

# Metal-Containing Residues from Industry and in the Environment: Geobiotechnological Urban Mining

Franz Glombitza and Susan Reichel

**Abstract** This chapter explains the manifold geobiotechnological possibilities to separate industrial valuable metals from various industrial residues and stored waste products of the past. In addition to an overview of the different microbially catalyzed chemical reactions applicable for a separation of metals and details of published studies, results of many individual investigations from various research projects are described. These concern the separation of rare earth elements from phosphorous production slags, the attempts of tin leaching from mining flotation residues, the separation of metals from spent catalysts, or the treatment of ashes as valuable metal-containing material. The residues of environmental technologies are integrated into this overview as well. The description of the different known microbial processes offers starting points for suitable and new technologies. In addition to the application of chemolithoautotrophic microorganisms the use of heterotrophic microorganisms is explained.

**Keywords** Ashes · Biohydrometallurgy · Bioleaching · Catalysts · Flotation residues · Industrial residues · Organic acids · Rare earth elements · Slags · Sludges · Tailings · Trace elements

## Abbreviations

BDS	Bacterial Dried Substances
BOP	Basic Oxygen Process
B12	Cobalamin
CTR	Continuous Tank Reactor
DS	Dried Substances
DSZM	German Collection of Microorganisms and Cell Cultures
ESM	Electronic Scrap Material

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EU	European Union
kt	Kilo tons (thousands of tons)
LD	Linz–Donawitz
LD Slag	Slag of the steel producing basic oxygen process (BOP) Linz–Donawitz process
MET	Methionine
MO	Microorganisms
n.d.	Not determined
PFS	Phosphorous Furnace Slag
pH	pH value (negative decade logarithm of the H <sup>+</sup> ion activity)
REE	Rare Earth Elements
REO	Rare Earth Oxides
TE	Trace Elements
THF	Tetrahydrofolic acid
TOC	Total Organic Carbon
UFZ	Helmholtz Centre for Environmental Research
w.s.	Water soluble

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## 1 Introduction

Raw materials and energy are essential for economic existence. Even if no growth is expected and only maintenance of the economic force is aspired to, enormous amounts of basic materials and energy sources are required. The satisfaction of needs is based on the exploration and exploitation of new resources and energy deposits as well as on the attempt to recover raw materials via recycling processes. Recycling processes depend on the state of development of separation techniques which are still imperfect. Most exploitation technologies create secondary materials that still contain valuable substances as well as unusable residues. Older exploitation technologies, especially, produced unexploitable residues containing much higher concentrations of valuable substances in these residues than in some mineral ores. The increase of the efficiency of resource exploitation is recommended as a most important challenge by the OECD [1].

Such metal-containing residues were accumulated in huge amounts in the past. These are waste materials from the smelters, mainly slags, but on the other hand there are flotation residues from mineral ore processing deposited in tailings, the iron and aluminum containing red mud from aluminum production, slags and residues from phosphate and phosphorous production, sludges from electroplating plants, ashes from incineration processes of gas, oil, or lignite and coal power stations as well as of the municipal waste incineration plants, dusts from various dust removing and air filtration plants, and the manifold residues from wastewater treatment and biogas formation plants in addition to the sludges from rivers and harbors.

These residues are not only remnants of the past, but are still constantly obtained from various purification and incineration processes. They comprise, for example, the sludges from (drinking) water treatment plants as well as the ashes from various incineration processes and mainly slags from running smelters. In contrast, the number of recycled materials is, however, much greater than in the past and is continuously increasing. It includes electronic scraps, spent catalysts, composite materials, and the residues of young industries such as the photovoltaic

or the chip industry. The proportion of recycled goods and residues from other processes such as color television and electronic tube production decreases or is almost negligible in contrast to the increase of the former residues.

The concentration of valuable substances in all these residues can be increased by novel accumulation and separation processes. In addition to pyro- and hydro-metallurgical extraction processes, there are many geomicrobiological processes applicable for the extraction of valuable substances by dissolving or transforming the inorganic matrix [2–5]. Most of the residues are oxides, hydroxides, phosphates, carbonates, or silicates that contain different important metals and trace elements, but cannot be used as an energy source for the microbial processes. The microbial decomposition is based on secondary processes such as the formation of acids or other water-soluble and/or volatile products related to different metabolic transformations. As there are numerous possible reactions based on various microbial processes, the challenge is to look for the most suitable solution to the problem [6–9].

Such reactions are the formation of inorganic acids, for example, sulphuric acid after the addition of sulphur or sulphides, but also the formation of nitric acid and carbonic acid which, in a second reaction, dissolve the inorganic materials, or the formation of organic acids that also dissolve the inorganic materials and act as chelating agents simultaneously. The dependence of industrial processes on natural biogeochemical cycles of matter is an important precondition for further sustainable development [1].

The acidolysis describes the destruction of the mineral matrix by inorganic acids inducing sulphuric acid, nitric acid, or carbonic acid, whereas organic acids simultaneously act as complexing agents. This process is designated as complexolysis. Additional extracellular substances such as siderophores also play a special role because they act as chelating substances with the ability to increase the solubility of metal oxides with small solubility products and enhance their bio-availability. Quite different mechanisms of microbial dissolution are based on the redoxolysis, the reduction and/or oxidation of cations in a mineral matrix, for example,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Fe}^{2+}$ , or  $\text{Fe}^{3+}$ . The microbial cyanide production induces their instability by the formation of water-soluble cyanide-containing complexes. In contrast to the acidic processes the latter process takes place under alkaline conditions. The transformation of metals into organometallic compounds via microbial processes such as methylation or ethylation and the formation of volatile metal organic compounds has scarcely been investigated or applied thus far. Microbial silicate solubilizing processes and the extraction of valuable materials from silicates should attain increased importance in the light of the increasing need of the global industrial society. They offer extensive possibilities for the extraction of rare elements.

The assessment of the European Union shows 14 elements and compounds that are expected probably to run short for European industries in the future. These elements and compounds are presented in Table 1.

**Table 1** Elements and compounds with critical availability in the future

Antimony	Tungsten
Beryllium	Tantalum
Cobalt	Indium
Gallium	Platinum metals
Germanium	Rare earth elements
Magnesium	Fluorspar
Niobium	Graphite

Attempts to recycle materials and to recover valuable substances have been undertaken for many years, including the consideration of microbial processes [10–16]. A compilation of running or developed technologies for the separation of valuable substances from anthropogenic residues is demonstrated in Sects. 4–8.

The following examples give an idea of the huge possibilities concerning the exploitation of raw materials by means of biotechnological recycling technologies. This list is not exhaustive and complete due to the complexity of this issue. For example, it does not contain the various running metal recovery processes from mine wastes such as dumps and heaps [17–23].

General conditions that limit the application of a biotechnological process depend on the prevailing economic and technological situations and legislative regulations. Such preconditions are:

- Market price of the product and market demand as well as market development
- Product and capital costs
- Influence of political development and legal interpretation (politically driven development).

## 2 Overview of Appropriate Microbial Reaction Mechanisms

The extraction of valuable substances from the named residues typically requires the dissolution or partial destruction of oxides, hydroxides, phosphates, carbonates, or silicates that contain the wanted metals, valuable substances, and trace elements. Usually these residues do not contain energy-supplying agents for the microorganisms. Processes from natural cycles of matter have to be analyzed and applied causing destruction of materials thereby. This destruction is achieved by secondary processes such as the microbial formation of acids, or the formation of water-soluble and/or volatile products due to microbial transformation or complexing agents as well as by reducing processes that transfer cations in a lower oxidation state with better water solubility.

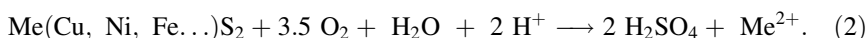
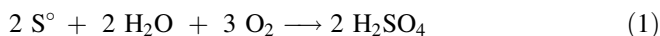
The following chapter provides a brief overview of the most important existing possibilities.

### 3 Acid Formation Processes (Acidolysis)

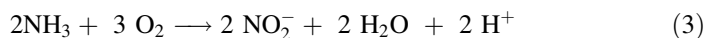
Microorganisms are able to produce inorganic and organic acids.

#### 3.1 Microbial Processes Related to the Formation of Inorganic Acids

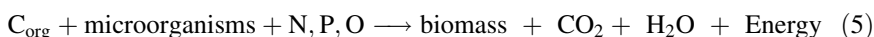
The most common process is the formation of sulphuric acid. Sulphur or sulphides from metal sulphides are oxidized to sulphuric acid by sulphur-oxidizing bacteria:



In addition to the formation of sulphuric acid, the formation of nitric acid has to be taken into account. Ammonia is oxidized via nitrite to nitrate by nitrifying archaea or bacteria such as *Nitrosomonas* and *Nitrobacter*:



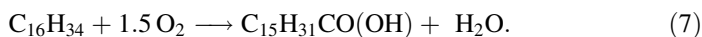
The formation of  $\text{H}_2\text{CO}_3$  is based on the release of  $\text{CO}_2$  during microbial growth:



#### 3.2 Microbial Processes Related to the Formation of Organic Acids

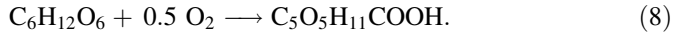
##### 3.2.1 Fatty Acids

Fatty acids belong to the aliphatic monocarboxylic acids. Sources of such acids are organic compounds such as saturated aliphatic hydrocarbons, paraffins, or iso-paraffins. They are oxidized to the corresponding organic acids under aerobic conditions and lack of nitrogen. For example, yeasts or hydrocarbon-utilizing bacteria form hexadecanoic acid (palmitic acid) from hexadecane [24, 25]:



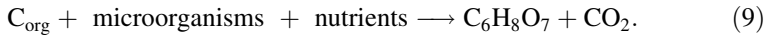
### 3.2.2 Gluconic Acid

Glucose or glucose-containing substances are oxidized to gluconic acid by microorganisms under aerobic conditions and in a nitrogen-free medium:



### 3.2.3 Citric Acid

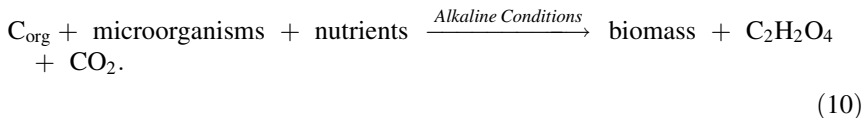
Citric acid is often produced by yeasts under stress and citric acid is released as a side product of the tricarboxylic acid cycle into the fermentation medium. Such stress factors can be the lack of nitrogen in the medium. The carbon-containing substrate cannot be transformed into biomass and is converted to  $\text{CO}_2$  and citric acid:



The formation of citric acid by fungi is different from the processes in yeasts. Citric acid is often produced by *Aspergillus niger* under iron deficiency during cultivation.

### 3.2.4 Oxalic Acid

Oxalic acid is also an intermediate product or constituent of the tricarboxylic acid cycle. Another mechanism is responsible for the microbial formation of oxalic acid by fungi. Oxalic acid is excreted under alkaline conditions:



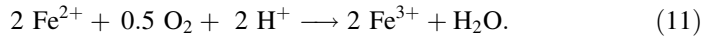
The formation and expression of citric acid, isocitric acid, and oxalic acid as well as some other acids are well known for various fungi, bacteria, and yeasts.

## 4 Oxidizing and Reduction Processes (Redoxolysis)

Microbial growth is always linked to energy transfer, which includes electron delivering (donator) and electron receiving (acceptor) processes. Because different metal and nonmetal ions are involved in this electron transfer, different oxidizing and reducing processes exist, relevant for a leaching process.

## 4.1 Oxidation Processes

### 4.1.1 Oxidation of Ferrous Iron ( $\text{Fe}^{2+}$ )



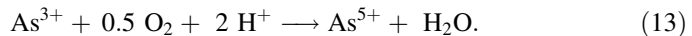
The formed  $\text{Fe}^{3+}$  can be separated as iron hydroxyl sulphate in an acidic and sulphate-containing medium.

### 4.1.2 Oxidation of Manganese Ions ( $\text{Mn}^{2+}$ )



The  $\text{Mn}^{4+}$  is mainly separated from solution as  $\text{MnO}_2$  after the oxidation.

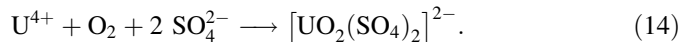
### 4.1.3 Oxidation of $\text{As}^{3+}$ and $\text{Sb}^{3+}$ (e.g., [26, 27])



$\text{As}^{5+}$  forms an arsenate anion and can be separated as  $[\text{AsO}_4]^{3-}$  by precipitation.

An analogous process takes place with the ions and compounds from trivalent antimony and the formation of  $[\text{SbO}_4]^{3-}$  [28].

### 4.1.4 Oxidation of Uranium ( $\text{U}^{4+}$ )



Uranium(IV) is transferred to uranium(VI) directly by microorganisms or indirectly by an oxidizing agent and forms a uranyl sulphate anion under acidic conditions with sulphuric anions [29].

## 4.2 Reduction Processes

Reduction is described as an electron receiving process. Many electron acceptors are known in combination with microbial actions, for example:



Chromium(VI) ions are reduced and form highly soluble chromium(III) ions [30, 31].

The reduction of  $\text{As}^{5+}$  and  $\text{Sb}^{5+}$  is also known:

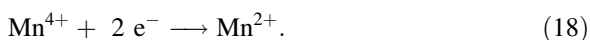


Compared to  $\text{As}^{5+}$  compounds the compounds of  $\text{As}^{3+}$  often have a higher solubility. This was demonstrated, for example, under reducing conditions in wetlands where the  $\text{As}_2\text{S}_5$  compounds are transformed into more soluble  $\text{As}_2\text{S}_3$  compounds resulting in an increased concentration of arsenic in the treated water.

Ferric ions are enzymatically reduced by acidophilic or neutrophilic microorganisms under anaerobic conditions [32–35, Chap. 1]. Organic carbon, hydrogen, or sulfur compounds can act as the electron donor in this reaction:



The reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$  is similar to the reduction of ferric iron. It is enzymatically catalyzed, for example, by *Geobacter* or *Shewanella* species. It takes place under anaerobic conditions also in the presence of sulphate-reducing bacteria (SRB) via a chemical reduction with their metabolic product sulphide [36]:



The reduction of uranium(VI) (anaerobic conditions) is connected with the formation of uraninite, an insoluble uranium-containing mineral [37]:



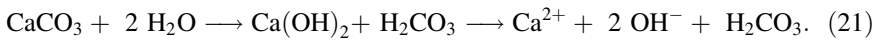
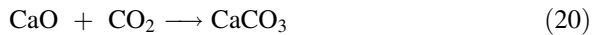
In addition to the direct enzymatic microbial reduction and oxidation of the cations an indirect reduction and oxidation occurs. This happens where the microbially formed products act as a reducing or oxidizing agent. The oxidizing action of  $\text{Fe}^{3+}$  on uranium(IV) to form uranium(VI) is such an example, and the formation of ferric iron again by a repeated microbial oxidation. Some other reactions focus on the relationship between  $\text{Fe}^{3+}$  and  $\text{S}^{2-}$ . Sulphide is oxidized to  $\text{S}^{\circ}$  and  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$ . Both substances are energy sources in a subsequent microbial process. A similar mechanism can be assumed between  $\text{Fe}^{3+}$  and  $\text{As}^{3+}$ .

The reduction of chromate is also important, because the toxicity of  $\text{Cr}^{3+}$  is much lower than that of  $\text{Cr}^{6+}$ . Such a reduction can be achieved by biologically produced hydrogen [38].

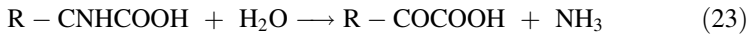
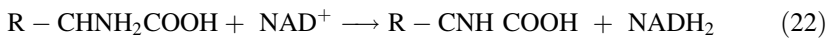
## 5 Alkalinity-Producing Reactions and Growth Under Alkaline Conditions (Alkalinolysis)

In addition to microbial processes under acidic conditions, there are processes under alkaline conditions [39, 40].

The alkaline conditions can be caused by chemical or microbial processes. Such a process is the carbonization of slags or other materials containing CaO reacting with CO<sub>2</sub> from the air and with water on the surface to CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>. This results in a high pH value (in part  $\geq 10$ ) and the hydrolysis of organic material into low-molecular-weight compounds serving as substrate for extreme alkaliphilic microorganisms. They form organic acids in subsequent metabolic processes as well as potential ligands that enhance the metal mobilization by complex formation [41]:



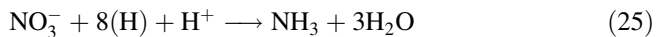
Another possibility exists if H<sup>+</sup> ions are removed and OH<sup>-</sup> ions remain in the water. Such a basic reaction is the interaction of NH<sub>3</sub> with water or the dissociation of some carbonates. The microbial formation of NH<sub>3</sub> can be achieved by the transfer of organic nitrogen from amino acids [Eqs. (22) and (23)] or a hydrolysis of urea catalyzed by the enzyme urease and urea cleavage microorganisms (Eq. 24) as *Sarcina urea* [42, 43],



or:



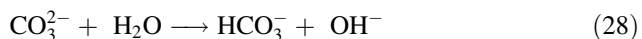
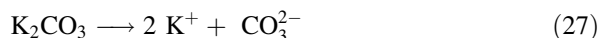
A third possibility is the nitrate ammonification [44, 45],



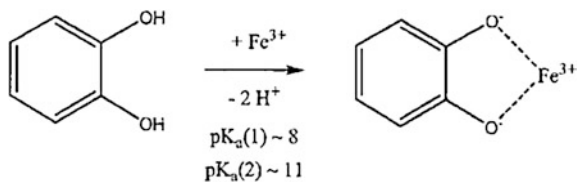
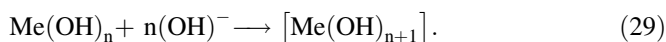
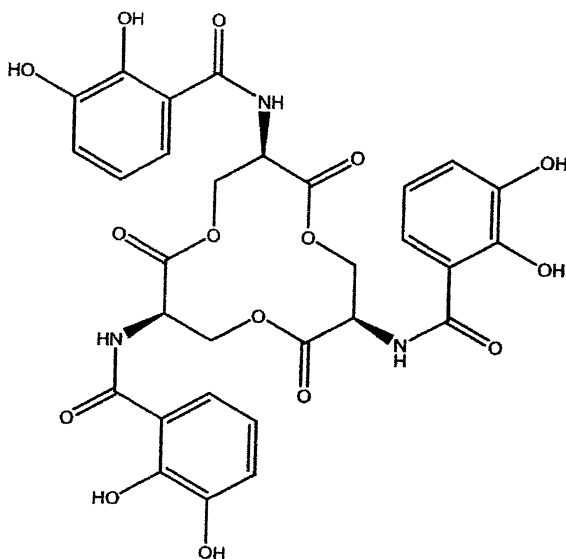
An example for the formation of carbonate is the transfer of orthoclase by CO<sub>2</sub>,



and the delivery of OH<sup>-</sup> in unbuffered systems



In addition, many metals form highly soluble complexes with (OH)<sup>-</sup> anions:

**Fig. 1** Complex formation of iron by catechol**Fig. 2** Enterobactin

This can be observed for Al or Zn which form aluminates or zincates.

## 6 Complexolysis

### 6.1 Siderophores

Some microorganisms are able to produce organic compounds that form stable complexes with heavy metals. Well known are siderophores which form stable compounds with iron [46].

They are formed by bacteria and fungi, for example, by *Escherichia coli*, *Pseudomonas picketti* (*Ralstonia*), or *Agrobacterium tumefaciens*. About 200 different natural siderophores are known. Because iron exists in insoluble compounds, the complexes often possess extremely high complex formation constants.

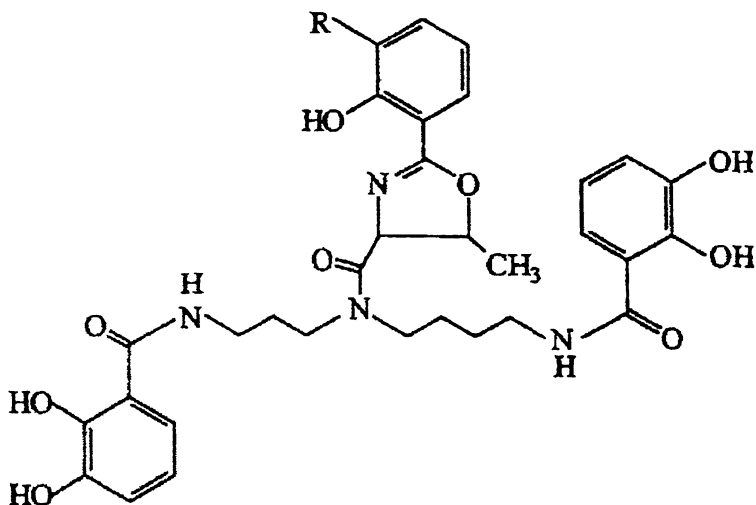
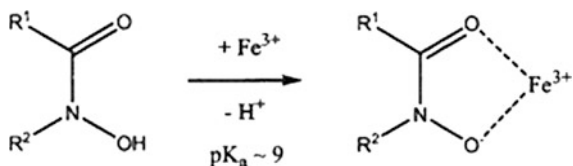


Fig. 3 Agrobactin

Fig. 4 Complex formation with hydroxamate



The stability of the complexes is very strong and in parallel is a precondition for the dissolution of iron oxides. This opens the possibility to leach iron-oxide-containing materials and to use them in microbial rust separation processes [47].

There are three different types of siderophores according to three main complexation mechanisms: catecholate, hydroxamate, and hydroxyl keto-carboxylate. The formation of a complex with catechol is demonstrated in Fig. 1.

Enterobactin and agrobactin are compounds related to catechol as demonstrated in Figs. 2 and 3. The formation of complexes with hydroxamate is shown in Fig. 4. Ferrichrome is one of the most known compounds of this type and is demonstrated in Fig. 5. The third kind of siderophore is based on the complex formation with alpha-keto-carboxylate (Fig. 6). This complex has a lower stability due to a lower pKa value.

Ferrichrome is the iron-containing compound as a representative of the hydroxamate compounds (Fig. 5).

Fig. 5 Ferrichrome

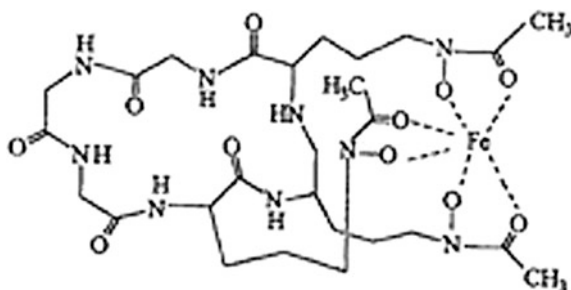
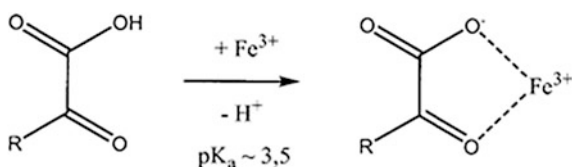
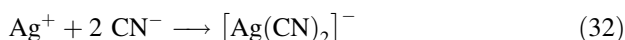
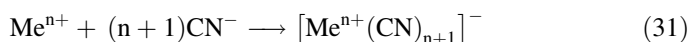
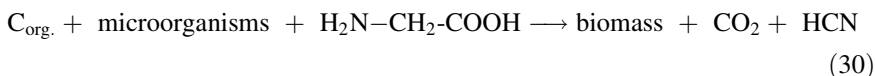


Fig. 6 Complex formation with alpha-keto-carboxylate



## 6.2 Cyanide Formation Processes

In addition to the iron complexation by siderophores, the formation of cyanide complexes is another quite different complex-forming process. Cyanide can be produced by microorganisms under alkaline conditions whereby glycine as a substrate and precursor is used [48–50]. This offers the possibility to form stable and water-soluble metal cyanide complexes. This is schematically demonstrated for the leaching of silver in the following equations.



In addition to silver many other metals form stable cyanide complexes and thus can be leached.

## 7 Transformation and Formation of Metal Organic Compounds

### 7.1 Methylation/Ethylation

The formation of metal organic compounds by methylation and ethylation is a very interesting process [51]. An alkylation takes place directly by a microbial transfer of methyl or ethyl groups or indirectly by microbially formed metabolites followed

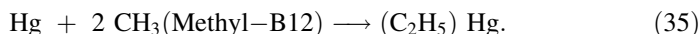
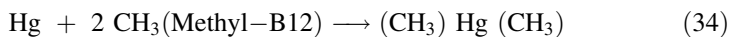
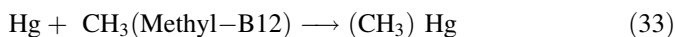
**Table 2** Metal(loid) organic compounds from different sources [140]

Waste disposal	Sewage sludge	Low contaminated soil
(CH <sub>3</sub> ) <sub>2</sub> AsH	(CH <sub>3</sub> )AsH <sub>2</sub>	(CH <sub>3</sub> )AsH <sub>2</sub>
(CH <sub>3</sub> ) <sub>3</sub> As	(CH <sub>3</sub> ) <sub>2</sub> AsH	(CH <sub>3</sub> ) <sub>2</sub> AsH
(CH <sub>3</sub> ) <sub>2</sub> AsC <sub>2</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>3</sub> As	(CH <sub>3</sub> ) <sub>3</sub> As
(CH <sub>3</sub> ) <sub>3</sub> Sb	(CH <sub>3</sub> ) <sub>3</sub> Sb	(CH <sub>3</sub> ) <sub>2</sub> BiH
(CH <sub>3</sub> ) <sub>3</sub> Bi	(CH <sub>3</sub> ) <sub>3</sub> Bi	(CH <sub>3</sub> ) <sub>3</sub> Bi
(CH <sub>3</sub> ) <sub>2</sub> Te	(CH <sub>3</sub> ) <sub>2</sub> Te	(CH <sub>3</sub> ) <sub>2</sub> Se
(CH <sub>3</sub> ) <sub>2</sub> Hg	(CH <sub>3</sub> ) <sub>4</sub> Sn	(CH <sub>3</sub> ) <sub>2</sub> Se <sub>2</sub>
(CH <sub>3</sub> ) <sub>4</sub> Sn		CH <sub>3</sub> TeH
(CH <sub>3</sub> ) <sub>4</sub> Pb		(CH <sub>3</sub> ) <sub>2</sub> Te
		(CH <sub>3</sub> ) <sub>2</sub> Hg
		(CH <sub>3</sub> ) <sub>4</sub> Sn
		(CH <sub>3</sub> ) <sub>4</sub> Pb

by cleavage under sunlight irradiation [52, 53]. The intracellular transfer of the methyl group is linked to the presence of methyl donors. Methyl donors are, for example, methyl-cobalamin (methyl B12), methionine (MET), and tetrahydrofolic acid (THF). This offers the possibility of separating heavy metals by microbially formed volatile compounds. Table 2 shows some microbially formed metal organic compounds in different habitats.

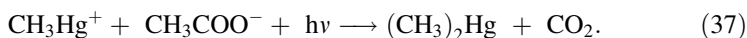
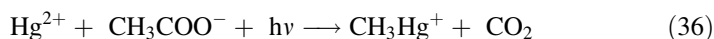
## 7.2 Mercury

A well-known mechanism is the transformation of Hg into methyl-, dimethyl-, or ethylmercury. In addition to the habitats listed in Table 2 it can be observed in sediments of harbors, rivers, or the sea:



The process occurs under anaerobic conditions and in the presence of sulphate-reducing bacteria.

The next equations demonstrate the formation of methyl-Hg with acetate as metabolite under sunlight irradiation ( $h\nu$ ):



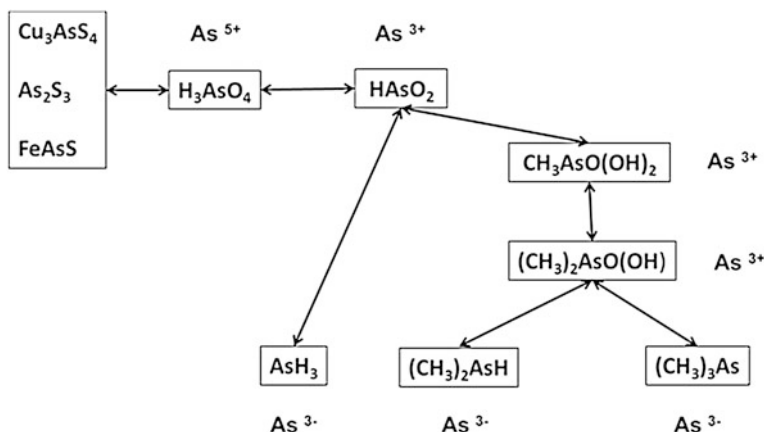


Fig. 7 Interactions of arsenic with microorganisms and change of the oxidation state [6]

### 7.3 Arsenic

Inorganic arsenic can be reduced by microorganisms and algae but also in vivo in mammals. The resulting formation of organic As compounds plays an important role in nature and the transformation can be used as a remediation process [54]. Similar processes are used for mercury-contaminated sites. Different microbially initiated processes are demonstrated in Fig. 7.

Another remarkable process is the alkylation of tin, because  $\text{Sn}^{4+}$  is very stable and forms oxides with a low water solubility. Hence, this is an important process, because it offers a new possibility of separating tin from ores and residues.

## 8 Preconditions for the Application of Microbial Leaching Processes

To select a suitable and effective leaching strategy, preconditions concerning the microbial growth conditions must be considered in addition to economic feasibility and legislative restriction. This means that leaching or dissolution under acidic conditions is possible, however,

- The Ca and Mg concentration has to be low in the raw material. In most cases Ca and Mg are bound as carbonate in minerals. This requires the destruction of the carbonate minerals as the first step. Ca reacts with sulphuric acid to form  $\text{CaSO}_4$  in a second reaction and prevents a further leaching process by clogging the capillaries and consuming the sulphuric acid. The recommendation for the application of an acidic leaching process is that the total concentration of Ca and  $\text{MgCO}_3$  be lower than 30 % [F. Glombitza, unpublished; 55].

The following is valid in general.

- The choice of a suitable pH value and the pH range determine the solubility of the dissolved ions. Therefore there are leaching processes under alkaline conditions but also under neutral, moderate acidophilic, and acidophilic conditions.
- Leaching is more effective, if many products of the leach solution can be exploited. A combination of the production of the leaching concentrate and the purification of the organic acid is much more effective in comparison with a pure acidic leaching process.
- Another strategy of leaching is the selection of some elements in a mineral matrix whose oxidation state can be changed by a microbial oxidizing or reducing process and cause the destabilization of the solid phase as a first step in the leaching process.

## **9 Residues from Mining and Metallurgical Industry**

If we designate residues from the industry, we mostly subsume sludges, ashes, dusts, slags, and the residues from flotation processes, the so-called tailings. In the next chapter residues from the mining and metallurgical industry are described for the potential recovery of valuable substances. The chapter is divided in two sections. The first section concerns slags from running smelter processes. The second section refers to stored residues and slags from the past.

## **10 Residues from Smelters: Slags**

### ***10.1 Introduction***

Slags are the residues of various pyrometallurgical processes and are obtained as a side product of zinc, lead, nickel, or copper production. Due to the decrease of mining activities and minimization of the number of smelter processes during the last decades disposal was covered with a water-impermeable top layer. Such sites are found in all old mining districts such as in Germany in the Harz Mountains, or in the Ore Mountains (Erzgebirge), for example, near Freiberg or in St. Egidien where a former nickel smelter operated in the past. The slags of these smelters are mainly silicates and oxides which always contain remarkable amounts of valuable substances. Other mining residues are products from the flotation tailings that are stored separately.

Table 3 gives examples of studies with residues from mining and metallurgical processes. It contains remarks concerning potential microbial leaching strategies of these materials and information about the main valuable substances. The

residues are the slags from different smelters and materials from flotation processes. The table lists the great variety of slags and residues. Some examples are from Germany, where different active smelters and many stored residues from the past exist. In addition, other authors are cited who have published investigations of and experiences from the leaching of such materials outside Germany.

## 10.2 Zinc Smelter Slags

The zinc recycling smelter in Freiberg, Germany, produces zinc from zinc-containing dusts of rotary kiln processes. In comparison to other plants the capacity is very high and amounts to an average of 50,000 t/a [56]. Previous analyses of the slags have demonstrated that neutrophilic and alkaliphilic microorganisms are able to extract metals including zinc, lead, and cadmium, whereas under acidic pH conditions zinc is extracted preferably.

Figure 8 demonstrates the leaching of zinc by *Acidithiobacillus* strains under acidic conditions and the attempts of a leaching of lead under alkaline conditions with an alkaliphilic mixed culture. A medium after Horikoshi was used for the cultivation of the alkaliphilic microorganisms [39]. The curves represent the average results for zinc and lead of different leaching experiments in shake-flasks. A notable concentration of zinc was measured. Only a few micrograms of cadmium were mobilized under alkaline conditions (not shown) but the concentration of lead ranged to some milligrams.

Another example for the treatment of slag resulting from a smelter process has been reported by Willscher et al. [57, Chap. 1]. They investigated the heterotrophic leaching of silicate-based and alkaline materials of slag from a smelter. About 38 % of Mn, 46 % of Mg, 68 % of Ca, 27 % of Zn, 15 % of Fe, 26 % of Ni, 40 % of Co, and 8 % of Pb could be dissolved. Other aspects include a strong alteration of the particle surfaces due to the microbial influence and the microbially mediated formation of secondary minerals such as calcite. The isolated microorganisms (e.g., the novel species *Nocardiopsis metallica*; [58]), were alkali-tolerant strains with the ability to grow in the culture medium at a pH value of 11.

## 10.3 Lead Smelter: Slags

The treatment of slags from lead smelters is different from that from other base metal smelters. Some slags are deposited; other slags are used as the building material Berzelit® for the construction of disposals or roads [59]. Alternative investigations revealed that up to 70–80 % of the remaining metals in the slag could be leached with a mixed population of moderately thermophilic and acidophilic microbes [60, 61].

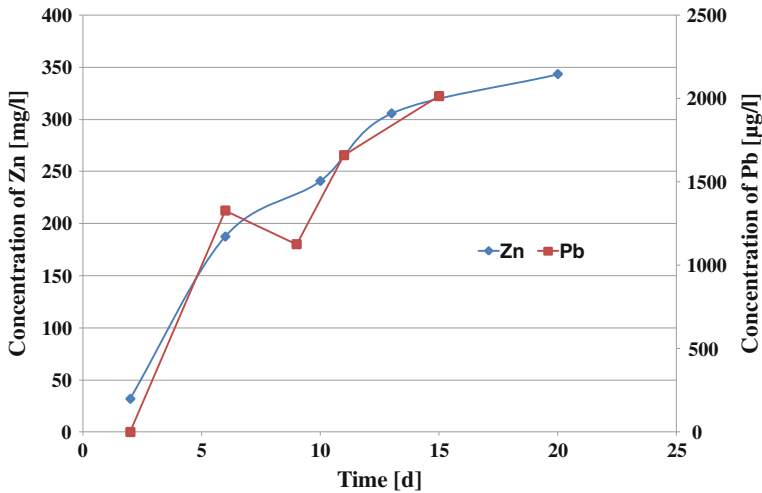
Table 3 Suitable microbial processes for leaching or destruction of slags and other mining residues

Residue/waste	Origin	Content/valuable substances	Treatment	References	Remarks
Slags	Lead/Zinc smelter	Al, Cu, Mn, Fe, Zn	Leaching with mixed culture— isolate of moderate— thermophilic bacteria, <i>Bacillus</i> spp. <i>Sporosarcina</i> spp. <i>Pseudomonas</i> spp	[60, 61, 141]	Leaching efficiency of about 80 % in average, shaking flasks, pH 1.5, >60 °C electrochemical investigation of the metal solubilization
	Zinc smelter	Zn, Pb, Cd	Acidic and/or alkaline leaching	[142]	Solubilisation of Zn, Pb, and Cd under alkaline condition, Zn under acidic conditions
	Nickel smelter, nickel ore residues	Ni, Cr, Co, Fe	Acidic autotrophic or heterotrophic leaching	[71, 72, 74]	Residues from Ni—laterite, Ni extraction is influenced by the iron and solid concentration in the medium, 90 % at 2 % solids are possible
	Phosphor production	Ca, Fe, Al, Si, Mg, Mn, REE	Heterotrophic leaching of REE	[80; 81, 84]	Leaching of the slag was carried out with gluconic acid producing <i>A.</i> <i>methanolicus</i>
	Copper smelter slag	Cu, Ni, Co	Acidic leaching with <i>At.</i> <i>ferrooxidans</i> , <i>At. thiooxidans</i>	[65, 66]	66 % Cu, 50 % Ni, 64 % Co are dissolved from particles of <75 Mm size slag
	Copper mining/ copper converter slag	Fe, Cu	Pulverized slag was leached with <i>At. ferrooxidans</i>	[69]	5 % pulp density, pH 1.9, 32 °C, Cu recovery is 77.5 %
	Steel producer	Fe, Ca, Si, V, TE	Alkaline heterotrophic leaching	[41, 67]	Heterotrophic leaching of LD slag by means of organic acids from wood,
	Waste incineration plant	Al, Cr, Cu, Ni, Pb, Zn	Leaching with acid producing autotrophic and heterotrophic bacteria and fungi	[143]	Extraction of Cu and Zn until 80–90 % depending on the process conditions

(continued)

Table 3 (continued)

Residue/waste	Origin	Content/valuable substances	Treatment	References	Remarks
Tailings/ flotation residues/ore residues	Tin mining	Sn	Leaching of sulphidic and oxidic tin minerals and flotation residues with <i>At. ferrooxidans</i>	[89–91]	Treatment of tin containing mine tails and residues with <i>At. ferrooxidans</i> and maximum concentration of tin from about 200 Mg/l
	Nickel mining	Ni, Cr, Co, Fe	Acidic leaching—autotrophic or heterotrophic	[21, 71, 72, 74]	Leaching of residues from Ni—laterite and lateritic ores, a delivery of Fe, Cr and Co takes place besides Ni



**Fig. 8** Average values of the release of zinc from slags by an acidic leaching process with *Acidithiobacillus* and lead leached with alkaliphilic strains of microorganisms

## 10.4 Copper Smelter Slag

During smelting of copper concentrates, in addition to copper and precious metals, an iron silicate smelt is obtained in the Aurubis copper smelter, which is converted into iron silicate stones and a granulated material [62]. About 95 % of the iron silicate stones consist of olivin  $(\text{Mg,Fe})_2[\text{SiO}_4]$  which is used in water engineering [63, 64].

Inasmuch as the slags also contain other valuable elements, their recovery is conceivable according to the known and cited microbial dissolution investigations reported by Mehta et al. [65, 66], Karsson et al. [41], Willscher and Bosecker [67], Carranca et al. [68], or Baghery and Oliazadeh [69]. All these authors reported a successful leaching of similar material using various strains and conditions.

## 11 Slag Deposits: A New Possibility for Resources

### 11.1 Nickel-Containing Ores and Residues

An example for the treatment of smelter residues is the former nickel smelter in St. Egidien, Saxony, Germany. After closure of the mine in 1990, a so-called high-contaminated industrial area remained. This area contains about 2.3 million t of slags, tailings, and some other waste materials from industrial processes. The major contaminants are nickel, chromium, and cobalt compounds [70]. Leaching of this material seems to be possible using special leaching technologies.

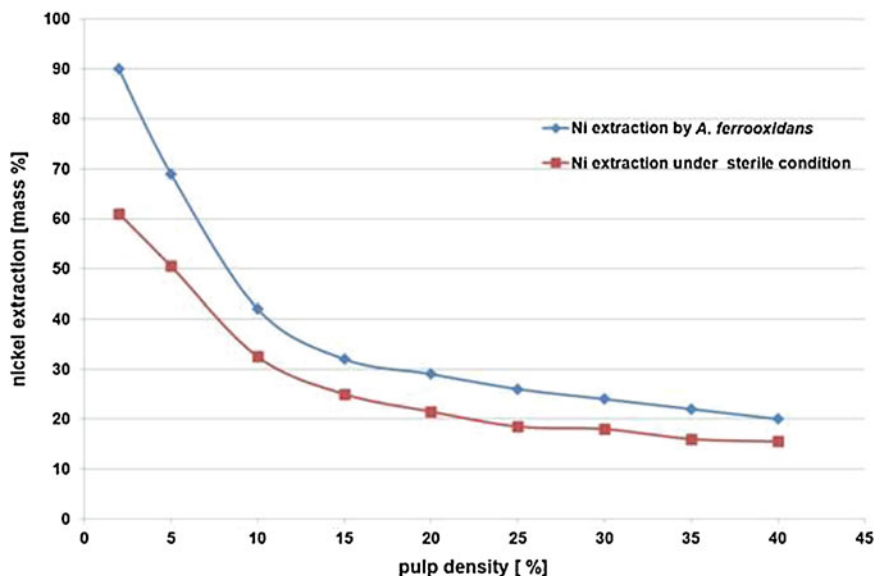
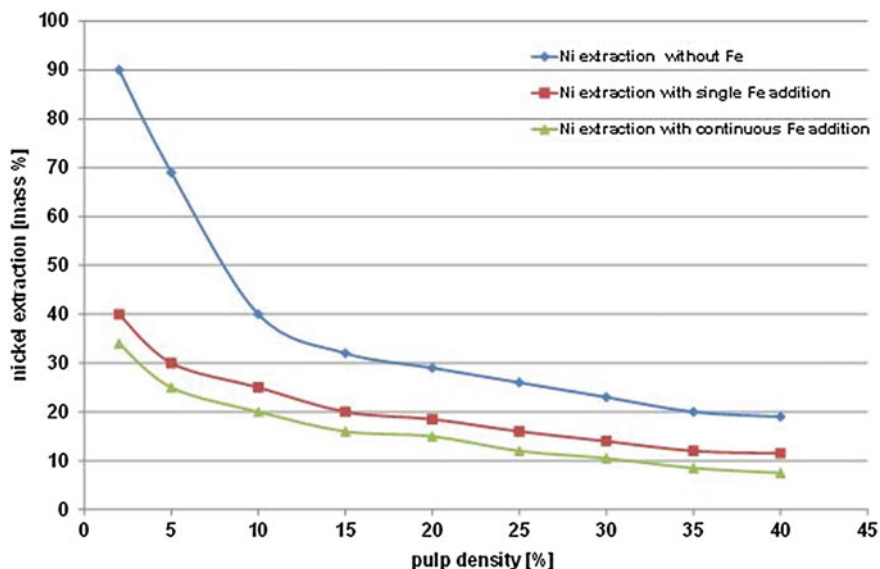


Fig. 9 Nickel extraction from hydrosilicate residues with and without microorganisms

Comprehensive investigations of nickel bioleaching from ores and residues were carried out [71, 72]. Because the nickel ore is a hydrosilicate with concentrations of 2,500–15,900 mg/kg Ni, 240–2,000 mg/kg Co, 2,400–7,000 mg/kg Cr and 1,900–9,000 mg/kg Mn and no energy-delivering substances for microbial leaching are available, a suitable leaching technology had to be developed. The leaching was carried out as submerged leaching [73] with different pulp densities with different strains of microorganisms. The influence of the ferrous iron concentration on the leaching process was investigated too. The results revealed a high extraction rate at a low solid concentration in the suspension and a decrease of the extraction efficiency with increasing solid concentration (Fig. 9). The figure displays the results of the leaching experiments with and without microorganisms and the investigations confirmed the positive influence of the bioleaching with *Acidithiobacillus ferrooxidans* on the nickel extraction. Figure 10 shows the attempt to increase the nickel extraction by increasing the concentration of ferrous iron. The results demonstrated a decrease of the nickel extraction due to an assumed precipitation of iron and a plugging of the porespace.

Table 4 shows the maximum concentrations and efficiency obtained with different microbial strains. The data result from separate investigations and are not related to each other. That means a concentration of 1,000 mg/l nickel in the leaching solution and a maximum average efficiency of 70 % were achieved [71].

In Fig. 11 the bioleaching of a nickel hydrosilicate with the extraction of iron, nickel, chromium, and cobalt is demonstrated. The process was driven by *Acidithiobacillus* strains with sulphur as the energy source and for sulphuric acid



**Fig. 10** Bioleaching of nickel from lateritic material with *A. ferrooxidans* and different  $\text{Fe}^{2+}$  supply

**Table 4** Leaching effectivity and maximum metal concentrations in the leaching solution

Microorganisms/metals	<i>Acidithiobacillus ferrooxidans</i>	<i>Acetobacter methanolicus</i>	Yeast <i>Rhodotorula</i> sp.	Yeast <i>Candida</i>
Ni				
Concentration (mg/l)	1000	30	160	169
Max. effectivity (%)	70	30	19	20
Mn				
Concentration (mg/l)	112	40	480	460
Max. effectivity (%)	10	47	57	55
Cr				
Concentration (mg/l)	2.15	2.5	15	13.6
Max. effectivity (%)	5.5	6	4	3.4
Co				
Concentration (mg/l)	25	n.d.	3.8	77
Max. effectivity (%)	5.5	n.d.	19.4	38

formation simultaneously [74]. The maximum yielded nickel concentration was about 1 g/L. The iron concentration was much higher and averaged some grams per liter.

Similar investigations with microbially produced organic and inorganic acids were reported by Coto et al. [21]. Comprehensive investigations on the influencing factors proven by statistical methods were published by Simate and Ndlovu [75].

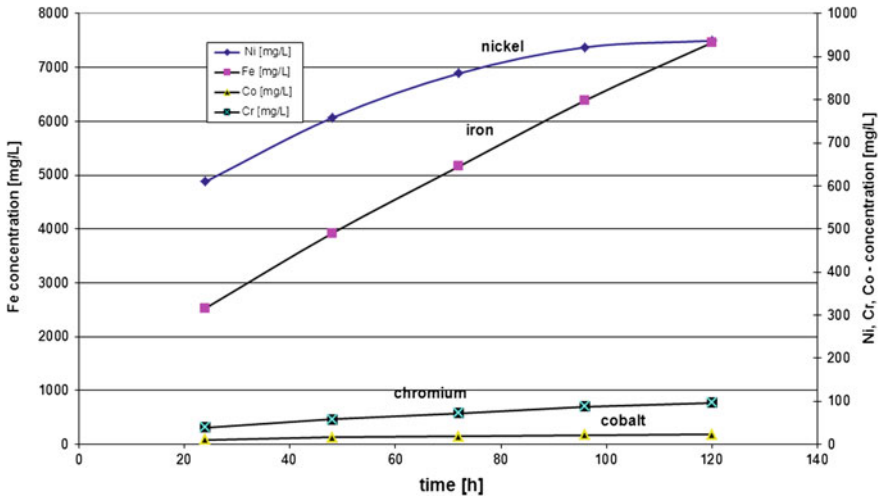


Fig. 11 Microbial acidic leaching of lateritic nickel ore [74]

A new technology for the leaching of nickel laterites involves the reduction of ferric iron ions under acidic anaerobic conditions with sulphur as electron donor. A cleavage of the mineral matrix caused by the reduction of ferric iron takes place and results in the dissolution of the metals [76, Chap. 1].

### 11.2 Rare Earth Elements Containing Residues

Slags usually consist of silicates and contain trace elements as well as rare earth elements. Such elements are very important for modern economics due to the needs of the electric and electronic industries. Covering the demand is really difficult because currently no economically recoverable primary mineral resources containing REE and trace elements exist. The importance of rare earth elements for a modern economy increases continuously. The EU demand for rare earth elements in 2008 was 23,013 t. About 90 % of the REE and REO are imported from China. Table 5 shows the amounts of Chinese production of rare earth oxides (REO) and of some single elements in 2006. Table 6 contains the global demand of REO in 2008 classified by different fields of application. It should be noted that China is not only a producer of REE but also a country with a big consumption [77].

Germany lacks high-grade REE deposits, therefore alternatives for the recovery of REE have been investigated in the past (and are still under investigation today).

One possibility is the separation of the REE from REE-containing residues. Such residues are various kinds of slags. This results in the analyses of slags and subsequent development of methods for the extraction of rare earth elements and trace elements from slags. An example is a slag obtained from the phosphorous production from apatite. Apatite contains between 0.4 and 1.2 % of REE and the

**Table 5** Produced amounts of rare earth oxides and single metals in China in 2006 [77]

La <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>	Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Eu <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Tb <sub>4</sub> O <sub>7</sub>	Dy <sub>2</sub> O <sub>3</sub>	Er <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Sum
19730	22579	2297	11343	1586	368	4625	607	2311	954	9027	75427
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Er	Y	
2034	–	–	7032	489	–	–	–	1280	–	–	10835

Data in t

**Table 6** Overview of global application of REO from different industrial branches in 2008 related to the global production in % derived from [77]

Application	Amount (t)	%
Glass, polishing, ceramics	33,000–42,000	ca. 30
Magnets	21,000–27,000	ca. 20
Catalysts	20,000–25,000	ca. 20
Metal alloys, batteries	17,000–23,000	ca. 18
Phosphorous, luminescence	9,000	ca. 7
Others		ca. 5

phosphorous furnace slag (PFS), as a residue of this process, therefore contains these REE as well.

Table 7 demonstrates the composition of the slag and the distribution of different REE. The slag contains about 0.7 % REE consisting of more than 80 % light and about 12 % heavy REE as displayed in the righthand columns.

Hence, the separation of the REE from the slag was an important objective in the past. In addition to chemical processing, microbial processes were applied. The leaching of the slag was done chemically using waste hydrochloric acid or nitric acid, respectively. The first microbial investigations focused on the leaching of the slag using *Acidithiobacillus* strains to destroy the material by the formation of sulphuric acid. The formation of free sulphuric acid was, however, impossible due to the high concentration of calcium and the transfer of the sulphate ions into gypsum. A stable pH value in the acidic range could not be reached and the pH value was changed to alkaline conditions. Another attempt was the leaching with autotrophic microorganisms and Fe<sup>2+</sup> as energy source for the growth of the microorganisms. Unfortunately, maintaining a stable acidic pH value was found to be difficult too.

The above-mentioned difficulties fostered research for alternative leaching techniques, for example, to connect the extraction of the rare earth and trace elements with the microbial formation of gluconic acid. The addition of an organic substrate was necessary because the slag doesn't contain any energy source for microorganisms [78–82, 83].

Gluconic acid is an important and most frequently used agent in the food industry and in healthcare. It can be separated by precipitation with some ions, for example, as Ca-gluconate from solution. This offers the chance to destroy the phosphorous furnace slag and to clean the organic acid.

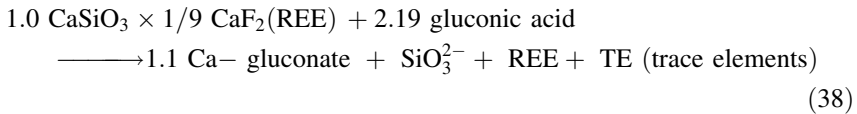
Gluconic acid is microbially formed during the oxidation of glucose by different microorganisms in a nitrogen-free cultivation medium. The leaching process

**Table 7** Composition of the phosphorous furnace slag (PFS) and the contained REE

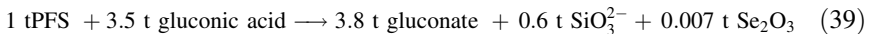
Compound/ element	Concentration (%)	Composition REE (100 %)	Concentration (%)	Total (%)
REE	0.7	La <sub>2</sub> O <sub>3</sub>	22.3	
CaO	45.0	CeO <sub>2</sub>	44.6	
SiO <sub>2</sub>	41.0	Pr <sub>6</sub> O <sub>n</sub>	1.7	
F	2.9	Nd <sub>2</sub> O <sub>3</sub>	16.7	
Al <sub>2</sub> O <sub>3</sub>	3.5	Sm <sub>2</sub> O <sub>3</sub>	1.1	
Fe <sub>2</sub> O <sub>3</sub>	0.4	Eu <sub>2</sub> O <sub>3</sub>	1.7	88.1
P <sub>2</sub> O <sub>5</sub>	1.0	Gd <sub>2</sub> O <sub>3</sub>	5.6	
K <sub>2</sub> O	1.0	Tb <sub>4</sub> O <sub>7</sub>	0.17	
Na <sub>2</sub> O	0.4	Dy <sub>2</sub> O <sub>3</sub>	2.2	
MgO	0.5	Er <sub>2</sub> O <sub>3</sub>	1.7	
SO <sub>3</sub>	0.5	Tm <sub>2</sub> O <sub>3</sub>	1.1	
MnO	0.2	Lu <sub>2</sub> O <sub>3</sub>	1.1	11.9

and the gluconic acid formation are carried out by various bacteria, for example, by *Acetobacter methanolicus* [84, 85]. Methanol is used as a suitable carbon source for the cultivation [82, 83]. The advantage is that the slag is destroyed by the formation of a water-insoluble calcium gluconate compound. The residue and the REE of the slag can be separated afterwards [86].

The process can be described by the following reaction equations [86].



or



It is generally believed that the leaching process is mainly influenced by the amount of formed gluconic acid and the amount of added slag. Because the calcium gluconate has a low solubility of approximately 3 g/l, the free gluconic acid in the leach solution decreases with a higher concentration of the slag. The formed amount of gluconic acid is important for the leaching process and depends on the precultivation conditions and the biomass concentration (Figs. 12 and 13). Precultivation conditions are the residence time of the cultivation process and the used carbon substrate or the biomass concentration [88].

Figure 12 shows that the highest concentration of gluconic acid is related to the highest amount of biomass and a short residence time during their cultivation. Figure 13 demonstrates the influence of different carbon sources on the concentration of formed gluconic acid. Methanol was the preferred substrate for a selective cultivation during the addition of slag to the medium, because providing glucose as a substrate at the technical scale that is used by a vast number of

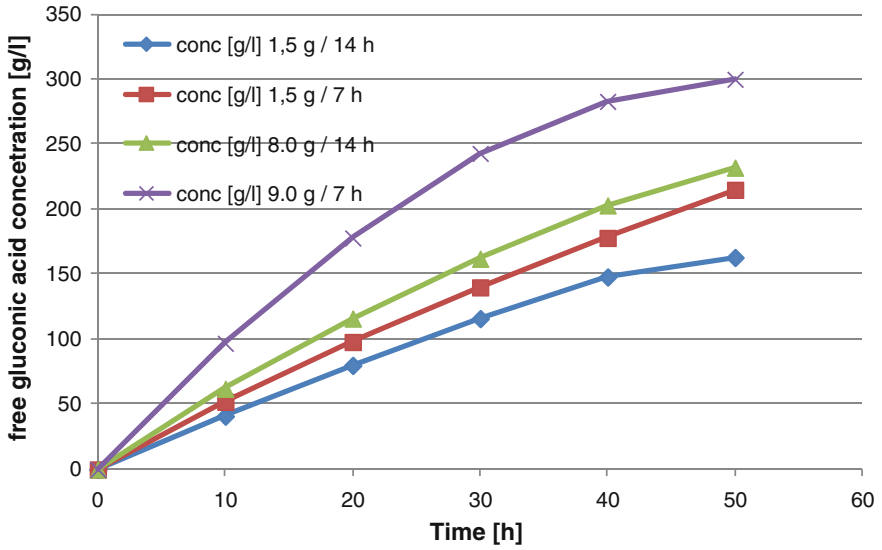


Fig. 12 Influence of the biomass concentration and residence time on the formed amount of gluconic acid with *A. methanolicus*

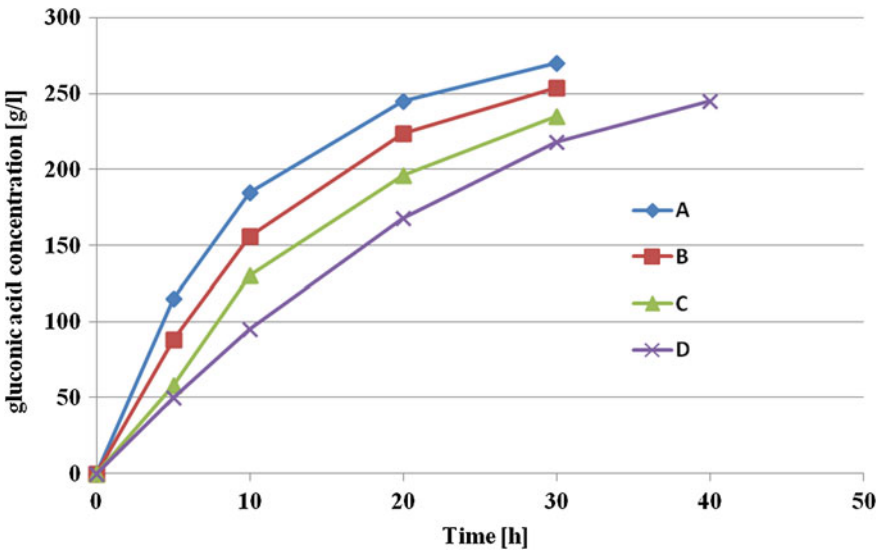
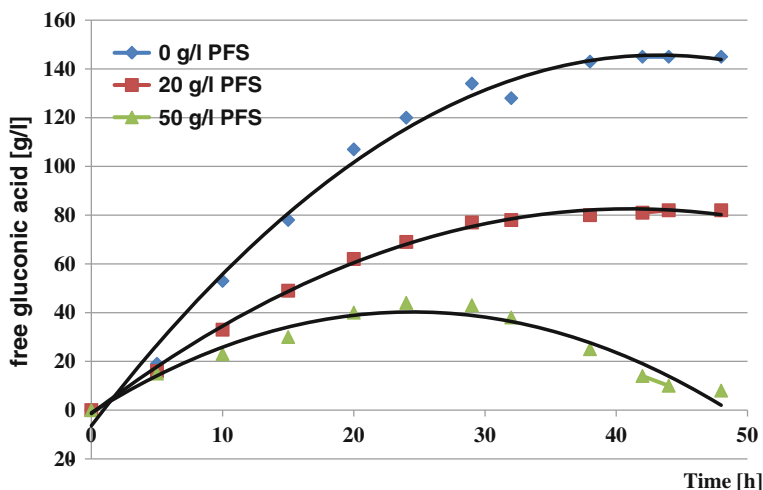


Fig. 13 Influence of the carbon source on the gluconic acid formation, A growth on glucose 5 g BDS/l; B growth on a mixture of methanol and glucose in a ratio 5:1; C growth on a mixture of methanol and gluconate in a ratio 5:1; D growth on methanol



**Fig. 14** Gluconic acid formation with different concentrations of PFS in the medium

microorganisms would have increased the risk of contamination by other microbial strains.

Figure 14 shows the decrease of free gluconic acid in the medium depending on the slag concentration. Inasmuch as the gluconic acid forms a stable compound with the Ca ions from the slag, a precipitation of calcium gluconate can be observed.

Figure 15 shows the amount of leached REE related to the total content of REE as a function of the formed concentration of gluconic acid. About 40 % of the REE were extracted from the slag at a gluconic acid concentration of 150 g/l.

Because the leaching system consisted of three different phases—two solid phases, namely the biomass and the slag and one liquid phase, the leaching solution—the distribution of the REE in these phases was investigated. Figure 16 demonstrates that more than 80 % of the leached REE were dissolved in the leaching solution and only 10–15 % of the REE were bound to the total biomass. The majority of REE were bound and stored in the biomass during the beginning of the leaching process. An increase of the REE concentration in the leaching solution can be observed after a saturation of the REE on the biomass. Comprehensive investigations of the sorption processes and the sorption capacity of the biomass confirmed this statement [78, 79]. Such a multiphase reaction system generates comprehensive difficulties due to the analytical determination and the establishment of a balance equation.

The results of such a discontinuous leaching process and the distribution of the REE in the leaching system as well as the dissolution of the slag as an example are shown in Table 8. Related to a volume of 1 l the leaching system was characterized by 50 g slag with a concentration of 0.59 % REE according to a total amount of 0.259 g/l, an average biomass content of 5 g and 165 g glucose. The expected

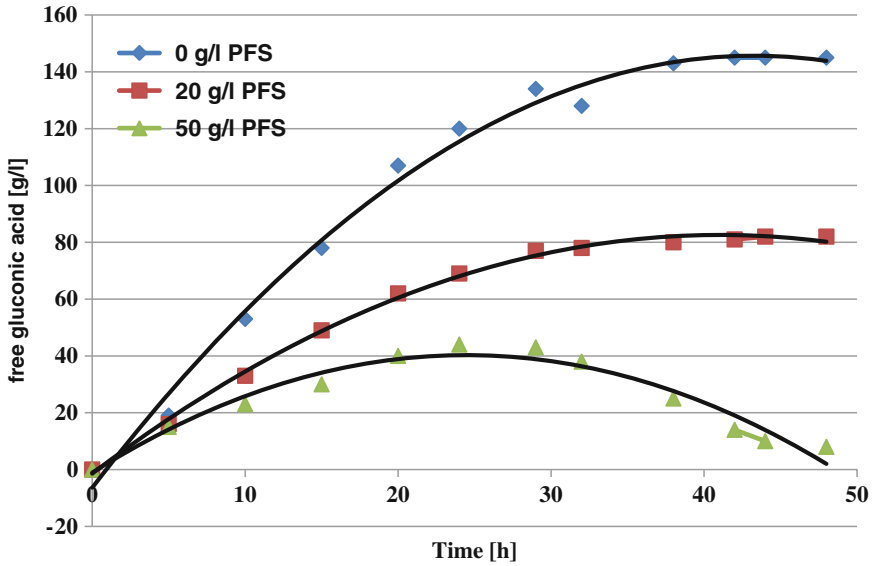


Fig. 15 Ratio of dissolved related to the total amount of rare earth elements depending on the produced amount of gluconic acid

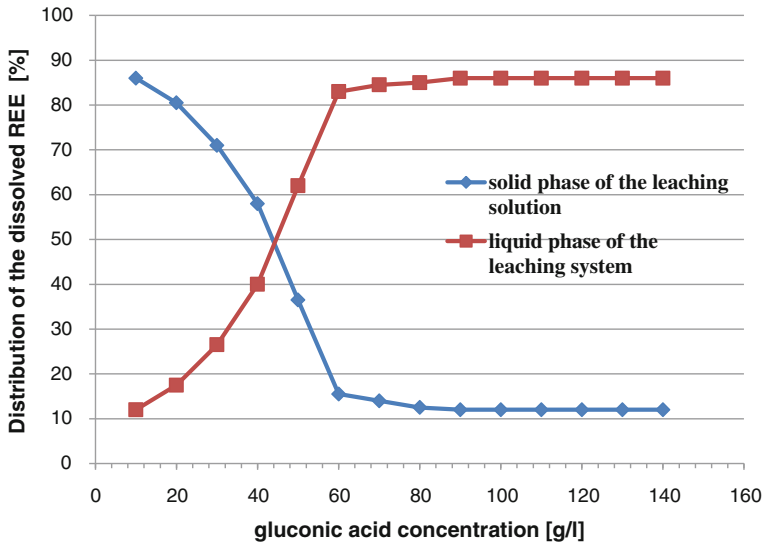


Fig. 16 Distribution of the leached REE in the leaching system

concentration of the formed gluconic acid was 140 g/l. The slag after the leaching was 19.1 g/l with a concentration of REE of 0.67 % (0.128 g/l). This means a leached amount of REE of about 56.6 % and a solubilized amount of slag of

**Table 8** Results of the phosphorous furnace slag leaching process with *A. methanolicus* [80, 87]

	Dimension	Slag	After the leaching process		
			Slag	Biomass in the leaching solution	Dry residues of the leaching solution
Amount	g/l	50	19.1	19	119
REE	%	0.59	0.67	0.262	0.07
REE	g/l	0.295	0.128	0.05	0.083
Solubilized slag:	%	61.8			
Leached SEE:	%	56.61			

61.8 %. The determination of the distribution of the leaching solution had given 19 g/l biomass containing solids with 0.262 % of REE or 0.05 g/l REE and 119 g/l: dry residues of the liquid phase with 0.07 % of REE or 0.083 g/l. Both phases contained 0.133 g/l REE according 79.6 % of the leached REE [87].

A huge amount of such slags is obtained from phosphorous production. About 120 kt/a were produced in Piesteritz over a long period and about 25 kt/a in Bitterfeld. The whole amount of slags produced in Germany can be assessed with 22.6 million t.

In addition to the REE-containing slags there are other residues from phosphoric acid production. In contrast to the slag this sludge contains gypsum because the production of phosphoric acid is achieved by the treatment of apatite with sulphuric acid. The calcium of the  $\text{Ca}_3(\text{PO}_4)_2$  forms not very soluble gypsum with the sulphuric acid and the phosphoric acid is released. REE and trace elements are precipitated in the sludge. The produced and deposited amount of sludge is estimated to be 34 million t.

## 12 Flotation Residues: Tailings

Mining of ores is often linked to the generation of flotation residues which were stored in special tailing ponds or dams in the past. These residues mostly contain various valuable substances due to less-efficient separation techniques in the past. The ore processing mainly focused on the production of one product and by-product metals were not exploited during this time.

The long-lasting mining activities in the Ore Mountains (“Erzgebirge”) created tailings with fine-grained residues of the tin flotation. The “Bielatal” tailing pond, Saxony, Germany, solely contains more than 10 million t of residues comprising 0.2 % of tin, 200 ppm of tungsten, 100 ppm of molybdenum, 200 ppm of bismuth, and additionally lithium, rubidium, manganese, titanium, cesium, and some trace elements [89]. This is a remarkable potential of resources. Table 9 displays the average concentrations of the target elements, Table 10 lists the concentration of the by-product elements in the flotation tailings, and Table 11 gives an overview of the structure and the composition of the material in the tailing pond.

**Table 9** Main components of tin flotation tailings at “Bielatal,” ore mountains (Erzgebirge), Saxony, Germany

Element	Concentration (mg/kg)		
	Average value	Min	Max
Sn	644	563	766
W	876	766	986
Bi	76	60	84
Mo	12.2	11.2	13.8

**Table 10** ICP analyses of the concentration of some by-product elements of the flotation tailings

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Ba	128	Ni	4
Be	12.5	Sc	7
Co	7	Sr	54
Cr	7	Ti	595
Cu	66	V	6
La	37	Y	47
Li	853	Zn	80
Mn	775	S total	<0.01 %

**Table 11** Concentration of the main compounds of the flotation tailings

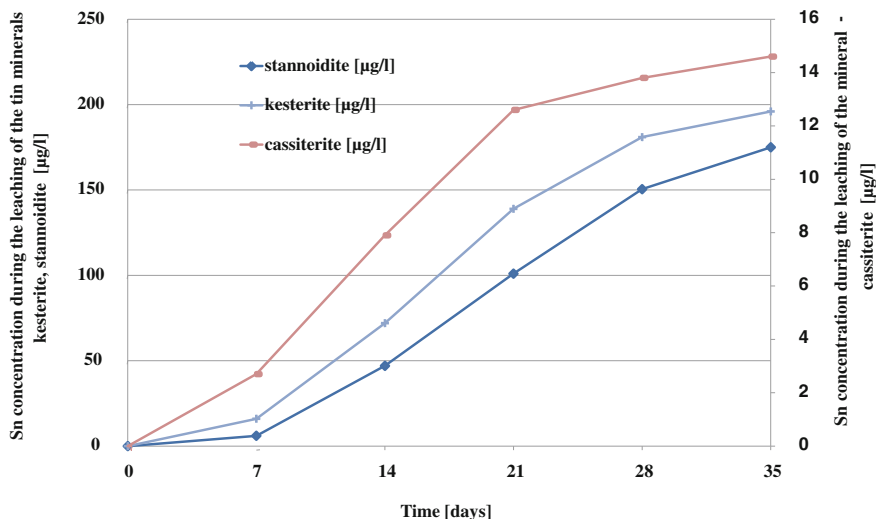
Compound	Percentage (%)	Compound	Percentage (%)
SiO <sub>2</sub>	72.1	CaO	0.96
TiO <sub>2</sub>	0.1	Na <sub>2</sub> O	n.d.
Al <sub>2</sub> O <sub>3</sub>	14.5	K <sub>2</sub> O	2.3
Fe <sub>2</sub> O <sub>3</sub>	4.36	P <sub>2</sub> O <sub>5</sub>	0.064
FeO	1.84	CO <sub>2</sub>	0.33
MnO	0.1	H <sub>2</sub> O	2.18
MgO	0.08		

The potential for microbial leaching of this material under acidic conditions was investigated with the aim of subsequent tin separation [89]. The leaching was carried out with a mixed culture of *Acidithiobacillus ferrooxidans* and Fe<sup>2+</sup> as energy source. The treated amount of solid residues varied between 2 and 30 % in the leaching system. The pH value ranged from 2.4 to 1.7 and the initial Fe<sup>2+</sup> concentration was between 10 and 12 g/l. Table 12 shows some results of the bioleaching processes. The first line in the table shows the content of solids in the medium; the second line displays the total amounts of tin in the solids related to the liquid phase. This is the potentially maximum leachable tin concentration. The next line includes information about the pH conditions and the added Fe<sup>2+</sup> concentration at the beginning and the end of the leaching experiment. The last line shows the tin concentration in the leaching solution after the leaching process. Only a few micrograms of tin could be separated from the flotation residues.

The extraction of tin from different tin compounds was investigated earlier by Teh et al. [90, 91; see Fig. 17]. The authors investigated the microbial leaching of the quaternary synthetic sulphidic tin minerals stannite, kesterite, and stannoidite,

**Table 12** Tin bioleaching of flotation residues from the Bielatal tailing pond

Pulp density (%)	2		5		20		30	
Maximum resulting tin concentration (mg/l)	40		100		400		600	
Process conditions	pH	Fe <sup>2+</sup> (g/l)	pH	Fe <sup>2+</sup> (g/l)	pH	Fe <sup>2+</sup> (g/l)	pH	Fe <sup>2+</sup> (g/l)
	2.4–1.7	10.3–0.2	2.4–1.7	10.98–0.23	2.4–1.8	11.2–9.0	2.4–1.7	12.35–7.98
Dissolved tin (µg/l)	90		120		130		215	

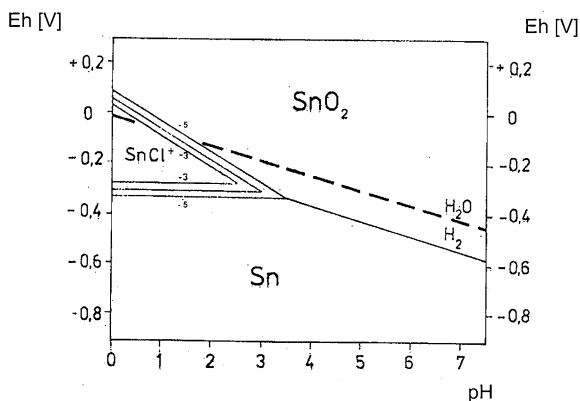
**Fig. 17** Bioleaching results of several tin minerals after [90, 91]

and the oxidic minerals cassiterite and varlamoffite. The leaching was carried out with *At. ferrooxidans* at 32 °C, 0.5 % pulp density, pH 2.5, and a particle size smaller than 0.16 mm. Investigations under sterile conditions were carried out simultaneously.

An influence of *At. ferrooxidans* strains could be observed, but the resulting concentrations were in the same range as in the aforementioned investigations. The results from the leaching of the sulphidic tin minerals stannite, kesterite, and stanniodite show concentrations of dissolved tin sometimes higher than those of the leached cassiterite. But the highest observed concentration was about 200 µg/l. These results demonstrate that the concentration of dissolved tin was low and that bioleaching was without remarkable success.

Investigations concerning the behavior of tin revealed that Sn<sup>4+</sup> is not stable in the leaching solution. Sn<sup>2+</sup> acts as a reducing agent with a potential of +0.15 V and forms Sn<sup>4+</sup>. This generates SnO<sub>2</sub> again which exhibits a very low solubility. Only  $1.2 \times 10^{-16}$  mass % are dissolved at 20 °C in water. But Sn<sup>4+</sup> ions form stable chloride complexes [SnCl<sub>6</sub>]<sup>2-</sup> under acidic conditions. This requires a chloride concentration between 1 and 3 mol/l to enhance the solubility of Sn in the leaching

**Fig. 18** pH Eh diagram of  $\text{SnO}_2$  in the system  $\text{Sn}-\text{Cl}-\text{H}_2\text{O}$  (Sn concentration  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$  mol/l, Cl concentration  $10^{-1}$  mol/l), [89]



solution. The calculation of the stability of tin and chloride in an aqueous system at different pH and Eh values is displayed in Fig. 18 and revealed stable conditions at low pH values and a negative redox potential [89].

Therefore bioleaching with *At. ferrooxidans* strains was repeated after the adaption to higher concentrations of chloride under aerobic conditions. The highest chosen concentration of chloride anions was 5 g/l, whereas the highest concentration of tin in the leaching solution with a pulp density of 30 % was 6 mg/l, much higher than in the previous experiments.

Considering this relationship, a separation of tin seems to be possible by a microbial leaching process under anaerobic and acidic conditions with chloride anions in the solution or via biomethylation resulting in a tin organic compound such as dimethyl tin.

## 13 Sludges from Industry and Environment

### 13.1 Industrial Sludges

There are a huge number of different types and volumes of deposited metal-containing sludges. Table 13 summarizes some processes that demonstrate the treatment of metal-containing sludges. The sludges have different origins. They are residues from industry or from water treatment plants as well as sediments from rivers and harbors. A review concerning the separation of heavy metals from contaminated sludge for soil remediation is given by Babel and Dacera [92].

Today sludges from galvanic plants and pickling processes are reprocessed very often by chemical and physical techniques. For their treatment, microbial processes were developed but are currently not applied [93–95].

A waste product of high commercial interest is the iron- and titanium-containing red mud from aluminum production. These sludges are water insoluble. In addition to iron, aluminum, and titanium, they contain trace elements as well as

**Table 13** Treatment of various metal-containing sludges

Residue/ Waste	Origin	Content/valuable substances	Treatment	References	Remarks
Sludges	Copper mining (Theisen sludge)	Zn, Pb, Sn, Cu	No successful treatment until now	[99]	Metals are bound in a sludge from the blast furnace gas washer containing bituminous carbon
	Electroplating plants	Cr, Cu, Ni, Zn	Leaching of the metal hydroxide	[144]	Leaching efficiency Zn 99 %, Ni 96 %, Cu 81 %, Cr 71 %
	Plating sludge	Zn, Cu, Ni, Pb, Cd, Cr	Leaching with <i>At. ferrooxidans</i>	[145]	97 % Zn, 96 % Cu, 93 % Ni, 84 % Pb, 67 % Cd, 34 % Cr are separated
	River/harbour sludges	Cd, Cu, Zn, Ni, Pb, Hg, As, Cr	Leaching of heavy metal polluted harbor sludge	[110]	Treatment consists of a two stage process, an anaerobic sulphate reducing process followed by an autotrophic acidic leaching process with <i>Acidithiobacillus</i> and <i>Leptospirillum</i> strains
	River sludge	Zn, Mn, Cr, Cu, Pb, Ni, Cd	Chemical and microbiological leaching in solid bed and percolator system	[106, 107, 163]	Up to 70 % of the metals were solubilized depending on the leaching conditions (content of S <sup>o</sup> , influence of surfactants, irrigation rate and height of the solid bed)
	Canal sediments	Cu, Ni, Zn	Sediments of a canal in an industrial area were treated with biosurfactants	[146]	Different concentration of rhamnolipid were used for washing the sediments. 15 % of Cu and 5 % of Zn were solubilized
	Sand/Soil	Cr, Ni, Zn	Leaching of a heavy metal contaminated sand by a two stage process	[147]	Heavy metals were solubilized by <i>At. thiooxidans</i> and separated from the leach liquor by sulphate reducing bacteria. 14.6 % Cr, 26.7 % Ni, 90.5 % Zn were solubilized, 2.2 % Cr, 54 % Ni, 28 % Zn were precipitated
		Cu, Zn, Cd	Alkaline heavy metal polluted soil was treated in situ by stimulating the activity of the indigenous soil microflora	[148]	The soil was treated with biodegradable organic materials and phosphate. Heavy metals were solubilized as complex with organic acids

Table 13 (continued)

Residue/ Waste	Content/valuable substances	Treatment	References	Remarks
Sewage sludge	Cr, Cu, Ni, Pb, Zn	Metals stored in the sludge are leached with indigenous S- oxidizing <i>Acidithiobacilli</i> strains	[149]	50.6 % Cr, 87 % Cu, 94.4 % Ni, 41.2 % Pb, 99.5 % Zn were solubilized
	Cu, Al, Cr, Zn, Ni, Pb, Fe	Leaching of the sludge with <i>At. thiooxidans</i>	[162]	Leaching was carried out with high solid concentration (130 g/l), no remarkable influence of the solid concentration on the bioleaching, high dependance on pH condition, leaching efficiency 91 % Zn, 51 % Cu, 47 % Cr, 30 % Pb, 84 % Ni, 29 % Al
Municipal sewage sludge	Cd, Cu	Separation of Cd and Cu with indigenous Fe and S oxidizing bacteria	[150]	Indigenous bacteria were selected and the sludge from a municipal treatment plant was leached, maximum leaching efficiency: 100 % Cd and 70 % Cu

silicic acid. An extraction of iron by microbial processes with a parallel dissolution of the silicate matrix also is possible. Other investigations include the microbial leaching of aluminum from red mud [96, 97]. A similar situation concerns the sludges of mines and drinking water treatment plants.

A special and interesting issue is the processing of residues from the former copper smelter in the Mansfeld region, Saxony-Anhalt, Germany. Copper production resulted in the generation of a special sludge, the so-called Theisen sludge. The Theisen sludge is a side product of the blast furnace flue dust washing plant, containing volatile organic bituminous substances as well as heavy metals. There was no technology for the treatment of the sludge after closing the plant in 1970, therefore the sludge was stored and the search for a suitable technology for the recovery failed until today. Between 200,000 and 450,000 t of sludge are stored in special dumps to avoid any risk to the environment [98–100]. The concentration of valuable substances is noteworthy. Theisen sludge contains about 18 % Zn, 14 % Pb, 1.2 % Cu, and 1.2 % Sn, in addition to trace and minor elements. Main components of the sludge are 17 % SiO<sub>2</sub>, 16 % S, and 11 % C wherein the carbon originates from the bitumen. Recent investigations demonstrated the possibility of the extraction of metals from bituminous matter related to the production of copper from copper shale [101]. The organic matrix can be destroyed microbially, releasing and mobilizing metals and trace elements [102, 40, 103].

Sludges from wastewater treatment plants are rich in organic carbon and exhibit high concentrations of heavy metals due to the ability of the microorganisms to accumulate and store heavy metals by biosorption processes. High concentrations of zinc and copper were found up to several g/kg in the dried sewage sludge. The concentrations increase if the sewage sludge is used for biogas formation in digestion processes related to the utilization of organic carbon. The metals are precipitated as sulphides, carbonates, or hydroxides via reduction of sulphate to sulphide, under neutral conditions accompanied by the formation of CO<sub>2</sub> as a side product of the methanogens. The composition of the sludge determines the chosen microbial leaching process. As well as metals, sewage sludge is an interesting phosphate resource. According to the environmental database, the produced amount of sludge from biogas formation was about 17 million t in 1990. Of these 60 % were deposited and 10 % were introduced in the municipal waste incineration process [104].

### ***13.2 River, Harbor, and Marine Sludges***

Small suspended particles that bind metal cations due to their high sorption capacity are stored in rivers and storage reservoirs. They have to be removed periodically to clean the rivers and storage reservoirs. Storage of the suspended particles also takes place in rivers where a barrier exists and sediments are formed. These sediments are enriched with heavy metals and trace elements. Investigations of a 2.5-km segment of the river Elster near the town Leipzig, Germany, revealed

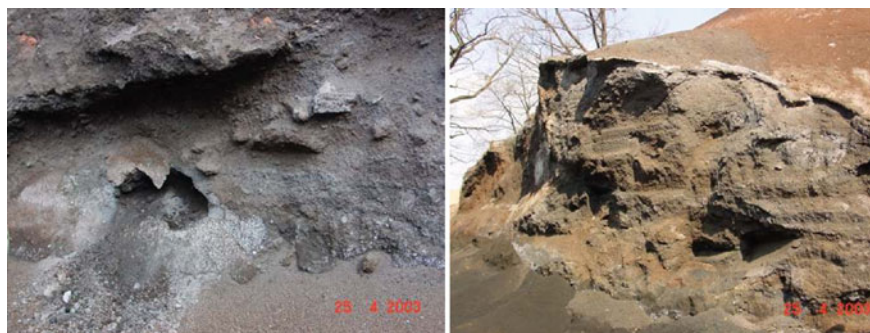
330,000 t of sediments with 1,300 t of zinc, 81 t of nickel, and 79 t of copper. A technique for recovering the metals from the sediments was successfully developed [105, 106]. Comprehensive investigations of the development of a treatment technology were conducted during the last 20 years in the environmental research center (UFZ). The bioleaching process was carried out as suspension and solid bed leaching after the treatment of the sludge. The treatment involved homogenization and analytical determination. The sludge was poor in inorganic carbon (below 0.05 %) and rich in organic matter (19 %) containing the following metals in mg/kg: 3,291 Zn, 954 Mn, 515 Cr, 322 Cu, 312 Pb, 286 Ni, and 36 Cd. Investigated parameters were, among others, the irrigation rate, the influence of sulphur addition, and the presence of surfactants [107]. Because freshly dredged sediment proved to be unsuitable for solid-bed leaching, due to its low permeability, an upstream process for sediment conditioning has been developed. This process involved the treatment of the sludge with helophytes converting it into a soil-like material [108]. After this pretreatment the bioleaching of the sludge was successful and 20,000 kg of the material were processed at large scale.

A special interaction exists between natural surface water and mining residues. Such fluvial materials (often tailings) are exposed to microbial oxidation processes and heavy or precious metals are mobilized. Willscher et al. [109, Chap. 1] investigated such processes and reported the bioleaching of fluvial residues of historical gold mining with autotrophic as well as heterotrophic microorganisms, detecting a quantitative separation of chromium and manganese during the heterotrophic process. The autotrophic leaching using an acidophilic mixed culture showed a quantitative separation of Cu, Al, Cr, and As.

The sludges in harbors bear similar characteristics. They are very often enriched in heavy metals and trace elements. A treatment of the sludges by leaching processes is also possible. Beolchini et al. [110] demonstrated a two-stage treatment. The processing involved anaerobic sulphate reduction followed by an acidic leaching process with the autotrophic bacteria *Acidithiobacillus* and *Leptospirillum* strains. The method is based on the transfer of heavy metals into sulphides under anaerobic conditions (Chap. 1) and a subsequent leaching of the sulphides under acidic conditions.

Marine sludges often exhibit high concentrations of heavy metals. The sludge is removed to ensure sufficient depth of shipping passages. Due to the anaerobic conditions the sulphate reduction is one of the driving processes and metals are precipitated as sulphides. On the other side huge amounts of carbonate exist as a result of the CO<sub>2</sub> formed. Therefore a successful bioleaching process depends on the ratio between sulphide and carbonate in the sludge.

The sludges of floodwaters are sometimes contaminated with heavy metals and stored as hazardous waste in disposals analogous to the river sludges. Thus a leaching process for the separation of these metals has to be considered.



**Fig. 19** Photos of a slag dump

## 14 Ashes and Dusts

### 14.1 Introduction

Many industrial processes are linked to the formation of dusts. They are separated from the air by special dust filter plants. Zinc-containing dusts are predominantly treated in smelters today and residues are stored in special disposals. The influence of different microbial strains on the release of some elected heavy metals was therefore investigated. Because of the neutral to alkaline pH conditions, in addition to acidophilic, also alkalophilic microorganisms were used for the bioleaching experiments, as well as humic acid and citric acid as organic leaching agents. Because the treated dusts are similar to slags, the results of some investigations are reported in Chap. 4.1.2

The pictures in Fig. 19 show a dump of stored residues from a zinc smelter and the influence of environmental and climate conditions on the deposited slag as visible by the changes in color.

Table 14 summarizes the characteristics of ashes and dusts from various incineration processes and from a copper-producing smelter in accordance with microbial leaching studies for the extraction of valuable substances.

### 14.2 Ashes from Lignite Electric Power Stations

Ashes are residues from incineration processes and contain various valuable elements. Table 15 shows a comparison of ashes from different lignite-fired power stations and power stations using other fuels. Unfortunately the data are incomplete, but they demonstrate the variation in the composition of the ashes and the huge number of valuable substances.

**Table 14** Valuable substances of different ashes and kind of dusts

Residue/ Waste	Origin	Content/Valuable substances	Treatment	References	Remarks
Ashes	Lignite power station	Ca, Mg, Al, Si, Fe, Mn, Cu, Ni, Ga, Nb, Ge, Ti, REE	Heterotrophic leaching with acid producing microorganisms	[116]	Depending on the kind of lignite, solubilization depends on the amount of formed acid
	Fuel power station	V, Ni, Fe, S, Ca, Mg, Co, Ti, Al, Mo, Ba	No leaching tests are reported	[117]	Investigations were carried out for energy saving in the metallurgical industry
	Gas power station	V (2–10 %), Ni (1–3 %)	No leaching tests are reported	[117]	Ash is stored in disposals or used in smelter processes
	Waste incineration plant	Al, Cd, Cr, Cu, Ni, Pb, Sn, V, Zn	Leaching with <i>A. niger</i>	[151]	Depending on the kind of waste material, extraction of Cu, Pb 60–70 %, Al, Mn, Zn, 80–100 %
	Municipal solid waste incineration ash	Al, Ca, Cu, Fe, K, Mg, Mn, Pb, Sr, Zn	Fly ash was treated with <i>A. niger</i> at different pulp densities, spore and sucrose concentrations	[152]	Optimum conditions are: pulp density 2.7 %, sucrose 150 g/l (for gluconic acid formation)
Dusts	Copper containing dust	Cu, Fe as different sulphides and oxides (Cu conc. 23–36 %)	Bioleaching from copper flue dust with a mixed mesophilic culture of <i>At. ferrooxidans</i> , <i>At. thiooxidans</i> and <i>Leptosyrillum</i>	[153]	Leaching carried out in CTR with a pulp density of 2–7 %, Cu extraction decreases from 92 to 87 %, with increasing density

**Table 15** Comparison of elemental composition of ashes from different electric power stations

Element	Power station ash refinery residues (mg/kg)	Power station ash oil firing (mg/kg)	Power station ash lignite Leipzig (mg/kg)	Power station ash lignite Lusatia average values (mg/kg)
Vanadium	42,500	70,000	10	84.5
Iron	31,800	65,400	56,000	132,000
Nickel	21,600	32,400	16	37
Sulphur	46,900	199,800	11,900	17,200
Silicon	48,300	6,800	234,000	217,500
Calcium	11,500	5,100	164,000	113,600
Magnesium	2,000	1,100	18,000	26,100
Cobalt	400	300	4	10.50
Titanium	1,500	200		4,025
Phosphorus	2,000	400		590
Barium	0.15	1,300	3	535
Molybdenum	0.05	100		4.5
Aluminium	17,100	3,400	64,000	52,100
Chromium	200		27	95.5
Arsenic			3	19
Tungsten	200			<1
Copper			17	74
Manganese			1125	1,060
Strontium			1756	1,340
Zinc			29	70.5

Lignites are organic substances that often contain and accumulate metals. These metals remain in the ash after the incineration process and reach higher concentrations than in lignite due to the reduced volume. The annual production of lignite is about 300 million t in Germany. The amount of ash from lignite ranges from 10 to 20 % of lignite dry weight. This means the total amount of ash accounts for approximately 15 million t per year. In addition to the main element Si, the ashes consist of Ca, Mg, Al, and contain various trace elements and REE depending on the kind of lignite. Main components of lignite ashes [111] and the average typical composition of East German lignites from different regions are presented by Holzapfel [112]. Table 16 includes the concentrations of heavy metals and trace elements in different lignites and ashes.

Ashes are valuable resources. If the value of 1 t of ash according to the valid prices of the contained elements without the element Si is calculated, a price exceeding €500/ton ash results. A suitable mineral processing for the separation of the valuable substances needs to be explored. This can be done by the combination of physical chemical or biotechnological treatment techniques. During leaching experiments the solubilization of Ca, Mg, Fe, and Al was detected depending on the pH value and the kind of water used [113].

According to the focused elements the leaching can be carried out under neutral, acidic, or alkaline conditions. A separation of aluminum by microbially produced organic acids was investigated by Singer et al. [114] and Torma and



**Table 17** Composition of a fly Ash from the lignite power station neurath [116] precleaned by Sieving [161]

Parameter/Element	Value
Dry residue (mass %)	99.8
TOC (mass %)	0.3
NH <sub>4</sub> -N (mg/kg)	<0.5
SiO <sub>2</sub> (mg/kg)	265,000
Na <sub>2</sub> O (mg/kg)	29,200
K <sub>2</sub> O (mg/kg)	14,600
P total (mg/kg)	<100
SO <sub>4</sub> <sup>2-</sup> (mg/kg)	10,500
NO <sub>3</sub> <sup>-</sup> (mg/kg)	<50
Sulfide (mg/kg)	950
Ca (mg/kg)	152,000
Al (mg/kg)	85,400
Fe (mg/kg)	52,500
Mg (mg/kg)	34,700
Mn (mg/kg)	480
Va (mg/kg)	240
Ni (mg/kg)	110
Zn (mg/kg)	99
As (mg/kg)	36
Mo (mg/kg)	36
Co (mg/kg)	21
Wo (mg/kg)	12
Cd (mg/kg)	<2

Singh [115]. Krejcik [116] tried to solubilize all elements. Table 18 contains the composition of a fly ash from a lignite power station. Calcium, aluminum, iron, and magnesium are the main metal components in addition to silicon dioxide. For leaching of the fly ash different microbial strains can be used (Table 17).

Figure 20 shows the leaching of iron by the neutrophilic strain *Bacillus circulans* and the organic acid producing strain *Acetobacter methanolica* at different concentrations of ashes in the leaching solution [116].

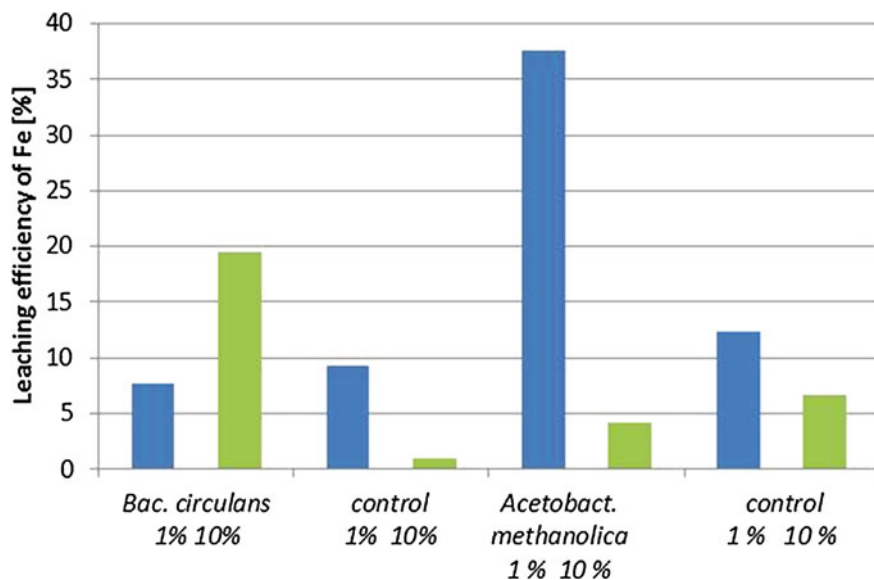
The bioleaching efficiency decreases with an increasing amount of ash due to the constant amount of organic acid formed by *A. methanolica*. In the case of *B. circulans* the increased efficiency can be explained by the shift of the pH into the alkaline region and better growth conditions of the neutrophilic–alkaliphilic strain. The leaching results without microorganisms are denoted as control. Therefore a selection of the most suitable leaching conditions for each element is recommended.

### 14.3 Ash from Oil- and Gas-Fired Power Stations

Ashes from oil- and gas-fired power stations as well as the filter dusts of the crude oil processing industry contain mainly vanadium with concentrations of 2–10 % and nickel with a concentration of 1–3 %. They are mixed with sodium carbonate

**Table 18** Valuable substances from water treatment plants

Origin	Content/valuable substances	Treatment	References	Remarks
Drinking water	Fe, Mn	Separation of Fe, Mn by microbial oxidation and precipitation	[131, 132]	Fe <sup>2+</sup> , Mn <sup>2+</sup> are microbially oxidized at neutral pH and separated as Fe <sup>3+</sup> and Mn <sup>4+</sup> hydroxide/oxide
Mine water	Separation of Mn <sup>2+</sup> from contaminated water	In situ removal of Mn <sup>2+</sup> from mine water but also drinking water and ground water with pH >4	[155]	A reactor using Mn <sup>4+</sup> coated pebbles is used for the microbial Mn <sup>2+</sup> oxidation and separation. Two fungi ( <i>Pleosporales</i> ) and one bacteria ( <i>Bosea thiooxidans</i> ) were isolated
Iron		Continuous oxidation of Fe <sup>2+</sup> with a moderate acidophilic mixed culture in a mine water treatment plant and precipitation as hydroxysulphate	[123, 124, 129, 130]	The reaction takes place in a continuous flowed and aerated basin with carriers for the growth of the microorganisms
Surface treatment effluents	Separation of heavy metals from surface water	Treatment consists in an application of sulphate reducing bacteria to transform metals into sulphides	[156]	Microbial production of S <sup>2-</sup> and precipitation of metals from surface water



**Fig. 20** Bioleaching of Fe from lignite combustion ash with *Acetobact. methanolica* and *Bac. circulans*, leaching conditions: *Acetobact. methanolica* strain DSZM: 5432, medium 569, *Bac. circulans* strain DSZM: 11, medium No 1, controls: ash plus sterilized nutrient solution, without microorganisms, pH adjusted with HCl

and melted in a drum furnace. As results, sodium vanadate ( $\text{Na}_4\text{V}_2\text{O}_7$ ) and iron and nickel sulphide compounds ( $\text{FeS}$ ,  $\text{NiS}$ ) are produced. Vanadium concentrate with a high concentration of organic carbon is deposited. An annual available amount of 100,000 t has been calculated for Europe [117] and a microbial leaching to extract the metals might be reasonable.

#### 14.4 Ashes from Waste Incineration Plants

The incineration of urban waste produces about 250 kg ash per ton of domestic waste. About 70 incineration plants for urban waste exist in Germany producing about 5 million t of ash from 20 million t of domestic waste per year with an increasing trend in the future [118, 119]. Only 8 % of the metals in the ash are recovered including only 1 % nonferrous metals. The major part of the ashes (75 %) is used in disposal and road construction. About 10 % are deposited [120]. Ashes from municipal waste incineration have a different composition depending on the kind of wastes. The concentration of nonferrous metals varies from 1,000–3,500 mg/kg for lead, 200–1,000 mg/kg for chromium, 1,000–10,000 mg/kg for copper, 100–500 mg/kg for nickel and 2,000–7,000 mg/kg for zinc [120, 121]. The copper concentration is in the range of the actually exploited copper ore bodies.

The improvement of the recovery of nonferrous metals can be achieved by an optimization of the downstream processing in combination with biotechnological techniques [122].

## 15 Residues from Water Treatment Plants

Because wastewater usually contains anions and cations and even heavy metals and some trace elements (TE), different technologies are used for separating these substances. Table 18 shows some examples for the separation of valuable substances from different water qualities.

A typical example for separating a metal in an industrial water treatment plant is the separation of iron from lignite mine water. The mine water is treated by aeration and the addition of lime milk to neutralize the water and oxidize the ferrous iron. The produced sludge contains trace elements as well as valuable substances. The sludge is stored in special deposits, transferred into flooded open cast mines, or transported into “dewatering fields,” producing a dried iron-containing sludge.

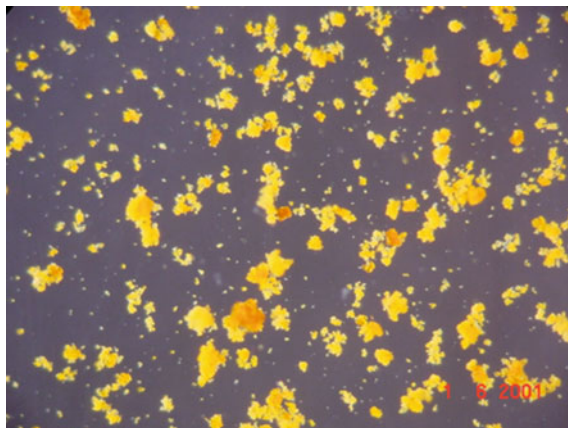
A new technology separates the iron before lime addition by a microbial process [123–125]. The process is based on the microbial oxidation of ferrous iron to ferric iron at low pH and the formation of an iron hydroxy sulphate mineral, called schwertmannite [126, Chap. 2].

The formed iron compounds precipitate and can easily be separated due to the low solubility of schwertmannite in water. The mineral has got a higher purity in comparison to the lime containing iron hydroxide sludge [123, 124]. Figure 21 shows the formed schwertmannite crystals in the treated mine water.

According to the amount of dissolved iron in the mine water at this site, about 10,000 t of the mineral could be produced and utilized. Different research projects focused on the production of adsorbents or iron oxide pigments from schwertmannite [127]. A pilot technology has been applied for 10 years now and confirms the stability of the process [128]. Comprehensive investigations concerning the composition of the microbial population revealed a moderate acidophilic mixed population consisting of two groups of *Betaproteobacteria* accompanied by “*Ferroplasma myxofaciens*” and strains related to *Gallionella ferruginea* as the main part [129, 130].

Another process concerns the separation of iron and manganese via neutrophilic iron and manganese oxidizing bacteria. These bacteria form a stable film at the surface of sand grains and oxidize the metal ions. In a second step a precipitation of ferric iron or  $Mn^{4+}$  takes place. This technology is applied in the treatment of drinking water or groundwater [131, 132].

**Fig. 21** Schwertmannite crystals in a treated mine water



## 16 Residues from the Electric and Electronic Industry and Spent Catalysts

Table 19 shows some microbial processes for the separation of heavy and precious metals from residues of the electric and electronic industry or from spent catalysts. A multitude of further recyclable residues are composite materials such as laminated boards and laminated papers, as well as metal-containing plastics that can be separated by microbial processes. A current treatment technology for these materials includes the incineration and separation of the metals. An alternative process could be microbial treatment where the organic material is utilized or transformed into water-soluble compounds and the metals are released.

The significance of electronic scrap has increased. Its components can be dissolved and separated by different microbial acid-forming processes [16, 133]. Heterotrophic as well as autotrophic microorganisms can be used for these processes. For example about 90 % of copper, about 50 % of zinc and 17 % of manganese could be bioleached by an autotrophic mixed culture [134] (Table 19).

Some other metals, for examples, lead could be separated by precipitation. This category also includes car shredding residues.

The treatment of this material with cyanide-forming microorganisms offers a similar yet new possibility. This is valid in particular for the treatment of electronic scrap as well as for the treatment of precious-metal-containing catalysts [50, 135]. Analogue processes are possible with spent catalysts [16]. Hydrogenating catalysts are used in the chemical industry. The spent catalysts contain between 1.5 and 3.5 % Ni, 4–11 % Mo, 35–50 % Al, about 15 % of Fe, and 5–18 % Ca. But they contain between 3.3 and 6.6 % sulphur, mostly occurring as sulphide. In the past the recovery of nickel and molybdenum was investigated by Iske et al. [55]. Analogue investigations using strains of *Aspergillus* demonstrated yields of 78 % of nickel, 82 % molybdenum, and 85 % aluminum [136].

**Table 19** Composition of valuable substances in catalysts and residues of the electronic industry

Residue/waste	Origin	Content/valuable substances	Treatment	References	Remarks
Catalysts	Motor car	0.1 % Pt, Cu	Pt leaching by CN <sup>-</sup> -forming microorganisms	[135]	<i>C. violaceum</i> are able to solubilize Cu and Pt
	Hydrogenating catalysts	Al, Ni, Mo, Fe, Ca	Leaching of Ni, Mo by moderately acidophilic autotrophic microorganisms	[55]	Separation of Ni and Mo from Ca, Fe, Al
	Spent refinery catalysts	Ni, V, Mo	Bioleaching of pretreated refinery catalysts—a mix of iron and sulphur oxidizing bacteria was used	[157]	The recovery by the Fe oxidizing bacteria was 90, 80, 54 % for Ni, V, Mo respectively, recovery using the S oxidizing bacteria was 88, 94, 46 % (Ni, V, Mo)
Residues/scrap from the electric/electronic industries	Electronic scrap (ESM)	35 % Sn, 65 % Pb, Zn, Al, Mn, >70 % Fe, Ni, Cu were mobilized	Leaching with <i>Aspergillus niger</i> , pulp density of 0.1–2.0 %	[133]	Two step leaching process due to the inhibitory effects of toxic metals
	Shreddered electronic scrap	Ag, Au, Pt	Solubilization of the precious metals by different (CN) <sup>-</sup> -forming microorganisms from electronic scrap	[50]	Au was mobilized as dicyanoaurate [Au(CN) <sub>2</sub> ] <sup>-</sup> , Ag as [Ag(CN) <sub>2</sub> ] <sup>-</sup> and Pt as [Pt(CN) <sub>4</sub> ] <sup>-</sup>
	Electrical appliance	Al, Cd, Co, Cr, Cu, Ni, Pb, Sn, W, Zn	Separation of nickel by bacteria and fungi	[158]	<i>Thiobacillus sp.</i> and fungi were grown in presence of computer scrap, scrap concentration >10 g/l inhibited the growth, an adaptation up to 100 g/l was possible, leaching efficiency of Cu and Sn were 65 %, Al, Pb, Ni, Zn >95 % at scrap concentration 5–10 g/l

Table 19 (continued)

Residue/ waste	Origin	Content/valuable substances	Treatment	References	Remarks
Printed circuit board		Cu, Zn, Cr, Ni, Pb, Mn	Leaching with a mixed culture of acidophilic Fe and S oxidizing and acidophilic heterotrophic bacteria	[134]	4 % of crushed circuit boards are treated in shake flasks with the mixed culture, all metals were removed from the boards but sometimes precipitated in the liquor
		Cu	Recovery of copper from printed circuit boards by leaching with <i>At. ferrooxidans</i>	[159]	The leached amount of Cu increased with the addition of Fe <sup>2+</sup> , max. Fe <sup>2+</sup> was 5.2 g/l. The recovery of Cu was 37 % without citric acid and >80 % in the presence of citric acid
Secondary sources		Pt group elements	Separation of PGM from leaching liquor by bioreduction with pretreated <i>E. coli</i> cells	[160]	Pd(II), Pt(II), Pt(IV), Rh(II) were enzymatically reduced and precipitated as metals under acidic conditions by a hydrogenase from <i>E. coli</i>
paint pigments of colour TV		Ca, Zn, Al, Y, Eu, Gd	Leaching with Fe and S oxidizing acidophilic microorganisms	[139]	Investigations of different composed colour films and pure fluorescent substance Y <sub>2</sub> O <sub>3</sub> S
Printed circuit boards		Cu, Pb, Sn, Zn, Cr, Ni, Mn	Leaching of crushed circuit boards with acidophilic iron and sulphur oxidizing and acidophilic heterotrophic strains	[134]	Average leaching efficiencies: 81–99 % Cu, 40–48 % Zn, 5–11 % Ni, 0.15 % Pb, 6–18 % Mn

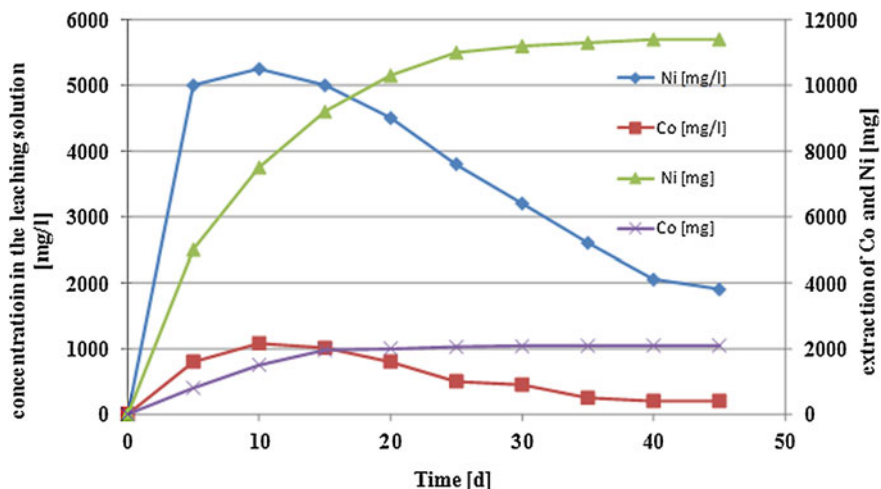


Fig. 22 Ni and Mo bioleaching from a hydrogenating catalyst [55]

The aforementioned bioleaching of Ni and Mo from spent catalysts was carried out by moderate acidophilic autotrophic microorganisms. Various mixed cultures isolated from the storage place of the catalysts as well as a moderate acidophilic *Acidithiobacillus* population isolated from copper shale leaching processes were used. The pH optimum of these strains was in the range of 4–5. This range was chosen, because the solubilization of iron, calcium, and aluminum is prevented at moderate acidic conditions.

The leaching was carried out in shake flasks, in columns (each filled with 1 kg material) and in a stirred tank reactor [55, 137]. The investigated material consisted of dust from the catalysts and the catalysts pill. Figure 22 displays the change of the nickel and molybdenum concentration in the leaching solution and the total amount of metals separated from the catalyst in the column leaching experiment. The highest concentration of nickel accounted for more than 5 g/l and the concentration of molybdenum for 1.2 g/l. The leaching efficiency was 50–60 % for nickel and 3.3–12.5 % for molybdenum. The leaching was carried out under saturated and unsaturated conditions in the column. A batch system represented the unsaturated conditions where 50 % of the leaching solution was exchanged by a fresh solution every 6, 12, 19, 30, and 47 h, to prevent an inhibition of the microbial process caused by the high nickel concentration. However, separate investigations of the influence of nickel on the microbial growth revealed much higher concentrations of up to 16 g/l without an inhibiting effect on the adapted microorganisms [138].

Other residues and dusts are the REE and trace elements containing dusts from colour TVs or fluorescent tubes with a concentration of 8–15 % of yttrium, 1–2 % of europium and some gadolinium, furthermore zinc, aluminum, cadmium, and iron. The leaching was investigated with oxidizing and acidic acid generating

microbial processes. The aim was to destroy the material and separate Eu, Gd, and Y. The results demonstrated the possibility to leach the sulphide-containing material and to concentrate yttrium in the pregnant leaching solution with up to 500 mg/l [139].

New industrial residues are wastes and nonconforming products of the photovoltaic industry with trace elements, for which suitable recycling technologies have not yet been investigated properly.

Further sources for recoverable valuable substances are old municipal waste disposals. The content of the valuable substances of ash disposals is adequate to the composition of the fuel but with higher concentrations. If the waste material contains a high fraction of organic compounds, the concentration of metals increases during the transformation of carbon into methane. A separation of the metals by different leaching processes is possible in both cases.

Examples for the treatment of other different catalysts and residues from the electric and electronic industry are summarized in Table 19. Because these materials are not sulphides or do not contain  $\text{Fe}^{2+}$ , a leaching mechanism based on the formation of inorganic and organic acids or complexing agents has to be developed. Nevertheless, all these tables reveal the huge diversification of valuable substances containing residues and the large number of treatment processes.

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<http://www.springer.com/978-3-642-54709-6>

Geobiotechnology I

Metal-related Issues

Schippers, A.; Glombitza, F.; Sand, W. (Eds.)

2014, VII, 241 p. 60 illus., 22 illus. in color., Hardcover

ISBN: 978-3-642-54709-6