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M. Siebenhofer[a]; H. Schweiger[a]; K. Lorber[b]
[a] VTU Engineering GmbH, Graz [b] Montanuniversitaet Leoben Inst. fuer Entsorgungs- und Deponietechnik, Leoben

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UPGRADING OF ZINC FROM GALVANIC SLUDGE AND STEEL FURNACE DUST

M. Siebenhofer, H. Schweiger
VTU Engineering GmbH
Grottenhofstraße 3 A-8010 Graz

K. Lorber
Montanuniversitaet Leoben
Inst. fuer Entsorgungs- und Deponietechnik
Peter Tunner Straße 15 A-8700 Leoben

ABSTRACT

Mining of zinc demands the upgrading of different residues of the refining process. A method, which had been used over a period of several years, was based on the so-called Dörschel process. From the chemical point of view, the Dörschel process is a high-temperature redox process, combined with a flash distillation (sublimation) step.

This process is based on the reduction of zinc compounds with coke at elevated temperature. The metal is then evaporated, reoxidized, precipitated by filtration, and refined hydro-/electrochemically. Zinc, lead, cadmium, nickel, cobalt, germanium, and copper can be refined from solid feed material by this process.

Modern waste management also needs such methods for the treatment of hazardous waste from different industrial processes, and the applicability of the Dörschel process in the upgrading of galvanic sludge, dust from steel furnaces, and scrap of portable batteries has been investigated. The feed material used for investigation has a mean zinc content of 15 to 25 wt% and a mean lead content up to 10 wt%. The presence of sulfate determines the anionic nature of feed material from galvanic sludge.

The capacity of the kiln used in the investigation is about 10,000 metric tons per year. The efficiency of zinc recovery is about 95% to 98%. The matrix substances of the feed were dissolved in neutral to caustic slag. Sulfur dioxide was recovered by absorption, purification, and condensation.

INTRODUCTION

Metal-containing residues are often environmental hazards. The objective of this study has been the development of a technology which is able to process this hazardous waste by splitting it into a useful product and an inert material suitable for disposal in landfills. An evaluation of several technologies considering chemical, electrochemical, and metallurgical processes (1) led to the conclusion that application of these processes would permit the recycling of significant quantities of metals. The residues left for disposal after treatment would still need a long-term control of the landfill. Further investigations also considered technologies already used in several mining processes.

Mining processes need different steps for the upgrading of residues. The Dörschel process has successfully been applied in the mining of zinc. The process was originally patented in 1937 (2) and designed for the recovery of lead from lead sulfate by reducing the feed material with coke in a molten slag of lime and quartz. Various improvements of the process have extended its application in the downstream processing of residues from hydrometallurgical processing of calcined zinc ores (3). The application of the technology in waste management is described in a recent patent (4). Application of this technology in the management of metal-containing waste should therefore meet the objectives of optimized recycling of the metals and the formation of a stable residue for disposal.

TECHNOLOGY AND PROCESS

The Dörschel processes is carried out in a so-called short-drum kiln. It is comparable with the Waeltz process (3). The main difference is in the mode of operation. Both processes are based on the reduction, evaporation, and reoxidation of the metal to be separated from the feed matrix. But the Waeltz process is continuous, and the Dörschel process is operated batchwise. The Dörschel process offers the possibility of treating feed material of varying composition. The scheme of the Dörschel kiln is shown in Figure 1.

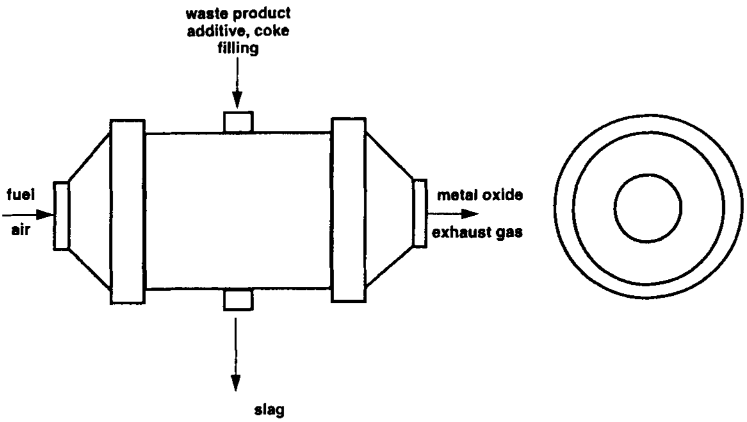

FIGURE 1. Scheme of the short-drum kiln applied in the Dörschel process.

The short-drum kiln is a cylindric kiln, equipped with an opening along the cylinder for the filling of the feed product and the additives. The kiln can be fired from one side, and the off-gas together with the metal oxide is removed at the opposite side. A second opening along the cylinder is used for the tapping of the slag.

The kiln is charged with the waste material and with additives. The mixture of additives and the amount of additives used determine the reducing atmosphere of the solid reaction mass and the quality of the slag. Carbon monoxide and metal vapor are formed just above the solids during operation. In the upper part of the drum, an oxidizing atmosphere is generated by the combustion air. During an upgrading campaign, the metal is reduced in the solid bulk and evaporated or melted. During the reduction step and the oxidation step, the matrix of the feed material should not melt, and evaporation of the metallic substance is preferred. For certain applications the recovery of the metal from the feed material by forming a metal bath covered with molten slag is possible. These principal modes of applying the Dörschel process depend on the chemical nature and composition of the feed material. Feed material with a high zinc content has to be treated in the reoxidizing mode, and the same route has to be applied for the recovery of cadmium. When lead is the major component in the feed material, the treatment remains in the reducing mode and forms a lead bath, covered with slag. Under reducing conditions only a small amount of lead will be evaporated, corresponding to the vapor pressure of lead.

Ordinarily the waste feed is split into metal oxides and the inert slag phase. When treating waste, it is very important to obtain both a reduction of volume and lower toxicity of the residual material. The slag must meet the specification for a non hazardous landfill.

Figure 2 shows the fundamental steps of the process. The waste material is heated under reducing conditions in the solid bulk. The metal salts and metal oxides are reduced to the metal and are evaporated immediately. In the vapor phase a surplus of oxygen guarantees the formation of the metal oxide. The metal oxides are separated from the off-gas by filtration.

The whole process is carried out batchwise and can produce slag with specified properties (5). It is possible to prepare the mix so that the slag is inert and ready for disposal in landfill areas. Depending on the composition of the feed, lead or mixtures of metals with lead do not form oxides but do form melts, which are separated from the slag by gravity settling.

The exhaust gas from the kiln contains the metal oxide and gaseous substances such as sulfur dioxide or hydrochloric acid. Therefore treatment of the off-gas after precipitation of the oxidic dust is necessary. In a post-combustion chamber, surplus carbon monoxide is destroyed. The heat in the off-gas is used for steam production. The metal oxidic dust is removed behind the heat recovery system with a bag filter. The off-gas then passes the wet gas purification plant, where acidic substances such as sulfur dioxide and the various halides are precipitated. The scheme of the plant is shown by Figure 3.

The processing of residues from leaching of calcined zinc ore has been a favored application of the Dörschel process. Feed material with a wide variety of cationic species and with sulfate as the main anionic substance can be split during such treatment.

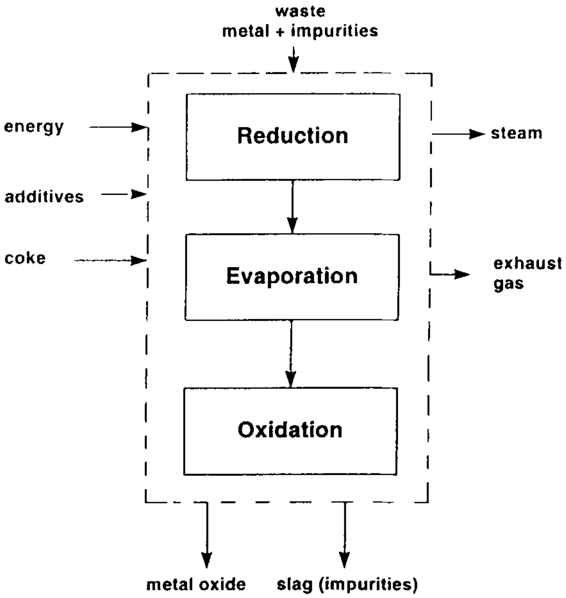

FIGURE 2. Fundamental steps of the Dörschel process

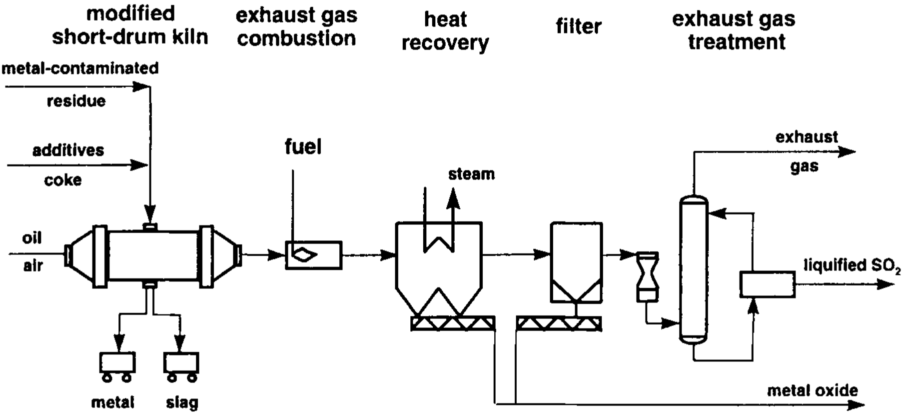

FIGURE 3. Scheme of the metal recycling plant.

Figure 4 represents the summary of the process mass balance for the treatment of sludge from ore leaching with ZnO. The major substance in the sludge is $ZnSO_4$. As mentioned, treatment of this material involves reduction in the solid bulk phase, evaporation of the reduced zinc, and reoxidation of the metal in the gas phase. Reduction and evaporation plus reoxidation all occur during the thermal treatment.

After starting a process batch, the concentration of sulfur dioxide in the off-gas increases and finally forms a peak before decreasing rapidly to a base level. This step is followed by the evaporation step, during which the temperature increases rapidly as the reoxidation process is exothermic. The maximum heat produced during reoxidation therefore limits the amount of the material to be treated in a single batch. As shown in Figure 4 the exhaust gas periodically carries a large amount of sulfur dioxide that is removed in the desulfurisation plant. Because of the large amount of sulfur dioxide involved, physical absorption with polyglycole and condensation have been preferred over precipitation processes.

THE RECYCLING PROCESS

By stripping the valuable metals from the feed by reducing with coke, evaporating, and reoxidizing the metals, it is then possible to transform metal-contaminated waste into metal oxide and inert slag material. From an economic point of view the process also needs to transform the metal oxides into valuable products. Different metallurgical processes may be applied. Because of the heterogenous nature of the oxidic dusts, hydrometallurgical processing and electrolytical precipitation offer a flexible method for purifying the metals. Figure 5 shows the scheme of process steps needed for the complete process. Combining the thermometallurgical waste treatment with downstream processing of the products finally leads to metallurgical processes being successfully transferred and applied in waste management.

It is possible to extend the process after installing pretreatment steps to also treat wastes such as portable batteries or fluorescent tubes. When processing this

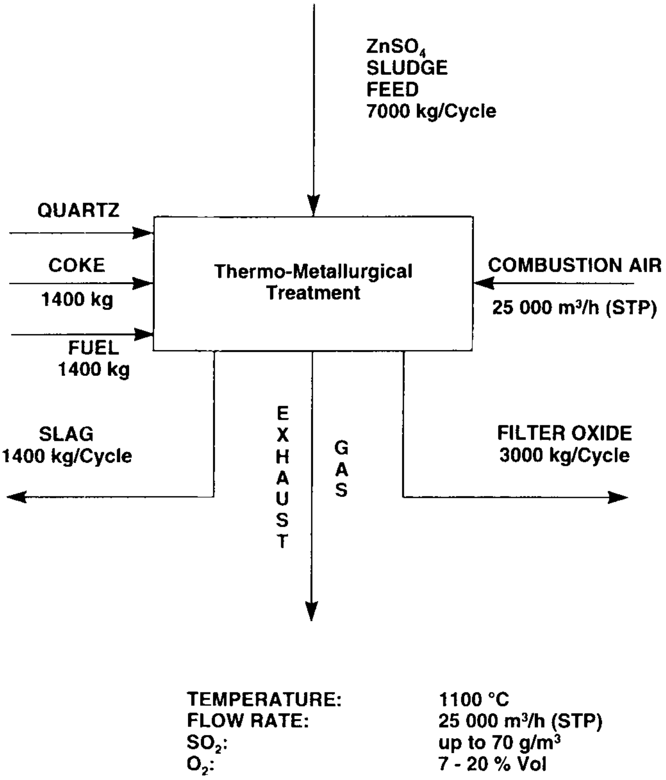

FIGURE 4. Mass balance for the treatment of residue from leaching of calcined zinc ore.

kind of waste, it is necessary to remove mercury before the thermometallurgical treatment. Thus a wide variety of hazardous waste materials can be treated by this process.

PROCESS AND MASS BALANCE

When processing galvanic sludge, steel furnace dust, and similiar feed material thermometallurgically, the principle of operation does not differ

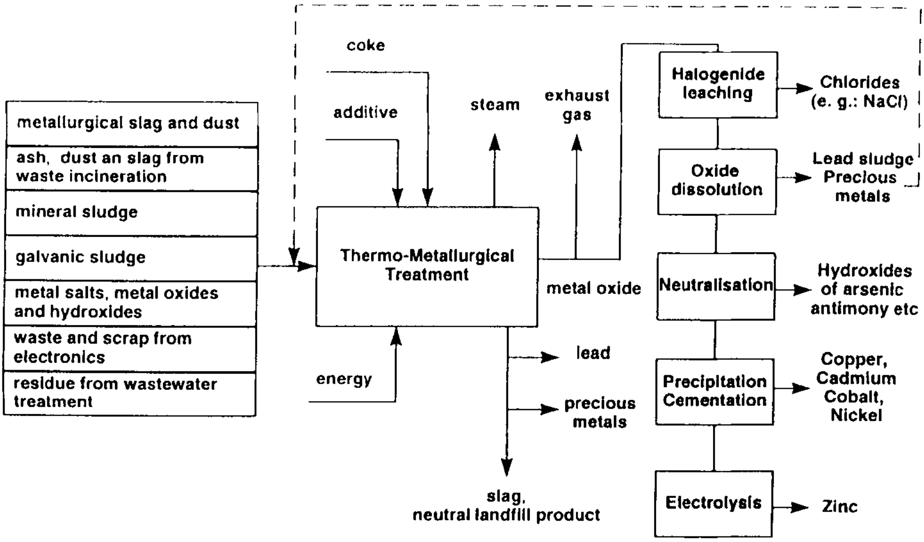

FIGURE 5. Scheme of the complete recycling process.

significantly from the standard mode of operation but one must consider the composition of the individual feed materials.

The addition of coke, the addition of slag-forming additives, and the temperature of reduction depend on the mean composition of the feed material. Table 1 shows the mean composition of residues formed during the leaching process of calcined zinc ore. The main reduction processes are as follows:

$$ZnO + C \rightarrow Zn + CO \qquad (1)$$

$$ZnSO_4 + 2C \rightarrow Zn + SO_2 + 2CO \qquad (2)$$

$$PbSO_4 + 2C \rightarrow Pb + SO_2 + 2CO \qquad (3)$$

$$CdSO_4 + 2C \rightarrow Cd + SO_2 + 2CO \qquad (4)$$

Since the reduction takes place in the solid phase, the rate of reaction is accelerated by the presence of carbon monoxide (6), as represented by equation 5.

TABLE 1. MEAN COMPOSITION OF DIFFERENT RESIDUES LEFT FROM LEACHING CALCINED ZINC ORE

Mean composition (wt%) of residues from leaching of calcined zinc ore			
Substance	**Sludge from neutral leaching**	**Sludge from acidic leaching**	**Sludge from waste water treatment**
Zn	4-23	5	8-12
Pb	6-10	50-55	0.2-0.8
Cd	0.2-0.5	0.3	0.03-0.1
Ge	0.12	< 0.005	< 0.001
SiO_2	2-3	1.5	< 0.03
Fe	9-12	1	0.3-0.5
Ca	5-8	1-2	20-25
Mg	appr. 1	< 0.5	
S	13-14	12	5
Cu	< 0.1	0.1	
Tl	< 0.03	< 0.07	
As	< 0.5	< 0.4	
Cl	0.01-0.20	< 0.05	< 0.1
F	< 0.05	< 0.01	7-14
Ni	< 0.005	< 0.004	< 0.005
Co	< 0.001	< 0.001	< 0.001
H_2O	15-30	appr. 20	60-65

$$ZnO + CO \rightarrow Zn + CO_2 \tag{5}$$

The reduction of sulfidic feed is supported by the formation of other metal sulfide with CaO or FeO:

$$MeS + CaO + C \rightarrow Me + CaS + CO \tag{6}$$

Depending on the composition of the feed, evaporation and reduction take place in parallel and with increasing temperature. At the same time, oxidation of the evaporated metals accelerates the process and increases the temperature to a maximum during each cycle. The end of the oxidation phase is indicated by a rapidly decreasing temperature of the off-gas.

Oxidation is caused by the atmosphere of the gaseous phase just above the solid bulk and follows main reactions 7-9.

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO \quad (7)$$

$$Pb + \frac{1}{2}O_2 \rightarrow PbO \quad (8)$$

$$Cd + \frac{1}{2}O_2 \rightarrow CdO \quad (9)$$

When treating sludge from neutral leaching, the process has to consider reduction, evaporation, and reoxidation. With regard to the low feed concentration of lead in this type of sludge, lead is also removed from the feed by evaporation, reoxidation, and collected in the bag filter. Unlike the treatment of feed waste with high lead concentration, the separation of a liquid lead phase from the solid bulk must be avoided.

The distribution of the elements and substances is shown in Table 2. As represented by Table 2, the stripping and precipitation of chloride is very much influenced by the interaction of hydrochloric acid with the caustic oxide. With regard to the operating temperature in the bag filter of about 400 K, hydrochloric acid is preferably precipitated there. It has to be mentioned that the composition of the slag is based on the molten residue, which is left in the kiln after 7 cycles.

As shown in Table 3, the composition of the off-gas changes during different stages of the process. After starting the process, the temperature has to be increased by direct firing. Composition and amount of the off-gas are determined by the combustion of fuel, by the water content of the feed material, and by the sulfate content.

The end of sulfur dioxide emission caused by chemical reaction indicates the shift from the reduction phase to the oxidation phase. In the oxidation phase the amount of off-gas and the temperature of the off-gas are determined by the energy of oxidation and by the capacity of the heat recovery system. Ordinarily the amount of off-gas decreases during oxidation and is a minimum at the end of a cycle.The kiln is then recharged, and the whole process is repeated.

With the experimental kiln, the procedure was repeated seven times during one campaign. After finishing the last cycle, the quality of the slag has to be corrected by adding further slag conditioners such as lime and quartz to the solid residual remaining in the kiln. The molten slag is then tapped into a water bath, and

TABLE 2. DISTRIBUTION OF ELEMENTS AND SUBSTANCES DURING TREATMENT OF SLUDGE FROM NEUTRAL LEACHING. FEED: 6500 KG OF SLUDGE PER CYCLE

Substance	Feed	Filter oxide	Additives	Slag	Off-gas
Zn	1269	1236		231	
Pb	688	672		112	
Cd	40	40		-	
Ge	6.5	6.5		-	
SiO_2	298	5.4	200	3448	
Fe	379	27		2464	
Ca	416	7.5		2860	
Mg	49	1.3		334	
S	1034	80.6		400	896
Ni	0.3	0.06		1.7	
Co	0.3	0.02		2	
Cu	0.6	0.27		2.3	
Tl	2.6	1.34		8.8	
As	36	35.5		3.5	
Chloride	9	9		-	
Fluoride	4.3	1.1		22.4	
comment:	per cycle	per cycle	per cycle	**after 7 cycles**	per cycle

the campaign is completed. The quality of the slag must correspond with strict landfill regulations. Table 4 shows representative results of solubility tests based on the regulations of DIN 38414, part 4.

The solubility data have been compared with the composition of the slag. The amount of valuable products is the main difference between feed material from neutral leaching of calcined zinc ore and waste products. The matrix is similiar. Table 5 shows a comparison of several feed materials used for this investigation.

HYDROMETALLURGICAL PROCESSING OF THE FILTER OXIDE

These oxidic dusts may be processed both pyrometallurgically and hydrometallurgically (7). Because of the heterogenous composition of the filter

TABLE 3. MEAN COMPOSITION OF THE OFF-GAS DURING REDUCTION PHASE AND DURING OXIDATION PHASE. FEED: 6500 KG SLUDGE PER CYCLE

Reduction phase

Off-gas (m^3/h. STP)	24,624
Temperature (K)	1,300
N_2 (m^3/h. STP)	19,750
O_2 (m^3/h. STP)	1,815
CO_2 (m^3/h. STP)	3,059
H_2O (kg/h)	579
SO_2 (kg/h)	1,805
HCl (kg/h)	(9.2)
Dust (kg/m^3)	-

Oxidation phase

Off-gas (m^3/h. STP)	19,143
Temperature (K)	≥ 1,370 to1,020
N_2 (m^3/h. STP)	15,800
O_2 (m^3/h. STP)	2,269
CO_2 (m^3/h. STP)	1,074
H_2O (kg/h)	771
SO_2 (kg/h)	13.7
Dust (kg/m^3)	0.14

TABLE 4. SOLUBILITY TESTS WITH SLAG ACCORDING TO DIN 38414

Mean composition of the slag and solubility in water		
Substance	**Composition (wt%)**	**Solubility in water (mg/l)**
Zn	1.25	< 0.5
Pb	0.095	< 0.05
Cd	0.0011	< 0.05
Cu		< 0.1
Ni		0.30
Cr		< 0.1

TABLE 5. MEAN COMPOSITION OF REPRESENTATIVE FEED PRODUCTS

Chemical composition (wt%) of different feed material			
Substance	**Galvanic Sludge**	**Steel furnace dust**	**Cupola furnace dust**
Zn	13.30	22.60	8.00
Pb	2.80	4.50	0.45
Cd	< 0.01	0.036	0.01
Ge	< 0.01	--	--
SiO_2	--	1.11	28.10
Fe	2.30	34.60	20.70
CaO	17.00	8.40	3.30
Mg	0.55	--	--
S	12.40	< 0.10	--
Cu	0.01	0.02	0.05
Tl	< 0.01	--	--
As	0.02	< 0.01	0.03
Cl	0.20	1.60	--
F	0.03	0.02	--
Ni	3.20	< 0.01	0.05
Co	0.01	0.10	< 0.02
H_2O	40	--	

oxide from different feed material, the hydrometallurgical processing of the filter oxide has some advantages.

As shown by the flow scheme of Figure 5, the hydrometallurgical process starts with the leaching of metal halogenides. The wastewater of this leaching process is purified by sulfide precipitation. The oxide is then dispersed in water and added to the spent electrolyte under pH control. The pH value is kept beyond 3. Under these conditions, lead sulfate will be precipitated and removed from the leach liquor by filtration. In case of germanium contamination, the electrolyte is then removed by tannate precipitation. Arsenic will also be removed by this step. Iron sulfate and manganese ore are added to the electrolyte, and the pH value is elevated to pH = 5 by adding more oxide to the solution. Lead, chromium, antimony and arsenic as well as germanium are stripped from the electrolyte during precipitation of iron hydroxide and are removed by a filtration step. The electrolyte is then ready for finishing. Finishing starts with cementation of copper, cadmium, and thallium by dispersing zinc dust in the electrolyte. Then the electrolyte has to be prepared for cementation of nickel and cobalt by adjusting the redox potential. Nickel and cobalt are removed from the electrolyte by adding zinc dust to the solution followed by filtration again.

The aqueous solution is then ready for electrolytical precipitation of zinc. The hydrometallurgical process needs a high standard of quality control and precise reproduction of the process instructions. The efficiency of the electrolytic precipitation of zinc definitely depends on the quality of the electrolyte. Increased attention has to be paid to the quality control of the hydrometallurgical process.

SUMMARY

The applicability of metallurgical upgrading in modern waste treatment has been investigated. The objective has been the evaluation of technologies, applicable in treating metal containing hazardous waste. Galvanic sludge and dust from steel works have been considered. The investigated process, which is based on an improved version of the Dörschel process, can be operated up to a temperature of 1700 K. It is led batchwise. During operation the feed product is split chemically by reduction with coke. The valuable substances are either removed by reduction, evaporation, and reoxidation or by reduction and melting. The residual matrix of the feed is stabilized by melting. The slag is tapped. The quality of the slag must meet strict leaching conditions.

The oxidic dust is treated hydro-/electrochemically in a further technological step. Depending on the composition of the feed, the off-gas has to be purified by filtration and absorption.

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