteria which recycle organic carbon (organotrophic) (e.g. the genus *Acidiphilium*) and fungi has been repeatedly demonstrated in mining heaps. Organotrophic microorganisms may lead to a mobilisation of heavy metals under acidic and even alkaline conditions by the formation of organometallic complexes.

The variety of heterotrophic microorganisms in the heap substrates essentially depends upon the pH value (acidophilic, acid-tolerant, neutrophilic, alkaline-tolerant species) and the existing supply of organic carbon. Heterotrophic microorganisms exist mainly in mineral tailing materials with microbial pyrites oxidation from the organic precipitates of iron and sulphur-oxidising bacteria. In lignite tip heaps from open-cast mining and/or coal mining heaps, these microorganisms can exist in addition to the remaining biodegradable components of coal.

A mobilisation of heavy metals and thus a risk to the environment can also take place in mining heaps under the exclusion of atmospheric oxygen. *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Acidiphilium* sp. are able to reduce iron(III) under acidic anaerobic conditions. At a neutral pH, it has been shown that iron(III) and manganese(IV)-reducing bacteria (e.g. *Geobacter* sp.) detected in sulphide mining heaps or tailing ponds lead to dissolution of iron(III) or manganese(IV) oxides and hydroxides. These often contain heavy metals, which can then be mobilised. This can be problematic, e.g. in the underwater storage of tailing materials.

Some of the more important processes involved in pyrites oxidation:

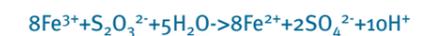


Fig. 5: *Thiobacillus ferrooxidans* under the microscope.

Protection of mining heaps

In order to inhibit biological leaching processes in mining heaps, the residues can be stored under water (in lakes and/or in the groundwater), the heaps can be covered, inhibitors introduced into the tailings, or the heaps planted. The underwater storage of sulphide tailings is quite common. The low diffusion of oxygen levels through the water leads to a significant, if not complete reduction of the bacterial count and hence to the metal sulphide oxidation rate. The securing of heap materials by storing them in a body of ground water of a former open-cast mining site which has been naturally regenerated – and at the same time incorporating proton-consuming barrier layers to stabilise the pH – is an extremely expensive process, which has been carried out e.g. by Wismut GmbH. Dry covers (e.g. made of clay or plastic, such as HDPE) reduce or prevent the penetration of atmospheric oxygen and water from precipitation into the heap or the mining pond, and thus the metal sulphide oxidation process. Furthermore, covers prevent the spread of heavy metal-containing dusts and allow planting. The technical requirements are quite considerable, so that efficient covers can be very expensive. The heat development of some heaps, amongst other things, may endanger the long-term stability of these covers. Although covers made of a simple layer of clay reduce the rate of biological oxidation, they cannot completely bring it to a halt, however.

Covers consisting of several layers are recommended, for example, a clay layer and an overlying cultured layer, which protects the clay layer from drying out and damage. The cultured layer has stabilising plant cover (erosion control), which further minimises the penetration of water and air into the heap substrate. In older heaps covered in this way (> 65 years), a significant reduction in the new formation of leachate and seepage – compared to just re-cultivation of the site – has been shown.



Fig. 6: Geschüttete Halden des Kupferbergbaus in Rosija Pojenie (Rumänien)

Substances to inhibit biological leaching can cause a change in the pH value, have a direct biocidal effect on bacteria or cause passivation of the pyrites surface. Lime is often successfully used to raise the pH value and as a buffer, which is however a significant cost factor. The increase in pH reduces the growth of acidophilic iron(II) and sulphur oxidising bacteria. Also, the addition of phosphates to form passivating iron phosphate layers around iron sulphides can be allocated to this avoidance category. Planting inhibits biological leaching in two different ways: firstly, the plant's roots system competes with the iron(II) and sulphur oxidising bacteria for atmospheric oxygen and, secondly, the plant's roots excrete organic substances that act in an inhibiting way. Also, the plant roots extract water from the heap material. These effects are summarised under the term "phytostabilisation". Planting directly on an untreated heap surface is problematic because the plants usually do not tolerate the high level of acidity and heavy metal content. Biological oxidation of pyrites can cause plants to die, even years after planting. Therefore, planting should be done preferably in combination with other measures such as liming or by the use of coverage.

The specific use of plants also allows pollutants (metals) to be extracted via the plant biomass (phytoremediation or phyto-extraction). Heaps can possibly be restored and precious metals can be selectively concentrated using this method. Also, the leachate quantity and seepage are reduced and, above all, heavy metals are "stored" in the upper ground layer, from which they can be slowly extracted by the plants.

It is necessary to consider a combination of measures (e.g. liming and underwater storage at Wismut GmbH) in every single case. This raises the question about the efficiency and costs. When selecting appropriate measures, investigations on the microbial environmental hazard potential of mining heaps should be carried out before the restoration, e.g. as compiled in the Guidelines of the Federal Office for Radiation Protection for estimating of the influence of microbial processes on groundwater or leachate.

As the restoration of large mining heaps can only be addressed with an immense financial and logistical effort, and a very long follow-up phase is to be expected despite the high level of costs and effort taken, the possibility of natural pollutant retention has also been examined (natural attenuation).

In some mining heaps, crusts are formed by an accumulation of crystalline or gel-like secondary phases. Depending on the climate, heap content and the order of the tipped materials, multiple secondary phases can occur in the pH ranges from <1 to >12. These crusts are characterised by a reduction in the pore space and thus the permeability of the heap, chemical-metallic concentration and/or depletion, as well as by characteristic new mineral formation, which is stable under the given pH conditions. The secondary phases accumulated in the crusts have a high binding capacity for pollutants.

The natural reduction of pollutants in lignite tailing tips is essentially based on the already short-term buffering effect of the acid water formed, whereby pollutant ions in secondary mineral phases are integrated or absorbed onto reactive surfaces (clay minerals, humic materials, iron hydroxides), and a medium to long-term acting microbial sulphate reduction takes place with subsequent precipitation of new sulphide mineral phases.

While buffering is mainly due to carbonates contained in the tailing materials, the microbial sulphate reduction represents a medium to long-term acting, sustainable and above all a sulphate load-lowering mechanism. In this respect, the sulphate reduction is to be understood as a stage in the sequence of microbial reduction reactions. The prior iron reduction for the groundwater of almost every tip proceeds in the same manner, as shown by the high iron(II) content levels. The driving force for the reductive process chain is the microbial implementation of the falling mass in tertiary organic matter (electron donors). The microbial sulphate reduction can be increased by adding organic matter as additional electron donors (enhanced natural attenuation).

Outlook

Recent global activities have opened up the door for metal extraction from mining heaps using biotechnical methods. The secondary raw material sources can also be developed in Germany by intelligent combinations of classic and new processing technologies. Bio-mining as a cheap reprocessing technology can occupy a key position here. With the extraction of precious metals from mining heaps, pollutants can be removed at the same time, allowing safe and environmentally sound storage of reprocessed tailing material. A more cost intensive follow-up such as the treatment of seepage water could thus be avoided. Such costs must be taken into account when assessing whether a heap can be economically recycled. Furthermore, economic processes have already been developed at laboratory scale for reprocessing wash-heaps which use bio-mining. The organic leaching and/or organic oxidation of sulphide flotation concentrates has been successfully tested for extracting gold, copper, nickel, silver, and uranium.

In order to open up secondary deposits and heaps with regard to their reprocessing potential, it is necessary to create a recyclable and/or pollutant register for Germany. Further future-oriented approaches for the recovery of metallic raw materials from secondary deposits are biotechnological process development especially for non-sulphide slag heaps, which represent an interesting option for anaerobic bioleaching, as well as the integration of biotechnology into an intelligent combination of reprocessing technologies. Heaps with low economic potential for treatment can likewise cause a significant environmental impact. Tips from lignite mining produce large amounts

of sulphate and acid, which can be counteracted by biotechnological exploitation of microbial sulphate reduction processes in combination with dumping technology and cultivation strategies for surrounding groundwater and surface water bodies. Research is required in any case in the upscaling of promising field and laboratory procedures, in order to test their applicability and cost-effectiveness, and to establish new biotechnological processes in the mining industry.

NEED FOR RESEARCH

- Preparation of a recyclable and/or pollutant materials land registry for Germany
- Development of biotechnological procedures for non-sulphide slag heaps
- Integration of biotechnology as part of an intelligent combination of reprocessing technologies
- Upscaling of promising field and laboratory procedures

3 Metal-containing mining waters – Avoidance, waste or raw material?

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Formation, types, examples

Acid mining waters from ore or coal mining, heaps, tailings, or tips pose a significant danger to the environment. Not only the low pH is problematic, they also contain high concentrations of sulphate and iron. Furthermore, they can be negatively loaded with other heavy metals and metalloids such as arsenic. As oxidised iron is involved in this process and dissolves better at a low pH, a self-perpetuating process may result.

In addition to acidic drainage waters, there also exist neutral drainage waters with relatively high heavy metal content. This occurs when sulphate and hydrogen ions are bound or sulphate is reduced anaerobically and these pollutants are released. In the first instance, mainly high zinc concentrations are involved, in the second case there are also increased iron, manganese and arsenic levels in addition to radium.

In order to select appropriate measures for water purification, the waters have to be differentiated using the following criteria:

- » Is the water from active or abandoned mining sites? In the first case, it is still possible to intervene in the design of heaps. In the second case, access of oxygen can be reduced by flooding.
- » What water volumes and bodies of water are involved? Is it a lake, e.g. a flooded pit left over from open-cast mining operations, or are flowing waters to be treated – if the latter, with which volume per unit of time?
- » What concentrations of what kind of water contents are present? This depends upon the respective storage depots and their mineral stock. Also, this point is dependent upon the age of the mining activities.
- » What is the redox potential, what is the oxidation state of the substances contained (speciation of the metals and metalloids as well as the sulphur)?
- » These points are related to the acidity and alkalinity of the water. This does not only refer to the current pH value. The acidity can alter in the presence of metal ions that form hydroxyl-complexes, or by redox reactions. For the level of alkalinity, ions (such as phosphate, bi-phosphate, silicate, etc.) play a role in addition to the carbonate content, depending upon the respective definition.

The following examples illustrate the characteristics of mining waters:

- » In areas with lignite open-cast mining, residual-mining holes are bound to remain following open-cast operations due to the volume reduction from coal production when surface mining has finished. In the



Fig. 7: Measurements of acid mining waters

Rhenish lignite mining area, this is going to affect especially the open-cast mining areas of Garzweiler, Hambach and Inden, the flooding of which is scheduled from 2030 and 2045 and is expected to last for about 40 years. The flooding of the residual mining holes in areas belonging to the New Federal States is partially already completed. In this way, lake landscapes have emerged (in Saxony, for example, 48 lakes with approximately 16,000 ha surface area, almost 2.2000 billion m³ volume, status in 2009). Pyrites levels can achieve up to 3% in the Lusatia region, and in places up to 8% in the Central German lignite district. For this reason, post-mining lakes there may have partly very low pH values and high metal and sulphate concentrations: in Saxony, three out of 22 post-mining lakes had a pH value of < 3.0 in the Leipzig area in 2007, and five had a pH value between 3 and 4.5; in the Lusatia region, 8 out of 26 post-mining lakes had a pH value of < 3.0 and 9 had a pH value between 3 and 4.5.

- » Active lignite open-cast mining can also lead to large water currents with a need for treatment. In this case, it is the water which is pumped out of lignite mines. This is raised from all around the respective open-cast mining to lower the groundwater level and to keep the open pit dry. Vattenfall cleans about 300 million m³ water in several mine water treatment plants in the Lusatia region every year. The untreated water from the mine water treatment plant Tzschelln at the open mining pit in Nochten, for example, has a pH 4-5, sulphate concentrations of about 3,100 mg/l and iron concentrations of 300-700 mg/l. Whereas the technique currently used of neutralisation and ventilation effectively limits the iron concentrations of the water pumped from the mine and raises the pH, the problem of sulphate loads remains. The burden of the subsequent receiving waters of the Spree is not without some objection in terms of the drinking water supply in Berlin and Frankfurt/Oder as well as with regard to its use as cooling water (concrete corrosion) and because of possible ecological consequences to the environment.
- » Seepage also emerges from coal mining heaps in the region around Zwickau with significant concentrations of Ni, Cu, Zn, Cd and U. In the Ruhr area, there is also seepage from mining heaps which give rise to mainly high local radium loads.
- » From the period 1946 to 1990, waters with a need for considerable long-term treatment resulted from the uranium mining area of Wismut AG in Thuringia and Saxony. The heaps have mostly either been redeveloped or filled back into the open pit and considerable progress has been made with the flooding of underground mines. Nevertheless, contaminated waters remain with a need for long-term treatment. Thus, uranium, iron, arsenic and radium are primarily separated from waters with different compositions at various plants, including, amongst other things, those located in Königstein, Ronneburg, Schlehma-Alberoda, Seelingstedt and Pöhla using different technologies.

Objectives

The obvious targets of water treatment are the removal of pollutants from the water pathway and the regulation of the pH value. Inorganic pollutants are not biodegradable like organic pollutants. The aim is thus typically to transform these into a less mobile form and to separate them by precipitation or sorption. Concentrated waters or sediments can either be put into landfills or further recycled – the purified waters are then released into receiving waters. Occupational safety and the time and effort required also play a role in the choice of procedure.

In view of the dwindling nature of mineral resources, the question in the meantime now arises whether some of the substances isolated from these waters can be returned to a meaningful use. This saves costs for landfills and, if necessary, can be also economically interesting in the light of higher raw material prices.

Treatment strategies

The priority objective in today's mining activities is to avoid the development of acid mining waters. Chapter 2 explains in some detail the possibilities available for securing heaps using covers or phytostabilisation. If this fails, or the site is an abandoned contaminated area, leaking acid water has to be treated.

1. Non-biological processes

The most important large-scale process used to reduce the iron load and to increase the pH is the neutralisation of acid mining water using **lime** in combination with **aeration** of the waters. With this technology, however, the sulphate content cannot be reduced below approx. 1600 mg/l due to the high solubility of gypsum. Furthermore, the provision of lime is both expensive and energy-intensive, and the iron oxide/hydroxide sludge formed can be poorly drained off.

One advantage in the formation of iron **oxides/hydroxides** is that they provide a basis for the **sorption of other ions** from metals and metalloids and immobilise them. This effect is used in order e.g. to remove arsenic compounds from uranium mining waters (Pöhla treatment plant). As the iron oxide from the treated water is not sufficient to bind arsenic, iron oxides must be added via a separate sorption plant and renewed regularly. The sorption of metals on iron oxides under oxidising conditions is also an important step in the immobilisation of elements from tailing heaps.

Also, the **addition of counter-ions** to form poorly soluble salts can be used to **precipitate** pollutants. Barium sulphate possesses a significantly lower solubility than gypsum; however, barium is toxic in soluble form and quite expensive, so that it is not considered for sulphate precipitation as a rule and is only used for reducing radium concentrations.

The removal of metal ions from water by **ion exchangers** is more complex. Such procedures play a role e.g. in the cleaning of water contaminated with uranium at Wismut GmbH.

Membrane processes (reverse osmosis, nanofiltration) always lead only to a concentration of salts and thus to a reduction in volume. Therefore, they have to be combined with other steps, e.g. precipitation. Scaling, i.e. the blocking of the membrane by precipitates, limits the extent of concentration and thus the effectiveness of the membrane process. Membrane processes, amongst other things, have been and still are being tested on a pilot scale on waters from open-cast lignite mining, as well as copper mining.

There are also membrane electrolysis processes (RODOSAN process) which are still in the pilot phase. In this case, water is electrolysed; iron hydroxides are precipitated in the cathode compartment, whereas sulphuric acid accumulates in the anode compartment. The performance of the cells could be further increased by supplying an infeed of CO₂.

2. Principles of biological water purification

In biological treatment of mining water, organisms which use the oxidation or reduction of iron or sulphur to produce energy play an outstanding role. Organisms that also derive energy from redox reactions of uranium or arsenic are of interest, as well as organisms involved in the carbon cycle (phototrophic (biomass formation), fermenters, methanogenic or aerobic heterotrophs). These only affect mining waters indirectly. Substances contained in water that are to be immobilised are either electron donors or electron acceptors; the respective missing partner for the desired reaction still has to be added. In view of the multitude of possible metabolic processes, one must



Fig. 8: Behandlung von Bergbauwässern

reckon with adverse competing reactions, as biological processes on a large scale cannot be kept sterile. However, as the process which allows the largest gain in energy usually dominates, thereby permitting biomass production under the given conditions, the design and control in this case therefore have to create advantages for the desired organisms. Alternatively, the cells would have to be cultivated separately and introduced again into the respective reactor after a certain number of process cycles.

The prerequisites also preclude that a carbon source and the necessary nutrients (e.g. nitrogen, phosphorus, and trace elements) are available. Carbon sources can be organic compounds for many heterotrophic sulphate reducers, which also serve as electron donors. In the case of inorganic electron donors such as Fe^{2+} or H_2 for sulphate reduction, CO_2 is usually the carbon source. Organic compounds are even harmful to some autotrophic organisms. The phosphorus supply is not trivial for iron oxidisers given the low solubility of iron phosphates. The same applies for trace metals in the case of sulphate reducers.

As the redox pair Fe(III)/Fe(II) has a positive reduction potential, whereas sulphate is reduced at a significantly more negative potential, sulphur is mainly present in oxidised form as sulphate and iron in the reduced form as Fe^{2+} . The starting material is thus incompletely oxidised. For this reason, oxidative treatment as well as reductive treatment can lead to the immobilisation of pollutants.

Treatment procedures are often divided into active and passive processes. Active processes are those requiring continuous or frequent intervention, whether in the form of maintenance or the addition of chemicals or energy. Passive processes are those which rarely require maintenance after they are constructed and revert to natural energy sources (such as photosynthesis). Usually passive processes require a lot more area than active ones, so that their application only makes sense for smaller volume flows and moderate concentrations of pollutants. Depending upon the construction of the facility, active processes also have the advantage that the precipitated and absorbed products are easier to recover. The boundary between active and passive processes, however, cannot be drawn distinctly, which becomes clear from the use of expressions such as “semi-passive processes” and this leads to the fact that some processes are classified differently, according to the respective author. Oxidation and reduction reactions as well as biosorption or bioaccumulation may play a role in both active as well as passive processes.

3. Precipitation by microbial redox processes

Where the problem of mining water is caused through oxidative processes, the obvious solution would be to use reductive processes. In fact, extremely low-soluble metal sulphides (e.g. FeS) are formed by microbial reduction of sulphate in the presence of metal ions, which are precipitated and thus removed from the water phase. For this reaction to take place, the sulphate reducers need either an organic electron donor (organic acids, alcohols, sugars) or an inorganic electron donor such as H_2 . When using an organic electron donor, methanogenesis can occur due to the activity of fermenters and methanogens as competing reactions, i.e. the formation of CO_2 and methane. Existing iron(III) may then possibly undergo preferential reduction by iron(III) reducers and thus be mobilised. In this case, further metals bound to iron(III) oxide or metalloid ions can be mobilised. This can also affect arsenate (H_2AsO_4^-) and/or microbially formed arsenite (As(OH)^-) which occurs under reducing conditions. An immobilisation can only be achieved, if necessary, with complete reduction to the corresponding sulphides.

Unlike iron, uranium – which is present as the oxidized moiety uranyl (UO_2^{2+}) – is immobilised by reduction. The result is uraninite (UO_2), which as such is also removed from the water phase.

Precipitation by oxidative processes relies on the formation of Fe(III) and possibly Mn(IV) compounds. It has the advantage that these compounds can further absorb ions and immobilise them. This strategy is similar to the conventional technique using lime and ventilation. However, the biological oxidation of iron – in contrast to the purely chemical method – can proceed relatively quickly even at low pH values. It should also be considered that further acidification occurs by the biological oxidation of iron. This takes place unplanned at a low pH in residual

mining lakes or pipelines for seepage waters – it can also be induced by specific aeration in appropriate facilities. Advantages over conventional treatment methods are the cost and energy savings for lime, the improved drainage compared to iron oxides/hydroxides, as well as in the immobilization of a part of the dissolved sulphate content. Carriers of the process are iron oxidising acidophilic bacteria. With the exception of Fe^{2+} , the existing partially oxidized sulphur (elementary sulphur, thiosulphate, polysulfides, polythionates) may be oxidized to sulphate or uraninite (UO_2) to uranyl ions (UO_2^{2+}) under oxidising conditions, if applicable.

4. Biosorption und Bioakkumulation

Biosorption describes the property of biomass or certain biomolecules to bind and concentrate metals. In contrast to bio-accumulation, this is a passive process. Functional groups such as carboxyl, hydroxyl, thiol groups, phosphates, sulphates or amines on cell surfaces or biomolecules or special surface structures are responsible. Their performance is comparable to that of ion exchange materials. They often provide better results than activated carbon or natural zeolite materials. One disadvantage is that these organic materials can only be used directly in a few cases as column material and therefore have to be immobilised with considerable effort mainly to preserve their good binding properties. Particular challenges in this case are achieving a high mechanical stability while maintaining accessibility to the reactive surface.

Biosorption has already been described for a variety of bio-polymers from different organisms and elements. In particular, alginate from seaweed and kelp, chitosan from fungi, peptidoglycans from bacteria, as well as the so-called S-layer proteins – bacterial surface proteins – exhibit special metal-binding properties. These studies have focused mainly on toxic metals and semi-metals such as lead, cadmium and arsenic, which are particularly relevant for the environment, but also elements such as uranium and thorium, which are released during the extraction of uranium and rare earths.

In addition to natural absorption, different targeted approaches are being pursued to optimise bio- components using genetic technology, in order to change their specificity and their affinity for metals. Thus, for example, the expression of cysteine-rich metal-binding proteins (metallothioneins) on the cell surface leads to a 15-20-fold increase in the binding of Cd^{2+} . Due to the de-novo design of peptides with repetitive metal bonding motifs, their fusion with surface proteins and heterologous expression in *E. coli*, it was possible to increase the bonding of cadmium or mercury 10-fold.

The application of biosorptive processes is particularly attractive for bioremediation, i.e. the removal of toxic heavy as well as semi-metals such as lead, cadmium, mercury, arsenic or uranium from water. Many studies have been carried out in this respect. Another area of application of growing interest is the concentration and recovery of valuable metals from recycling processes, as well as from mining waters. Concentrations of more than 2.4 mg/l for the rare earths, especially gadolinium, neodymium, ytterbium, and yttrium have been detected in the Gessen heap in Gessenbach, at the former Ronneburg uranium mining area.

By the combination of “classical” biotechnology with genetic engineering methods and the integration of material science, it is possible to develop new approaches for the well investigated phenomenon of biosorption, which has been known for a long time. If the absorption of metals is reversible and if the materials are renewable, the technology will also be attractive from a cost point of view and can then compete with ion exchangers. For example, the use of biosorptive materials has been examined for the recovery of platinum, palladium and gold and rare earth elements such as scandium, yttrium, lanthanum, cerium, europium and ytterbium.



Fig. 9: Reduktionsbecken

In contrast to biosorption, bioaccumulation involves the active absorption and concentration of metals in cells. This process is driven by selective metal transporters or by diffusion processes, due to large differences in concentration. In contrast to biosorption, one has to rely on living cells when using these processes. The materials are often not renewable. Therefore, recovery of these metals can only take place via incineration or time-consuming extraction processes. As, however, bio-accumulative processes are generally more selective than biosorption, their application for the recovery of low-concentrated and poorly accessible elements using conventional processes can still be attractive. In particular, bio-accumulative processes are very attractive for the bioremediation. A well-researched example is the assimilation of mercury by microorganisms. Many bacteria are able to take up Hg^{2+} and to reduce it enzymatically to Hg^0 inside the cell, which then exits the cells by diffusion. These mechanisms have been used for the removal of mercury from industrial waters and installed in pilot plants. Bio-accumulative processes have already found practical applications e.g. in sewage treatment plants (“bioaccumulation carp”). Plants, such as sunflowers or Indian mustard, have also been used in the restoration of soil by phytoremediation for extracting heavy metals from soil.

5. Passive processes in abandoned mining sites and residual lakes

The simplest passive processes are those in which mining water runs through limestone channels and it is neutralised in the process. A distinction is made between open channels with oxidising conditions and closed channels with anoxic conditions. In both cases, biology does not play any essential role.

In aerobically constructed wetlands, cattails, reeds, or rushes are planted. These marsh plants possess aerenchyma, a tissue through which air can reach the rhizosphere, the space around the root. As a result, chemical or microbial oxidation is enabled there and hence the precipitation of e.g. iron. Because protons are released in the hydrolysis of iron due to oxidation, acidification occurs. Excessive acidification is harmful for the plant. That is why aerobically constructed wetlands should only be used if there is sufficient alkalinity and a sufficiently high pH value. Plants may also absorb a part of the metals (phytoextraction), if applicable, and also reduce the flow rate of water. Phyto-extraction with stonewort algae for bioaccumulation of radium was temporarily tested by Wismut GmbH at the Pöhla site, but this has been discontinued due to unfavourable conditions.



Fig. 10: Aerobically constructed wetlands

In constructed wetlands that contain compost, this is used as a slowly decomposing electron donor source for microbial sulphate reduction. In order that sulphate reduction takes place, oxygen has to be consumed and also iron(III) reduced as far as possible. Metal ions are precipitated in these wetlands as sulphides. A critical factor is the permeability of the compost.

In so-called RAPS (Reducing and Alkalinity Producing Systems), the anoxic limestone channel is combined with the compost contained in the wetlands. The mining water first flows through the compost and is reduced. Then it flows through the limestone channel to raise the pH and/or the alkalinity. As only a small part of the sulphate is reduced to sulphides in the compost, it is to be assumed that the sulphate load does not significantly decrease.

The so-called “reactive walls” – which are constructions made underground – are to be included with the passive methods, which should have a positive influence on contaminated ground water. In this case, reduction by elementary iron can play a role as well as absorption to iron oxides/hydroxides or precipitation with phosphates.

A procedure was developed for the treatment of open-cast mining lakes by the Helmholtz Centre for Environmental Research, in order to stimulate microbial sulphate reduction by adding carbolime and straw bales. This was tested

in the residual pit 111 in Lauchhammer in Lusatia in cooperation with the GKSS Research Centre Geesthacht, using enclosures 30 m in diameter. The sulphate reduction could actually be stimulated, especially beneath the straw bales, which were submerged in the lake. The rate, however, remained restricted for this reaction, due to the low volume. The higher velocity of the iron(III) reduction also caused problems, which led to the re-mobilised Fe^{2+} reaching oxidising zones. There it was oxidised again and entered into competition once again with sulphate as an electron acceptor.

6. Active processes

Recent technological approaches separate the iron by microbial oxidation of Fe^{2+} in the acidic pH range and recover clean ferrous hydroxy sulphate that is suitable for different purposes. The process, which also removes part of the sulphate, is carried by novel acidophilic iron-oxidising bacteria. Rough calculations have shown that about 10000 t of material can be obtained in this way. This can then be processed to iron and iron-containing adsorbents for the purification of water contaminated with arsenic or for sulphide separation in biogas plants. The company G.E.O.S. Freiberg has developed a possibility to use schwertmannite which results from the water cleaning process (idealised formula: $Fe_{16}[O_{16}(OH)_{10}(SO_4)_3] \cdot 10 H_2O$) as a base material for dyes. Similar recycling strategies are possible with the iron and manganese-containing sludge from drinking water plants.

Processes, by which microorganisms use organic electron donors, or H_2/CO_2 reduces sulphate, often run in fixed-bed bioreactors. Attachment of sulphate-reducing microorganisms to the fixed bed material prevents a washout of the microorganisms from the reactor. Alternatively, the microorganisms can be used in a UASB (Upflow Anaerobic Sludge Blanket) reactor. In the meantime, such procedures are classified with the “semi-passive methods”; however, the implementation in bioreactors combined with the effort required for measurement and control technology to optimise the process justifies their allocation to the active processes. A group of processes developed by the Dutch company PAQUES is the most well-known. In this respect, a part of the H_2S formed by sulphate reduction is used to precipitate a number of metals as sulphides, before being introduced into the bioreactor. At the same time, another part is partially oxidised to elementary sulphur. A large-scale process was implemented in 1992 for cleaning up the mining waters of a zinc smelter. The company G.E.O.S has developed a methanol-based fixed-bed process for cleaning up mining waters in Lusatia. Studies of the GFI Dresden aim to use hydrogen for cleaning up tip groundwater in horizontal *in-situ* reactors. Ongoing efforts at the BTU Cottbus could be considered borderline passive processes to accelerate the reductive processes in open-cast lignite mining tips by the addition of glycerol or methanol directly into the groundwater flow.

In order to accelerate the sulphate reduction in residual mining lakes, an active version of the process using carbolime and straw bales has been designed by the UFZ, in which the lake water is pumped through straw bales. The BTU Cottbus has gone even further in this respect using floating bioreactors for methanol-driven sulphate reduction.

Whereas sulphate reduction was traditionally carried out at around neutral pH values, it has increasingly emerged that this is also possible even under acidic conditions. This offers the opportunity to remove metals by sulphate reduction not only in total from these waters, but to carry out selective precipitation at different pH values depending on the solubility of the sulphides.

The remediation of waters burdened with U(VI) has been intensively modified by adding organic compounds (e.g. acetate) in field trials, especially in the United States. $Fe(III)$ as well as sulphate-reducing bacteria were able to reduce the uranyl ion level to uraninite and immobilise it. An application of these processes for the restoration of partial areas of the uranium pit in Königstein seems to be conceivable.

Challenges

Despite the frequent benefits of biotechnological procedures with regard to energy and chemical consumption or capital costs, the drawback compared to purely chemical-physical methods is their susceptibility to breakdowns (possible toxicity of pollutants especially with peak loads) as well as in their complexity, which makes it difficult to predict results. This complexity is reflected, for example, at the above-mentioned level of competitive symbiosis between sulphate reduction and methanogenesis, or between sulphate reduction and iron(III) reduction. The role of heavy metals for microorganisms is also ambivalent: on the one hand, they act as toxic pollutants, on the other, as essential trace elements. In addition – perhaps as a result of this misunderstood complexity – inadequate turnover rates, high hydraulic retention times, and thus high investment costs impede the application of biotechnological procedures. Therefore, it is a major scientific challenge to understand the biology of the process carriers better in order to adapt the conditions in technical facilities accordingly and to avoid disturbing variables by the use of optimised control systems. For example, work on Fe^{2+} was almost exclusively focused on *Acidithiobacillus ferrooxidans* for decades. Today, we know that this organism does not play a role at slightly elevated pH values in natural systems. Thanks to the increasingly powerful methods used in molecular biology, such as genome, transcriptome or proteome analyses, it is possible to gain new insights into microbial diversity. If one understands the process carriers, their physiological needs and limitations better, the susceptibility to breakdowns and the necessary hydraulic holding times can be reduced.

The complexity of conditions outside a bioreactor or constructed wetlands, i.e. in the tip or post-mining lake itself, is particularly high. At the same time, problem solving on site is often the most cost-effective. It is also a challenge to implement a well-controlled *in-situ* remediation process.

The combination of biotechnical with chemical/physical processes can certainly be further extended. For example, one could initially concentrate mining water by membrane processes and then precipitate the substances contained using biotechnology.

For a long time, the treatment of mining water was seen only from the perspective of water purification. In view of rising energy prices and the increasing scarcity of resources, the question arises whether elements can be recovered from the contaminated water and given a new use. Some already achieved examples are the recovery of elementary sulphur in the THIOPAQ process or the use of precipitated schwertmannite for the production of pigments or adsorbents. Challenges for the future will be to extract further elements from these waters and use the means available for selective separation to facilitate the extraction of pure substances

NEED FOR RESEARCH

- Examination of relevant organisms also using the -Omics methodology
- Biotechnological optimisation of bioadsorbents
- Development of controlled *in-situ* remediation processes
- New processes for recovery of metals

4 Metal-containing residues from industry and the environment – biogeotechnological reprocessing?

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Introduction

New deposits of raw materials are being continuously developed to meet the economic needs for raw materials and energy. In addition, an attempt is being made to recover at least part of the raw material requirement (recycling). The extent to which this is achieved will depend significantly upon the ability to successfully separate these various materials; however, these separation processes have currently still not been perfected. For this reason, residual amounts of materials are still incurred during recycling operations that contain significant amounts of recyclables. From today's perspective, residues from older recovery technologies in particular contain concentrations that are partially higher than those in mining ores which are considered economically recoverable. Therefore, an increase in the efficiency of resource usage is seen as one of the most urgent challenges by the OECD.

We encounter today large quantities of metal-containing industrial residues: these are residues from iron smelters, usually as slags and from ore reprocessing plants, which are stored as flotation residues, or tailings. In addition, we also find iron-rich red sludge from aluminium recovery, slag and residues from phosphorus and phosphate production, filter residues from the manufacture of titanium oxide and sludge from galvanic plants. This also includes ash from different incineration processes used in gas, oil and coal-fired power plants, as well as waste incinerators, and dusts from dust extraction and filtering systems. Finally, many residues occur in sewage and bio-gas plants as well as river and harbour sludge. These residues are mainly oxides and hydroxides, phosphates, carbonates and silicates, which contain a number of important metals and trace elements. They are not only relics of the past, but still arise in the various combustion, cleaning and recycling processes even today. These include in particular the sludge from drinking water and water treatment plants, as well as the ash from various incineration processes and slag from metallurgical production plants. In addition to these residues, the number of recycling products and goods to be returned into the economic cycle, such as electronic scrap, catalytic converters and composite materials is constantly increasing. There are also residues from new industries, such as the photovoltaic or chip industry. The concentrations of recyclable materials in these residues are also often far higher than those which are present in deposits, or they can be increased to such an extent by enrichment and concentration processes.

It is problematic that as a rule none of the 'usual' energy sources for microorganisms are available in the recycling or separation of recyclables by microbial processes from these residues. However, there are a number of geo-microbial processes, which can be derived from the natural material cycles and used for recovering recyclables.

There is an enormous variety of microorganisms to choose from, which opens up a variety of possible reactions for the dissolution or transformation of the matrix. The dissolution of the matrix – called acidolysis – occurs by formation of inorganic acids such as sulphuric acid, nitric acid, or carbonic acid. Organic acids often act concomitantly as complexing agents; this process is therefore called complexolysis. Also, extracellular substances play a special role. So-called siderophores are able to complex metal oxides with low solubilities and to make these accessible. Other destructive and dissolution mechanisms are based on redoxolysis – the reduction and oxidation of cations such as Mn^{4+} or Fe^{2+} and Fe^{3+} in a mineral matrix, resulting in their destabilisation. The formation of water-soluble

cyano-complexes by microbial cyanide formation is possible, even in the alkaline pH range. The transformation of metals into organometallic compounds by microbial processes, such as methylation or ethylation and the formation of volatile metallorganic compounds, has been rarely analysed and implemented in technologies up until now. The microbial digestion of silicate opens up possibilities for extracting recyclable materials which were unimaginable until now.

The following examples are intended to give an impression of the diverse approaches used in biotechnical (recovery) extraction technologies. It is a very complex subject, so that the overview does not claim to be complete.

Residues from the industry

Sludge

The type, number and quantity of incurred and deposited sludge is tremendously large. Sludges from etching processes and galvanising plants are largely reprocessed today. Microbial processes are also known for this purpose. This does not yet apply to the iron and titanium oxide-containing red sludges from the aluminium production. Red sludges are the water-insoluble residues left after extraction of aluminium with sodium hydroxide and contain different silicic acid compounds in addition to iron and titanium oxides. Recovery of iron using known microbial processes, but also by dissolution of the silicate matrix is feasible.

This also applies to the sludges from pit water and drinking water treatment plants. Theisen sludges are a particular problem. They arise in the smelting of copper slate. Their levels of trace and precious metals are high, but so far a suitable reprocessing technology has been lacking. In the Mansfeld mining district, copper ores were not separated by flotation from the accompanying material, but were introduced directly into the smelting process. This resulted in flue dusts containing volatile substances and heavy metals. With the introduction of flue dust scrubbing and the use of the Theisen scrubber, a coupling product accrued. It contained particles stuck together with bitumen from copper shale and volatile heavy metals. Up until the beginning of the 1970's, these were reprocessed in the lead smelting site in Hettstedt. The recycling chain has been broken since the smelter was closed. Therefore, the Theisen sludges were stored in the hope that a suitable recycling technology would be found. The information regarding quantities vary from between about 200,000 t and approx. 450 000 t of sludge, which are supposedly stored in the mono-landfill Pond 10 on the site of the primary smelter in Helbra. The recyclable material potential is very high with 18% zinc, 14% lead, 1.2% copper, and 1.2% tin, as well as a number of other trace and auxiliary elements. Other main components are 17% silicon dioxide, 16% sulphur, and 11% carbon. Recent studies in connection with the recovery of copper from bituminous copper shale have shown that the organic components can be degraded microbially and the metals can thus be mobilised.

Sludges from wastewater treatment plants usually also contain high concentrations of metals. This is based on the ability of microorganisms to store metals by absorption and accumulation processes. Particularly high concentrations – up to several grams / kg dry sludge – can often be found for zinc and copper. If biomass is used for bio-gas formation, the concentrations in the residues are often significantly higher. Due to methane formation and the reduction of sulphate, the metals are usually precipitated as sulphides, hydroxides or carbonates. The composition determines the nature of possible leaching by microorganisms. In addition to metals, the high phosphate concentrations make this sewage sludge interesting for recycling. According to an environmental database, the amount incurred in 1990 was approximately 17 million t after digestion, of which approximately 60% was deposited and approximately 10% was given up for waste incineration.

Flotation residues

A large number of wash heaps have arisen following decades of mining activities, which contain different recyclable materials. Tin mining in Altenberg has left behind three large landfills in recent decades with the Schwarzwasser heap, the Tiefenbach heap and the Bielatal heap, which consist of very finely grained sediments. In the Bielatal

heap alone, 10.5 million m³ of tailings are stored today. They contain approx. 0.2% tin, approx. 200 ppm tungsten, approx. 100 ppm molybdenum, 200 ppm bismuth, 850 ppm lithium and rubidium, manganese, titanium, and caesium, in addition to other trace elements – offering a considerable resource potential. The recovery of tin through microbial processes has already been tried several times and published, but due to the very low solubility of Sn⁴⁺ this has been considered problematic. A separation seems to be possible here, however, if it is possible to successfully reduce Sn⁴⁺ to Sn²⁺ in a pH range below 3, or the separation as methylated tin after a bio-methylation process.

In the fluorite and barite spar production, which is currently being established in the Erzgebirge region, approx. 6000 t/a of sulphide-containing residues from flotation processes are to be expected, which are intended to be smelted. Microbial leaching and metal recovery seems to be possible in this case, too.

Dusts

Dusts occur in various processes and are separated by filter plants. Zinc containing dusts are nowadays mainly smelted. Dusts from colour television and fluorescent tube production contain relevant amounts of rare earths – about 8-15% yttrium, 1-2% europium and <0.1% gadolinium – in addition to zinc, aluminium, cadmium and iron. In order to separate the recyclable materials – in particular europium, gadolinium and yttrium – an attempt was made to liberate the materials with oxidising and acid-forming microbial processes. In this respect, it was shown that microbial leaching of sulphide-containing materials for TV screens is possible and yttrium concentrations up to 500 mg/l can be achieved.

Ash

Ash as a residue from incineration processes contains a variety of valuable elements. For example, lignite is a good absorption and storage medium for metals. Currently, about 300 million t of lignite are produced every year in Germany. The ash content is approx. 10% to max. 20%, based on the dry starting material. This means an annual ash production of at least 15 million t. These ashes consist mainly of calcium, magnesium, aluminium in addition to silicon and furthermore contain considerable amounts of trace elements and rare earths, depending on the type of coal and the deposit. 1 t ash is currently worth approx. € 520 on the basis of the prices of the metals contained therein, without silicon. So far, ashes have been deposited, used as aggregate for the immobilisation of pollutants or in the construction industry. Recovery of metals from these ashes by different microbial leaching processes is feasible and has already partly been tested. It can be carried out in acidic, neutral or alkaline pH ranges, depending upon the concept used and the target element, and leads to different recyclable materials. Analogous considerations apply to coal ash.

The ash from the oil and gas fired plants and the filter dusts from the petroleum refining industry contain above all 2-10% vanadium and 1-3% nickel. This is melted in drum furnaces with the addition of soda. In this way, sodium vanadate (Na₄V₂O₇) and ferrous nickel matte (FeS and Ni₃S₂) are recovered. Vanadium concentrates with a high content of elementary carbon have been mostly put into landfills so far. An annual amount of approx. 100,000 t of such filter dusts is estimated for Europe. Microbial leaching for the recovery of these metals appears to be promising.

Flotation: Enrichment process used in mining, paper recycling, water preparation or soil remediation operations. It is based on the different wetting properties of particles with gas bubbles; well-wetted particles collect in the foam on the surface of the suspension. By the addition of additives, it is possible to change the wetting properties.

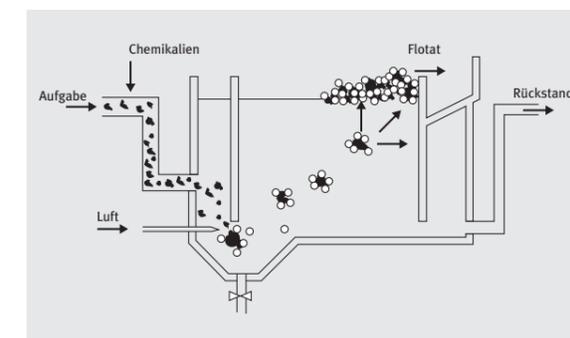


Fig. 11: Flotation processes (Source: Manual "Bodenwäsche", Landesanstalt für Umweltschutz Baden-Württemberg (1993), S. 81)

In laboratory experiments with power plant flue ash, significant amounts of cadmium, chromium, copper, nickel, lead and zinc could be separated by microbial leaching processes using *Bacillus megasterium*, *Pseudomonas putida*, *Acidithiobacillus* sp. and *Aspergillus niger*, whereby the yield amounted to up to 80% and depended upon the respective strains used.

Ashes from incineration plants are particularly interesting. Due to the pre-sorting of the 'fuel', higher concentrations can be expected than in other ash, according to the composition of the respective starting substances. An average of 250 kg/t household waste incineration ash (HMVA) is produced during the incineration of municipal solid waste. With a current capacity of about 20 million t/a for the approx. 70 large-scale waste incineration plants in Germany, this results in approx. 5 million t of ash, which will significantly increase in the next few years. Currently, only approx. 8% metals, of which approx. 1% are non-ferrous, are recovered from HMVA. The largest part – about 75% – is used in landfill and road construction. About 10% are stored in landfills. HMVA exhibits a wide range of solid material parameters due to the heterogeneous composition of waste used in incineration. For example, raw and aged ashes contain 1,000-3,500 mg/kg of lead, 200-1,000 mg/kg chromium, 1,000- 10,000 mg/kg copper, 100-500 mg/kg of nickel and 2,000-7,000 mg/kg zinc. In particular, the average concentrations of copper are already in the range of primary mining copper deposits. In order to improve the recycling of non-ferrous metals in HMVA, reprocessing primarily has to be optimised, for example, using separation technology based on eddy current or induction separators, as well as crushing the coarse fraction before further classification. In the reprocessing of fine fractions, biotechnological processes such as e.g. bioleaching can contribute to better recovery of recyclable materials in addition to (wet) mechanical reprocessing steps.

Slag

Slag is the residue left after different smelting processes. It currently occurs primarily in smelters during the extraction of zinc, lead, copper, and nickel. With the decline in production, the slag landfills at old smelter sites have been restored and are usually covered by a surface water-reducing layer. Such sites can be found, amongst others, in the Harz mountains, in Freiberg, and in St. Egidien from the nickel smelter. Slag from productive smelters, which can still contain significant amounts of recyclable materials, are mainly silicates.

In the zinc recycling smelter in Freiberg, roller oxide leaching has been developed and introduced on an industrial scale to recover zinc from dusts. The throughput is comparatively very high with 50,000 t per year. Analysis of slag behaviour has shown that it is possible to extract the remaining heavy metals such as zinc, lead, and cadmium from slag with neutrophilic and alkalophilic microorganisms. Only zinc is separated in the acidic pH range.

Slag arising in lead smelters is handled differently. In this case, slag from the secondary lead smelter MRU Freiberg (Muldenhütten Recycling und Umwelttechnik GmbH) is landfilled, whereas silicate slag arising from the primary lead smelter BBH Berzelius Bleihütte Stolberg – some approx. 60,000 t/a – is mainly used in landfills and for road construction as Berzelit®.

In the smelting of copper concentrates, the Aurubis copper smelter (formerly Norddeutsche Affinerie) produces, besides copper and precious metals, an iron silicate smelt which is processed in two different ways into iron silicate-containing rock and/or granules. The copper concentrates, which are used for smelting, include copper and sulphur and also approx. 30% iron, and are bound in the mineral phase. With the addition of quartz sand, a pyrometallurgical iron-silicate smelt is created at a temperature of approx. 1,250°C. By slowly cooling down, a high-quality, crystalline rock is produced. This consists of approx. 95% mineral olivine (Mg, Fe)₂[SiO₄] and is comparable with igneous rocks such as basalt, diabase and gabbro. After shock-cooling under a water jet, amorphous granulate is produced which is comparable to washed sand 0-4 mm. This iron silicate granulate is processed to the standardised abrasive blasting agent Nastra, whereas the iron silicate rock is used as a building material. As a multitude of other elements possibly also exist in the slag, further recovery of recyclable materials analogously to the above-mentioned microbial slag dissolution is feasible.

St. Egidien provides an example for the treatment of slag heaps. With the closure of the nickel smelter in 1990, a huge industrial area became an abandoned site. In total, there existed a company landfill (rinsing pond) with approx. 2.3 million t of slag and other production residues, in addition to a core area polluted with nickel, chromium and cobalt compounds.

These silicates can be liberated microbially as has been shown by the break-up of phosphorus furnace slag (POS) in the past using different processes. POS is a calcium silicate-containing residue, which is left following the electro-thermal production of phosphorus from apatite; it contains about 1% of rare earths and 2% strontium. Over a longer period of time, about 120,000 t/a have been produced in Piesteritz and approx. 25,000 t/a in Bitterfeld. The entire amount of slag which has accumulated in Germany is currently estimated at approx. 22.6 million t. In Bitterfeld and Piesteritz, various investigations were made before 1990 to utilise phosphorous slag or to refine it. The biotechnical work had as its goal the digestion of these silicates using acid-forming processes via autotrophic and heterotrophic microorganisms. The separation of rare earths took place by chemical and/or microbially initiated chemical leaching processes. In Bitterfeld, the digestion was investigated using waste hydrochloric acid and microbially with gluconic acid; at the same time, active silicic acid, sodium silicate, zeolites, and rare earths were recovered in addition to organic products such as calcium gluconate. In Piesteritz, the digestion was processed using nitric acid for the recovery of rare earths and strontium.

In addition to POS, extensive amounts of phosphate gypsum were incurred from the wet-chemical production of phosphoric acid by the digestion of apatite with sulphuric acid, which were then also landfilled. The total amount is estimated to be approx. 34 million t. The content of rare earths is approx. 0.3-0.4% for phosphate gypsum from Kola apatite. In the special waste landfill Knapsack-Hürth, 6 million t of phosphate gypsum are said to have been landfilled, in addition to calcium silicate slag.

Recyclable production residues

Many recyclable residues in the industry can be separated by microbial processes; these include, for example, composite materials made of cardboard, paper as well as plastics and metals. These materials are currently incinerated and the metals are separated. An alternative is to break down the organic substrates or transform them into water-soluble compounds microbially.

Electronic waste can be solubilised by different acid-generating microbial processes and broken down into its component parts. For this purpose, autotrophic as well as heterotrophic microorganisms can be used. The same applies when shredding residues from scrapped cars, which can also undergo a leaching process after pre-treatment, as well as used catalytic converters. It had already been shown in the 1980's that nickel and molybdenum can be recovered by nickel-resistant moderate acidophilic microorganisms from hydrogenation catalysts, containing 1.5-3% nickel and 4-11% molybdenum, in addition to aluminium, iron and calcium. Analogously, studies with modified *Aspergillus* strains led to yields of 78% nickel, 82% molybdenum and 65% aluminium.

Up until now, proven recycling technologies for the waste and faulty batches of photovoltaic production are lacking. In the production of thin-film modules, semiconductor materials such as cadmium telluride and copper-indium-gallium selenide (CuIn(Ga)Se₂) arise, amongst other things. So far, only a large scale wet chemical recycling process exists for the recovery of cadmium telluride (First Solar). Other recycling technologies are in the pilot phase. In this case, the use of biotechnology would have to be examined and tested.

Residues in the environment

Landfills

Abandoned household waste landfills are another source of recyclable materials. The recyclable content of ash landfills corresponds to the composition of the combustibles at correspondingly higher concentrations. If the share of organic compounds is high in the landfill material, the concentrations of metals increase due to the conversion of the organic material into landfill gas, provided that they are not removed with the seepage water. Usage is feasible after completion of the methane formation phase.

River, harbour, sea, flooding sludge

Suspended particles and fine particles accumulate in rivers and reservoirs, which can bind metal cations by their high adsorption capacity. They are removed regularly in order to keep rivers navigable. Likewise, sediments settle on artificial barriers in rivers, which are typically rich in heavy metals and trace elements. Approximately 330,000 t of sediment alone are present along a 2.5 km section of the Weisse Elster River in the city of Leipzig, which includes, amongst other things, 1,300 t zinc, 81 t nickel and 79 t copper. Also, harbour sludge, sea sludge which occur especially during clean-up operations in the waters of the Bodden, and sludge from flooding are loaded with heavy metals.



Fig. 12: Behandlung schwermetallhaltiger Sedimente durch Phytoremediation

NEED FOR RESEARCH AND ACTION

- Central registry of residues, residual substances and waste with details of the content substances and their concentration
- Studies on the efficiency of microbial reprocessing of different metal-containing secondary raw materials
- Development of reasonably priced naturally oriented processes for reprocessing and separation of oxide and hydroxide, silicate, carbonate, phosphate containing residues with the aim of recovering recyclable materials and the minimisation of residues.
- Development of reduction processes for metals in strongly acidic (e.g. tin), but and especially also in a neutral pH range.
- Analysis of the formation of metallo-organic water soluble or volatile compounds and the effect of siderophores.
- Analysis of the enzymatic processes, which are the basis for recovery, and the development of enzyme catalytic processes.
- Analysis of the genetic principles of microbial reactions and the combination of different specific genetically fixed reactions in microorganisms, as the basis for the development of new technologies.

5 Geomicrobiology underground – opportunities for geobiotechnology

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Deposits – Microbiology & MEOR strategies

For decades, it has been known that methane is formed by microbial activity directly in oil, gas and coal deposits. Methane is produced from hydrocarbons, which are transformed by anaerobic microorganisms in the absence of oxygen. The understanding of these processes in deep oil, gas or coal deposits, as well as other geo-systems such as marine sediments, is not only scientifically interesting, but is also of great economic and social importance, as the quality of the oil changes; this influences the exploration and recovery of energy raw materials significantly.

Examples of problems caused by microorganisms in the production of oil and natural gas are (I) the formation of toxic and corrosive hydrogen sulphide in sulphate-rich deposits (“acidification”), (II) the formation of heavy crude oils which are difficult to exploit and (III) microbial corrosion caused by biofilms in pipelines and production facilities. Therefore, it is important to be able to assess the degree of degradation of storage deposits for the exploration industry.

However, microorganisms in these deposits not only have a negative effect. Their use in MEOR strategies (Microbially Enhanced Oil Recovery) offers considerable potential for more effective exploitation of reserves. One must first determine the extent reached for recent methane formation by microorganisms in coal and oil deposits, and which microorganisms are involved. This should lead to a reliable prediction regarding the possible economic use of this process. A cost-effective biotechnological process to convert amounts of petroleum or coal, which are difficult to extract, into compounds which are easier to recover, such as methane, would provide additional energy resources which are environmentally friendly. A respective change in the geological or geochemical conditions will also contribute to the more efficient use of storage deposits. Examples of microbially catalysed reactions which can be used include the formation of bio-surfactants or acids for solubilizing petroleum, the formation of large quantities of gas to increase the pressure as well as to seal pore spaces. The behaviour and direction of the flow of oil or water (“selective plugging”) can be influenced with the help of specific biofilm formation.



Fig. 13: Tiefenprobennahme in einem Gasfeld

Gas storage (H₂, CH₄)

In view of the growing fluctuating electricity generation from renewable energy sources, such as wind and solar energy, new storage technologies are needed. For this purpose, the transformation of electricity into hydrogen or methane is currently being discussed, with subsequent storage of gases in pore and gas storage caverns. Likewise, the feeding of biogas into the existing gas network and thus possibly also into gas storage facilities is being discussed.

The storage of natural gas in pore and storage caverns has been practiced successfully in Germany for many decades. However, the underground storage of hydrogen gas or biogas (methane) in particular places special demands due to the specific physical, chemical and biological properties of hydrogen. If bacterial growth is stimulated by hydrogen in pore storage facilities, hydrogen sulphide and organic acids can be formed, which are corrosive. Bacteria or their organic metabolic products can clog pore spaces. In addition, there is a loss of gas due to microbial degradation, which can attain relevant orders of magnitude. Unfortunately, only insufficiently documented experience exists from coke oven gas storage, which was practiced up until the 1970's for underground storage of hydrogen in pore storage facilities. In this respect, there is high demand for research to be carried out here.

Geothermal energy

Deep geothermal energy offers an economic and climatically friendly alternative to fossil fuels at many locations. In recent years, more than 15 new geothermal plants have been built in some of the Federal States that use hot water from great depths for the district heating supply and also partly for generating electricity. The requirements for plant and production equipment vary and these are influenced by the chemistry and temperature of the fluid, the quantity and the composition of dissolved gases and the desired production amounts. However, microbiology also plays a role: microorganisms from the aquifers can be introduced into the system via the thermal water. This can lead to local damage caused by microbial corrosion or the reduction of flow rates by the formation of deposits and biofilms. The temperature changes in the substrate also affect the hydro-geochemical conditions and the microbiology. For estimating the medium to long-term operational safety, it is important to know whether and to what extent microbial biocoenosis and local geochemistry in thermal water aquifers have changed during production and passage through the plant, as well as during the re-injection of thermal water after it has cooled down.

Carbon dioxide storage (CCS)

Germany wants to reduce its greenhouse gas emissions by at least 80% by 2050. For this purpose, the separation and storage of CO₂ in deep geological formations is also being examined in addition to the central approaches for energy efficiency and renewable energy. This so-called CCS technology (Carbon Dioxide Capture and Storage) is of long-term importance, especially for coal-fired power plants. The technology has been tested on an industrial scale for several years in Norway and Algeria. Similar storage projects are in preparation in many industrialised countries. With the current state of our knowledge, it is not possible to predict how microbial activities and their associated geochemical reactions and processes affect the capacity, efficiency and long-term reliability of CO₂ storage facilities. The aim of ongoing research projects is to investigate how high CO₂ concentrations affect physiological activities and the composition of microorganism populations and how these geochemical catalysts behave under storage deposit conditions. Active, highly-adapted microorganisms, which play important roles in biogeochemical material cycles, live in such extreme environments. They are also crucial for long-term conversion of CO₂ into methane or biomass. The results of these studies will lead to a substantiated selection of storage sites, as well as a better assessment of the capacity, efficiency and long-term reliability of planned CO₂ storage deposits.

Recent research work is concerned with the consequences of possible leakage from CCS storage sites for groundwater and deep biogeochemical processes. The ecological implications on natural microbial communities by pH reduction and high CO₂ partial pressures in the geosphere have not been conclusively clarified and are important for the implementation of CCS activities.

Final disposal of radioactive waste

Microbial processes also play a role in the final disposal of radioactive waste underground. Investigations in this respect were carried for the geological barriers granite and argillaceous rock. A low-level of colonisation with microorganisms could be established. Sulphate reducing bacteria are of particular importance, which form the corrosive gas hydrogen sulphide which can cause corrosion problems in technical barriers (metal canisters). Microorganisms underground also catalyse the formation and degradation of carbon dioxide, hydrogen and methane, the degradation and the formation of organic carbon as well as the reduction of atmospheric oxygen. Furthermore, microorganisms affect reducing and oxidising processes. They play a role in the mobilisation and immobilisation of metals and radio-nuclides. In addition, metals are absorbed onto biomass. It remains to be clarified to what extent microbial processes are stimulated by the dispersion of geological barriers and the storage of waste (temperature rise). Above all, the interfaces such as the surface of the geological barrier or the transition from the clay rock bentonite to the metal canister are important. The microbial processes have to be simulated and quantified and incorporated into mathematical models in order to provide even stronger evidence in the safety analysis.

Microbial degradation of organic pollutants – Bioremediation

In Europe, there are more than 3 million abandoned sites with suspected contamination. About 250,000 of them are classified as requiring restoration according to previous state of our knowledge. The standing committee for contaminated sites of the Federal/State Working Group for Soil Protection has compiled more than 300,000 abandoned sites suspected of contamination in Germany alone, from which currently 4000 have been restored. As site inspections will still continue, the number of sites classified as in need of restoration could rise by 50% up to the year 2025.

Active restoration (*'ex-situ'*) of contaminated sites using soil excavation, soil washing and landfilling, Pump & Treat, etc. – has proven to be not very practicable in many locations: in populated areas, *ex-situ* technologies are often not technically feasible or are economically impracticable. In the face of the immense number of contaminated sites, it is urgently necessary to develop minimally invasive, energy-saving, efficient and economically sustainable site management and restoration strategies. The pollutant should be eliminated directly into the contaminated environmental compartment (*'in-situ'*).

The starting point for the development of innovative in situ safety and restoration concepts is the understanding of biological degradation processes. Examples include (I) the aerobic degradation in the air sparging or the Pump & Treat process, (II) the acceleration of anaerobic degradation of pollutants (Enhanced Natural Attenuation, ENA), or (III) just the observation of the natural course taken by degradation processes (Monitored Natural Attenuation, MNA) to secure the site. In order to ensure that the biological self-cleaning potential is able to sustainably reduce the pollutant load at a site, the effective processes must be measured qualitatively and quantitatively. Requirements for pollutant monitoring methods are high. Natural degradation processes are relatively slow, which is why MNA activities typically take a long time (years or even decades). This places high demands on the planning and monitoring of these activities and thus the long-term forecast for

Pump & Treat: Process in which water for the treatment is pumped from underground.

Air Sparging: Introduction of a flow of air into the ground. Volatile compounds are then suctioned up and the soil air is subsequently reprocessed.



Abb 14: Kernbeprobungen im Gasfeld zum Monitoring

the damage to develop. In particular, it is important that waters or adjacent soil and ground water areas are not contaminated. If it is established that the natural degradation potential is not sufficient to reduce the pollutant load quickly enough, an attempt can be made using ENA to accelerate the degradation of pollutants. In order to implement MNA or ENA concepts in contaminated site processing, the efficiency of pollutant degradation at a site has to be demonstrated and forecast over long periods of time. A key issue in the planning of restoration projects is therefore the factors which determine – or possibly limit – the microbial degradation performance.

Only a few processes exist for the direct detection and evaluation of pollutant removal. They are mostly only applicable for certain classes of pollutants and not for all types of contamination. The need for research is necessary to develop quantitative methods for monitoring degradation. There are also combinations of methods which allow verification (I) of the biodegradation of contaminants which require little time, effort and costs, (II) assessment of the potential for microbial pollutant degradation, and (III) preparation of justified long-term projections concerning degradation performance.

If one estimates the stoichiometry of degradation and plans MNA and ENA measures, one has to consider biogeochemical transformations of inorganic compounds. Intermediate or end products of anaerobic respiration processes – e.g. reduced sulphur compounds (sulphide or elementary sulphur), ammonium, reduced iron (Fe^{2+}) – can be oxidised and compete with organic contaminants for electron acceptors. The reductive de-halogenation of chlorinated organic compounds may also slow down in the presence of more energetically favourable electron acceptors.

We still do not know much about the composition of microbial communities that reduce and mineralise pollutants in the environment. The key organisms of degradation at the respective site are mostly unknown, and only a fraction of the entire microbial community is cultivable in the laboratory. The microbial degradation of pollutants is often a joint effort of various microorganisms, resulting from the symbiotic interaction. In soils, or more exactly in the rhizosphere (root zone), a combination of bacteria, fungi, and plants is frequently observed. Such complex symbiosis can be classified using modern, molecular biological methods, which are independent of cultivation. If one knows the composition of the symbiosis of the microorganisms to degrade the pollutants, this opens up new possibilities for the deliberate manipulation and improved degradation result. The latest techniques from molecular biology – proteomics and metabolomics – are used to answer questions about the ecology of pollutant degradation.

The in situ degradation of pollutants and simultaneous biogeochemical processes can be non-invasive and therefore very elegantly characterised and quantified using isotopic fractionation techniques. A new approach is multidimensional isotope analysis, with which specific degradation pathways can be detected in the field. Methodological limitations – such as the lack of cost-effective routine methodology for hydrogen and chlorine isotopes, difficulties in isotope analysis of trace concentrations – currently restrict the use of isotope analyses in contaminated site research, but offer approaches for analytical development.

At most contaminated sites, the various pollutants are present as mixtures ('pollutant cocktails'). How individual substances in pollutant cocktails are degraded, and what inhibition or acceleration affects the degradation of individual substances, has so far been insufficiently studied. Herein lies the potential for further fundamental and applied investigations.

Many chemical compounds can act as electron acceptors in anaerobic degradation; in order to better understand the ecology of pollutant degradation, new techniques are needed for high-resolution characterisation of coupled electron transfer processes. The anaerobic degradation of many contaminants has been hardly investigated, both biochemically and microbially; more accurate knowledge of anaerobic degradation potential is important to assess the environmental behaviour of chemicals. The anaerobic degradation of pollutants in groundwater and sed-

iments has so far received scarce consideration when evaluating chemicals, although sediments and groundwater compartments are mostly micro-aerobic or anoxic. The anaerobic degradation of "emerging contaminants" from diffuse input sources has been little examined up until today and offers an attractive field for study in the future.

"Emerging contaminants" can be e.g. pesticides, surfactants, pharmaceuticals, plasticizers or stabilisers. A methodological challenge for assessing these diffuse contaminations forms the monitoring of degradation processes on a scale from water catchment area or deposition room.

NEED FOR RESEARCH

- Compilation and characterisation of microorganisms in deep underground
- Investigation of the effects of geothermy and CCS on microbial colonisation
- Understanding of natural biological degradation processes and monitoring procedures
- Involvement of microorganisms in scaling and biocorrosion
- Development of geobioetchnological processes for deep underground

6 Training in Geobiotechnology

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Geobiotechnology includes all microbial processes used in mining and environmental protection. These comprise of

- » the biotechnological recovery of recyclable materials from deposits, mining residues, waste or processing water (from biomining, biohydrometallurgy, bioleaching, biooxidation, biomineralisation, bioaccumulation, biosorption, bio-reduction, bio-precipitation, bioflotation, bioflocking),
- » the cleaning and quality improvement of soils, water and air by the fixing and degradation of pollutants (bioremediation processes) and the resulting minimisation of discharge, and
- » the monitoring of changes to substances by biosensors

In addition to knowledge of the general natural sciences (mathematics, physics, chemistry), geobiotechnologists, who deal with these complex fields of activity, should possess special knowledge about geology/mineralogy, environmental analysis, ecology, biotechnology (molecular biology, microbiology, biochemistry), bioinformatics and process technology (bioprocess technology). In order to develop processes for the recovery of recyclable materials and the breakdown of residual materials, up-to-date knowledge of molecular biology and the selection as well as taxonomy of microorganisms are imperative.

Nature and quality of current training courses

According to the knowledge of the authors, no course of studies is offered in “biogeotechnology” at German universities. Many courses of study offer modules as specialisation or elective subjects, which cover the basic biotechnical principles in the context of geological problems. Modules, which are concerned generally with microorganisms or specialise in soil conservation, are almost exclusively offered as partial or elective modules. These mostly involve the diagnosis of environmental and soil pollution problems. Only in a few cases are retrospective and preventive aspects addressed. Quite often, no previous microbial knowledge is necessary as a prerequisite or is mediated for modules dealing with these subjects. The curriculum only includes chemical or physical methods for reprocessing abandoned polluted sites, land use and protection or also for the recovery of materials. Biological methods are not discussed.

The Mining Academy of the Technical University in Freiberg should be mentioned here, as a good example. It offers the degree course (diploma) in “Geotechnology and Mining” studies, which specialises in the mining, monitoring and recovery of raw materials from flat and deep mining operations. Biogeotechnological contents are only briefly covered – an emphasis is placed on environmental and geotechnical training aspects. Since the winter semester 1996/97, the TU Mining Academy in Freiberg also offers a course of studies “Geoecology”, which can be completed after 6 semesters with a bachelor degree or after 9 semesters with a diploma. As part of this degree course, it is also necessary to gain credits in environmental microbiology/biotechnology. The main focus of training lies in the area of nature, environmental, soil and water conservation. With these principles, it is difficult to promote further develop in biogeological technologies.

However, there are courses of studies with more emphasis on biotechnology. For example, the University of Trier offers two Master’s Degree Courses, which do come closer in their approach to the subject – on the one hand, the Master of Science in “BioGeo-Analysis with the main focus on Biogeography, Ecology and Monitoring (BÖM)” and, on the other hand, the Master of Science in “BioGeo-Analysis with the main focus on the Molecular Biology

of Environmental Substances and Environmental Influences”. Both courses of study are more concerned with the analysis of environmental influences and environment management than biogeochemical processes.

At the Friedrich-Schiller University in Jena, attention is clearly drawn to the Bachelor of Science as well as the Master of Science in Biogeosciences that the “course provides education and training in the interface area between the biological and the geosciences” (http://www.uni-jena.de/unijenamedia/Downloads/studium/grundstaendig/bachelor/BSc_Biogeowissenschaften-p-21789.pdf). Despite the inclusion of extensive biotechnological modules and a basic course in the fundamentals of the subject, the main focus is placed also on remediation and restoration strategies. This does not necessarily exclude, however, that – both here as well as at other universities – individual lectures do also have some biogeotechnological content. Thus, for example, in the compulsory module Environmental Technology (series of lectures by Prof. B. Ondruschka) a chapter about “Recovering raw materials by the leaching of ores” is included. At the University of Anhalt (FH), biogeotechnological content is covered as part of the module on Environmental Bioprocess Engineering (lecture series by Prof. R. Pätz). The same applies for the University of Mittweida (FH), where some biogeotechnological content is included as part of the introduction to biotechnology lectures (Prof. P. Radehaus) as part of the Bachelor Degree Course of Studies in Biotechnology/Bioinformatics. In general, it applies for many universities in Germany that the main focus of the study courses offered lies primarily in areas other than biogeotechnology, a field with increasing importance for the future.

The Table in Annex 1 shows the biogeotechnological curricula offered at German universities, without attempting to be complete. The source of this information is from the descriptions provided for these courses of study and modules described by the universities in the Internet. Naturally, it cannot be assessed to what extent the teaching staff deviate from the descriptions of the modules. It is to be assumed that more interdisciplinary knowledge is imparted, without it being formally taken from the pure description of the module.

In summary, it can be said that courses of study which cover the essential aspects of biogeotechnology are not offered up until now and still have to be developed. In this respect, the need for specialists has to be looked at more closely, in order to align the present and future needs of the economy and the labour market.

Need for geobiotechnology graduates

Previous chapters have illustrated the economic significance of bioleaching, as well as biogeotechnical processes for soil and water reprocessing. It may be assumed that the use of biotechnical processes will increase and thus the need for trained and qualified biogeotechnologists will continue to grow in both Germany and throughout the world [P. Sackett 2012, www.thesolutionsjournal.com/node/1107].

So far, however, Germany is not adequately prepared for this development. Besides the already existing environmental and geoecology courses of study, there is a lack of specialisation opportunities being offered in the form of Diploma or Master Degree Courses of Study in biogeotechnology. Because this is a highly complex interdisciplinary subject, geobiotechnological education at the Bachelor Degree level is not recommended, as it demands some very fundamental and quite considerable amounts of knowledge and methodological competence as a prerequisite. A specialisation in geobiotechnology should, however, be based on this.

NEED FOR ACTION

- Dedicated master or diploma programs in geobiotechnology should be established in Germany to prevent skills shortage

Table 1 Geobiotechnological studies at German universities

Study program	University	Degree	Name of the module	Content
Applied geoscience with environmental geoscience and technology focus	Technische Universität Darmstadt	Master of Science	Pollutants	Biological remediation methods
			Interdisciplinary compulsory optional subject	Lectures on biology (microbiology, physiology of microorganisms, ecology)
			Crystals and minerals	Biominalisation and biomaterials
Applied geoscience	Karlsruher Institut für Technologie	Master of Science	Hydrogeology III – Protection and quality	Pathogenic microorganisms, hydro-bio-geochemical processes in ground water
			Hydrogeology IV – Ecology and climate	Fundamentals of groundwater microbiology
Geoecology	Karlsruher Institut für Technologie	Bachelor of Science	Biosphere – Flora	Anatomy and taxonomy of procaryots, fungi, algae, moss, ferns, plants
			Soil mineralogy	Biominalisation: Role of microorganisms
			Introduction to soil science	Soil conservation and biological processes in soil
BioGeo-Analysis with focus on biogeography, ecology and monitoring	Universität Trier	Master of Science	Genetic engineering and genetic monitoring	Handling of GMOs
			Molecular biogeography	Recent developments in molecular biogeography, genetics in environmental protection
			Advanced Aspects in Environmental Soil Science	Soil capacity, interactions, hydrologic inventory
			Soil Use and Sustainable Management:	Use of organic residues, sustainable soil use
BioGeo-Analysis with focus on molecular biology of environmentally relevant substances and environmental impact	Universität Trier	Master of Science	Ecotoxicology	Research on molecular biological impact
			Soil Biology and Soil Functioning	Role of soil organisms as inhabitants and designers
			Sustainable Chemistry	Application of sustainability criteria on material and energy cycles, utilization potential of renewable resources and biomass residues
Bio-Geo-Sciences	Universität Jena	Bachelor of Science	Material cycles	Understanding of material conversions including microbial conversions in soil
			Environmental mineralogy I	Causes and development of current pollution
			Quarternary geology and introduction to soil science	Soil science from a scientific perspective
			Limnology I	Central role of microorganisms in the polluted habitat water
			Mikrobiologie I	Methods of biotechnology in water/soil/rock
			Limnology II	Current problems in waste water and water treatment
			Mikrobiologie II	Fundamentals of the application of microbes in biotechnology and genetic engineering

Study program	University	Degree	Name of the module	Content
Bio-Geo-Sciences	Universität Jena	Master of Science	Bioremediation	Impact of substances in soil: bioremediation, reuse of brownfields
			Geomicrobiology/ Aquatic Microbiology	Interaction of microorganisms in minerals in aquatic and terrestrial habitats
			Applied microbiology/ Biotechnology	Relevant environmental organisms in soil; degradation of problematic substances; biofilms; microbial communication; fermentation; metagenomics
			Soil microbiology	Molecular biological techniques and methods of genomics; genetic engineering
BioGeoSciences	Universität Koblenz-Landau	Bachelor of Science	Interaction of organisms with the environment II	Frequency, degradation of pollutants, taxonomy - microorganisms
			Mikrobiologie	Microbial ecology
BioGeoSciences	Universität Koblenz-Landau	Master of Science	Ecophysiology of heterotrophic organisms	Aquatic microorganisms
			Research Lab Microbiology	Topics in microbial ecology; surface-associated, independent and symbiotic microorganisms
Soil use and soil conservation	Hochschule Osnabrück	Master of Science	Soil remediation	Microbial processes / phytoremediation
			Soil ecology and environmental monitoring	Methods of soil ecology; microbial biomass, marker substances
Geoenvironmental Engineering	TU Clausthal	Master of Science	Soil remediation	Biological methods for soil purification
			Water treatment, wastewater technology	Special biological wastewater technology
Geoecology	Universität Bayreuth	Bachelor of Science	Plant ecology and microbiology	Ecophysiological processes, morphological adaptation of plants to limited resources, stress and competition; biology and life forms of microorganisms and metabolic processes
			Biosphere	Fundamentals of distribution of life on earth; concepts and techniques
Geoecology	Universität Bayreuth	Master of Science	Biogeochemistry	Soil ecology, soil contamination, environmental forensics
Geoecology	TU Braunschweig	Bachelor of Science	Biology	Botany, ecology, zoology, microbiology: Chemical and cellular bricks – cell structure and lifestyle – metabolism and energy conversion – taxonomy and diversity – classic and molecular methods
			Pedosphere	Soil science; water and matter balance

Study program	University	Degree	Name of the module	Content
Geotechnology and mining	TU Bergakademie Freiberg	Diplom-Ingenieur	General environmental history	Current developments and initiatives in the context of societal developments
			Solid mineral resources – formation processes of mineral deposits and mine geology	Availability of solid mineral resources; exploration and evaluation of resources; analytics of ore and industrial minerals
			Geology, genesis and prospecting of coals and hydrocarbons	Fundamental knowledge of methods, processes and economy of searching and exploring deposits; accumulation and maturation of organic substance; comparison of methods; detection and evaluation of resources; economy of deposits
			Fundamentals of exploitation/geotechnological exploitation	Differentiation versus classical exploitation methods; dissolution – leaching – fracking – geothermal methods – hydraulic/hydronechanical methods
			Fundamentals of hydrogeology	Dissolved and particular ingredients; bacteria; viruses; dispersion, diffusion; contamination and remediation
			Engineering geology III/ Environmental geotechnology	1) Heap building and industrial tailings ponds 2) Introduction to brownfields 3) Geotechnical protection and remediation of former mines
			Recultivation	Scientific principles of recultivation; use requirements and implementation in mining landscapes
			Socio-economical environmental assessment	1) Environmental aspects, impacts, risks; modeling of environmental risk 2) Environmental cost accounting 3) Planning, installation, implementation and monitoring of integrated management systems
Geology/Mineralogy	TU Bergakademie Freiberg	Bachelor of Science	General deposit theory	Commodity markets; economic geology; processes in deposit generation; processes of accumulation, textural and substantial conversion of organic substance in geologic spaces of time
			Applied geoscience III	1) Environmental Geology: air pollution, brownfields, environmental impact of mining, dumps including ultimate disposal of radioactive and highly toxic waste 2) Principles of near-surface drilling engineering and dissociation for sample taking 3) Practical experience in current projects (dumps, remediation, etc)
			Applied mineralogy I	Connection between characteristics and industrial applications; overview on genesis, deposits, raw material situation, mineral processing and specific implementation parameters
			Applied stratigraphy and facies	Principles of micropaleontology; biostratigraphy; relevance of the most important microfossil groups; macro and micro paleontology

Study program	University	Degree	Name of the module	Content
Geology/Mineralogy	TU Bergakademie Freiberg	Bachelor of Science	Sedimentology/ Stratigraphy I	Transport- and deposition processes; petrography of sediments; syn- and postsedimentary textures; deposition systems
Geoecology	TU Bergakademie Freiberg	Bachelor of Science	Introduction to genetic engineering	Strategies, enzymes, vectors and their properties; safety; law; methods (isolation, subcloning, restriction digestion, Southern blot...)
			Principles of biochemistry and microbiology	Structure and functionality of biomolecules; DNA replication; phylogenetic classification and identification of microorganisms; dissociation of natural substances; N-, S- and Fe-cycles
			Principles of environmental protection	Administrative processes in environmental protection; methodical competencies; management of biotopes and landscape conservation
			Microbiological-biochemical laboratory	Microbiological and biochemical methods; aseptic techniques; enrichment, isolation and identification of bacteria; types of metabolism; leaching of sulphides; N ₂ -fixation; synthesis of antibiotics
			Environmental geochemistry and ecotoxicology	Impact of changes in geo and eco systems on living nature; anthropogenic influence on material cycles; model systems – bioindicators – biomonitoring
			Environmental microbiology	Microorganisms for the dissociation of organic pollutants and mobilization/ immobilization of anorganic pollutants; ecological strategies; proof of damaging properties of chemicals
			Geoecology	TU Bergakademie Freiberg
				Mechanisms of negative impacts of pollutants and other stressors; analysis of exposition and effects; pharmacology and impact analysis
			Biotechnological production processes	Knowledge and competency of biotechnological methods in production processes; biorefinery; renewable resources; upstream and downstream processing
			Management of biotopes and landscapes	Use of modern methods in landscape ecology; analysis and assessment of landscapes and remediation ecology; development frameworks
			Biotechnology in Mining	1) Basics: microbial energy metabolism, redox reactions; 2) Microbial leaching: MO involved in mechanisms of leaching, production of copper, gold and diamonds; 3) oxidation
			Engineering geology III/ Environmental geotechnology	1) Heap building and industrial tailing ponds 2) Introduction to brownfields 3) Geotechnical protection and remediation of mining landscapes

Study program	University	Degree	Name of the module	Content
Geoecology	TU Bergakademie Freiberg	Master of Science	Microbiology of Fossile and Regenerative Energy Resources	mechanisms of aerobic an anaerobic degradation of organic compounds; microbiological processes affecting oil and gas deposits and CO ₂ storage
			Microbiological-biochemical lab	Microbiological and biochemical methods; aseptic techniques; enrichment, isolation and identification of bacteria; types of metabolism; leaching of sulphides; N ₂ -fixation; synthesis of antibiotics
			Molecular Ecology of Microorganisms	molecular techniques to analyse microbial communities; molecular methods for the identification of isolated bacteria
			Recultivation	Scientific principles of recultivation; use requirements and implementation in mining landscapes
			Trace analytics	Methods of trace element analysis; atomic emission, atomic absorption, mass spectroscopy, electrochemistry, enrichment and separation processes, speciation
			Stress physiology and ecotoxicology	Adapation reactions and mechanisms of damage; defense against toxic substances; deputy organisms; biotest batteries
			Environmental bioprocess engineering	Relations between biology and process engineering; commodity industry; biological conversion in production and end-of-pipe processes
			Environmental microbiology	Microorganisms for the dissociation of organic pollutants and mobilization/ immobilization of anorganic pollutants; ecological strategies; proof of damaging properties of chemicals
			Behaviour of organic pollutants in the environment	1) Chemodynamics: Substance assessment; abiotic transformation processes, models of fugacity 2) Biological dissociation; persistency, complete dissociation vs co-metabolism; biotensides, bioavailability 3) Ecotoxicology, bioaccumulation, dose-effect relationship, combinatory effects
			Subsoil remediation	Risk analysis of damage events; modern methods for subsoil remediation and monitoring; processes in saturated and unsaturated zones relevant for remediation
International Master Program Geoscience	TU Bergakademie Freiberg	Master of Science	Groundwater Chemistry I	Chemistry of the elements Si, Al, Na, K, C, Ca, Mg, halogens, S, Fe, Mn, N, P and trace elements; radioactivity
			Molecular Ecology of MO	molecular techniques to analyse microbial communities; molecular methods for the identification of isolated bacteria
			Rheology, Lattice Preferred Orientation, Microtectonics	principles in rocks and minerals; kinematic analysis of microstructures, rheology of major rock-forming minerals

Study program	University	Degree	Name of the module	Content
International Master Program Geoscience	TU Bergakademie Freiberg	Master of Science	Subsoil remediation	Risk analysis of damage events; modern methods for subsoil remediation and monitoring; processes in saturated and unsaturated zones relevant for remediation

7 Overview on websites and further information sources

(no claim to be complete, ranking does not reflect valuation)

Associations

**DECHEMA Gesellschaft für chemische Technik und Biotechnologie e.V.,
Temporärer Arbeitskreis Geobiotechnologie**
<http://biotech.dechema.de/Fachgemeinschaft+Biotechnologie/Gremien+der+Fachgemeinschaft/Geobiotechnologie.html>

**DECHEMA Gesellschaft für chemische Technik und Biotechnologie e.V.,
Fachgruppe Mikrobielle Materialzerstörung und Materialschutz**
<http://biotech.dechema.de/Fachgemeinschaft+Biotechnologie/Gremien+der+Fachgemeinschaft/Mikrobielle+Materialzerst%C3%B6rung.html>

- Microbially induced corrosion of materials and methods for protection against microbial corrosion

Biosaxony e.V.
www.biosaxony.com

- Association for biotechnology and related fields from material science to medical technology in Saxony

**Deutsche Gesellschaft für Geowissenschaften e.V.,
Arbeitskreis Bergbaufolgen**
www.dgg.de

- Promotion of geosciences in research and teaching, in industry and administration

**Geokompetenzzentrum Freiberg e.V.,
Arbeitsgruppe Geobiotechnologie**
www.gkz-ev.de

- Research and development, continuing education and promotion of the microbiological processes in mining and environmental protection

Innovationsforum Geobiotechnologie – mikrobiologische Verfahren in Bergbau und Umweltschutz
www.geobiotechnologie.de

- Joint program within the Unternehmen Region – BMBF-Innovationsinitiative Neue Länder

Institutionen

**Bundesanstalt für Geowissenschaften und Rohstoffe (BGR),
Arbeitsbereich Geomikrobiologie**
www.bgr.bund.de/DE/Themen/GG_Geomikrobiol/gg_geomikrobiol_node.html

- Research and consulting on geomicrobiology and geobiotechnology with a focus on biomining and MEOR

**Bundesanstalt für Materialforschung und -prüfung (BAM),
Abteilung Material und Umwelt**
www.bam.de/de/kompetenzen/fachabteilungen/abteilung_4

- Assessment of relationships between material and the environment by multidisciplinary cooperation of engineers, chemists, geologists and biologists; research of long-term stress at the material/environment interface considering technological, ecological and economic aspects

**Helmholtz-Zentrum Dresden-Rossendorf, Helmholtz-Institut Freiberg für Ressourcentechnologie,
Gruppe Biotechnologie**
www.hzdr.de/db/Cms?pOid=35570&pNid=2772

- The research focusses on the development of biotechnological processes for the exploitation of metals from primary and secondary resources and the development of applications of bacterial proteins

**Helmholtz-Zentrum für Umweltforschung-UFZ,
Fachbereich Umwelttechnologie**
www.ufz.de/index.php?de=13997

- Research of complex interactions of people and the environment in used and disturbed landscapes, especially closely populated urban and industrial agglomerations as well as near-natural landscapes

**Hochschule Lausitz,
Angewandte Mikrobiologie**
www2.fh-lausitz.de/fhl/cv/www-Stahm

- Research and development of remediation of mining areas

**Hochschule Mittweida, Fakultät Mathematik, Naturwissenschaften, Informatik,
Arbeitsgruppe Biotechnologie**
www.mni.hs-mittweida.de/professoren/biotechnologie/prof-radehaus.html

- Development and optimization of processes for treatment of mining and industrial waters

**TU Bergakademie Freiberg, Interdisziplinäres Ökologisches Zentrum,
Arbeitsgruppe Umweltmikrobiologie**
http://tu-freiberg.de/fakult2/bio/ag_mikrobio/index.html

- Research and education in the fields of ecology, geoecology, environmental microbiology

TU Dresden, Fakultät Umweltwissenschaften, Institut für Abfallwirtschaft und Altlasten
http://tu-dresden.de/die_tu_dresden/fakultaeten/fakultaet_forst_geo_und_hydrowissenschaften/fachrichtung_wasserwesen/iaa

- Research and education on remediation of mining landscapes and brownfields

Universität Duisburg-Essen, Fakultät für Chemie – Biofilm Centre
www.uni-due.de/biofilm-centre

- Research and education focussing on biofilms, bioleaching and biogenic concrete and metal corrosion

Universität Jena, Institut für Mikrobiologie
www.mikrobiologie.uni-jena.de/cms/index.php/de/das-institut-mainmenu-1

- Research on the phytoextraction of metals

Companies

Bauer Umwelt GmbH
www.bauerenvironment.com/de/index.html

- Environmental service provider; treats and purifies water, soil, air

G.E.O.S. Ingenieurgesellschaft mbH
www.geosfreiberg.de

- Microbiological processes for water treatment and recycling of valuable materials, bioleaching

GFI Grundwasserforschungsinstitut GmbH Dresden
www.gwz-dresden.de/gfi-gmbh.html

- Research and development for remediation of mining areas

MicroPro GmbH

www.microprolabs.de/index.htm?PHPSESSID=647bd80dacfbb0674432eb19736282fb

- Services and research in the fields of geomicrobiology and applied microbiology, microbial exploration of novel hydrocarbon deposits and microbial enhanced oil recovery

Research funding**Allianz Industrie Forschung, Aif**

www.aif.de/aif/aif-im-profil.html

- Funding for applied research and development for SMEs

Geotechnologien

www.geotechnologien.de/portal/cms/Geotechnologien/Home

- Geoscientific research and development program of BMBF and DFG

Projekträger Jülich

www.geotechnologien.de/portal/cms/Geotechnologien/Home

- Research and innovation funding programs in the fields of biotechnology, energy, materials science, environmental technology and sustainability, ocean and polar research, shipping and marine technology, technology transfer and founding of businesses as well as regional technology platforms and clusters

Websites of stakeholders and activities outside Germany**European Association of Mining Industries, Metal Ores & Industrial Minerals, (EUROMINES)**

www.euromines.org

European Federation of Biotechnology, Section on Environmental Biotechnology

www.efb-central.org/index.php/Main/section_on_environmental_biotechnology

European Technology Platform on Sustainable Mineral Resources

www.etpsmr.org/index.php?option=com_content&view=article&id=1&Itemid=2

Minerals Engineering International: the largest source of information on mineral processing & extractive metallurgy on the net

www.min-eng.com

Project Biomine – Biotechnology for metal bearing materials in Europe

<http://biomine.brgm.fr>

Project Bioshale – Search for a sustainable way of exploiting Black Shale Ores using Biotechnologies

<http://bioshale.brgm.fr>

Project ProMine – Nanoparticle products from new mineral resources in Europe

<http://promine.gtk.fi>

4th International Symposium on Applied Microbiology and Molecular Biology in Oil Systems

www.ismos-4.org

20th International Biohydrometallurgy Symposium – IBS 2013

www.ibs2013.com/english

An updated list is available at www.dechema.de/geobiotechnologie

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