

**Applicability of the EMPF® process for treatment of
zinc- and/or lead containing wastes**

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Summary

In commission of Elkem Technology the Netherlands Organisation for Applied Scientific Research (TNO) made an inventory of the zinc and/or lead containing wastes that are produced in EC countries.

The main objective of this study was to provide Elkem Technology with information in order to determine the potential market for the Elkem Multi-Purpose Furnace® (EMPF®).

For the selection of types of industries where zinc and/or lead containing wastes are produced the chains of these wastes have been described. The chains describe the use of the metal from winning, production, use in products, recycling until final disposal as waste.

Elkem and TNO agreed upon a selection of 13 types of industries. The selected industries can be clustered as follows:

- The primary and secondary production of metals (zinc, lead and iron).
- The shaping of the metals (accumulator- and basic metal-industry).
- The production/use of metal compounds (zinc oxide- and synthetic fibre-industry).
- Surface treatment (thermal- and electro-metalplating).
- Waste incineration (hazardous- and municipal-waste and tires).

The wastes that are produced in these types of industries are described by the way the waste is generated, the chemical composition, in particular the Zn and Pb content, the physical composition, the amounts produced (per country or per company) and both current and future routes of processing of the waste (treatment/disposal routes).

On basis of criteria such as the amounts produced, processability in the EMPF® process, economic value of recovered metals, current disposal costs and competition with respect to treatment by other technologies, a ranking has been carried out and the types of waste have been given first, second or low priority.

The most interesting materials for treatment in the EMPF® process are the zinc- and lead-containing materials from primary zinc and lead production (i.e. Blast Furnace and ISP smelters).

Also the wastes from primary (Blast Furnace dusts from steel production) and secondary ferrous industries (EAF dust) have first priority.

Secondary priority has been given to the lead-containing slags from the secondary lead production (Reverberatory Rotary Furnace) and the fine dust fraction from C-steel production. Treatment of the wastes from primary (electrolytical) zinc production (jarosite and goethite) also has secondary priority. The fly ashes from municipal waste incineration might be interesting although they are difficult to treat in the EMPF® process due to the high salt-content, in particular chlorides and sulphates. Also secondary priority have the bottom ashes from municipal waste incineration and slags and ashes from hazardous waste incineration if they can be co-processed.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

From an economic point of view, several waste materials, such as slags from zinc oxide production or flue dusts from lead refining, are interesting, but they are produced in a limited amount and construction of a dedicated plant will not be feasible. For this reason they have been given low priority. However these waste materials might be interesting for co-processing if an EMPF® furnace has been built for one or more other waste streams.

An important issue regarding the handling, processing and disposal of wastes is legislation. In the EC this is currently determined by national governments of the Member States; this will also be the case in the near future.

It is only recently that the European legislation, made at EC level, is becoming more important. So far, only the framework of legislation has been made which will not come into force before 1 April 1993. All the other Directives will come into force after this date.

Table of contents

	Summary	2
1	Introduction	7
1.1	Elkem Multi-Purpose Furnace® Process.....	7
1.2	Objectives of the project.....	7
1.3	Collection of general and specific information on waste materials.....	8
2	The zinc and lead chain	9
2.1	General concept	9
2.2	The zinc chain.....	9
2.3	The lead chain.....	10
2.4	Survey of industries producing zinc- and lead-containing wastes.....	12
2.5	References.....	12
3	Industrial sectors producing zinc- and lead-containing wastes	13
3.1	Iron and steel industry	13
3.1.1	General	13
3.1.2	Processes and wastes.....	14
3.1.3	Producers and waste production.....	17
3.1.4	New technologies and developments	17
3.1.5	References	20
3.2	Primary zinc production	26
3.2.1	General	26
3.2.2	Processes and wastes.....	26
3.2.3	Producers and waste production.....	29
3.2.4	New technologies and developments	30
3.2.5	References	31
3.3	Secondary zinc production	38
3.3.1	General	38
3.3.2	Processes and wastes.....	38
3.3.3	Producers and waste production.....	39
3.3.4	New technologies and developments	40
3.3.5	References	40
3.4	Zinc oxide/zinc powder production	42
3.4.1	General	42
3.4.2	Processes and wastes.....	42
3.4.3	Producers and waste production.....	44
3.4.4	References	46
3.5	Synthetic fibre industry	46
3.5.1	General	46
3.5.2	Processes and wastes.....	46
3.5.3	Production and waste production	47
3.5.4	New technologies and developments	47
3.5.5	References	49

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

3.6	Thermal metalplating industry.....	49
3.6.1	General	49
3.6.2	Processes and wastes	49
3.6.3	Producers and waste production.....	51
3.6.4	New technologies and developments	52
3.6.5	References	52
3.7	Electro metalplating industry.....	54
3.7.1	General	54
3.7.2	Processes and wastes	54
3.7.3	Producers and waste production.....	55
3.7.4	New technologies and developments	56
3.7.5	References	57
3.8	Basic metal industry	59
3.8.1	General	59
3.8.2	Processes and wastes	60
3.8.3	Producers and waste production.....	61
3.8.4	New technologies and developments	62
3.8.5	References	63
3.9	Primary and secondary lead production	65
3.9.1	General	65
3.9.2	Processes and wastes	65
3.9.3	Producers and waste production.....	70
3.9.4	New technologies and developments	71
3.9.5	References	71
3.10	Accumulator industry	78
3.10.1	General	78
3.10.2	Processes and wastes	78
3.10.3	Producers and waste production.....	79
3.10.4	New technologies and developments	79
3.10.5	References	79
3.11	Municipal waste incineration.....	81
3.11.1	General	81
3.11.2	Processes and wastes	81
3.11.3	Producers and waste production.....	83
3.11.4	New technologies and developments	84
3.11.5	References	85
3.12	Hazardous waste incineration.....	87
3.12.1	General	87
3.12.2	Processes and wastes	87
3.12.3	Producers and waste production.....	89
3.12.4	New technologies and developments	89
3.12.5	References	90
3.13	Rubber and tyre incineration	92
3.13.1	General	92
3.13.2	Processes and wastes	92
3.13.3	Producers and waste production.....	93
3.13.4	New technologies and developments	93
3.13.5	References	93

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

4	Waste legislation.....	96
4.1	The Waste Directive	96
4.2	The Hazardous Waste Directive	97
4.3	International Movements of Waste.....	98
4.4	Landfilling of waste	98
4.5	Other waste measures	99
4.6	References.....	99
5	Discussion.....	101
5.1	Waste materials for the EMPF® process.....	101
5.2	Legislation	105
5.3	Comparison between EMPF® process and Waelz process	105
5.4	References.....	107
6	Conclusions	108
7	Authentication	109

1 Introduction

1.1 Elkem Multi-Purpose Furnace® Process

Elkem Technology is one of the world's leaders in the field of the design, engineering, fabrication, start-up, maintenance, and operation of electric smelting furnaces. The experience and know-how gained over the years is now effectively used to develop processes for waste destruction and metal recovery. One of the hazardous waste streams, for which Elkem has developed a process, is electric arc furnace dust (EAF-dust). In this process, hereinafter referred to as EMPF® process (abbreviation for Elkem Multi-Purpose Furnace® process), the EAF dust is worked up to marketable zinc and lead products and a slag-granulate that meets very stringent leaching requirements. The EMPF® process has been tested on a pilot-plant scale; the construction of a 40,000 tons/y installation is in progress.

In view of the problems related to metal containing wastes, it is of great interest to investigate whether the EMPF® process is applicable to zinc and/or lead containing wastes, other than EAF dust.

1.2 Objectives of the project

The objectives of the project are:

- To obtain an insight into all zinc- and/or lead-containing wastes, generated in the EC countries, that can be processed with the EMPF® process as such;
- To obtain a basis for a further development of the EMPF® process in order to make it suitable as a broad-spectrum technology for processing metal-containing wastes, in particular zinc- and/or lead-containing wastes:
To achieve this purpose, each type of waste is described as completely as possible by stating the following data:
 1. Chemical composition, like
 - Zn and Pb content
 - Other metals
 - State of metals (metallic, oxide, salt)
 2. Physical composition, like
 - physical form (slag/ash/sludge, etc.),
 - other characteristics like moisture content, particle distribution, specific mass/weight
 3. Amounts produced (per country/company)
 4. Processing:
 - present routes of disposal
 - costs
 - developments (techniques)
 - future legislation
- To quantify the potential market for the EMPF® process in the EC-countries.

1.3 Collection of general and specific information on waste materials

Shortly after the start of the project it became clear that, in order to obtain as complete an insight as possible into both the types of zinc- and/or lead-containing wastes relevant for the project, and the types of industries involved, it is essential to have an understanding of the zinc and lead chain. On the basis of these chains, a number of industrial sectors were selected for further examination. The first approach which was followed was to gather information about individual producers of zinc- and lead-containing wastes through an inquiry and from literature.

For information about the producers, requests were sent to national and international institutions and governments. General information available in reports, studies, etc. was also requested. However, the response from these institutions was poor, even after an additional approach by telephone. This fact, as well as other recent disappointing experiences by TNO regarding inquiries, asked for a change in approach.

From the data found in literature it was clear that specific information about the quantity of wastes for each producer is hardly available. However, generic data about the wastes produced by producers is very often available. Data about the amount of products or the production capacity are also very often known.

An estimation of the amount of waste produced can be obtained on the basis of the ratio between the amount of production and the amount of waste. With this "waste production factor", the amount of waste per producer can be estimated. By collecting information from single producers and associations, combined with information from literature and statistics, the data for the wastes were obtained.

Chapter 2 gives an overview of the zinc and lead chains, while also a selection of types of industries is made.

In chapter 3, all selected industrial sectors are described. Chapter 4 gives an overview of regulations concerning waste legislation. The applicability of the EMPF® process is discussed in chapter 5.

2 The zinc and lead chain

2.1 General concept

The chain of a component, e.g. a metal, can best be described as the route that is followed from winning the component through production processes and applying it in products, to final disposal as a waste material. Obviously, the production of waste materials containing specific components will occur in industries involved in the chains of these components.

2.2 The zinc chain

Throughout the world, approximately 7 million tons of zinc were produced and consumed in 1989. In Western Europe, approximately 2 million tons were consumed [1]; 25-35% of this amount are obtained as recovered metal from recycled materials (scrap residues) [2].

Zinc and zinc compounds have a broad range of applications. The major application is in the galvanising of steel and iron objects. Zinc and zinc compounds are further used as components in alloys, pigments, batteries, pharmaceuticals, as hardener of synthetic fibres and as vulcanisation activator. Figure 1 gives a simplified scheme of the zinc chain and the industries involved. The principal uses of zinc in the Western world are given in Table 1.

Table 1 Principal uses of zinc in 1989 [1]

Application	Amount (%)
Galvanising	46.3
Brass	20.0
Die-casting alloys	14.3
Zinc semi-manufactures	6.8
Chemicals	9.6
Other applications	3.0

The zinc consumption is expected to grow in the 1990s with a rate of about 2% per year [3]. The galvanising industry will take 3/4 of this growth, as the use of zinc-covered steel will increase, specifically in the car and construction industry. A modest growth is expected for the die-casting of alloys, while also some growth is expected in the use of zinc sheets for architectural applications.

2.3 The lead chain

Throughout the world, approximately 6 million tons of lead were produced and consumed in 1989. In Western Europe, approximately 1.7 million tons were consumed; 50% of this amount are obtained as recovered metal from recycled materials (scrap residues) [1].

Lead and lead compounds are mostly used in lead acid accumulators. Other applications for lead are found in alloys, chemicals and products like sheets and cable sheathings. Figure 2 gives a simplified scheme of the lead chain and the industries involved. In Table 2, the principal uses of lead in the Western world are given.

Table 2 Principal uses of lead in 1989 [1]

Application	Amount (%)
Accumulators	61.6
Alloys	3.4
Lead semi-manufactures	10.2
Chemicals	15.8
Other applications	4.1

The lead consumption is expected to grow because of an increased use of accumulators in cars. The growth is expected to be in the same order as the general worldwide economic development [4].

In the future, accumulators will account for about 65% of the lead consumption. Applications in the form of construction material (sheets) are also likely to grow. The use of lead in the chemical industry will decrease, since lead compounds will be banned of as an antiknocking agent in gasoline.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

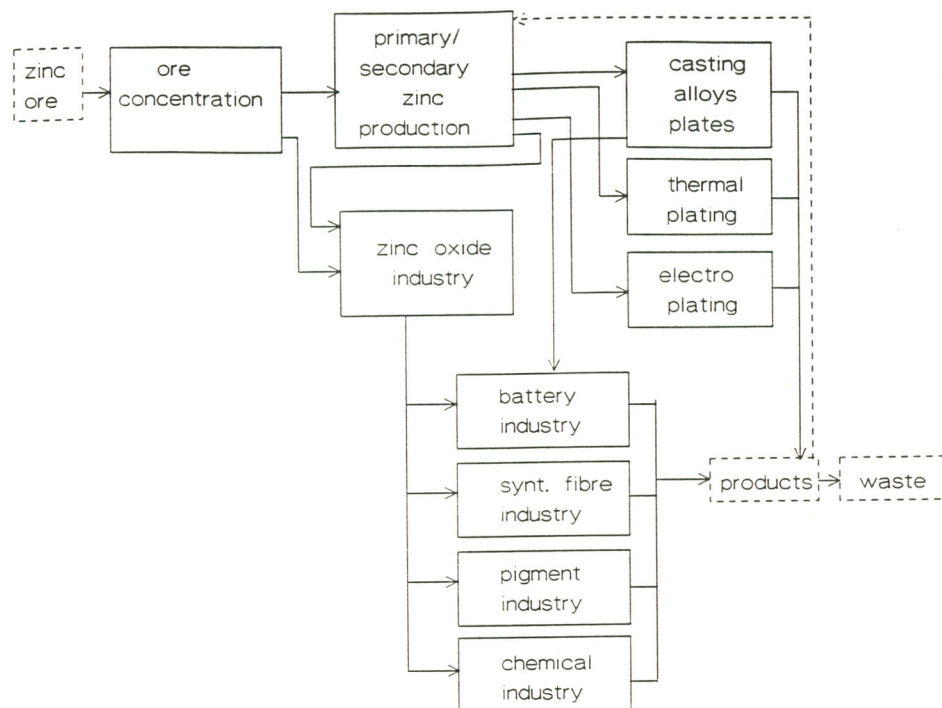


Figure 1 The zinc chain

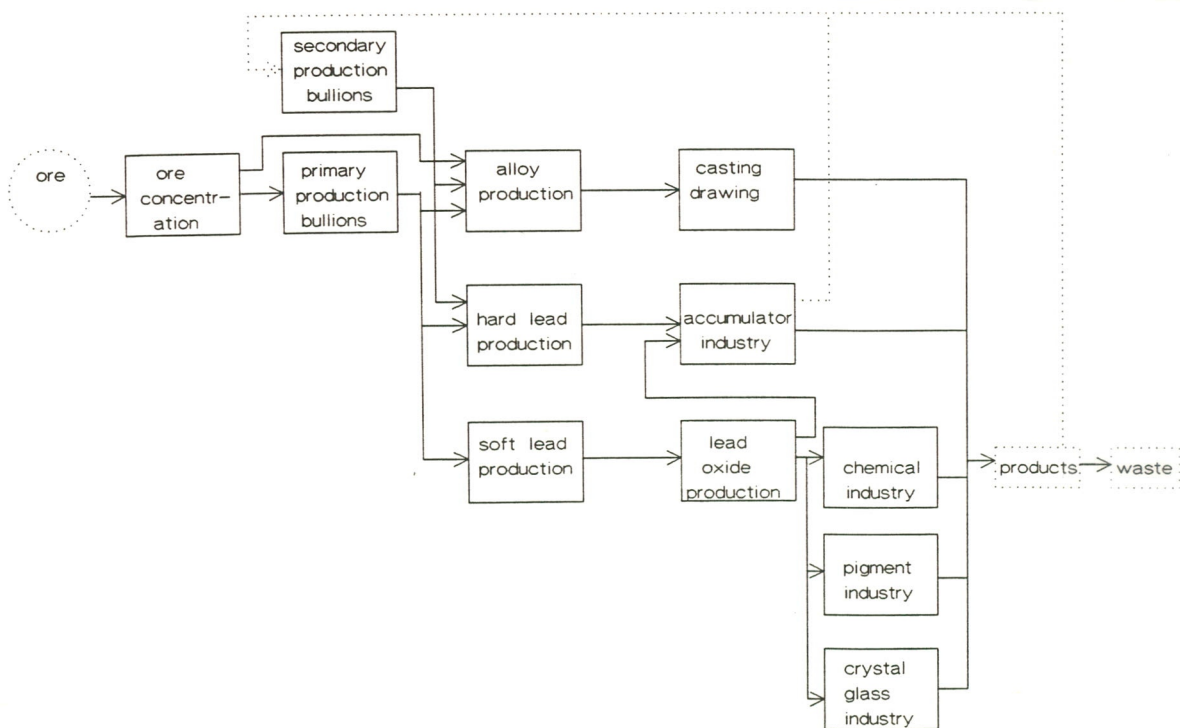


Figure 2 The lead chain

2.4 Survey of industries producing zinc- and lead-containing wastes

In the previous sections, surveys have been given of the zinc and lead chain and the industrial sectors involved in these chains. In addition to the industrial sectors directly involved in winning, producing and applying zinc and lead (or compounds thereof), the generation of wastes containing these metals also occurs with two types of industries involved in processing and treating post-consumer waste materials, i.e. the scrap-processing iron and steel industry, and the incineration of municipal and hazardous waste and tires.

Criteria for the selection of types of industries are the estimated amount produced and the composition of the waste, in particular the concentration of zinc and lead. In order to gather more information, Elkem and TNO agreed upon a selection of types of industries as described in Table 3.

Table 3 Types of industries with relevant zinc- and lead-containing waste streams

Wastes from	Zn	Pb
– iron and steel industry	X	X
– primary zinc production	X	X
– secondary zinc production	X	X
– zinc oxide/zinc powder industry	X	
– synthetic fibre industry	X	
– thermal metalplating industry	X	
– electro metalplating industry	X	
– basic metal industry	X	X
– primary and secondary lead industry	X	X
– accumulator industry		X
– municipal waste incineration	X	X
– hazardous waste incineration	X	X
– rubber and tyre incineration	X	

2.5 References

- [1] Statistical Yearbook 1989, Metaleurop.
- [2] OECD, Information from H. Yacowitz.
- [3] Ruess H.J., Cominco, Paper presented at the conference "Recycling lead and zinc", Rome, Italy, 11-13 June 1991.
- [4] Zelms J.L., Lead-Zinc '90, pp. 5-13, 1990.

3 Industrial sectors producing zinc- and lead-containing wastes

3.1 Iron and steel industry

3.1.1 General

Iron and steel production at integrated plants is accomplished by a number of interrelated processes. Next to these, many plants produce a variety of special steels.

An integrated plant consists of installations for the production of coke, sinter, pig iron, steel, semifinished and finished products. These are supported with installations for energy supply and the handling and transport of raw materials, intermediate products, and wastes.

Coke is used as a reduction agent. Sinter is an agglomerate of ore, coke breeze, limestone, and waste materials (mill scale and flue dust) to be used as feed material for the blast furnaces. Selection of ores for sinter production allows control of pig iron quality. Sinter is produced by moving a shallow bed of the raw materials on a travelling grate (sinter strand). After ignition of the coke, self-supporting combustion causes surface melting and agglomeration. Air is drawn downward through the bed. The cooled sinter is crushed and screened, fines are recycled. Sinter production acts as a “sink” for certain types of waste materials. Some steel plants produce agglomerates by pelletising; more often this has already been done at the mining plant.

Pig iron is produced in blast furnaces. In these shaft furnaces, iron oxides are reduced by carbon monoxide and carbon, both supplied by the coke fraction of the feed. The by-product gas is used as a low-grade fuel.

Iron and slag are periodically removed from the furnace (casting). The slag is transported to a slag pit; the molten iron is, sometimes after desulphurisation, transferred to the steel plant.

Steel is produced by removing most of the carbon from the pig iron, thereby improving physical and mechanical properties. For a wide variety of steels, both pig iron and scrap are used as raw materials. Raw steel is largely produced by the basic oxygen process (BOP, converter process) in which oxygen is injected in one way or several ways to oxidise carbon and other impurities. In the open hearth furnace (OHF-process, Siemens-Martin process, progressively passing into disuse), refining is accomplished by gas burners above and at the side of the furnace. Oxygen lances speed up melting and refining. Carbon steel and special steels are produced in electric arc furnaces (EAF). The feed is exclusively scrap material. Electricity, passed through carbon electrodes, provides melting heat.

Molten steel is poured into ingots subsequently to be shaped into slabs, blooms, and billets (slimline blooms). It can, however, also be directly cast into end products. Surface defects of these products are removed by oxygen jets (scarfing). Finally, rolling is the major step in forming shaped end products.

3.1.2 Processes and wastes

3.1.2.1 General

All these processes generate dusts (with reference to particle size, steel making also generates fumes). The particulate matter is controlled in various ways, by gravity separation, cyclones, dry or wet electrostatic precipitators, scrubbers, and baghouses. High carrier gas temperatures and very small particle sizes are problems to be solved. Coarse and fine fractions may or may not be separately treated.

As a consequence, reported particle size distributions of dusts from a certain type of process can vary considerably. The same is true of the composition of dusts, which depends on raw materials composition and process conditions. Heavy metal impurities of metals with low boiling points (Cd, Pb, Zn) are enriched in the fine particles by adsorption and sublimation.

3.1.2.2 Sinter production

Dust, collected from the different stages of the process is completely recycled, if necessary, after removing Pb and Zn by pyro- and hydrometallurgical processes [1]. Dust generation is reported to be 14 kg/tons of sinter [1].

3.1.2.3 Blast furnace

In the blast furnace, the process gas entrains abraded particulate matter from the feed material. The angularly shaped dust particles are removed by gravity separation to collect the coarse fraction and subsequent gas cleaning in one, two, or several ways. Coarse blast furnace dust is often recycled together with sinter dust. The fines, however, cannot be treated simply in this way. Low-boiling metal impurities, including Na and K, which are enriched in this material, would accumulate in the furnace. By evaporation in the lower part, sublimation in the upper zone, downward transport with the feed material and re-evaporation in the lower part, increasing amounts of these metals in the cooler upper zone would have an adverse effect on the process of ironmaking. This fraction, present in the form of a sludge (after wet separation), is therefore dewatered and dumped. Blast furnace dust as a waste material may also be present as a mixture of coarse and fine fractions if they are dumped together. Chemical composition data are a summary of literature data which are presented in Table 8.

Particle size characteristics, unless reported as such, are interpolated (or sometimes extrapolated) from reported size distribution data after plotting on a RRS graph [17]. The lower figure for the fine fraction is the more plausible one, referring to desagglomerated material.

The zinc content of this fraction is an order of magnitude higher than that of the coarse material. The lead content is between one and two orders of magnitude higher. The annual generation of these two metals is also presented in the table. The figures are, of course, not more than indications.

3.1.2.4 Steelmaking

3.1.2.4.1 Basic Oxygen Process

In the Basic Oxygen Furnace (or converter), molten pig iron together with scrap are refined with oxygen. Usually, the scrap fraction is 20-35%. In an exothermic reaction, carbon and other impurities are oxidised. A large quantity of CO is formed, which can be burnt at the exit of the furnace. Tiny droplets are entrained in the waste gas which, after solidifying, form the characteristic spherical particles of steelmaking fume. Charging and tapping are also sources of dust.

Particles are removed by separation of a coarse fraction, followed by further cleaning with wet or dry techniques. The method that is applied most is wet treatment [27]. The iron content and slag constituents are higher than those of blast furnace dust, as is shown in Table 8, but zinc and lead contents are comparable. The large average particle size of the fine material found in the literature [14] indicates a certain degree of agglomeration. Its specific surface, as compared to the coarse fraction, describes its physical shape probably better ($2600 \text{ m}^2.\text{kg}^{-1}$ and $200 \text{ m}^2.\text{kg}^{-1}$ respectively, BET sp.surf.).

The fine particles in steelmaking dust are different from the coarse ones with respect to iron species. The iron in the fines is present as 28, 30 and 42% as Fe, Fe^{2+} and Fe^{3+} respectively. For the coarse fraction, the percentages are 85, 10 and 5 [13, 14].

At Hoogovens IJmuiden (the Netherlands), the development of a processing route, aimed at maximum recycling of compounds contained by the dust, has been an ongoing effort since the late seventies. The first step of the process consists of a physico-mechanical concentration of zinc and lead by means of slurry-hydrocyclonage (Figure 3). The coarse particle fraction resulting from hydrocyclonage (the quantity of which amounts to 70% wt. of the blast furnace dust) contains low concentrations of zinc and lead and can be reused in the sintering plant.

The slurry-hydrocyclonage plant has been in operation at Hoogovens IJmuiden since 1984. It produces approximately 10,000 tons (dry weight) per year of fine particle fraction, and contains 90% of the quantity of zinc in the blast furnace dust. The fine fraction is stored at the Hoogovens area. Table 8 gives some major chemical and physical characteristics of the fine fraction [26]. The water content is about 35% after filtration [27]. Data of the disposal costs are not available; however, as the measurements are taken according to the "IBC-criteria", the disposal costs must be in order of magnitude of US\$ 10/ton. In the future, a penalty for disposal to be imposed by the government is a realistic possibility [27]. Two treatment options for this waste material are considered, e.g. high pressure leaching and a thermal process (The Inmetco process has been calculated). After treatment, the iron residue must be used as source material for steel production [27].

3.1.2.4.2 Electric Arc Process

The composition of the feed material for the Electric Arc Furnace (scrap) makes the composition of EAF fumes clearly different from converter fumes. Its high zinc content is, for a large part, due to automobile scrap; although the generation rate is lower than that of the oxygen process, waste zinc comes primarily from electric arc furnaces, as can be seen from Tables 6 and 8. This type of furnace is also used for the production of alloy steels. Dust generated from the production of these steels usually contains heavy metals, such as Ni and Cr, in amounts that make this waste material too valuable to dump. This is in contrast with the dumping of dust from EAF carbon steel dust [1].

3.1.2.5 Other processes

Casting, rolling, and reheating operations cause surfaces of semifinished products to oxidise. Removal of these oxides produces mill scale. This waste material may be generated in a quantity of 35 kg per ton of steel [3]. It mainly consists of iron oxides, and holds only trace amounts of zinc and lead (two orders of magnitude less than coarse blast furnace or coarse converter dust [3]). The majority, therefore, is recycled into sinter strands or blast furnaces after screening. Only the fines, usually contaminated with oil, are dumped. Table 7 gives the numbers of sites of the main dust-generating units, i.e. combinations of blast furnaces and oxygen steelmaking, and electric arc furnaces (that are often installed at locations other than where pig-iron is produced).

3.1.2.6 Waste characteristics

In Table 4, the characteristics of the dusts from the iron and steel industry are given. The waste production factor is the amount of waste (kg) per ton produced iron or steel.

Table 4 Characteristics of wastes from the iron and steel industry

Waste	Zn (%)	Pb (%)	Factor
BF dust, coarse	0.1-0.3	0.01-0.05	17 (10-20)
BF dust, fine	1-5	0.5-2	8 (5-10)
Steelmaking, oxygen, coarse	0.2-0.4	0.05-0.2	6 (4-8)
Steelmaking, oxygen, fine	2	0.5 (0.2-2)	12 (10-18)
Steelmaking EAF	17 (10-23)	3 (1-5)	10-15
Stainless steel, EAF	1-3	0.5-1.5	10-15

3.1.3 Producers and waste production

Production data of crude iron and steel, combined with the generation data of Table 4, yield estimates of amounts of waste dusts and amounts of zinc and lead in these. As composition data have a wider range than rate data, average rates were multiplied with composition ranges. Results are given in Table 5.

Differences between these figures and occasionally reported data were ignored. It is not known whether the latter are derived from enquiries or are estimates themselves. The figures in Table 5 at least have consistency in their uncertainty.

To the 4.6 Mtons of waste dusts from this table could be added about 1.5 Mtons of sinter dust and an estimated 5 Mtons of mill scale, or, about 8% of crude steel production. However, the majority of this volume is recycled. Only the fine fractions should be considered as real wastes. Their total amount is about 2.5 Mtons in the EC.

The fine fractions of waste dusts, often present as sludges, are usually dumped. In Germany (1987), all blast furnace sludge and 75% of converter sludge, converter dust, and EAF dust were dumped [1]. The British Steel Corporation (1974/75) dumped 25% of blast furnace dust, 78% of blast furnace sludge, all EAF dust, and half of the converter dust/sludge [3]. The remaining amounts are recycled. Allegedly, in Europe all converter sludge is currently dumped, but in Germany, centralised/thermal processing is being studied [18]. In the EC, then, 0.5-1.0 Mtons of blast furnace and converter dust, and 1.5-2 Mtons of blast furnace- and converter sludge, together with 0.4 Mtons of EAF dust/sludge, might be dumped annually. More than 90% of the Zn and Pb in these wastes are produced in six countries (Table 6).

In the Netherlands "Nedstaal" produces about 2500 tons EAF dust annually, with a zinc content of 25% and a lead content of about 3%.

3.1.4 New technologies and developments

Many investigations and many proposals have been made to recover iron from waste dusts, and to lower zinc and lead contents down to acceptable levels, but only few processes are operative [10].

One of these is in use at Thyssen's Bruckhausen plant [13, 14]. Converter dust is hot-briquetted, coarse and fine fractions being treated separately. Briquettes are fed into the converter. Fines containing too much zinc can be used in an EAF. Savings were reported to be high [13]. Some variants of this process exist [10, 18]. It has also been attempted without agglomeration [15]. Recycling by a sinter strand was tried as well [11]. Flotation, magnetic separation of iron oxides, and wet removal of zinc and lead with acid have been investigated for blast furnace sludge [2]. These processes, as well as leaching, do not come into consideration for technical reasons according to others, who developed an alternative leaching process using waste pickling acid in an atmosphere of oxygen under pressure [9, 18].

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

For EAF dust, only the Waelz process seems to be operative [4, 10]. In this process, pelletised dust is reduced with coke breeze in a rotating furnace. The total capacity of Waelz processes in Europe is about 180,000 tons/y [20]. The produced amount of EAF dust is about 440,000 tons/y. This means that approximately 45% of the EAF dust are treated by Waelz processes. EAF dust is collected with a dry method [22]. Before being treated in the kiln, the EAF dusts are pelletised and wetted. Products are slag with low zinc and lead contents, and 'Waelz-oxide' enriched with these metals. The Waelz-oxide is treated in an Imperial Smelting shaft Furnace (ISF process) to remove zinc and lead from it. Waelz plants are found in Germany, Spain, and Italy; ISF plants are in Germany, the UK, France, and Yugoslavia.

Two of the Waelz processes are operated by Berzelius Metallhütten Gesellschaft. Berzelius owns plants in Duisburg, Germany, and in Bilbao, Spain. The capacities of these Waelz plants for EAF dusts are given in Table 10. It can be concluded that only the UK and Italy produce considerable amounts of EAF-dust for which insufficient treatment capacity is available. The capacity of the Bilbao plant in Spain is 70,000-80,000 tons/y [19,25], giving rise to some 18,000 tons of zinc in the form of zinc oxides. About 40% of the EAF dusts are of national origin and the remainder is imported. Since no Imperial Smelting Furnace is available in Spain, all Waelz oxides are exported [25].

In the future, a new Waelz plant is planned with a capacity of about 50,000-100,000 tons/y [19]; it is to be built in Noyelles Godault, near Lille in France, Berzelius together with Metaleurop. The plant with a planned capacity of 70,000 tons/y [23] will treat residues from France and the Benelux countries. The other project is a possible participation in the Waelz plant in Ponte Nossa in Italy.

Costs for treating EAF dusts by Waelz processes are in order of magnitude of US\$ 70-100/ton of dust [21]. The break-even point for payment is 24% zinc [19]. For every percentage less than agreed upon in a contract, Berzelius charges a penalty of about US\$ 3/% [22]. EAF dusts are accepted by Berzelius only after pretreatment, e.g. briquetting [22].

Costs for hydrometallurgical treatment are US\$ 10-60/ton of dust, according to Dreisinger et al. [8].

The price in the Netherlands for secured landfilling of EAF dust is about US\$ 75/ton.

It is expected that in the near future the zinc content of scrap will increase due to a larger supply of automobile scrap. The processing of EAF dust, therefore, will be of increasing interest. The only industrially applied process for EAF dust is the Waelz process. A few alternatives have been developed based on electrical processes.

However, differences in costs for electrical energy and energy derived from fuel are considerable in most countries.

For the recycling of EAF dusts from stainless steel production (about 50 kt.y⁻¹ in the EC), two processes are operative [10]. Both the Inmetco and the Plasmadust processes use coke as a reducing agent; the product is fed into the EAF. Two small-capacity plants are currently operating a TETRONIC furnace for the recovery of metals contained in steel mill dusts, using plasma technology.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Legislation:

Disposal of EAF dust is allowed in the following EC countries [19]:

the Netherlands, Belgium, France, UK, Greece, Spain, and Portugal.

In Denmark, Germany, Italy, Scandinavia, and Switzerland, landfilling of EAF dust is forbidden. Although the EC is currently not preparing stricter legislation concerning EAF dust (only a study is being carried out), it is to be expected that stricter regulations will be imposed in the near future.

Position of the EMPF® regarding competition:

The most important High Temperature Metals Recovery Processes for EAF dusts are:

- | | |
|---|------------------------------------|
| — Davy McKee | - Hi Plas Furnace |
| — Elkem | - Multi-Purpose Furnace |
| — Horsehead Resources Development (HRD) | - Flame Reactor |
| — Scan Arc | - Plasmadust Process |
| — Tetronics | - Plasma Arc Furnace |
| — Horsehead Resources Development (HRD) | - Waelz Kiln |
| — ZIA Technologies | - Inclined Rotary Reduction System |

When comparing the Davy McKee process with the EMPF® process, the later has some superior features, such as airtight operation.

The main disadvantage of the Horsehead technologies, e.g. the Flame Reactor and the Waelz process, is the production of a crude zinc oxide, which requires further processing, rather than giving a saleable zinc product.

The Tetronic process encounters problems in the existing operation; it has limited scale-up potential.

The most critical part of any HTMR process is the metallic zinc recovery or zinc condenser stage. This stage has consistently been the most troublesome one for developers, requiring sophistication in both design and operational techniques.

The economic viability of the process is dependent on the production of saleable products. This affects economics in two ways. First, the credit from producing saleable products is essential to offset the operating costs. More critically, the costs of landfilling any residue which cannot be sold may overwhelm the other cost factors. Besides producing "Prime Western" grade zinc and lead products, the process must also produce a slag or a direct reduced iron (DRI) product which can be either recycled or sold.

As a result of an evaluation by the International Technology Corporation three processes appeared to be technically and economically superior: the Elkem process, the ZIA process, and the Scan Arc process.

The two-stage reduction processes (ZIA and Scan Arc) have the advantage of providing a higher quality gas stream to the condenser. The gas is higher in zinc concentration, contains no moisture, and is free of metallic iron. All these factors improve the operation of the condenser. In addition, these processes provide a higher degree of control, and are more tolerant of dust variations. These processes, however, are associated with a higher capital cost than the single-stage EMPF® process.

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Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

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Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 5 Dusts from the primary iron- and steel industry in CEC member countries, annual amounts, Zn and Pb contents. Estimated from 1988 production data

Country	Production of iron and steel (Mt) ¹⁾				Dust generated (kt)						Zinc and lead in dusts (kt)	
	Crude iron	Crude steel			Blast furnace		Carbon steel		EAF	Stainless steel	Zn	Pb
		oxygen	EAF	%SS			coarse	fine				
Belgium	9.18	10.30	0.92	19	155	75	60	125	9	2	4-10	0.7-5
Denmark	-	-	0.65	0	-	-	-	-	8	-	0.8-2	0.1-0.4
France	14.79	14.08	4.52	17	250	120	85	170	45	9	10-20	1.5-9
Fed.Rep.of Germany	32.45	33.94	7.09	18	550	260	205	410	75	15	20-40	3-18
Greece	-	-	0.96	0	-	-	-	-	12	-	1-3	0.1-0.6
Ireland	-	-	0.27	0	-	-	-	-	3	-	0.3-0.7	< 0.2
Italy	11.38	10.54	13.23	6	195	90	63	125	150	10	18-45	2-12
Luxemburg	2.52	3.66	-	-	43	20	22	44	-	-	1-2	0.2-1.3
The Netherlands	4.99	5.26	0.26	0	35	40	30	63	3	-	2-4	0.3-2.3
Portugal	0.45	0.47	0.34	0	8	4	3	6	4	-	0.5-1.5	0.1-0.4
Spain	4.69	4.75	7.13	7	80	38	30	57	80	6	10-20	1-6
United Kingdom	13.24	14.01	4.95	10	225	110	85	170	53	6	10-20	1.5-9
CEC	93.69	97.01	40.32		1590	750	585	1165	440	48	70-170	10-60

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 6 Major contributors to zinc and lead in waste dusts from the primary iron- and steel industry in the CEC (wt.%)

	Zinc				Lead			
	Blast furnace fines	Oxygen fines	EAF	Total	Blast furnace fines	Oxygen fines	EAF	Total
Belgium	2	2	1	5	3	3	1	7
France	3	3	6	12	4	4	7	15
Fed.Rep. of Germany	7	7	11	25	10	11	6	27
Italy	2	2	20	24	3	3	13	19
Spain	1	1	11	13	2	2	7	11
United Kingdom	3	3	7	13	4	4	5	13
Other countries	<u>2</u>	<u>2</u>	<u>4</u>	<u>8</u>	<u>2</u>	<u>3</u>	<u>3</u>	<u>8</u>
CEC	20	20	60	100	28	30	42	100

Table 7 Numbers of sites of blast furnaces and electric arc furnaces in the CEC

	Blast furnace sites	EAF sites
Belgium	7	5
Denmark	—	1
France	13	25
Fed.Rep. of Germany	16	23
Greece	1	3
Ireland	—	1
Italy	5	90
Luxemburg	3	—
The Netherlands	1	1
Portugal	1	1
Spain	6	37
UK	<u>5</u>	<u>26</u>
	58	213

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 8 Dust from the primary iron- and steel industry; rates and properties

		Blast furnace			Steelmaking, oxygen			Steelmaking, EAF		Stainless steel, EAF	
		coarse	fine	ref.	coarse	fine	ref.		ref.		ref.
Generation rate (kg.t ⁻¹)		17(10-20)	8(5-10)	1,2,4,11	6(4-8)	12(10-18)	1,4,11,14	10-15	4	10-15	4
Main const. (wt.%)	C	30(20-40)		2-4,12	0.5-2		3,4,14,15	0.3-3	1,3,4,7,16	0.3-0.6	4
	Fe	30(20-40)		1-4,9,12	65(50-75)		1,3-5,9,11,14,15	30(20-40)	1,3-5,7-9,16	20-40	3,4,6
Impurities (wt.%)	Zn	0.1-0.3	1-5	1-4,9,12	0.2-0.4	2	1,3,11,14,15	17(10-23)	1,3-5,7-10,16	1-3	3,4,6
	Pb	0.01-0.05	0.5-2	1-4,9,12	0.05-0.2	0.5-(0.2-2)	1,3-5,9,11,14	3(1-5)	1,3-5,7-10,16	0.5-1.5	3,4
	Cd							0.1-0.5	4,8,16		
	Cr							0.1-0.2	7,8	10-15	3,4,6
	Cu	0.01		4	0.01		4	0.1-0.4	4,8	0.2	4
	Mn	1.6		3	0.1-1.5		3	2-4	3,7,8	2,3,7	6, resp. 3
	Mo									1-2	4
	Ni							< 0.1	8	2-5	3,4,6
	Al	0.3-4		1	0.1		1	0.3-0.6	1,7,8		
	Ca	5-15		1	1-5		1,15	3-12	1,4,7,8		
	Mg	1-3		1				1.5-5	1,7,8		
	Na+K	0.2-0.5		3,12	0.2; 1-2		3, resp. 15	1-5	7,8,16		
	S	1-2		12	0.02	0.1-0.5	3,5,13,14	0.3-0.5; 1.5-2.5	3,7,8, resp. 4		
	Cl							2-5	4,8,16		
	P				0.05-0.06	0.05-0.06	13	0.2	7		
	Si	1-5		1	0.5-1		1	1-3	1,4,7,8		
Av. particle size, d ₅₀ (μm)		210	125	3	80		15	1.5	3		
			10-15 10?	2 1	300 180		14	< 1	1		

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 9 Chemical composition (in % dry wt.) and particle size distribution (in %) of the fine fraction from blast furnace dust

Chemical composition		Particle size distribution (1987 situation)	
Compound	Concentration	Size	Fraction
Zn	2 - 8	> 60 μm	2.1
Pb	0.5 - 1.5	30 - 60 μm	2.9
C	25 - 35	20 - 30 μm	2.8
Fe	18 - 35	9 - 20 μm	9.8
Al_2O_3	3 - 5	6 - 9 μm	7.2
SiO_2	1 - 2	< 6 μm	75.2
CaO	3 - 5		
MgO	1 - 2		
MnO	0.3 - 0.5		

Table 10 Capacities of Waelz processes in the EC for EAF dusts

Country	Location	Production of EAF-dust (tons/y)	Treatment capacity (tons/y)	Percentage of treatment cap. ref. available
Germany	Duisburg	75,000	60,000	19,20,24 80%
Spain	Bilbao	80,000	70,000	20,24 88%
Italy	Porto Vesme	150,000	50,000	20,23 30%

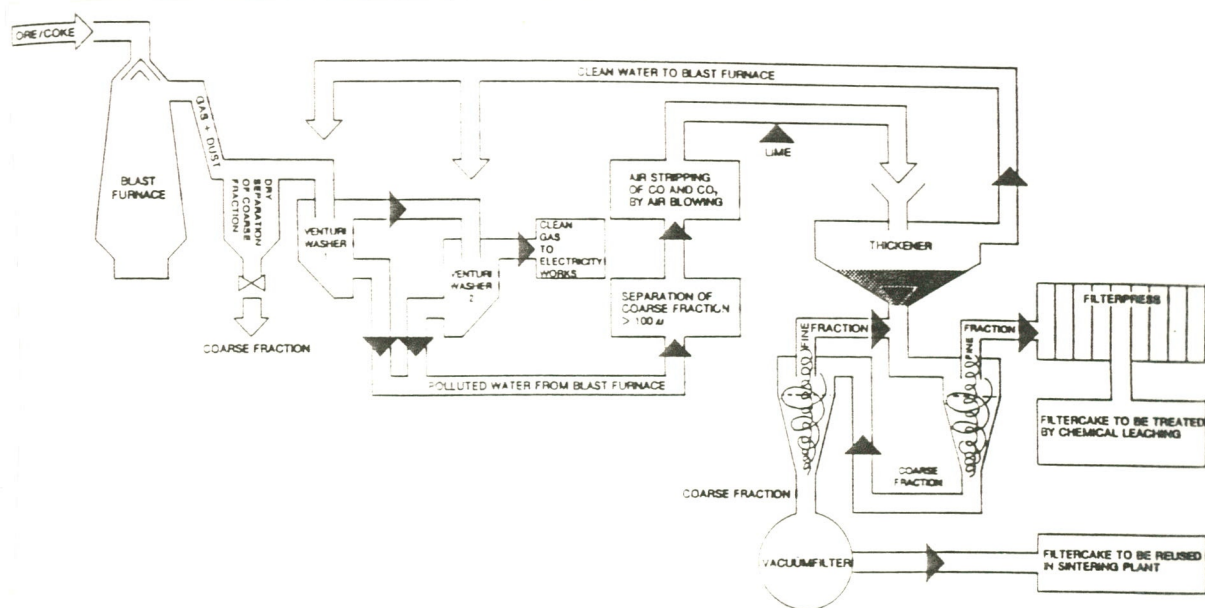


Figure 3 Treatment of Blast Furnace dust

3.2 Primary zinc production

3.2.1 General

For the production of primary zinc, enriched ores are used, containing high concentrations of zinc sulphide (approximately 85%) and iron sulphide (8-10%). The zinc concentration in these ores is about 50%. Other metals such as cadmium, arsenic, lead, cobalt, copper, and silver are also present in low concentrations. The enriched ores used for producing primary zinc in EC-countries are predominantly obtained from countries outside Europe, where the mineral ores are found. The production of zinc from enriched ores takes place at about 30-40 plants throughout the world.

As to the types of processes used, the production of primary zinc takes place with hydrometallurgic processes, including electrolysis, or pyrometallurgic processes. Because of lower cost and fewer environmental problems, the production of zinc by hydrometallurgic processes has increased significantly during the last decades. In 1980 the worldwide (excluding Eastern Europe and China) electrolytical zinc production accounted for approximately 85% of total primary zinc production.

3.2.2 Processes and wastes

3.2.2.1 Hydrometallurgic processes

All the hydrometallurgic processes have a common first step, where enriched ores or concentrates are processed through a roasting step.

Before electrolysis of zinc is carried out, iron and other impurities must be removed from the zinc solution. Iron, the main contaminant in zinc ores, is removed by precipitation, thereby capturing a small amount of zinc.

Several iron precipitates can be formed, depending on the process. The names of the processes (three main hydrometallurgical processes are applied for the zinc production) refer to the types of iron precipitate, i.e. jarosite $((\text{NH}_4)_2\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12})$, goethite $((\text{FeO}.\text{OH}))$ and hematite (Fe_2O_3) .

Other configurations of the primary zinc production process are possible. In Australia for instance, the "low contaminant jarosite" process is used, while Budelco uses a different type of jarosite process.

3.2.2.1.1 The jarosite process

The roasted feed is leached in a mixture of spent electrolyte and acid solution returning from the jarosite precipitation step (see Figure 4). In this neutral leaching step, zinc oxide dissolves, as well as soluble iron compounds carrying with them impurities that are harmful to electrolysis.

The remainder, insoluble under the neutral leaching conditions (mainly zinc ferrite), forms the neutral leach residue. This residue and the solution are separated, the latter proceeding to purification and zinc electrolysis, the former to the hot acid leaching, where it reacts with a mixture of spent electrolyte and sulphuric acid at a temperature of 90°C. The residue of the hot leaching is subjected to an extra-hot leaching step, whereby a Pb/Ag-residue is produced. The resulting solution is partly neutralised by adding roasted feed, and jarosite is precipitated in the presence of complexing ions, commonly sodium or ammonium. The pulp is separated, usually by thickening and filtration into a jarosite residue and a solution which is returned to the neutral leach [1, 2]. The jarosite residue typically contains 2-6% zinc and 0.2-2% lead.

After an extra hot acid leaching, a Pb/Ag residue is produced that contains 2-10% Zn and 2-22% Pb.

In the process at Budelco in the Netherlands, both residues, i.e. Pb/Ag residue and jarosite sludge, are combined in the process.

This jarosite sludge from Budelco contains 1.5-2.5% zinc and 5-6% lead. A more detailed composition of this sludge is given in Table 12. The density of the jarosite sludge is about 1.5-1.6 g/cm³ and the water content approximately 50%.

3.2.2.1.2 The goethite process

The roasted feed is treated subsequently by a neutral leaching, a mild acid leaching, a hot acid leaching, and an extra hot acid leaching. After this leaching, a Pb/Ag residue is left. This Pb/Ag residue contains 1.5-3% zinc and 25-30% lead (Table 12).

The zinc solution from the hot acid leaching is reduced and a sulphur containing residue is produced which is returned to the roasting step. The solution is further neutralised; in the next step, iron is removed from the zinc solution as a goethite precipitate. Goethite sludge contains 5-9% zinc [1] and about 1% lead [3]. The water content is approximately 50% (Table 12).

3.2.2.1.3 The hematite process

In the neutral leaching step, zinc oxide is leached from the roasted feed. This solution is separated from the solids (pulp), purified (cementation of copper and cobalt) and transferred to the zinc electrolysis. The pulp is leached in the hot acid leaching and, subsequently, in a strong acid leaching. After separation, a Pb/Ag residue is produced.

Iron in the solution from the hot acid leaching is reduced and, subsequently, a copper residue is produced. The solution is treated twice with roasted feed or lime. When lime is used, gypsum is formed in these two steps. When roasted feed is used, the solids are returned to the hot acid leaching. The first residue (gypsum preneutralisation) can be used as a building material (zinc concentration 0.24% and lead concentration 0.01%). The second residue (gypsum postneutralisation) is too much contaminated (zinc concentration is about 5% [1] and considerable amounts of gallium and indium are present).

After neutralisation, the solution is treated at elevated pressure (20 Bar), temperature (200°C), and oxygen concentration (1-3 bar oxygen pressure) to produce hematite. Hematite sludge contains about 1% zinc. At Ruhrzinc GmbH in Germany, which is the only company in Europe that uses this process, the zinc content will be further reduced in the future to < 0.2% by process modification [1]. The lead content in the hematite sludge is about 0.01% (see Table 12). The water content is approximately 10%.

3.2.2.1.4 Purification

In the electrolytic zinc production, drosses are produced in the melt bath, which is carried out as a purification step prior to electrolysis. The production is about 0.01 ton dross/ton of produced zinc. The zinc content in these drosses is about 80% (40% is metallic zinc) and they are either returned to the beginning of the process (roasting) or sold to the secondary zinc industry.

3.2.2.2 Pyrometallurgic Processes

The most important pyrometallurgic process is the Imperial Smelting Process (ISP). In the ISP, zinc and lead are simultaneously recovered from concentrated ores. The Imperial Smelting furnace is charged with zinc-lead sinter, coke, and recirculated drosses and dusts. Lead is reduced and tapped, along with slags from the bottom of the furnace. The lead is separated from the slags and ready for refining. At furnace temperatures of 950-1150°C, zinc is vaporised and condensed as it passes through a shower of liquid lead droplets. Liquid zinc is separated from the lead in an external cooling circuit and is then sent to a thermal zinc refinery to produce SHG and Prime Western product grades. The lead from the zinc condenser is recirculated.

Slag is the only residue from this process [5]. Usually zinc-bearing ores are processed together with secondary waste materials. The amount of secondary lead feed to the furnaces as a proportion of total lead feed is generally much lower than that of zinc.

The amount of slag produced in the furnace varies from 0.5 to 1.15 tons/ ton of zinc produced [4, 6]. The zinc content of slag can be lower than 5%, but normally averages about 7% (the lead content is normally 0.5-1.2%) [6]. Furnace slag is granulated in a water spray and is used for several purposes in different parts of the world, such as landfill and land reclamation from the sea, as a grit blasting medium, and as a component (iron source) in cement manufacture. At one plant, a slag-fuming operation has been used for many years; two plants are developing processes for this. The plant in Poland has fed its slag to a Waelz Kiln, but it is not known whether this is still practised [6].

3.2.2.3 Waste characteristics

Table 11 gives the characteristics of the wastes in the primary zinc. The waste production factor is the amount of waste per ton of produced zinc.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 11 Characteristics of wastes from the primary zinc production

Process	Zn (%)	Pb (%)	Factor [1, 7]
jarosite	2 - 6	0.2 - 2	0.5 - 0.64
Pb/Ag residue jarosite (jarosite Budelco)	2 - 10 1.5	2 - 22 6	0.10 0.75
goethite	5 - 9	1	0.32 - 0.45
Pb/Ag residue goethite	1.5 - 3	25 - 30	0.10
hematite	1	0.01	0.2 - 0.3
gypsum (pre)	0.24	0.01	?
gypsum (post)	5	?	?
slags ISF	7	0.5 - 1.2	0.5

3.2.3 Producers and waste production

In Table 14a, European producers of zinc that use a hydrometallurgic process and the type of process are described. The two most important processes are the jarosite and the goethite processes.

Worldwide, the most important process is the jarosite process (approximately 70% of the world production [8]).

In these hydrometallurgic processes, two residue streams are of importance: the iron residue and the Pb/Ag residue. The amount of iron residues is 0.45 ton/ton for the goethite process, and 0.64 ton/ton for the jarosite process, respectively. The amount of Pb/Ag residue is approximately 0.10 ton/ton.

According to the literature, the total amount of iron residue is 525,000 tons of jarosite and 260,000 tons of goethite produced annually by the most important companies in the EC (see Table 15), corresponding with approximately 10,000 tons of zinc ($x 0.50 \times 0.04$) for all jarosite residues and approximately 9,000 tons of zinc ($x 0.50 \times 0.07$) for all goethite residues. The amount of hematite is relatively low (41,000 tons/y), corresponding to approximately 400 tons of zinc. On the basis of calculation (waste production factor and capacity), these amounts are slightly higher.

The second important residue is the Pb/Ag residue. This residue is either produced separately from the iron residue and used as a source material for the lead industry or disposed of, together with the iron residue (see Table 16).

In the case the goethite process is applied, the Pb/Ag residue is treated at lead smelters, except the residue of Vieille Montagne in Aubry. Here silver is recovered and the lead containing residue disposed of [9].

In the case a jarosite process is applied, disposal of the Pb/Ag residue is more often practised. The Pb/Ag residue from the only company with the hematite process, Ruhrzinc GmbH, is treated by Berzelius.

This means that the Pb/Ag residue seems to be not a potential source material for the EMPF® process. The most suitable option is the lead residue of Vieille Montagne in Aubry, with a (calculated) waste stream of about 20,000 tons/year.

Disposal of jarosite at Outokumpu, Finland, is not under pressure. They have permission to dispose of until 2010. On the other hand, Metaleurop in Germany (Nordenham) is put under pressure by the authorities to solve their waste problem [9]. The costs for secured landfilling of the jarosite in the Netherlands (Budelco) in the new pond amounts to US\$ 50/ton of jarosite [9].

A small fraction of the world's primary zinc (about 12%) is produced by pyrometallurgical processes usually an Imperial Smelting process [10]. In Table 14b, the European producers that use a pyrometallurgical process are described. All companies use the Imperial Smelting process, except Metaleurop in Germany (Harlingerode), which company uses a vertical retort furnace [11]. Slags from Berzelius, Nuova Samim, Metaleurop, and Commonwealth Smelting (see Table 14b) are granulated and dumped.

3.2.4 New technologies and developments

A major reduction of waste production from electrolytical zinc production can be achieved with a less contaminated iron residue. Scientific research is emphasising this topic. The hematite process is, in fact, an example of a less contaminated iron residue.

Potential processing routes for treating jarosite were extensively studied by Budelco B.V., in association with Billiton Research B.V and the international "Jarosite R&D Group". On the basis of pilot-plant experiments it was concluded that pyrometallurgical treatment in an oxysmelt-process offers the best perspectives. The oxysmelt process for treating jarosite is a joint development of Budelco/Billiton, Outokumpu Research, and Pasminco Ltd. The jarosite oxysmelt-process consists of two thermal steps. Before the thermal treatment, the iron precipitate is filterpressed (belt filter press) and dried by means of a kind of spray dryer [9].

In the first step, the jarosite is treated in an oxysmelter at a temperature of 2000°C. Under these conditions metals like zinc, lead, arsenic, and silver will evaporate. The slag that is produced is treated under sub-stoichiometric oxygen conditions in a "CSIRO-lance" furnace to reduce its metal content further. The applicability of the slag is presently studied. Possible options are e.g. use as a raw material in the production of iron and steel, artificial gravel, or cement.

The evaporated metals are collected in the fly ash, which is further treated to produce a zinc solution (from which zinc and cadmium are recovered by electrolysis), a lead/silver residue, and an iron/arsenic residue. The former residue can be used as a raw material in a lead smelter. Further upgrading of the iron-arsenic residue is unlikely at this stage; the quantity to be disposed of, however, is relatively low (approximately 3.5% wt on intake). A flow sheet of the process is given in Figure 5.

The consultancy company Davy McKee is currently working out the concept for the plant [9].

3.2.5 References

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- [2] Arregui, Gordon, Steintveit, The Jarosite process, past, present and future, Congress Lead-zinc-tin, 1980.
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Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 12 Chemical composition of the residues in percentages of dry weight [1]

Process	Zn	Pb	Fe	Cd	SiO ₂	SO ₄	(H ₂ O)
jarosite	2- 6	0.2-2	24-30	0.05-0.2	?	30-36	(50)
Pb/Ag-residue	2-10	2-22	5-30	0.05-0.5	?	27-60	?
(jarosite Budelco)	1.5	6	27-30	0.04	?	?	(50)
goethite	5-9	1 ¹	40-42	?	2	12	(40-50)
Pb/Ag-residue	1.5-3	25-30	?	?	10-14	45-60	?
hematite	1	0.01	59	0.02	0.1	8	(10)
gypsum (pre)	0.24	0.01	0.17	0.01	?	?	?
gypsum (post)	5	?	9	0.01	?	39	?

1 [3]

Table 13 Average composition of jarosite (%) ($X_2 Fe_6 (SO_4)_4 (OH)_{12}$, $X = NH_4, Na, K$) from Budelco [8]

	Average (%)	Range (%)
iron	25	
zinc	2.5	
lead	5	3 - 5
ammonium	1.7	1.5 - 2.0
antimony	0.03	-
arsenic	0.2	-
cadmium	0.04	0.04 - 0.05
calcium	3 (as oxide)	2 - 3
chromium	0.03	-
cobalt	0.01	-
copper	0.07	-
magnesium	0.2 (as oxide)	1 - 2
silicon	5 (as oxide)	2 - 5
silver	0.02	0.01 - 0.02
sulphur	14	-
aluminum	1	-
oxygen	40	-
mercury	?	0 - 0.005

Physical composition:

water content sludge : 40-50%

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 14a Primary electrolytical zinc companies in Europe (capacities according to [12])

Company	Country (location)	Capacity in ktons/y
Jarosite:		
Astuariana de Zinc	Spain (Avilles)	225
Budelco	Netherlands (Budel)	210
Preussag-Weser-Zink (= Metaleurope)	Germany (Nordenham)	130
Hemijska Industrija Zorka	Yugoslavia (Sabac)	30
Rudarsko Metalursko	Yugoslavia (Trepca)	80
Norzink AS	Norway (Odda)	140
Otokumpu Oy	Finland (Kokkola)	170
Goethite:		
Metallurgy Hoboken Overpelt (MHO)	Belgium (Overpelt)	120 ³
Nuova Samim	Italy (Porto Vesme)	83 ¹
Pertusola	Italy (Crotona)	100
Veille Montagne	France (Auby)	200
Veille Montagne	Belgium (Balen)	180
Hematite:		
Ruhr Zink ²	Germany (Datteln)	135
Other electrolytical primary zinc producers (Unknown type of iron residue)		
Espanola de Zinc	Spain (Cartagena)	60
Metal Quimica del Nervion	Spain (Bilbao)	8
V.E.B. Bergbau und Hutten Komb. A. Funk	Germany (Freiberg)	21
Bleiberger Bergwerks Union AG	Austria (Gailitz/Arnoldstein)	30
Quimigal	Portugal (Barreiro)	11
Huta Metali Niezelaznych	Poland (Katowice)	23
Komb.Gorniczo-Hutniczy	Poland (Krakow)	90
KSM Dimitar Blagoev	Bulgaria (Kurdjali&Plovdiv)	90

¹ also Imperial Smelting

² Hematite is being sold mainly to cement makers

³ additionally 25 ktons/y of secondary materials

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 14b Companies with pyrometallurgical primary zinc production in Europe, 1989 production [11, 5]

Company	Country (location)	Production (kton/y)	
		zinc	lead
Berzelius Metallhütten Gesell.	Germany (Duisburg)	86	41
Nuova Samim	Italy (Porto Vesme)	76	34
Pennarroya (= Metaleurop)	France (Noyelles-Godault)	104	44
Commonwealth Smelting Ltd	UK (Avonmouth)	84	41
Harz zink GmbH (= Metaleurop)	Germany (Harlingerode)	30 ¹	
Topilnica Zletovo	Yugoslavia (Titov Veles)	56	28
Huta Cynku	Poland (Miasteczko)	72	32
Metalurgica de Metale Neferoase	Romania (Copsa-Mica)	70	

¹ Additionally to this primary production, Harz zink GmbH uses secondary materials (40 ktons/y) as a source material.

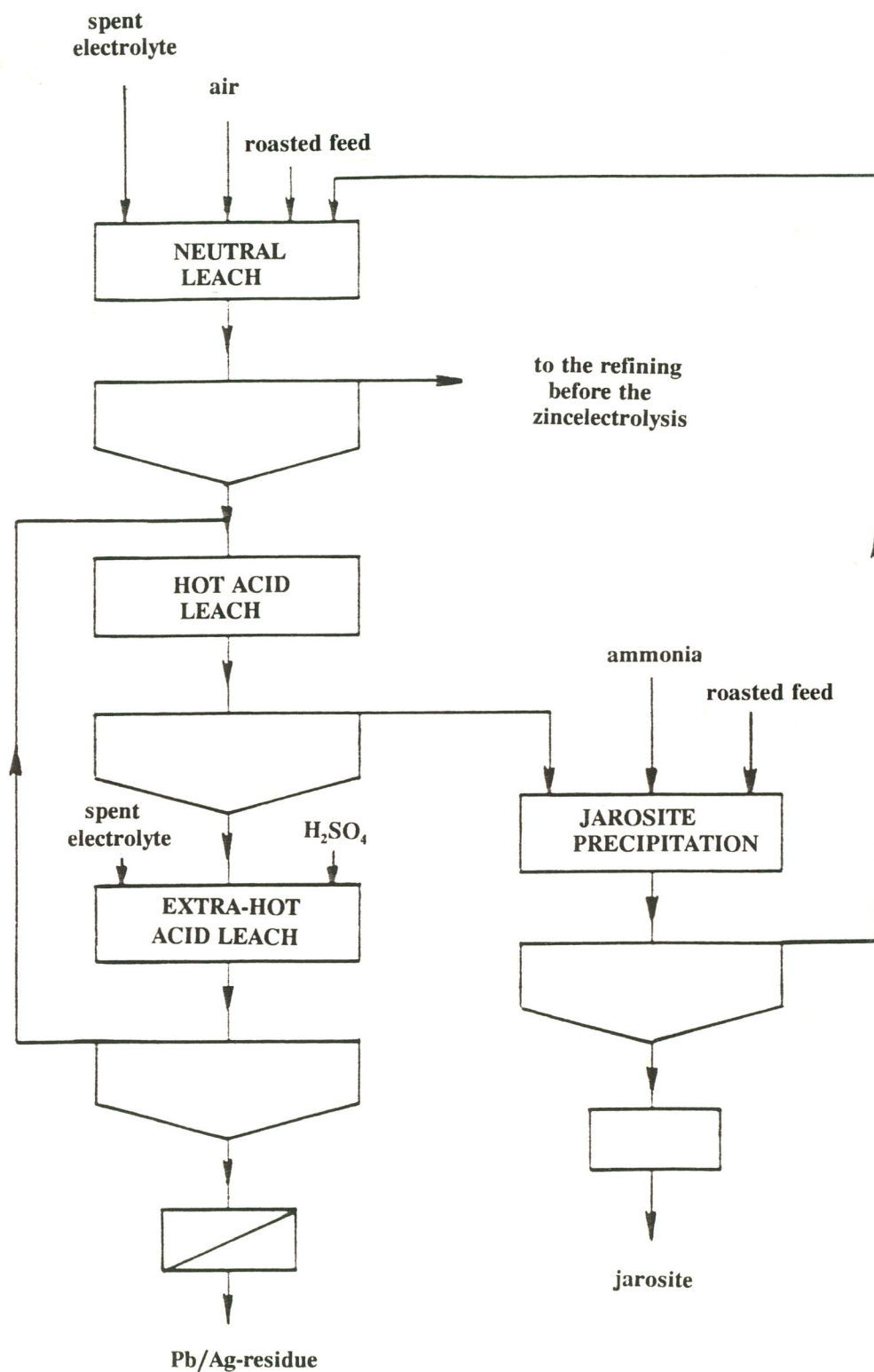
Table 15 Amounts of iron residues (calculated amounts and data from the literature)

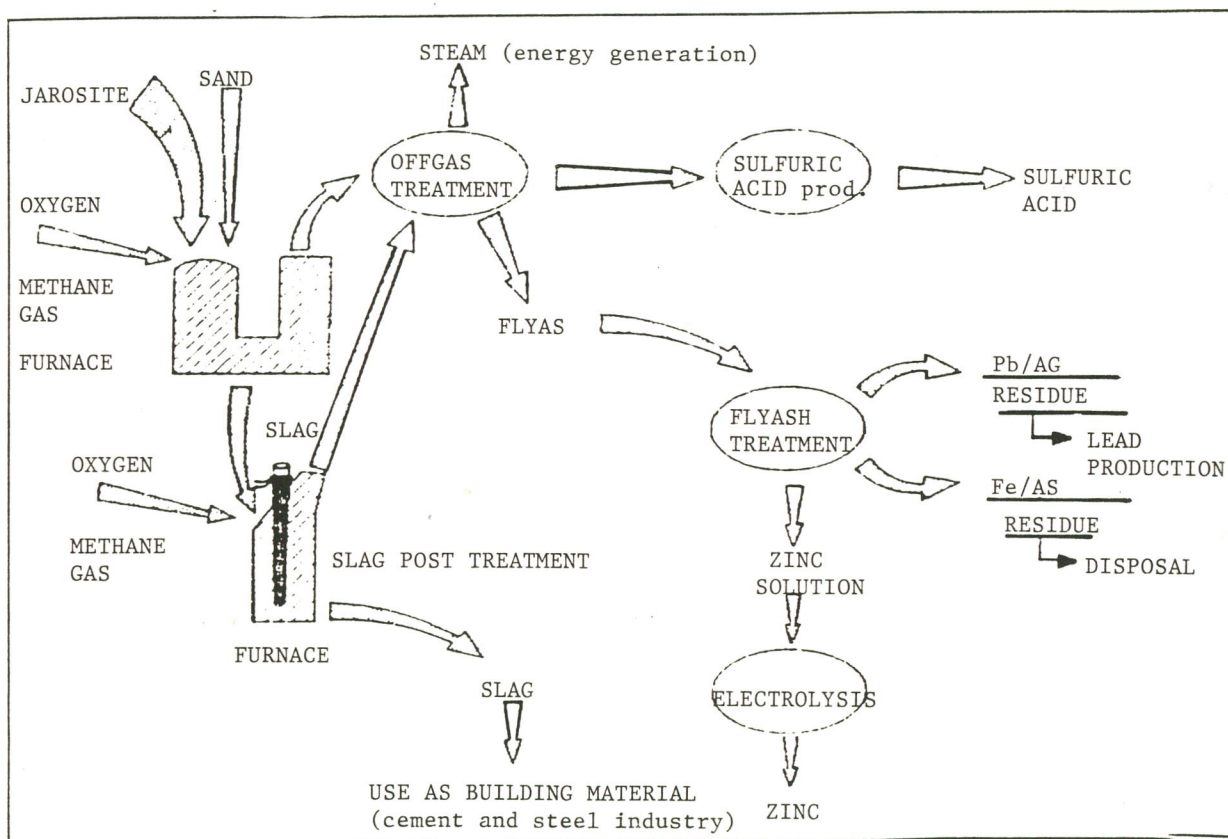
	Zn-prod. capacity ktons/y	Calculated dry ktons/y	Literature data [8] dry ktons/y
Jarosite:			
Astuariana (Spain)	225	144	115
Budelco (Budel)	210	156	120
Metaleurop (Nordenham)	130	83	75
Hemijiska Ind. Zorka (Yug)	30	19	25
Yugoslavia (Trepca)	80	51	15
Norzink AS (Norway)	140	90	75
Outokumpu Oy (Finland)	170	109	100
Goethite:			
MHO (Overpelt)	120	54	50
Samin (Porto Vesma)	83	37	30
Pertusola (Crotona)	100	45	40
Veille Montage (Auby)	200	90	75
Veille Montage (Balén)	180	80	65
Hematite:			
Ruhrzink (Datteln)	135	41	35

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 16 Calculated amounts of Ag/Pb residue (dry weight) and the application of residue [9]

	Zn prod.	calculated dry	residue
	ktons/y	ktons/y	
Jarosite:			
Astuariana (Spain)	225	-	disposal with jarosite
Budelco (Budel)	210	-	disposal with jarosite
Metaleurop (Nordenham)	130	13	to leadsmelter Metaleurop
Hemijska Ind. Zorka (Yug.)	30	3	?
Yugoslavia (Trepca)	80	8	?
Norzink AS (Norway)	140	14	to leadsmelter Boliden
Otokumpu Oy (Finland)	170	-	disposal with jarosite
Goethite:			
Vieille Montagne MHO (Overpelt)	120	12	to: leadsmelter Hoboken
Samin (Porto Vesma)	83	8	leadsmelter Samin
Pertusola (Crotona)	100	10	leadsmelter Noy.Godault
Veille Montage (Auby)	200	20	Ag winning, Pb deposit
Veille Montage (Balen)	180	18	leadsmelter Hoboken (?)
Hematite:			
Ruhrzink (Datteln)	135	18	to leadsmelter Berzelius

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes*Figure 4 The conventional jarosite process*

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes*Figure 5 Oxysmelt process for jarosite*

3.3 Secondary zinc production

3.3.1 General

Recycled zinc is growing steadily in importance as an essential metal. Over 1.6 million tons of zinc used each year in the Western world are now being recovered by reprocessing of secondary materials, accounting for 24% of zinc consumption [1]. As in more and more countries efforts are increased towards maximising recovery levels, these tonnages are expected to keep on rising during the 1990s.

3.3.2 Processes and wastes

Corresponding to the wide spectrum of their use, a variety of zinc bearing waste materials arise which can be processed into zinc or zinc-bearing products by different routes. Determining the method of treatment to be selected is usually a question of the most cost-favourable route to arrive at a specific saleable product from a waste material.

The waste materials can be divided into three main groups [2]:

a. Metallic residues

Metallic residues such as:

- old zinc;
- brass scrap;
- die-casting scrap;
- hard zinc;
- shredder scrap.

Remelting plants convert these residues back into saleable products. Zinc metallic residues are hardly polluted with other compounds and do not cause considerable amounts of residues to occur in the remelting process.

In some cases, these secondary materials are used as a raw material for the production of zinc dust or zinc oxide.

b. Cleaner oxidic wastes

Cleaner oxidic wastes such as:

- galvaniser's ashes;
- technical zinc oxide from remelting.

These residues are taken up preferentially by the chemical industry. Zinc oxide, zinc pigment, flux, and zinc chloride are made from them. Amounts in excess of demand go to the smelter, where they are processed into metal, equal in value to that recovered from primary sources.

Ashes from the thermal metalplating industry contain considerable amounts of metallic zinc particles and a high content of zinc oxide. Some companies separate the relatively large metallic zinc particles (by air sifting) from the zinc oxide ("fine ash"). Iron particles are removed by magnets. The metallic zinc particles are remelted; the zinc oxide (dusts) is used as a source material in the zinc oxide industry.

c. Impure oxidic wastes

Examples of impure oxidic waste are:

- galvaniser's ashes;
- dross from remelting plants;
- fine dusts;
- residues from alloying plants;
- spent zinc catalysts;
- steelwork dust.

These materials are distilled and melted to metal. Only under exceptional circumstances do they serve for zinc oxide production. The process that is used for distillation of these secondary materials is the Imperial Smelting Process (see 3.2 primary zinc production).

3.3.3 Producers and waste production

The most important European melters of scrap are summarised in Table 17. One of the biggest secondary smelters is Dinslaken in Germany with a capacity of more than 20,000 tons/year [3].

Ashes from the thermal metalplating industry are treated by a limited number of companies, i.e. Mapral in France, Rezinal in Belgium, Grillo Zincoxyde in Germany and Ercoreco in Spain. The metallic zinc is remelted and the zinc oxide or the "fine ashes" are used as a source material in the zinc oxide industry [3, 4]. The fine ashes from Rezinal and Mapral are treated by AFOX in Belgium, where lead and chloride are removed; the treated material is used as a source material at Zinkwit (zinc oxide producer) in the Netherlands. The removed lead is used for the production of lithopone (used as paint; mixture of zinc sulphide and barium sulphate) in the Sachtleben company in Germany [4].

Metaleurop (Pennaroya) in France (Noyelles-Godault), Commonwealth Smelting Ltd. in the UK (Avonmouth), Berzelius Metallhütten Gesellschaft in Germany (Duisburg), Nuova Samim in Italy (Porto Vesme) use Imperial Smelting Furnaces, see Table 18 [3]. These companies use enriched concentrates (primary zinc) in co-processing with secondary materials (impure oxidic wastes) as a source material.

Secondary materials can be fed to the ISP furnace in two ways, either as a raw material at the sinter plant or as a direct feed to the furnace shaft. The quantities fed to the various smelters depend on many factors and therefore the range of proportions varies considerably. At the Berzelius plant, 35% of the furnace zinc feed comes from secondary materials. For several years, the Miasteczko smelter in Poland has operated one of its furnaces entirely on secondary materials for several years. The amount of secondary lead feed to the furnaces as a proportion of total lead feed is generally much lower than that for zinc. Slags are normally disposed.

Another process is used by Harz zink GmbH (= Metaleurop) in Germany (Harlingerode), namely vertical retort furnaces with a capacity of 30 ktons/y of primary materials and 40 ktons/y of secondary materials as a source material.

3.3.4 New technologies and developments

No changes are expected.

3.3.5 References

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- [2] Possibilities of recycling zinc residues in the Imperial Smelting Furnace, paper delivered at the international Recycling Congress, Berlin, April 1982.
- [3] Information from Mr Meijers, Rezinal.
- [4] Information Rezinal, Belgium.
- [5] Information from Mr M. Smith, Imperial Smelting Furnaces.
- [6] World directory: Secondary Zinc Plants, International Lead and Zinc Study Group, 1988, London.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 17 Important secondary zinc industries in Europe using remelting processes [6]

Country	Company	Location	Capacity (tons/y)
Austria	Grillo & Reeseneerger	Tattendorf	1000
	Metallona Metallh. Verwertungs G.	Klosterneuburg	1000
Belgium	Rezinal N.V.	Zolder	18000
	Vieille Montagne	Overpelt	9000
France	Aldevienne	L'Isle Joudain	1500
	Banda	Metz	4000
	Mapral	Fecamp	5000
	Georges Ostrowiak S.A.	La Plaine St.Denis	12000
	Ramb	Paris	3500
	Société Nouvelle Metaux	Luneville	2500
Germany	A. Edelman GmbH	St. Ingbert	5000
	W. Grillo Werke	Duisburg-Hamborn	5000
	Metallwerk Dinslaken GmbH	Dinslaken	10000 ¹⁾
	Hetzel & Co GmbH	Nuremberg	1500
	Metallhuettengesell. Schumacher	Rommerskirchen	1500
	Preussag AG Metall Feuerverzink.	Neumuenster	4000
	Helmut Hahn KG	Hamburg	1200
	Alex Jost KG	Suemmern	600
Italy	Capitelli, S.p.a.	Barugo Molgora	5000
	Metalsider S.p.a.	S. Martino di Rio	5000
	Nuova Samin S.p.a.	Ponte Nossia, Rome	10000
Portugal	Societade Metalurgica Antonio	Matosinhos	1000
Spain	Fund. Triqueros	Madrid	3500
	Lainden S.A.	Barcelona	1500
	Ercoreco	?	?
UK	Abram Alloys Ltd	Cheshire	6000
	Brock Metal Co. Ltd.	Near Cannock	5000
	ISC Alloys Ltd.	Bloxwich	4000
	Metals and Ores Ltd.	Bromgrove	10000
	Zinteg Alloys Ltd.	Telford	10000
Norway	Larvik Pigments Fabrik	Larvik	12000

¹ According to Rezinal, production is at least 20,000 tons/y.

Table 18 Companies with pyrometallurgical primary zinc production in ISF plants in Europe, 1989 [2]

Company	Country (location)	Production (ktons/y)	
		zinc	lead
Berzelius Metallhütten Gesell.	Germany (Duisburg)	86	41
Nuova Samim	Italy (Porto Vesme)	76	34
Pennarroya (= Metaleurop)	France (Noyelles-Godault)	104	44
Commonwealth Smelting Ltd	UK (Avonmounth)	84	41
Topilnica Zletovo	Yugoslavia (Titov Veles)	56	28
Huta Cynku	Poland (Miasteczko)	72	32
Metalurgica de Metale Neferoase Romania (Copsa-Mica)	Romania (Copsa-Mica)	70	

3.4 Zinc oxide/zinc powder production

3.4.1 General

The application of zinc as zinc oxide throughout the world is approximately 4-5% of the total zinc consumption.

Zinc oxide is applied in many industrial processes such as [1]:

- rubbers and tires (as vulcanisation activator);
- paints;
- rayon and synthetic fibres (as hardener);
- ceramic products;
- animal fodder;
- cosmetics;
- pharmaceuticals;
- chemical and petrochemical applications (glue, metal surface treatment, stabilisers, catalysts).

The major application of zinc dust and powder is found in the chemical and the paint industries (primers).

3.4.2 Processes and wastes

3.4.2.1 Zinc oxide

Zinc oxide can be produced by two different processes: the direct (American) process and the indirect (French) process. In both processes, the source material is heated up to 900 - 1000°C, and anthracite is added as a reducing agent. Zinc oxide in the source material is reduced to zinc and is immediately oxidised again to zinc oxide with oxygen from the air after volatisation. The residue of the process is a zinc-containing slag.

The direct process:

Different direct processes can be mentioned, such as the “Wetherill process”, the “electrothermic” process, the process developed by Vieille Montagne (a cupola furnace) and the process in a rotating furnace.

The direct process uses an impure source material, usually ashes from thermal metalplating (see also chapter 3.3 Secondary Zinc Production); the production of residue is relatively large, approximately 10% [2, 3]. Zinc content in the slag is about 25-30% [3, 4]. The composition of the slag is given in Table 20.

The indirect process:

Different indirect processes are applied, such as the “distillation process in retorts”, the “New Jersey” process, and the “Smelting” process.

The indirect process uses metallic zinc, usually electrolytic zinc or “hard” zinc from the thermal metalplating industry, as a source material.

Compared to the direct zinc oxide production, the production of slag from the indirect process is very low, e.g. 0.33% [1]. The zinc content is high (approximately 80%). The metal value is 50-60% of the zinc price; this material is sold as a source material to the secondary industry.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 19 gives the characteristics of wastes from the zinc oxide industry. The waste production factor is the amount of slag per ton of rce material.

Table 19 Characteristics of slags from the zinc oxide industry

Process	Zn (%)	Pb (%)	Factor
Direct	5 - 60	0.01 - 0.5	0.10
Indirect	80	?	0.0033

3.4.2.2 Zinc dust or zinc powder

Zinc dust and powder are produced if the process of zinc distillation is carried out under reducing conditions. This reducing environment is obtained by argon gas addition. As the production processes for zinc oxide and zinc dust are comparable, it can be assumed that the waste characteristics (slag) are also comparable.

3.4.3 Producers and waste production

3.4.3.1 Zinc oxide

In the EC, 22 companies are involved in the production of zinc oxide, see Table 21 [5]. The production of slag as waste material only occurs at the companies with a direct process. In Europe, only four companies use the direct process, i.e. Vieille Montagne (Zinkwit, or KMZM) in the Netherlands, Grillo Zinkoxyde in Germany, Vieille Montagne (Creil) in France, and Vieille Montagne (Blanc de zinc in Marseille) in France. The production of these four companies is approximately 25,000 tons of zinc oxide/y [4]. The company with the largest zinc oxide production is Zinkwit in the Netherlands (15,000 tons/y).

The other companies use the indirect process with usually "hard" zinc as a source material. This production is about 125,000 tons zinc oxide/y [4]. As stated before, the amount of slag from the indirect process is negligible.

Zinkwit, the Netherlands:

The company with the largest production is Zinkwit in the Netherlands, whose capacity will grow in the future. Zinkwit has two production lines: a direct and an indirect process.

Its production is 15,000 tons/y of zinc oxide and 6,000 tons of a technical zinc oxide that is sold to the fodder industry. Source materials are ashes (fine fraction, 30,000 tons/y) from metalplating for the direct process and electrolytic zinc for the indirect process.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

The production of slag from the direct process is 1500 tons/y and will grow to 2000 tons/y in the future. The zinc content is 25-30% Zn, the lead content is negligible, as the source material has been pretreated (removal of lead and chloride at Afox, Belgium). The particle size is 0.9 - 30 cm. According to Dutch regulations, this slag has to be regarded as a hazardous waste. The slags can still be dumped at the factory site (sealed), but this situation will change.

At Grillo Zinkoxyde GmbH in Germany, ashes from thermal metalplating are separated into metal zinc and fine ashes. The fine ashes are worked up to zinc oxide after removal of lead and chloride [4]. No information about residue production is available.

3.4.3.2 Zinc dust

The largest zinc dust producers are Vieille Montagne (Angleur, Belgium) and Harzer Zinkoxyde (Heubach, special column for zinc oxide production and zinc dust production).

3.4.4 References

- [1] Information from Zinkwit/Crosfield Chemie Eysden the Netherlands.
- [2] PBI, Verspreiding van de zware-metalenbevattende afvalstoffen van de K.M.Z.M. in de regio Zuid Limburg en de effecten hiervan op de bodem, 1986 (in Dutch).
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- [4] Information from Mr Meyers, Rezinal.
- [5] Panorama EC.
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- [7] Secondary lead and zinc, Special Meeting of the Recycling Subcommittee, 1988.
- [8] Information from British Zinc Association.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 20 Chemical composition of slags from the direct process [2]

Compound	Range (%)	Typical (Zinkwit [1]) (%)
zinc	5 - 60	22 - 42
(Zinc oxide		27 - 53)
lead	0.01 - 0.5	0.005 - 0.01
cadmium	0.00 - 0.04	< 0.001
arsenic	0 - 0.1	
copper	0.1 - 1	0.1 - 0.25
barium	0.01 - 0.3	
Al ₂ O ₃		12 - 20
Fe ₂ O ₃		6 - 12
Mn ₃ O ₄		0.3 - 0.6
TiO ₂		0.6 - 0.8
SiO ₂		14 - 21
CaO + MgO		5 - 9
Na ₂ O + K ₂ O		1 - 2
SO ₃		2 - 4
C		1 - 7

Table 21 Companies with zinc oxide production (direct + indirect process)

Country	Company (location)	Ref.	Capacity ktons/y
Netherlands	total capacity	3	15
	Zinkwit (Eysden)	3	15
Belgium	total capacity	6	18
	De Creane	4	18
France	total capacity	6	33
	Vieille Montagne (Creil)	4	
	Blanc de zinc de la Méditerranée (Marseille)	4	
	other companies		
Italy	total production capacity	6	22
	Pertusola (Crotona)	7	8
	Nuova Samim, "Zinco Lombardi" (Porto Vesme)	7	8.5
	Zinco Ossidi	7	5
	A Esse	7	3
Spain	total production capacity	6	9
	Foret (Barcelona)	5	
	Asturiana de zinc (San Juan de Nieve)	5	(13)
	Ercoreco	4	
UK	total production capacity	6	23
	Barking Zinc Oxide Ltd (Barking)	8	
	James M. Brown Ltd (Fenton)	8	
	Durham Chemicals (Durham)	8	
	Manchem Ltd. (Manchester)	8	
Germany	total production capacity	6	?
	Grillo Zinkoxyde	4	
	Harzer Zinkoxyde	4	

3.5 Synthetic fibre industry

3.5.1 General

The chemical company AKZO produces a zinc containing sludge as a by-product of the rayon-viscose fibre production or cellulose fibre. Zinc is used as a retarder in the coalescence process. Cellulose fibre is used in textiles and as technical fibre in car tires (for instance Michelin). In Europe, the only producer of rayon-viscose fibre is AKZO. AKZO possesses five rayon fibre factories: two in the Netherlands and three in Germany.

3.5.2 Processes and wastes

The cellulose solution is coagulated in a sulphuric acid bath. In this bath, zinc sulphate is present, where it acts as a retarder of the coalescence process. During post-treatment of the produced fibres zinc is removed from the fibres with water by washing. The waste water is treated with the main purpose of removing zinc and organic compounds. Zinc is removed by precipitation with the sludge containing mainly zinc hydroxide and small amounts of zinc sulphide [1]. The zinc content of the sludge varies between 1.8 and 8% on a dry substance basis, see Table 23 [2]. The composition of a typical sludge is given in Table 24.

Table 22 presents the waste characteristics from the synthetic fibre industry. The waste production factors are not given, since the exact amounts of waste per production plant are known.

Table 22 Waste characteristics from the synthetic fibre industry

Waste	Zn (%)	Pb (%)
Sludge	1.8-8	0.007-0.03

3.5.3 Production and waste production

As stated above, AKZO possesses five rayon fibre factories, two in the Netherlands and three in Germany. One of the three factories in Germany has permission to treat its waste water in a domestic wastewater treatment plant. As a result, the zinc content in the sludge is very low. The sludge quantities of the other four companies are given in Table 25 [2].

The production of sludge at the Ede factory in the Netherlands is 6,000 tons/y, but an additional amount of 90,000 tons of historical wastes is disposed of at the factory site. AKZO is seeking a solution for these historical wastes. The permeability of the wastes is very low, which makes leaching techniques very difficult [3].

3.5.4 New technologies and developments

In the "Kleefse Waard" factory zinc is selectively recovered from the process water by means of solvent extraction. As a result of this process step, the zinc content in the sludge is decreased considerably to such a level that the sludge is no longer regarded as hazardous waste (zinc concentration < 2%). It can be expected that if sludge disposal becomes difficult the solvent extraction technique will be applied in the other factories as well [2].

Process measurement (probably implementation of solvent extraction) will be taken in the "Ede" factory in order to reduce the zinc content in the sludge to a percentage below 2% per January 1994. Sludge with this concentration is not regarded as chemical waste in the Netherlands and can be disposed of without problems.

3.5.5 References

- [1] Enka, Toelichting bij de aanvraag voor een vergunning in het kader van de hinderwet en de wet op de luchtverontreiniging, 1978 (in Dutch).
- [2] Information by Mr Van Kinschot, AKZO-Arnhem.
- [3] Information by Mr Topma, AKZO-Ede.

Table 23 Zinc and lead concentrations in rayon-viscose sludges

Location	Zn ¹ (%)	Pb ¹ (%)	Water content (%)	Organic content ¹ (%)
Ede	7	0.0072	40	50
Kleefse Waard	1.8	0.0086	78	57
Oberbruch	2.9	<0.05	61	10
Kelsterbach	8	0.03	67	20

¹ based on dry substance.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 24 Composition of a typical rayon sludge (Ede factory, the Netherlands), based on dry substance [2]

Metal	Concentration (%)		
Zn	4	-	7
Pb	0.0107	-	0.0136
Fe	0.22	-	0.24
Mg	0.62	-	0.83
Cu	0.0018	-	0.0166
Cd	0.0007	-	0.0033
Cr	0.0012	-	0.0026
Hg	0.0002	-	0.0004
Mn	0.0365	-	0.0417
Al	0.25		
Ag	< 0.002		

Table 25 AKZO-locations with rayon-viscose production [2]

Country	Location	Capacity (tons/y)
The Netherlands	Ede	6000
	Kleefse Waard	3000
Germany	Oberbruch	13000
	Kelsterbach	4000

3.6 Thermal metalplating industry

3.6.1 General

Thermal metalplating or hot dip galvanising is used to protect steel products. For zinc plated steel the average zinc content is about 8%. Thermal metalplating is done in two manners:

1. continuously, used for mass production of galvanised pipes and plates.
2. discontinuously, used for the finishing of single products, such as bolts or car parts.

Regarding the consumption of zinc, the thermal metalplating industry is an important industry, it consumes about 37% of the world's zinc production [1]. The zinc consumption is still growing in particular because of the increased application of zinc-plated products in cars [2].

3.6.2 Processes and wastes

After pickling and fluxing, products to be treated are dipped, in a bath of molten zinc at a temperature of about 430 - 460°C. The zinc reacts with the iron and steel to form a series of alloy layers on the surface, each successive layer containing a higher proportion of zinc until, in the outer layer, the coating consists of ductile unalloyed zinc. The zinc is thus effectively bonded to the basis metal to form a protective coating with excellent resistance to corrosion and rough handling.

In continuous metalplating, the steel surface is first oxidised by air and then reduced by a mixture of hydrogen and nitrogen gas to obtain the desired surface characteristics. After cooling until 450°C, the zinc is attached to the steel. During continuous metalplating, drosses are produced, the zinc content of which is 80-96%. No other wastes are produced in the process. Condemned products are not dezincing, but sold as low-quality products.

Figure 6 shows the process of discontinuous metalplating and the production of residues.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

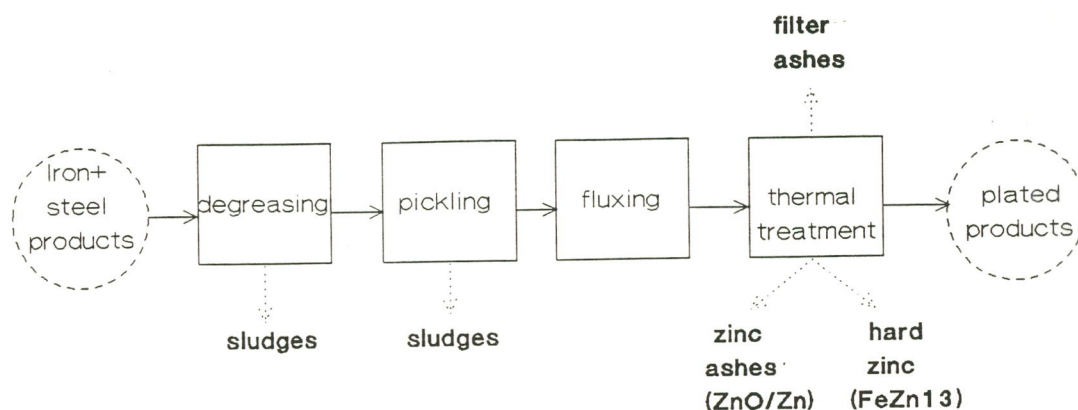


Figure 6 Stages in discontinuous thermal metalplating

In discontinuous metalplating, the products are first degreased and then pickled to remove oxides. The product is either dipped in a separate flux bath ($\text{NH}_4\text{Cl}/\text{ZnCl}_2$ solution) and successively dipped into the molten zinc bath or it is directly dipped into the molten zinc with a flux layer (NH_4Cl salt) on top of the bath. In the Netherlands, five out of the 21 companies use a flux layer. There is a molten lead layer at the bottom of the zinc bath to protect the bottom and collect hard zinc. The product is finally taken out of the bath and dried.

Discontinuous metalplating produces the following wastes [2]:

- Sludges produced during degreasing in the alkaline baths (sand, metal carbonates, metal hydroxides).
- Pickling baths; the exhausted pickling acids contain the following main components: 30-170 g/l of zinc (normally about 100), 40-100 g/l of iron (normally about 100) and some 300 g/l of chlorides. The pickling acids can be used for a considerable period, but must be removed regularly. Zinc originates from the dezincing of old or condemned products, and the baskets in which small products are plated.
- Zinc salmiak slags (only when a flux layer on the liquid zinc is used), with a zinc content of about 50%. The production is < 0.01 ton per ton of zinc applied. They are sold profitably to zinc producers.
- Zinc ashes, zinc oxides containing 80-90% zinc. They are produced because air oxidises the liquid zinc layer. The production is 0.1-0.3 ton per ton of zinc applied. They are sold profitably to zinc producers.
- Drosses, a precipitate of FeZn_{13} ("hard zinc"), containing 94-97% zinc. In the liquid lead layer, the crystals sink to the bottom of the bath and are regularly removed from the bath. The production is 0.1-0.2 ton per ton of zinc applied. They are sold to zinc producers.
- Dusts, from filtering the air above the zinc bath. Until now filtering is not always applied. In the Netherlands the first deduster was installed in 1988; in 1990, 17 of the 21 companies use filtering. The dusts are sold to zinc producers.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 27 gives the chemical compositions of the exhausted pickling acids and dusts from the discontinuous metalplating and the drosses from the continuous metalplating.

In Table 26, the characteristics of wastes from the thermal metalplating are given. The waste production factor is the amount of waste per ton of zinc consumption.

Table 26 Characteristics of wastes from thermal metalplating

Waste	Zn (%)	Pb (%)	Factor
Dross	94-97	0.14	0.15
Ashes	80-90	?	0.2
Pickling acids	10	0.05	0.5
Zinc salmiak slags	50	?	<0.01
Dust	15-20	0.02	0.007

3.6.3 Producers and waste production

Table 28 presents the quantities of zinc-plated products per country in Western Europe as per 1989. In general, about 8% of the steel products consist of zinc.

The data refer to discontinuous metalplating. It is not known whether the data also include continuous metalplating [3]. It is assumed that the data refer only to discontinuous metalplating, except for the Netherlands where continuous metalplating is included in the figures (193 kt/y discontinuous and 17 kt/y continuous) [2].

Also given in Table 28 are the quantities of the residues produced per country. The production figure of the residues is the zinc amount of the plated products multiplied with the factor from Table 26.

According to Dutch regulations, the exhausted pickling acids are classified as a hazardous waste. The acids produced in the Netherlands with a zinc concentration > 10%, are now treated by Wocklum at Balve in Germany at considerable costs (US\$ 125-150 per ton of waste [2]). The thermal metalplating industry in the Netherlands is under pressure of the authorities to realise the treatment of pickling acids in the Netherlands.

Wocklum also treats pickling acids from the German metalplating industry. The chlorides are used for the production of barium chloride. The remainder, probably a waste material, is further treated on site or in the chemical industry.

3.6.4 New technologies and developments

Pickling acids are the only residue worth developing a treatment route, since all the other residues from the thermal metalplating are presently well treated.

TNO's Department of Environmental Technology is currently involved in developing a process for the recovery of zinc from pickling acids. This process is based on solvent extraction with tributylphosphate as an extractant. Zinc is selectively removed from the acid and is finally collected as a high-purity zinc sulphate. From the experimental work it was concluded that the process offers good perspectives. At present, pilot-plant experiments on a 40-80 l/h scale are in progress [4].

3.6.5 References

- [1] Metal Statistik 1979-1989, Metallgesellschaft, Frankfurt am Main, 1990.
- [2] Information from Mr P.J. Meijer, RIVM/LAE, 1990 (in Dutch).
- [3] Information from the European General Galvanisers Association.
- [4] TNO, Department of Environmental Technology, 1991.
- [5] Second symposium on environmental control in the steel industry, 1979, pp. 2/8/145/1-7.

Table 27 Chemical compositions of residues [2, 5], all data in %

Compound	Exhausted pickling acids ¹	Dusts ²
zinc	3-17 (aver. 10)	15 - 20
lead	0.05	0.02
iron	4-10 (aver. 10)	0.56
cadmium	0.002	<0.01
aluminum	-	0.32
tin	-	0.04
chloride	3-30	55.0
ammonium	-	26.0
grease	-	2.0
water	remainder	2.0

¹ on wet basis

² on dry basis

*Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes**Table 28 Production of zinc-plated products and residues in Western Europe, 1989 [3]*

Country	Production (ktons/y)	Dross (ktons/y)	Ashes (ktons/y)	Pickling acids (ktons/y)
Germany	881	10.6	14.1	35.2
Italy	773	9.3	12.4	30.9
France	562	6.7	9.0	22.5
UK + Ireland	528	6.3	8.4	21.1
Spain	221	2.7	3.5	8.9
Netherlands	210	2.5	3.4	8.4
Belgium	152	1.8	2.4	6.1
Denmark	100	1.2	1.6	4.0
Portugal	39	0.5	0.6	1.6
Sweden	103	1.2	1.6	4.1
Norway	70	0.8	1.1	2.8
Finland	70	0.8	1.1	2.8
Switzerland	101	1.2	1.6	4.0
Austria	91	1.1	1.5	3.6

3.7 Electro metalplating industry

3.7.1 General

In the electro metalplating industry a metal layer is applied on steel products. The main metals used are zinc, nickel, copper, and chromium. Very often producers apply different metals at one single plant. The thickness of the zinc layer applied electrochemically is 5-25 µm, compared to 50-150 µm for thermal metalplating.

Thus, the consumption of zinc in the electro metalplating industry is much lower than that in the thermal metalplating industry. The electro metalplating industry consumes about 2% of the world zinc consumption, whereas 37% is consumed by the thermal metalplating industry.

Processes in the electroplating industry can be divided into pretreatment, main process, and post-treatment. During pretreatment, the surface is cleaned; during the main treatment a nonoxidising layer is applied electrolytically. Post-treatment applications are colouring or painting with the objective to protect the surface.

3.7.2 Processes and wastes

In the electro plating industry, baths are used for the various process steps. Bath used for zinc plating are [1]:

- Degreasing baths.
- Pickling baths, for the removal of the metal oxides in:
 - dilute sulphuric acid,
 - dilute HCl,
 - acetic acid;
 - sodium hydroxide,
 - sodium cyanide,
- Zinc plating baths, containing:
 - zinc chloride, ammonium chloride,
 - zinc cyanide/hydroxide, sodium cyanide/hydroxide,
 - zinc sulphate, ammonium chloride/sulphate.

After the baths have been used intensively, they are neutralised in a wastewater treatment plant where the heavy metals are precipitated as hydroxides. This results in a sludge or filtercake which usually has to be disposed of as a hazardous waste. Also treated is contaminated waste water, in which the plated products are rinsed.

In practice, different baths and waste water are often mixed before neutralisation and because of this the waste sludge will contain a variety of components. Figure 7 presents the process in which the sludge is produced.

The exhausted pickling baths are separately removed as waste. The baths also contain several metals.

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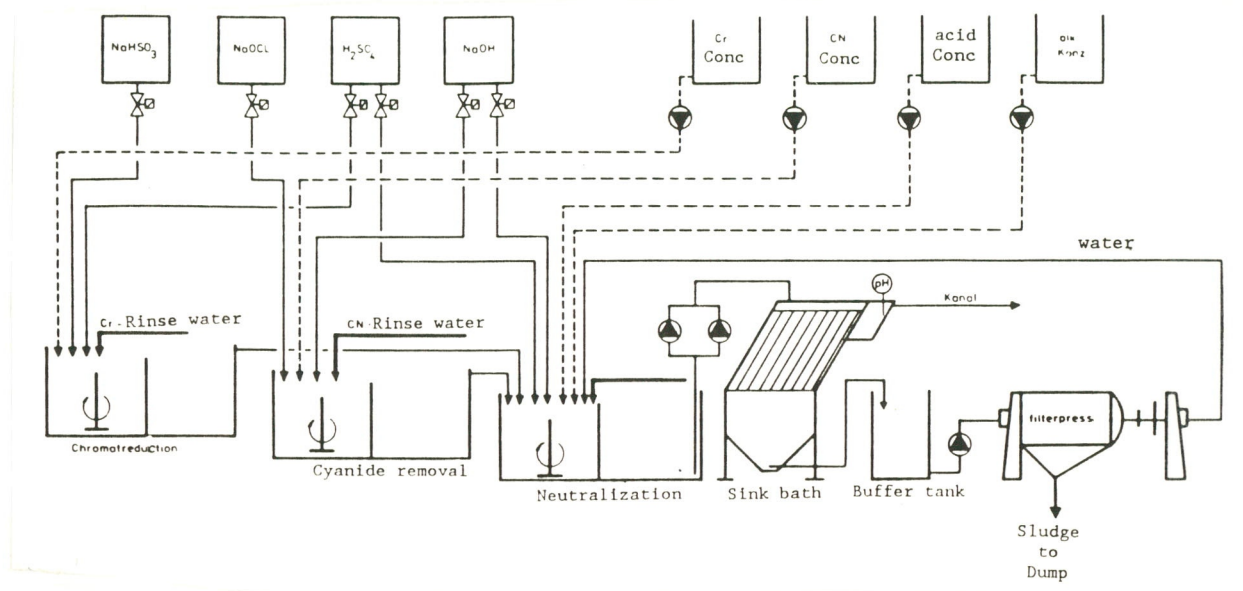


Figure 7 Flow scheme for detoxifying and neutralizing waste water and baths

As an average for metalplating, the sludge produced contains 63% water and 5% heavy metals [2]. Table 30 gives the composition of the sludge.

In Table 29, the waste characteristics are given. The waste production factor is given as the amount of zinc (ton) in the sludge per ton of consumed zinc.

Table 29 Characteristics of waste from the electro metalplating industry

Waste	Zn (%)	Pb (%)	Factor
sludge	7.6 - 9	0.01 - 0.44	0.1

3.7.3 Producers and waste production

Details about the quantities of electroplated products produced are not directly available. This is caused by the fact that electroplating and thermal metalplating are combined in statistics. The main results of an inquiry held at national associations in Europe to obtain production and sludge production figures were:

- UK: No information available.
- Germany: Producers are not linked together.
- Italy: There is no production of galvanic sludges.
- Spain, Sweden, Austria, Belgium, Switzerland, France: No reaction at all.

Literature [3] mentions the zinc consumption by the galvanising industry, including electro and thermal metalplating, for most European countries. It is assumed is that 4% of this zinc is used for electro metalplating [5].

If the figure for the galvanising industry was not available, the entire annual zinc consumption was used for the calculations, assuming 2% to be used in the electro metalplating industry.

On the basis of figures from the Netherlands, a rough estimation for the production of sludges in Europe can be obtained [2, 4]:

1. The annual zinc consumption by the electroplating industry is 1000 tons.
2. The total amount of zinc in the wastes is about 100 tons. It is assumed that all zinc is precipitated in the sludges. On the basis of the Dutch figures, the production factor of zinc in the sludge for the electroplating industry is 10% of the zinc consumption in the electro metalplating industry.
3. The amount of zinc in the sludge is 0.4% of the zinc consumed in the entire Dutch galvanising industry or 0.2% of the Dutch annual zinc consumption. A figure for the separate sludges cannot be given since the sludges are very often mixed.

In Table 31, the amount of zinc in the sludges is given. On basis of the assumptions, it is calculated that in Europe approximately 2800-3500 tons of zinc are disposed of by sludges from the electro metalplating industry.

For some countries, especially the South European ones, it is uncertain whether sludges are produced. In Italy, wastewater equipment is not used and therefore no sludges are produced.

Sludges with a mixture of metals (almost all zinc containing sludges) are disposed of in secured landfills. Sludges containing only one metal, such as nickel, cadmium or copper, are sometimes treated and the metals recovered.

The sludges in Germany and the Netherlands are disposed of in chemical waste storage basins [5].

The amount of exhausted pickling baths in the Netherlands is small, about 200 tons/y, containing about 22 tons zinc [4].

3.7.4 New technologies and developments

A promising approach to reduce the wastes produced are the so called “process-integrated measures”. This means either that revision of the process is accomplished in order to avoid residues or that processes are implemented in order to recover metals from process liquors that contain single metals. Examples of these recovery techniques are solvent extraction and membrane electrolysis. An overall decrease of 20-40% in the amount of sludges should be obtainable with these measures [2].

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

3.7.5 References

- [1] Oppervlaktebehandeling materialen, deel 1 metalen, VOM, 1981 (in Dutch).
- [2] Galvanische bewerkingen, VOM, 1991 (in Dutch).
- [3] Metallstatistik 1979-1989, Metallgesellschaft, 1990.
- [4] TNO, Department of Environmental Technology, 1991.
- [5] Johnen H., Zink-Taschenbuch (in German), Metallverlag, 1981.
- [6] Mr Scheepens, Metaalinstituut, TNO.
- [7] Statistical yearbook 1989, Metaleurop, 1990.

Table 30 Average composition of sludges from electro metalplating industry on the basis of dry substance. All data in %

Situation in	Germany [6]	the Netherlands [4]		
		Range		Average
zinc	8.9	3.5	- 16	7.6
lead	0.44	0	- 0.022	0.010
iron	8.9	4.3	- 38	16
cadmium	0.04	0.0001	- 0.9	0.31
nickel	1.6	0.0001	- 0.1	0.05
chromium	3.3	0.2	- 4.0	1.6
copper	1.7	0.007	- 1.5	0.6
aluminum	-	0	- 1.6	0.5
tin	-	0.004	- 1.6	¹
chloride	-	11.5	- 13.3	¹
sulphur	-	0.2	- 3.8	¹

¹ only 2 data available.
The water content of the sludge is 55-76%, average 63% (Ref. 8)

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 31 Zinc use and wastes in the electro metalplating industry in Europe, 1989 [7]

Country	Total consumption (tons)	Galvanising ¹ (tons)	Amount of zinc in sludge (tons)
Germany		153240	580 - 700
Belgium/Luxemburg	174900	?	320 - 390
France		141400	530 - 650
UK		104300	390 - 470
Italy		129500	470 - 570 ²
The Netherlands		27000	100 - 120
Spain		51800	200 - 240 ²
Greece	19900	?	30 - 50 ²
Denmark	10900	?	10 - 30
Portugal	11000	?	10 - 30 ²
Austria		23000	90 - 110
Norway	21200	?	30 - 50
Sweden	42100	?	70 - 90

¹ Both thermal metalplating and electro metalplating.

² Probably no sludges are produced.

3.8 Basic metal industry

3.8.1 General

In the basic metal industry products are made of either pure metals or alloys. After melting the liquid metals are shaped into a cast, in which the metals solidify into the final product.

Zinc or lead containing residues can be produced only where zinc or lead are present in the melting operation. The basic metal industry using zinc and/or lead can be divided into different sectors:

- a. iron foundries;
- b. light metal casting (zinc-aluminum alloys);
- c. copper alloy casting (brass and bronze foundries).

ad a: Iron foundries:

The iron foundries do not produce zinc or lead containing products. However, when the source material, for example galvanised scrap, is contaminated with zinc or lead, waste containing zinc or lead is produced as dust in the melting operation.

ad b: The light metal casting:

Die-casting is the process most often used for shaping zinc alloys. Other components, besides zinc, are aluminum (3.5-28%), copper (0.25-2.5%), and small amounts of magnesium, iron, lead, cadmium, and tin. These metals are added to improve the strength and the workability of the products. The metals are melted in a furnace and shaped in a die-casting machine.

The automotive industry is by far the largest user of zinc alloys. Applications are all kind of mechanical parts, e.g. carburettors and grilles. Other uses of zinc alloys are tools and mechanical parts in all kinds of machines.

ad c: Copper alloy casting:

Copper brass is an alloy of zinc and copper. It is melted and cast into a mould. Brass is used for a range of applications, such as ornaments and plumbing goods.

Bronze is an alloy of copper and tin. Sometimes zinc and lead are added to improve the characteristics of the alloy.

3.8.2 Processes and wastes

3.8.2.1 Iron foundries

Cupola furnaces, electric furnaces, and reverberatory furnaces are commonly used for the melting process. The raw materials used are pig iron, scrap, return material from the foundry, coke and limestone, silicon briquettes, carburising graphite, and melt treatment. Scrap contains paint residues, galvanic coats, and nonferrous metals. In general, the percentage of scrap is 60-70% [1]. The liquid iron is poured into molds and allowed to cool, after which the casting is shaken out of the mould.

During the melting of iron, volatile particles, e.g. zinc and lead, are emitted as dust [2]. No dusts are produced during the melting of steel [1].

The composition of the dust from an iron foundry is given in Table 33 [3]. The zinc content is 1%, the lead content 2%.

3.8.2.2 Zinc-aluminum alloys

The temperature (390-420°C) at which the zinc alloys are die-cast is just above the melting point of the alloy, which is about 387°C [4]. The emission of dust containing metals, therefore, hardly occurs; the emission factor is 0.004 kg of zinc oxide per ton of melt [2].

3.8.2.3 Copper alloys

The melting temperature of copper brass is 1083°C. As the melting temperature is higher than the boiling temperature of zinc (906°C), a fraction of the zinc will vaporise. After oxidation with oxygen from the air a zinc oxide is formed. This zinc oxide, which contains a small amount of copper, can be collected in a baghouse filter.

Also slags are formed at the surface of the smelting bath as a result of the oxidation of zinc and copper. The slags can be returned to the primary producers [5].

The zinc/copper ratio in the slags is almost the same as in the alloy, on the average 30% zinc and 70% copper. The zinc content in the ashes can amount up to 60%, most zinc is present as zinc oxide. Also some copper will evaporate and collect in the ash. More information about the composition of both residues is not available.

3.8.2.4 Waste characteristics

Table 32 gives the characteristics of waste from the foundries. The waste production factors are the amounts of waste (tons) per ton of produced castings.

Table 32 Characteristics of waste from foundries

Waste	Zn (%)	Pb (%)	Factor ton/ton
Cupola dust iron foundry	1.0	2.1	0.0075 - 0.009
Zinc die casting dust	?	?	0.000004
Ashes brass foundry	60	?	0.044
Slags brass foundry	30	?	0.120

3.8.3 Producers and waste production

3.8.3.1 Iron foundries

The amount of iron used in foundries in the EC is given in Table 34. Separate data for the three types of furnaces are not available. In the Netherlands, there are 30 foundries, 6 of which use cupola furnaces, sometimes in combination with electric furnaces [1].

The amount of dust produced is [2, 6]:

- Cupola furnaces: 5 - 18 kg/ton of melt.
- Reverbatory furnaces: 0 - 1 kg/ton of melt.
- Electric furnaces: 0 - 1 kg/ton of melt.

In the Netherlands, the production of cupola furnace dust is 1,000-1,200 tons/y. The amounts of dusts from the other types of furnaces is much smaller.

The amount of iron used in the Dutch iron foundries is 133 ktons/y. The production factor for cupola furnace dust is, therefore, 7.5-9 kg/ton iron. The production of cupola furnace dust in the EC is calculated with this factor. Data are given in Table 34. It is assumed that the Dutch ratio between the production in cupola furnaces and that in the other furnaces is valid for the EC.

The dusts produced in the Netherlands are disposed of in a secured landfill.

3.8.3.2 Zinc-aluminum alloys

As mentioned, the amount of waste per ton of product is very low. Therefore, no effort has been made to provide data on producers of waste.

3.8.3.3 Copper alloys

The European production of brass is concentrated in the region between Lyon, France, and Bréscia, Italy. Germany is another large producer. The consumption of zinc in brass for most Western European countries is given in Table 35. No data are available for the other countries. Zinc present in brass scrap is not included. In general, about 30% of the brass produced consists of zinc.

In the Netherlands, the amount of zinc consumed is 11 kton/y by 2 brass foundries. The amount of ashes produced is 485 tons/y, which gives a factor of 44 kg ash/ton of consumed zinc. The amount of slags produced is 1,300 tons/y, which gives a factor of 120 kg slag/ton of consumed zinc.

The production of brass in the Netherlands for the two production sites is 30 ktons/y (Boliden) and 33 ktons/y (Outokumpu).

The slags and the filter dusts are sold. This covers the costs for the whole waste disposal [8].

The European production of ashes from the brass industry is estimated at 6,000 to 7,000 tons/y [7]. According to the calculations in Table 35, it is 19,000 tons/y. Annual fluctuations in the amount of wastes per producer, the percentage of scrap used, and the fact that the calculations are based on two producers may account for the difference.

3.8.4 New technologies and developments

The companies Rezinal in Belgium and Gambari in Italy are planning to set up a plant for the treatment of ashes from the brass industry. The plant is planned at Bordeaux in France, with a capacity of 2,500 tons/y. It is still uncertain whether the processing will take place by means of a hydro- or a pyrometallurgical process. The advantage of the hydrometallurgical process is the higher efficiency of recovery of zinc and copper, but the residue is more difficult to dispose of because of the approximately 20% water content. However, Rezinal claims to have found a company that is willing to pay for the residue. The amount of residue is approximately 1,500 tons/y.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

3.8.5 References

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- [2] Handbook of Emission Factors, VROM.
- [3] Information from Leto Recycling, The Netherlands.
- [4] Materials and Technology 3, Metals and Ores, Longman & De Bussy, 1970.
- [5] Kunes T., Solid waste disposal, CRC-press, Boca Raton, USA, 1987, pp 57-82.
- [6] Information from AGA Gas, the Netherlands.
- [7] Information from Mr F. Strubber, Rezinal, Belgium.
- [8] Information from Outukumpu, The Netherlands.
- [9] Industrial Statistics Yearbook 1985, UN.
- [10] Metall Statistik 1979-1989.

Table 33 Chemical composition of a typical iron foundry dust [3]

Compound	Concentration (%)
zinc	1.0
lead	2.1
arsenic	0.019
mercury	0.00025
nickel	0.0061
copper	0.062
chromium	0.036
cadmium	0.0012

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 34 Iron consumption in foundries and production of cupola furnace dust in Western Europe, 1990 [1]

Country	Iron (ktons)	Cupola dust (tons)
Belgium	161	1200 - 1400
France	2034	15000 - 18000
Germany	3369	25000 - 30000
Greece	140 ¹	1100 - 1300
Italy	1406	11000 - 13000
UK	1121	8400 - 10000
Portugal	83	600 - 700
The Netherlands	133	1000 - 1200

¹ data from 1985 [9].

Table 35 Zinc bullion consumption in brass in Western Europe, 1989 [10]

Country	Consumed Zn (ktons/y)	Ashes (tons/y)	Slags (tons/y)
France	56	2500	6600
Germany	118	5200	13900
Italy	188	8300	22200
United Kingdom	51	2200	6000
the Netherlands	11	485	1300
Spain	11	485	1300

3.9 Primary and secondary lead production

3.9.1 General

Throughout the world, 5.8 million tons of lead are produced annually. The total production in Western Europe is 1.6 million tons [1]. Applications of lead can be divided into two main groups: alloys and lead compounds for chemical applications.

Lead production processes are based on smelting of the lead containing input materials, followed by separation of liquid lead (bullions) and slag materials. After the separation, the lead is refined to standard quality grades. Three lead grades are produced: a) soft (pure) lead, b) hard (containing antimony) lead, and c) alloys (containing e.g. copper, calcium, tin).

In the primary industry, concentrated ores, having a lead amount of 40-70% (mostly 70%), are used. The lead-containing mineral is predominantly galena (PbS). Zinc concentrations are up to 15%; other metallic impurities are: gold, silver, copper, arsenic, antimony, iron, and bismuth [2].

In the secondary lead industry, accumulators are the main feed materials. The recycling rate for accumulators is high, 86% in Europe. The used accumulators are usually shredded into mud. This mud contains 68.9% lead, 0.45% antimony, 0.04% arsenic, the rest are sulphates, water, and polystyrene [3].

Other lead scrap is usually high-grade lead collected from sheets, pipes or cable sheathings. The purity of the produced lead is not such that it can be used as soft lead.

There is a considerable production of lead at plants that are specialised in treating scrap. These plants generally operate at a much smaller scale than the primary producers. Due to more stringent environmental regulations and economy-of-scale effects, the number of secondary lead producers has been decreasing since the early 1980s.

Electrolytical processes are also used for treating accumulators [3,4]. At the moment, only one process is operating on a commercial scale in Europe, i.e. at Nuova Samin, Italy.

Recycled lead is also used in the primary lead production by adding scrap with the concentrated ores to the furnace.

3.9.2 Processes and wastes

3.9.2.1 General

Figure 8 presents the basic route from ores/scrap to refined lead and slags for both primary and secondary production. It is important to mention that not all these steps are necessarily performed in each process. The only steps that all processes have in common are smelting and refining. The necessity of the other steps depends on the kind of process and the feed materials. Some given steps can be performed together, such as the smelting of feed materials and the immediate reduction in a blast furnace of lead oxides to metallic lead in the slags.

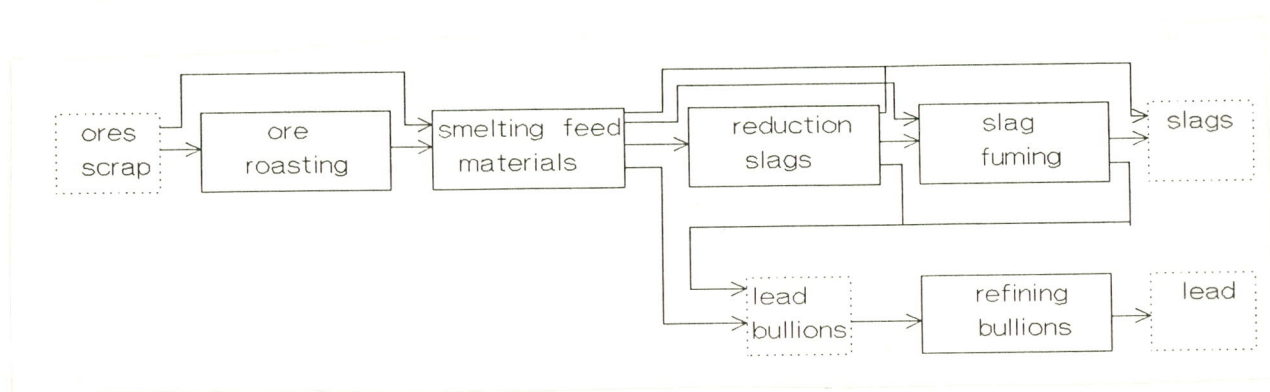


Figure 8 Principles of lead production

3.9.2.2 Smelting

Several pyrometallurgical processes are applied for the primary production of lead bullions from concentrates. In each process, lead-containing slags and flue dusts are formed. The temperature in all the smelting processes is about 1150°C. Valuable metals in the slags, especially zinc, are, if profitable, separated by additional processing, like zinc fuming. Because of the relatively low lead prices, recovery of lead from the slags is not economically profitable for a lead content below 25% [5]. The remaining slags are disposed of in landfills.

The flue dusts from the smelting operations are recirculated in the furnace or sintering plant.

The Blast Furnace and Imperial Smelting are the processes that are mostly used. Smelting processes for the production of lead bullions from concentrated ores are:

- Blast Furnace (BF) process;
- Imperial Smelting Furnace (ISF);
- Top Blown Rotary Converter (TBRC) or Boliden Kaldo process;
- Outokompu Lead Flash Smelting (OLFS) process;
- Electric Furnace (EF) process by Boliden;
- Queneau Schuhmann Lurgi (QSL) process;
- Kivcet CS process.

For many years, the Blast Furnace process has been the standard process for primary lead production. But environmental regulations, especially for SO₂, tend to make other processes more favourable. These processes are yet not widely used or are even in a pilot stage.

Metaleurop (3 primary BF) believes that the BF can be improved in such a way that it will be economically and environmentally healthy. They expect that the operating profits from new technologies (like QSL and Kivcet) are insufficient to meet the required very high investments [20].

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Metallgesellschaft has developed the QSL-technology to a level in which it is commercially operating. The results from the QSL-plant in Stolberg, Germany, show that this technology is capable of successful operation. The originally installed electric furnace for cleaning the slags has been removed for economic reasons [21].

The pyrometallurgical processes used in the secondary production are comparable to those used in the primary production. A much used process for the secondary production is the Rotary Reverberatory Furnace (RR).

In the BF process, the ore is first roasted to remove sulphur. Fluxes are added to produce a sintered material. Dusts are returned in the process. The sulphur dioxide containing off-gas is transformed into marketable sulphuric acid.

The roasted sinter is charged into the blast furnace, along with suitable fluxes and coke as a reducing agent. Lead oxides and other metal oxides are reduced to metals. The lead serves as a solvent for other (valuable) metallic impurities; it is tapped and transported for refining. The residue (gangue) is separated as slag and removed from the furnace. The lead content of the slag is about 1-4% [6]. The BF is also used for the production of secondary lead from accumulators.

The ISP furnace (see primary zinc production) is also used for the lead production.

In the TBRC process, dried lead concentrate, flux and return dust are charged into the converter. Oxygen-enriched air is injected to carry out the smelting process, as oxidation of the sulphur-containing concentrates is an exothermic process. Once smelting is completed, the air is shut off and the reduction carried out by adding an oxygen-fuel mixture. After reduction, slag with 1-2% lead is skimmed for disposal. Most of the zinc is collected in the slag and transferred to a slag-fuming plant for recovery of zinc and residual lead. Lead bullions are then cast for refining [6].

A similar process is the Isasmelt process, the difference being that Isasmelt uses a stationary furnace [8, pp. 608].

The OLFS uses dried lead concentrates and limestone-, pyrite- and silica-fluxes. These materials are smelted as they descend in the smelter through oxygen-enriched air. Lead is tapped off and a slag containing lead oxide is collected. The slag is reduced in an electric furnace, thereby producing lead bullions and zinc fume. The final waste slag contains 3-4% zinc and 1-3% lead [6].

The Boliden Electric Smelting process is a process which is similar to the OLFS. Lead concentrates are smelted by oxygen addition to the concentrates and then reduced in an electric furnace by adding coke [6].

In the QSL process, pelletised lead concentrates, flux materials and coal are smelted in a horizontal furnace. The charge is oxidised by an oxygen gas stream, which is injected at the bottom of the furnace. In another part of the furnace, coal is added to reduce the metals. Continually, slags and molten metal are separately tapped. Lead is present in the molten metal and can be refined, zinc is collected in the slag. The lead content of the slag is less than 5% [9]. The slags from the QSL plant at Cominco's Trail, Canada, are fumed in a separate furnace. The zinc content decreases from 8-10% to 1-3% [8, pp. 29].

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

The Kivcet CS process uses feed materials that are similar to the TBRC process. The process is based on oxygen smelting, using a shaft furnace in conjunction with an electric furnace. Slag with less than 3% lead and 3% zinc is skimmed and discarded. Lead bullions are tapped continuously for refining [6]. Zinc is recovered by leaching as zinc oxides from the fumes at the Kivcet plant of Nuova Samin, Italy. The leachate is treated in the electrolytical zinc plant [8, pp 913].

In the RR furnace, lead-containing secondary materials, especially the lead-containing parts of accumulators, are charged into the furnace with sinter materials. Oil and air are used to heat the furnace. The lead is reduced to metal and antimony is oxidised. The lead is tapped and further refined. An antimony-rich slag is collected, with a lead content of 3-5%. [10]. Slag cleaning is not performed. If the accumulators as a whole are melted, the amount of slag is 0.9 ton per ton of lead. This process, however, is very polluting and is used only at one plant in Germany.

3.9.2.3 Zinc fuming

Some lead smelters, who treat concentrates with an appreciable amount of zinc, recover zinc by fuming [11]. In some new processes, e.g. the OLFS process, zinc is recovered from the dusts which are produced in the slag-reduction process. At the Kivcet plant of Nuova Samin, Italy, zinc fuming is part of the process.

Boliden performs zinc-fuming primarily for the recovery of zinc from the slags from its copper plant. As the equipment is available, the lead slags are also treated. The slag is contacted with a carbonaceous reductant in a Blast Furnace. Zinc and lead are reduced to metals and vaporise. Both metals are immediately oxidised to a mixed ZnO-PbO fume. This fume is collected after cooling in either a baghouse filter or an electrostatic precipitator. After treatment, a reasonably pure zinc oxide is obtained. The zinc content of the slag is reduced from 8-10% to 1-3%, depending on economic factors. The silica content of the slag must be smaller than 38-40%, because otherwise the remaining slag will cause handling problems.

The Ausmelt process is based on the Sirosmelt process and can also be used for slag cleaning. In this process, fuel and air are injected into the liquid slags. Zinc oxide is reduced to zinc and vaporises. The zinc content of the slags after treatment is < 0.5%. Lead contents are between 0.04 and 0.20% in pilot-plant trials [8, p. 619].

At MHO, Belgium, slags from the BF are cleaned in an electric furnace. The process is profitable because of the feed material contains considerable amounts of precious metals, which are recovered.

The temperature of the liquid slags is 1350°C. Coke, distributed on the top of the bath, is used as a reductant. Zinc is vaporised and collected as zinc oxide. Lead is tapped from the bottom of the furnace. Slags with 7.2% zinc and 2.5% lead are cleaned to 5.7% zinc and 0.6% lead [8, p. 944]. The precious metals are tapped along with the lead, and are recovered during the refining.

3.9.2.4 Refining

Independent of the type of smelting process applied the pig lead has to be refined. Ore-treating plants nearly always perform the refining process as well. Depending on the impurities to be removed, several processes are applied. After smelting, secondary lead from accumulators is very often used for the production of accumulator plates, which makes removal of the antimony unnecessary.

Lead ashes and slags are collected during refining. They can be recirculated or sold because of their high metal content, especially lead.

Arsenic-containing flue dusts are also produced during refining by the primary lead production; they cannot be recirculated. The dusts are disposed of through landfilling or treated. This treatment consists of fuming or leaching processes, which separate the disturbing elements, allowing the remainder to be recycled [12]. In Figure 9, the refining process is given.

The first step in refining is the removal of copper by forming drosses by means of sulphur addition to molten furnace bullion. In secondary lead production, the copper content of the feed material is considerably lower.

In case of a copper-rich feed, sulphur is added, followed by skimming of the dross from the molten lead. The resulting copper-rich drosses are treated in a furnace to produce a high copper matte, which is further treated elsewhere for copper recovery.

In case of low-copper feed materials, soda ash, baghouse fume, coke and sulphur are added. This gives, besides lead bullions, speiss. This can be used as an alloying element.

Furnace kettle refining is based on the higher oxidation potentials of the impurities antimony, arsenic, and tin, in comparison to lead. This process is also called lead softening. The antimony residues are used in the production of lead-antimony. In this process, arsenic-containing flue dusts are collected.

In the Parkes process, noble metals are removed by adding zinc to liquid lead. Zinc decreases the solubility of the noble metals and forms insoluble compounds which can be skimmed off the top of the molten lead bath as the temperature is lowered.

An electrolytic refining process is based on the oxidation of lead with fluorosilicic acid to form lead fluorosilicate. The lead is recovered and the impurities are collected in a slime which is separated and purified for the recovery of valuable compounds [2].

3.9.2.5 Waste characteristics

The compositions of the wastes are given in Tables 40 through 42. The most important waste are the slags. The composition of the slags depend on the composition of the feed materials. Particularly in the secondary production, the slag composition can vary considerably.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

All the wastes are classified as hazardous wastes, according to Dutch regulations. For lead, as a metal and as a metal compound, a waste is classified as hazardous when its concentration is more than 0.5%.

The drosses from the refining section can be sold because of their high intrinsic metal value.

Table 36 presents the basic data for the production of residues in the primary and secondary lead industry. The waste production factor is the amount of waste (ton) per ton of produced lead.

Table 36 Characteristics of wastes from the lead production

Process	Waste	No slag fuming		Slag-fuming		Factor
		Zn (%)	Pb (%)	Zn (%)	Pb (%)	
BF-smelting	slag	6-18	1-4	2	0.6	1.8 ¹ , 0.2 ²
RR-smelting	slag	?	3-5	x	x	0.1-0.2
ISF-process	slag	9-10	5	0.5-1.5	0.04-0.2	1.7
EF-smelting	slag	17	4	x	x	?
TBRC-smelting	slag	15	1-2	1-3	?	?
OLF-smelting	slag	3-4	1-3	x	x	0.11
Kivcet CS	slag	3	3	0.52	1.8	0.7
QSL-process	slag	14.6	<5	1-3	?	0.50
Refining	As-dust	10.3	41.0	x	x	0.1-3*10 ⁻³

¹ primary production,

² secondary production

? = data not known

x = no slag fuming

3.9.3 Producers and waste production

In Table 37, the primary and secondary producers of lead in Western Europe are given [1, 13]. There are 13 primary and 37 secondary producers. Stated in the table are company name, location, capacity, and kind of process.

Data of the production per company are not available. However, when the total production of primary and secondary lead per country is compared with the total capacity per country, an estimation of the production can be obtained. The total production per country is divided by the total capacity per country. This factor is assumed to be representative for all companies in that country. This factor is also given in Table 37 for each country: it varies per country between 35 and 100%, but the average for the large, producing countries is 73-88%.

The United Kingdom (210,000 tons), Germany (242,000 tons), and France (150,000 tons) are the largest producers of primary lead.

The United Kingdom (272,000 tons) and Germany (261,000 tons) are also the largest producers of secondary lead.

In Table 38, the quantities of produced residues for the primary production per country are calculated by combining the production with the residue production factors of Table 36 for the used process. This is necessary since the production of residues is dependent on the production and not on the capacity.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

The disposal routes for the slags from primary production are landfilling or use as a construction material (slags from Kivcet in the USSR).

In Table 39, the produced quantities for the secondary lead industry are given. The slags from Billiton, the Netherlands, are presently landfilled in Germany at a cost of US\$ 150 per ton [16]. The slags from Metallgesellschaft, Braubach, are partly landfilled and partly used in the primary lead production. The relative amounts are not known. The landfilling will be ended in the near future [14]. The alternative is not known.

Some producers have stockpiles of old slags at their factory site. Metaleurop in Noyelles Godault [5] is an example of this. Names of other producers are not known; information is not available at all.

3.9.4 New technologies and developments

Arsenic-containing flue dusts are produced in the dressing operation. The arsenic content of approximately 10% prevents the dust from being recycled. In an experimental study [15], the flue dust is leached with sulphuric acid. Lead and silver remain unsolved and can be recycled back to the smelting process. Arsenic, zinc, cadmium, and indium are solved in the acid. The arsenic is selectively removed from the solution by precipitation with $\text{Fe}_2(\text{SO}_4)_3$ and CaCO_3 . Zinc can be recovered by standard electrolytical zinc processes.

Cadmium from flue dusts has to be removed as the cadmium concentration reaches 5%. Several methods exist for this removal [12]:

- The dust can be fumed to form a concentrated cadmium product, which can be electrolytically refined.
- Treatment of the dust with chlorine gas, followed by precipitating the cadmium with zinc.
- Concentration of the dust by fuming, followed by acid leaching. The cadmium is then precipitated from the leach solution with zinc.
- Direct leaching of the dust with sulphuric acid. The cadmium is recovered from the leach solution by electrolytical methods.

3.9.5 References

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Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

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Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 37 Primary and secondary lead production in Western Europe [1, 13]

Company	Location	Capacity (Kt/yr)	Process
France		302	prod:267 (88%)
Metaleurop SA	Noyelles Godault	40	ISF-TRaf
		110	BF-TRaf
	Villefranche-sur-Saone	402	RR-TRaf
	Escaudoeuvres	272	RR-TRaf
Societe de Traitement Chimique des Métaux	Toulouse	252	RR-TRaf
	Bazoches-les Gallerandes	302	RR-TRaf
Métal Blanc	Bourg Fidèle	102	RR-TRaf
G.A.S.T.	Point Sainte Maxence	202	TRaf
Germany		461	prod:350 (76%)
Berzelius Metallhütten	Duisburg-Wanheim	32	ISF
	Binsfeldhammer	90	BF-TRaf
Blei-und Silberhütte Braubach (Metallgesellschaft)	Braubach	40 ¹	2RR-TRaf
Norddeutsche Affinerie Aktiengesellschaft	Hamburg	30	BF-TRaf
Metaleurop Weser Blei	Nordenham	90	BF-TRaf
Metaleurop Harz Metall	Oker	70	2TRaf
Alfred Bauer	Berlin	6	2RR-TRaf
Metallhüttengesellschaft Schumacher	Rommerskirchen	15	2RR-TRaf
Varta Batterie A.G.	Krautscheid	30	2BF-TRaf
Hetzel & Co GmbH	Nürnberg	20	2RR-TRaf
VEB Albert Funk	Muldenhütten	80	2BF-TRaf
Belgium		160	prod:93 (58%)
Métallurgie Hoboken- Overpelt	Hoboken	125	BF-TRaf
Chemisch Metallurgische Bedrijf Campine	Beerse	10	2BF-TRaf
Fonderie et Manufacture des Métaux	Bruxelles	25	2RR-TRaf
Spain		155	prod:113 (73%)
Sdad Minera y Metalurgica de Peñarroya España	Carthagène	90	BF-TRaf
Tudor	Soria	44	2RR-TRaf
Derivados de Minerales y Metales	Barcelona	5	2TRaf
Metalurgia de Cubas SA	Madrid	10	2TRaf
Elacon SA	Murcia	6	2TRaf
Greece		20	prod:7 (35%)
E.M.M.E.L.	Lavrion	20	BF-TRaf
Ireland		27	prod:12 (44%)
Metal refiners	Dublin	27	2TRaf
Italy		210	prod:181 (86%)
Nuova Samin S.p.A.	San Gavino	35	El-TRaf
		35	TRaf
	Paderno-Dugnano	50	2BF-TRaf
	Marcianise	40	2RR-TRaf
	Porto Vesme	30	ISF
		100	Kivcet
Metalli Derivati	Arcola	15	2RR-TRaf
Plomboleghie	Brugherio	15	2RR-TRaf
Plombifera Bresciana	Maclodio	20	2RR-TRaf

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 37 continued Primary and secondary lead production in Western Europe [1, 13]

Company	Location	Capacity (Kt/yr)	Process
the Netherlands		55	prod:42 (76%)
Hollandse Metallurgische Industrie Billiton	Arnhem	35	2RR-TRaf
Uzimet	Delft	20	2TRaf
Portugal		7	prod:7 (100%)
Metal Portuguesa Sarl	Castanheiro do Ribatejo	7	2RR-TRaf
United Kingdom		442	prod:350 (79%)
Brittania Refined Metals Ltd	Northfleet	170	TRaf
		23	2TB-TRaf
Brittania Recycling Ltd	Wakefield	30	2RR-TRaf
Cookson Industrial	Newcastle-upon-Tyne	95	2RR-TRaf
Commonwealth Smelting Ltd	Avonmouth	40	ISF
H.J.Enthoven & Sons	Darley dale	60	2RR-TRaf
B.L.M.Girdler	London	14	2TRaf
B.L.M. North	St. Helens	14	2TRaf
B.L.M. South	Welwyn Garden City	14	2TRaf
Wilson & Jubb Ltd	Leeds	10	2RR-TRaf
Capper Pass & Sons Ltd	North Ferriby	12	2BF-TRaf
Sweden		125	prod:71 (57%)
Boliden Metall AB	Rönnskar	65	EIF-TRaf
		20	TB
Boliden-Bergsoë AB	Landskrona	40	2TB-TRaf

¹ melting of non shredded accumulators

Definitions of Processes:

2: secondary production
 BF: Blast Furnace
 ISF: Imperial Smelting Furnace
 RR: Rotary Reveratory Furnace
 EIF: Electric Furnace
 TB: Top Blown Rotary Converter
 EI: Electrolytical process
 TRaf: Thermic Refining

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 38 Production of residues from primary industry in Western Europe [Ref 1, 13]

Country	Slag (Kt/yr)	Process	Flue dust (tons/yr)	Amount Pb (tons)	Amount Zn (tons)
France	60	ISF		3000	5800
	175	BF		4375	21000
Germany			198	81	10
	41	ISF		2050	3900
	287	BF		7175	34400
Belgium			239	98	12
	131	BF		3275	5700 ¹
Spain			109	45	5
	119	BF		2975	14300
Greece			99	41	5
	13	BF		325	1600
Italy			11	5	1
	44	ISF		2200	4200
	60	Kivcet		1080	300 ¹
United Kingdom			45	19	2
	57	ISF		285	5500
Sweden			201	82	10
		EIF		?	?
			56	23	3

¹ Slag fuming taken into account.

Table 39 Production of residues from secondary industry in Western Europe

Country	Slag (Kt/yr)	Process	Amount lead (tons)
France	15	RR	590
Germany	42	RR	1700
	17	BF	425
Belgium	1	BF	25
	2	RR	70
Spain	4	RR	160
Italy	9	BF	225
	10	RR	390
the Netherlands	3	RR	120
Portugal	1	RR	33
United Kingdom	?	TBRC	?
	19	RR	770
Sweden	2	BF	50
	?	TBRC	?

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 40 Chemical composition of lead smelter slags

Process: Ref:	BF [2,11] ⁺	RR [16] [*]	ISF [14] [*]	EF [11] ⁺	TBRC [11] ⁺	OLFS [6] ⁺	Kivcet [17] [*]	QSL [8] [*]
lead	1-4	3-5	5.4	4	1-2	1-3	1.8	<5
zinc	6-18 ¹	-	9.6 ¹	17 ¹	15 ¹	3-4	7.7 ¹	14.6 ¹
copper	0.2-0.4	-	2.4	0.08	-	12-14	2.2	0.1
iron	25-30	20-35	29.1	8	22	14-21	20.5	28.0
silica	20-25	2.5-5	7	24	23	11-13	16.0	-
aluminum ox	1.5-2.5	-	5	-	-	-	-	7.0
manganese ox	2-5	-	-	-	-	-	-	-
calcium ox	9-20	1-2.5	17.7	34	20	-	22.7	13.8
silver	0.0006	-	0.012	-	-	-	-	-
sulphur	2	10-15	0.2	-	-	0.1-0.2	1.4	0.3
magnesium	-	-	1.4	-	-	-	-	-
arsenic	-	<2	0.33	-	-	-	-	0.1
antimony	-	<2	-	-	-	-	-	0.2
sodium ox	-	13-27	-	-	-	-	-	-

All data in mass %.

¹ Before slagfuming

⁺ Representative for whole industry

^{*} Based on data from one production site

The state of the lead is metallic for 85%; the remainder is in the form of sulphides and oxides. Specific gravity is 3.6 g/cm³.

Both metal and salt components are observed. Lead is present as Pb₃O₄, PbCl₂ and PbO.PbSO₄. Zinc is present as ZnS, ZnO, and ZnSO₄.

Table 41 Chemical composition of dross from the refining section from Billiton, the Netherlands [16]

Compound	Concentration
lead	67.0
zinc	0.68
iron	0.8
antimony	8 - 11
insolubles in 200-350g HCl:	6.5

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 42 Chemical composition of arsenic containing flue dusts [12, 18, 19]

Compound	Concentration (%)		
lead	30	-	55
zinc	0.01	-	11
iron	0.3	-	0.4
copper	0.001	-	1.0
antimony	0.01	-	3.5
cadmium	0.01	-	10
arsenic	0.01	-	10
nickel	0.002		
sulphur	4.5		
chloride	0.14		
indium	0.26		

The dust are finely divided material (85 weight % < 400 mesh, 25% < 20 µm).

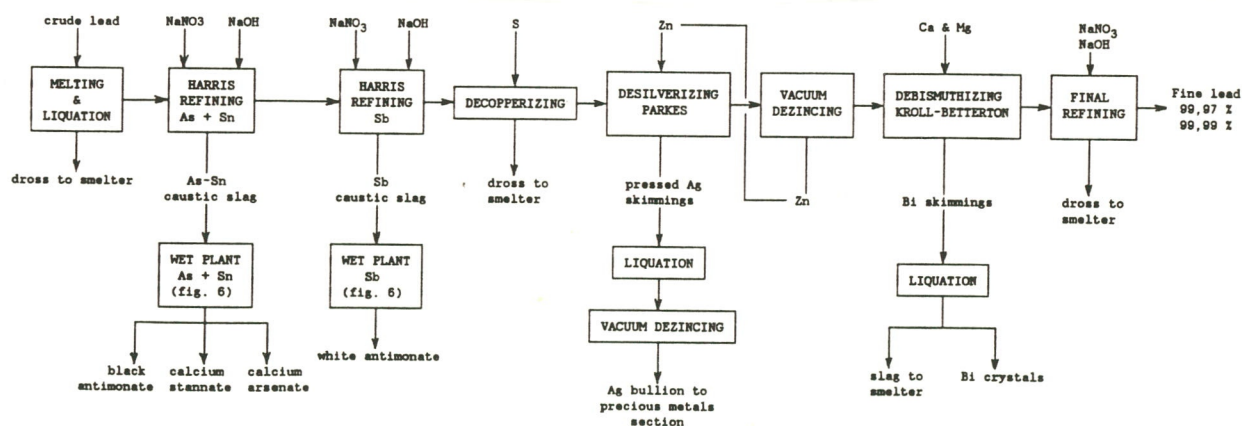


Figure 9 Flow-sheet of lead-refining

3.10 Accumulator industry

3.10.1 General

The accumulator industry is the most important consumer of lead. Accumulators are primarily used as car starter batteries. Other areas of application are: drive batteries for electric carrier vehicles; and fixed-installation batteries used to provide emergency power supplies. The most widespread operating principle is the lead-sulphuric acid system. To illustrate the importance of this industrial sector, some data are given.

In Europe, approximately 1.5 million tons of lead are consumed annually; the accumulator industry consumes 700,000 tons per year (46%).

Approximately 80% of the batteries produced are starter batteries, the remaining 20% are industrial batteries. In 1985, about 30 lead accumulator manufacturers existed in the EC.

The recycling rate in this industrial sector is very high; in the European accumulator industry approximately 600,000 tons/y of lead are used from secondary material (86%) [1]. In Germany, the recycling rate is even higher: more than 95% of the lead used in accumulators is recycled [2].

3.10.2 Processes and wastes

The accumulator consists of lead-antimony plates, sulphuric acid, separators, and a plastic container. The plates are covered with the active materials, either pure lead (negative electrode) or lead oxide (positive electrode). The plates serve as a support for the active materials and for conducting the current. The separators are microporous sheets made out of paper, rubber, glass or plastic.

The lead-antimony plates are manufactured by casting. The antimony content varies between 2 and 12%. The melting pot is heated either electrically or by gas to 427-524°C. The pot capacity is over 100 kg of alloy. Drosses from the molten metal are periodically removed by skimming. Fumes are collected in baghouse filters. The molten alloy is then poured into a preheated grid mould.

After cooling, the cast plates are separated from the mould and minor imperfections, e.g. rough edges, are removed.

The active materials are not directly pasted on the plates. On the positive electrode, PbO and some (<20%) Pb₃O₄ is pasted on the plate. On the negative electrode, mainly PbO and some additions (like barium sulphate (<3%) and certain organic components) are used.

The pasted grids are cured in 80-100% humidity for several days. The plates become active as they are placed in a tank containing dilute sulphuric acid. As a voltage is placed over the plates, PbO is converted in PbO₂ on the positively charged plates, while on the negatively charged plates PbO is converted into Pb. After drying, the plates are ready for assembly in cells. The cells consist of a number of parallelly connected pairs of positive and negative plates, separated by microporous sheets. The container is finally sealed and filled with sulphuric acid [3].

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

The dross produced during the melting process contains about 50% pure lead and 50% lead oxide. The amount of dross produced is about 1-1.5% of the amount of lead which is consumed in the accumulator production.

In Table 43, the waste characteristics of waste from the accumulator industry are given. The waste production factors are the amount of waste per ton of used lead.

Table 43 Waste characteristics from accumulator industry

Waste	Zn (%)	Pb(%)	Factor
Dross	?	96	0.01-0.015

3.10.3 Producers and waste production

Some large companies, such as Bosch, GM, specialise in the production of starter batteries. Most of the other large corporations, for example Chloride, Ceac and Varta, manufacture drive batteries and fixed-installation batteries alongside starter batteries. In 1985, the EC produced 47,000 accumulators [1].

Table 44 lists the producers of accumulators in Europe [2]. Production figures are not available, information by Eurobat is confidential.

In Western Europe, the total amount of dross produced is approximately 7,000-10,500 tons. The dross is sold to the secondary lead industry [4]. The amount of dusts produced is much lower.

3.10.4 New technologies and developments

Since all the drosses and dust are sold, no developments are expected.

3.10.5 References

- [1] Panorama of EC industry, Brussels, 1989.
- [2] Information from Eurobat, Association of Battery Producers.
- [3] Kirk-Ottmer, Vol. 3, pp. 649-659.
- [4] Information from Centurion, The Netherlands.

*Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes**Table 44 Producers of accumulators in Western Europe [2]*

Producer	Location	Country
Robert Bosch	Stuttgart	Ger
DETA Akkumulatorenwerk GmbH	Bad Lauterberg	Ger
Akkumulatorenwerke Hoppecke		
Akkumulatorenfabrik	Brilon	Ger
Akkumulatorenfabrik Moll GmbH	Staffelstein	Ger
Akkumulatorenfabrik Sonnenschein	Büdingen	Ger
Hagen Batterie AG	Soest	Ger
VARTA Batterie Ag	Hannover	Ger
Co.Française d'Electro-Chimie	Chlichy	Fr
General Motors France	Sarreguemines	Fr
Hawker Batteries Ltd.	Bristol	UK
Chloride Group PLC	London	UK
Femsa	Madrid	Sp
Sociedad Española del		
Accumulator Tudor S.A.	Madris	Sp
Uranio SpA	Veronella	It
Fiamm SpA	Montecchio Maggiore	It
Magneti Marelli SpA	Cinisello Balsamo	It
Ets. Daniel Doyen S.A.	Bruxelles	Bel
Accumulateurs Tudor S.A.	Archennes	Bel
Accumuladores Autosil Sarl.	Paço de Arcos	Por
Centurion	Venlo	Nl
Akkumulatoren-Fabrik Oerlikon	Zürich	Sui
Plus AG	Aesch	Sui
Electrona S.A.	Boudry	Sui
Leclanché S.A.	Yverdon	Sui
Säntis Batteriefabrik	Rühti	Sui
Dr. Leopold Jungfer	Feistlitz	Aus
Neste Battery Ltd Oy	Espoo	Fin
Anker- Sonnak A/S	Horten	No

3.11 Municipal waste incineration

3.11.1 General

Incineration, instead of landfilling, is an increasingly applied route for disposing of municipal and non-hazardous industrial wastes (hereafter called MSW). As MSW is incinerated, two different kinds of metal-containing wastes are produced: fly ashes and bottom ashes. Both residues contain lead and zinc, since lead and zinc are present in various products in the MSW, e.g. in plastics, batteries, rubber, paper and board.

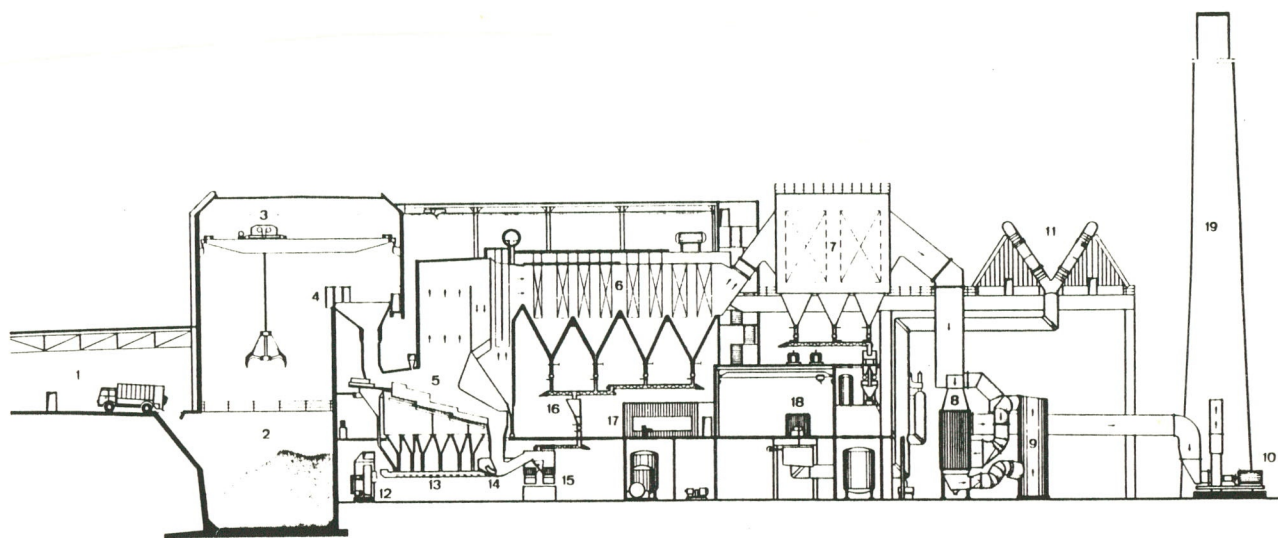
In Western Europe, the standards of incineration are quite variable from one country to another. Differences can be observed in the maximum allowable emissions of toxic compounds into the air and the standards for disposing of incinerator residues. Also the attitudes towards incineration are quite different.

For the future, it is expected that the importance of incineration will increase; in the Netherlands, for example, the amount of incinerated MSW is expected to grow from 2,800 ktons in 1986 to 7,000 ktons in 2000.

3.11.2 Processes and wastes

MSW is usually incinerated in a furnace with a grate, using energy recovery. The MSW is dumped onto a tipping floor, where bulky or hazardous materials are removed. Iron and steel are removed by magnetic separators. Noncombustible fractions like glass are removed by using trommel screens. The large parts of the remainder are reduced in size in a hammermill shredder and then mixed with the small fraction. The shredded MSW is combusted by preheated air. The heat is converted into steam, which is used for generating electricity. Figure 10 gives a scheme of such an incinerator plant.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes



- | | |
|--------------------------|-------------------------------|
| 1. Discharge hall | 11. Air condenser |
| 2. MSW-bunker | 12. Air fan |
| 3. Crane | 13. Conveyor belt |
| 4. Crane guide | 14. De-slagging unit |
| 5. Furnace with grate | 15. Transport of bottom ashes |
| 6. Steam boiler | 16. Transport of fly ashes |
| 7. Electrofilter | 17. Control room |
| 8. Offgas heat exchanger | 18. Turbine room |
| 9. Offgas cleaner | 19. Concrete chimney |
| 10. Offgas fan | |

Figure 10 MSW-Incinerator [1]

Bottom ashes are removed from the furnace and collected. The fly ashes are collected in electrostatic filters. An additional step is applied to the gases passing the electrostatic filters. In this step, the gases are washed with wet lime (CaO) to remove HCl and SO_2 . In some countries, this washing step is not applied at all (Denmark, France and UK); in Germany, two thirds of the incinerator plants use washing equipment [2].

Heavy metals present in the MSW are volatilised and deposited in the fly ashes. Especially metals, such as mercury, arsenic, cadmium and zinc, are relatively volatile under 1000°C at atmospheric pressure. These metals will be collected in the fly ash. The emission of inorganic compounds is dependent on the combustion temperatures and reactions with acid compounds in the waste [3]. Metals in the fly ash are bound to alkalichlorides and metal sulphides [4].

Nonvolatile metals, such as iron, nickel, chromium and others, are collected in the bottom ashes which are present at the bottom of the shaft. Lead will accumulate in both bottom and fly ash.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

The production of fly ash is 30 kg per ton MSW [2, 5]; the production of bottom ashes is 340 kg [2, 3].

The production of the sludges from the wet scrubbing of the offgas is 1 kg [1, p. 904].

In Table 46, the compositions of the fly and bottom ashes are given. The data are based on different analyses from Danish, Dutch and German incinerators. The composition of these wastes is rather homogeneous.

Fly ashes have an average zinc content of 2.2%, their lead content is 0.9%.

The small particles (< 20 µm) in the fly ashes have a higher zinc (2-6%) and lead (1-2%) content than the larger particles (> 20 µm).

The particle size of the bottom ash is on average 7.2 mm, with a maximum of 30 mm and a minimum of 0.04 mm [3, pp. 5B-26].

Table 45 gives the waste characteristics from the incineration of municipal waste. The waste production factors are the amount of waste per ton of incinerated waste.

Table 45 Waste characteristics from MSW incineration

Waste	Zn (%)	Pb (%)	Factor
Bottom ash	0.7-0.9	0.2-0.6	0.34
Fly ash	1.2-3.0	0.5-1.4	0.03
Scrubber residue	0.7	0.4	0.001

Pb/Zn concentrations based on dry solid.

3.11.3 Producers and waste production

In Table 47, details about the MSW incinerators in Western Europe are given, based on the 1987 situation. For each country, the total amount of MSW produced, the amount of MSW incinerated, and the number of incinerators are given. The situation greatly differs per country. The incinerators can be divided into two types. First, the old ones which no longer meet present environmental standards. Modernisation is often too expensive, but due to the lack of alternatives they are not shut down. The second type of incinerators meets all environmental standards and is usually much larger. This type of incinerator will most probably be used more frequently in the near future, as it is expected that increasing quantities will have to be incinerated.

A time lag of about 10 years is expected between countries with strict environmental standards and those with more lenient standards. The current attitudes of individual countries towards MSW incineration are [3]:

- MSW incineration is virtually absent in Greece, Portugal and Ireland. Mediterranean refuse is rich in organics and moist, which depresses the combustion temperature and leads to emissions of toxic organic compounds, including dioxins.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

- Italy is quite sensitive to this problem, because of the Seveso-accident; hence numerous old incinerator plants were closed, however building of multiple incinerators is planned for the future.
- In the UK, landfill of MSW is regarded as common sense and a cheap way of disposal, even in co-disposal with specific hazardous wastes. Modernisation of the existing plants is not foreseen. Emission codes for the few existing MSW incinerators have remained relatively lenient.
- In Belgium, there is a multitude of small plants. In its Northern (Flemish) region, the importance of MSW incineration has augmented dramatically (from 28% in 1981 to 51% in 1987).
- In the Netherlands, the number of incinerators will increase in the future.
- In France, a number of plants will be shut down, because of the high investment costs needed for attaining the environmental regulations.
- Germany has a high percentage of incinerated MSW, the use of flue-gas washing equipment is the highest in Western Europe.

In Table 47, the produced amount of residues per country is given. The data are based on the amount of incinerated waste multiplied with the waste production factor. Germany and France are the largest producers of both wastes.

Fly ashes are usually landfilled; however, methods for treatment are available. Fly ashes are also used as a filler material (e.g. in asphalt). Due to environmental regulations, the application of fly ashes is currently increasingly put under pressure in countries, such as Germany and the Netherlands.

The bottom ashes are less hazardous. After treatment, about 50% are used in construction in Germany [6]. The remaining 50% is landfilled, which is comparable to the Dutch situation.

The metal fraction from bottom ashes is about 10% and can be separated and sold [3, pp. 5B-2]. The remainder is likely to be used as a low-grade substitute for gravel or sand [3, pp. 6]. It can possibly be used as a construction material in roads [3, pp. 5B-2].

3.11.4 New technologies and developments

A number of treatments for the residues are available:

- solidification of the ashes.
- thermal treatment; sintering or glassification: DEGLOR.
- washing of the ashes: 3R.

Solidification of the residues is executed to reduce the leachability of toxic metallic compounds. As solidification agents, materials like cement are used. The agent forms a matrix in which the compounds are chemically or physically bound. The final product can be used as a construction material or is landfilled, depending on its leaching characteristics. A process on a commercial scale is, to our knowledge, not applied: efforts in research are, however, made. Examples are:

- In Bamberg, Germany, fly ashes are mixed with the sludge containing lime from the offgas cleaning. After mixing a solid product is obtained which can be landfilled. The process reduces the absorption of water [7].

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

- Research at the University of New Hampshire, USA, is conducted after adding cement, lime and asphalt to mixed fly ashes and bottom ashes. The three immobilisation agents can reduce the leachability of most heavy metals to a large extent, thereby producing a solid material [3, pp. 4B-42].

The DEGLOR process stands for Decontamination and Glassification of Residues. It is developed for treating fly ashes by ABB W+E, a large producer of waste incinerators [8].

The ashes are melted down above 1200°C in an electric furnace. Organic substances like dioxins are thermally destroyed, volatile metallic compounds evaporate and are, after cooling with cold air, collected in a baghouse filter. Zinc and lead are the main materials (each about 10%); silver, copper, and cadmium are also present. The metals are concentrated and used as a raw material in the metallurgic industry.

The remainder in the electric furnace will form a glass-like material, which has a volume of one quarter of the original volume. The glass-like material has low leaching rates, well under the wastewater standards. After quenching, the final product is a granular glass. This material can be deposited or reused.

The energy consumption of the process amounts to 1 kWh per kg of fly ash.

In an incineration plant, an experimental method for cleaning the fly ashes is examined on a pilot scale [6]. This method, developed by the Kernforschungszentrum Karlsruhe in Germany, is named the 3R-process.

The fly ashes are collected as usual in an electrostatic filter. The ashes are then washed under acid conditions, where easily soluble metal compounds are solved. These compounds are removed from the water by ion exchange. The remaining solid particles are separated and pelletised. The pelletised particles are fed back into the furnace, where they are roasted, thereby immobilising several metals. Leaching characteristics of the roasted particles are well below the requirements. Toxic organic compounds are destroyed during roasting.

3.11.5 References

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- [2] Dickhäuser K, Umwelt 3/88, 1988, pp. 71-72.
- [3] MWC, Proceedings conference Florida, 1989.
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- [6] Wagenknecht P., Weiss V.; Entsorgungspraxis 1-2/90, 1990, pp. 25-30.
- [7] Göttlicher R.; Anton P., AbfallwirtschaftsJournal 2, 1990, no. 6.
- [8] W+E News 1/90, 1990.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

[9] OECD Environmental data compendium 1987, 1987.

Table 46 Composition of MSW incinerator residues [1, 5]

Element	Fly ash (%)	Bottom ash (%)	Scrubber residues (%)
Lead	0.3-1.4	0.1-0.6	0.4
Zinc	0.7-3.0	0.1-0.9	0.7
Arsenic	0.004-0.03	0.0001-0.005	0.002
Chromium	0.014-0.045	0.02-2.6	0.02
Cadmium	0.028-0.080	0.002-0.013	0.02
Nickel	0.005-0.084	0.01-0.04	0.06
Copper	0.08-0.21	0.1-2.6	0.1
Iron	1.4-5.0	2.5-6.0	19.5
Magnesium	1.8-2.9	1.5-1.8	-
Aluminum	5-11	3-5	-
Mercury	0.0005-0.0009	-	0.3
Barium	0.039-0.59	-	-
Calcium	3-13	3-8	-
Sodium	1.6-6.9	1-6	-
Potassium	2.65	-	-
Phosphor	1.0	-	-
Sulphate	3-7	0.4-1.2	-
Chloride	1-5	0.4-0.6	-
Silicon	17-21	24-31	-
Org. Carbon	0.8-2.2	0.9-1.5	-

The water content of the scrubber sludge is 84.2%. The data in the table are based on dry solid.

Table 47 MSW-incineration and production of residues in Western Europe [2, 9]

Country	Produced (Mtons/y)	Incinerated (Mtons/y)	Number plants	Scrub step (%)	Fly ash (ktons/y)	Bottom ash (Mtons/y)
Belgium	2.8	0.35	29	38	11	0.1
Germany	19	6.5	47	66	195	2.1
Greece	2.5	0	0	0	0	0
Denmark	1.8	1.45	46	0	44	0.5
France	17	7.0	284	0	210	2.3
UK	18	1.8	38	0	54	0.6
Italy	14	2.5	80	4	7	0.8
Ireland	1.1	0	0	0	0	0
Portugal	1.7	0	0	0	0	0
Spain	10.6	0.48	8	?	14	0.2
the Netherlands	4.3	1.7	11	9	51	0.6
Austria	1.6	0.35	3	33	11	0.1
Switzerland	2.2	1.7	34	18	51	0.6
Sweden	2.5	1.40	23	22	42	0.5
Norway	1.7	0.14	?	?	4	0.05

3.12 Hazardous waste incineration

3.12.1 General

A common method for treating hazardous wastes is incineration. The type of furnace used is usually a rotary kiln. The residues produced are fly ashes and bottom ashes. The composition of the residues from hazardous waste incineration is quite variable, which is caused by the differences in composition of the incinerated hazardous wastes.

Among the incinerated wastes are liquids, sludges and solids, such as oil, solvents, cleaning sludges, paint, resins, glue, plastics, car shredder dust, medicines, oil filters, residues from the chemical and pharmaceutical industry, insecticides, pesticides, and spray cans.

3.12.2 Processes and wastes

The temperature of the furnace varies between 1000-1200°C [1]. The collection of the residues from the incineration of hazardous wastes is comparable with MSW-incineration. Cleaning of the offgas is executed with an electrostatic filter or a venturi scrubber. Because of the high contamination, the wet washing step for the offgas is always applied. Figure 11 gives a diagram of a rotary kiln system [1].

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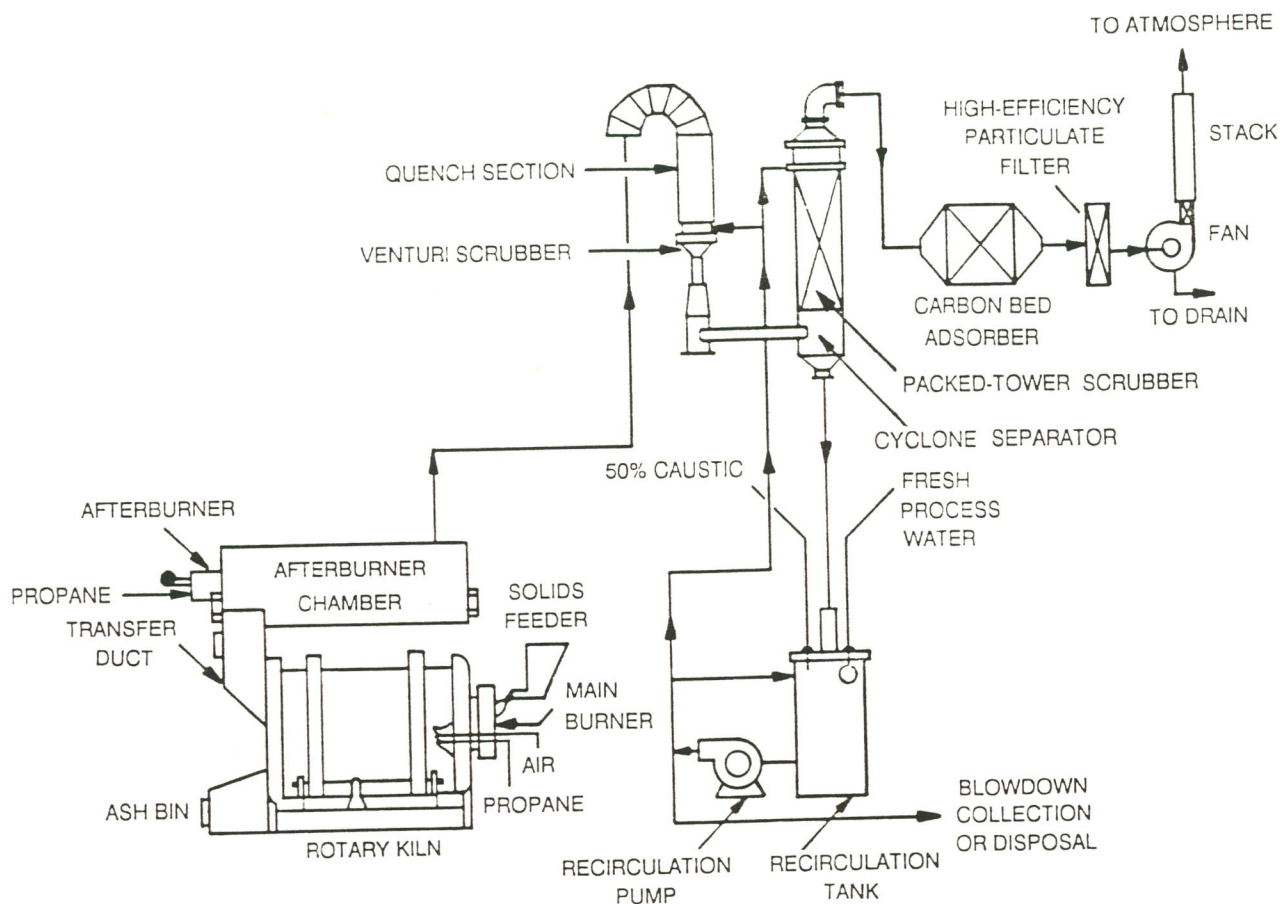


Figure 11 Schematic diagram of rotary kiln system

Table 49 gives the compositions of the fly and bottom ashes. These compositions are quite variable, since they depend on the kind of incinerated waste.

Table 48 states the characteristics of wastes from the incineration of hazardous waste. The waste production factor is the amount of waste per ton of incinerated waste.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 48 Characteristics of wastes from hazardous waste incineration

Residue	Zn (%)	Pb (%)	Factor
Bottom ash	< 2	< 0.5	0.24 ¹
Fly ash	0.5-6.5	1.2-7.5	0.0067 ¹
Scrubbing sludge	?	?	0.006 ²

¹ Based on data from German incinerators [2].

² Based on data from a Dutch incinerator (AVR) [3].

3.12.3 Producers and waste production

In Table 50, details about the hazardous waste incinerators in Western Europe are given, based on the 1987 situation. For each country are given the total produced amount of waste, the amount of incinerated waste, and the number of incinerators [4]. Germany has the largest amount of incinerated waste.

Also given in table 3 is the produced amount of residues per country. The data are based on the amount of incinerated hazardous waste multiplied with the waste production factor.

Currently, all the residues in Europe are landfilled [3]. The fly ashes and bottom ashes, produced in Germany, are landfilled in either controlled sites or underground in salt mines in Germany [2].

The fly ash and bottom ash from AVR, the Netherlands, are disposed in a special storage for hazardous wastes, which costs about US\$ 175/ton [5].

3.12.4 New technologies and developments

Processes for treating the residues are not applied.

A different incineration process for hazardous wastes, developed by Voest-Alpine-Industrieanlagenbau, is the High Temperature Gasification process [6]. This process, which produces fewer wastes, is in a pilot-plant stage.

The wastes are incinerated at a temperature of 1600°C. Oil and dusts are burnt at the bottom of the furnace; sludges and shredded solids are fed in the smelt. Molten material drops into a collector; after granulation, a nonleachable construction material is obtained. The gases pass through a cokes bed filter. The dusts from the offgas are collected and recirculated in the furnace. The cleaned offgas is washed twice, first to remove HCl and second to remove H₂S. The waste water from the HCl washing step is neutralised with gypsum. The remaining filtering sludge, in which most of the heavy metals are concentrated, is landfilled. The amount of the sludge is 1%, compared to the original waste.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

3.12.5 References

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- [8] OECD Environmental Data Compendium, 1987.
- [9] Figures for Hazardous Wastes 1989, VROM, 1990 (in Dutch).

Table 49 Composition of hazardous waste incinerator residues [5, 7]

Element	Fly ash (%)	Bottom ash (%)
Lead	1.2-7.5	< 0.5
Zinc	0.5-6.5	< 2
Arsenic	0.01-0.05	0.0005-0.004
Chromium	0.26-0.32	0.05-0.15
Cadmium	0.05	0.0002-0.035
Nickel	0.1-2.5	-
Copper	0.25	-
Antimony	0.2-0.5	0.0003-0.04
Iron	0	-
Molybdenum	0.05-3.0	0.01-0.5
Mercury	0.0005-0.005	0.0001-0.006
Chloride	1.3-28.0	0.4-1.5

The composition of the sludge from the washing step is not known.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 50 Hazardous waste incineration and production of residues in Western Europe [4, 8]

Country	Produced (ktons/y)	Incinerated (ktons/y)	Number plants	Bottom ash (ktons/y)	Fly ash (ktons/y)
Belgium	915	45 ⁴	1 ⁴	0	0
Germany	4900	461	27	110.6	3.1
Greece	?	0	0	0	0
Denmark	90	30	1	7.2	0.2
France	2000	200	9	48.0	1.3
UK	1500	39	7	9.4	0.3
Italy	1000-3000	35	1	8.4	0.2
Ireland	20	?	?	?	?
Portugal	?	0	0	0	0
Spain	?	0	0	0	0
the Netherlands	1200 ³	90	1	21.6 ¹	0.6 ²
Austria	100	?	?	?	?
Switzerland	100	?	?	?	?
Sweden	550	?	?	?	?
Norway	120	?	?	?	?

¹ [3]: in 1990 12.4 ktons.

² [3]: in 1990 1.7 ktons.

³ [9].

⁴ since 1989.

3.13 Rubber and tyre incineration

3.13.1 General

World generation of used tires and rubber wastes amounts to more than 9 million tons per year. Almost the entire quantity of rubber waste consists of tires. Rubber waste can be used as an energy source for industrial installations, or provide raw material for the production of rubber reclaim and crumb [1]. The current percentage of waste recycling varies, according to country, between 1% (for instance Spain) and 50% (Denmark, [1]).

The calorific value of spent tires is 33.6 MJ/kg [1], which is a real inducement for the incineration of rubber wastes (Coal 25-29 MJ/kg).

The heat produced during the process may be used for steam production or cement production [1].

Car tires also contain zinc oxide, which is added as a vulcanisation enhancer and as a heat conductor. The content is between 1.2 and 2.7% zinc oxide [2].

When spent tires are incinerated, iron is collected in the slags and zinc oxide is volatilised and recovered in the fly ashes.

3.13.2 Processes and wastes

Car tires are incinerated at a temperature of 1250°C under oxidising conditions [3]. When car tires are used as fuel in cement furnaces, temperatures are over 1400°C. Metals and sulphur are bound chemically in the cement. The zinc oxide content in fly ash from car tyre incineration is very high. According to [4], the zinc oxide content is 51.5% and the carbon content 32.2%. Probably, the incineration process has not been complete.

According to [5], the zinc oxide content is 83.6%, the carbon content 1.75%, and the sulphate content 10.5%. A complete analysis of fly ash is given in Table 52 [4].

At Marangoni in Italy, the fly ash contains approximately 80% zinc oxide, with a particle diameter of about 50 microns [1].

The production of fly ash is 4.5% on intake, the production of slag 13-18% [2]. The slags contain mainly iron.

In Table 51, the characteristics of wastes from the incineration of tires are given. The waste production factor is the amount of waste per ton of incinerated tires.

Table 51 Characteristics of wastes from the incineration of tires

Waste	Zn (%)	Pb (%)	Factor
fly ash	41-67	0.20	0.045
slag	?	?	0.13-0.18

3.13.3 Producers and waste production

46 car tyre incinerators are summarised in Table 53. In Germany, 475,000 tons of tires are produced annually, 170,000 tons of which are incinerated. The largest fraction (157,000 tons/y) is incinerated in the cement industry (21 furnaces [3]). In this case no zinc containing fly ash can be recovered.

3.13.4 New technologies and developments

In the EC, the following treatment methods are aimed at: 60% recycling in new tires, 30% recycling in other applications; and 10% reduction/prevention.

Before this high degree of recycling is achieved, more incineration will be applied in the near future, mainly in cement kilns.

3.13.5 References

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Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 52 Chemical composition of tyre incineration fly ash [4]

Component			Concentration (%)
Zn	as	zinc oxide	51.48
Pb	as	lead oxide	0.22
Fe	as	Fe ₂ O ₃	6.33
Cr	as	Cr ₂ O ₃	0.03
Cu	as	CuO	0.55
Ni	as	NiO	0.03
As	as	AsO ₃	0.02
Al	as	AlO ₃	0.76
Mg	as	MgO	0.50
Na	as	Na ₂ O	< 0.01
K	as	K ₂ O	0.01
Mn	as	MnO ₂	0.35
Sn	as	SnO	0.03
Si	as	SiO ₂	6.85
Cd	as	CdO	0.05
C	as	C	32.20

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 53 Tyre incinerators

COMPANY	SYSTEM/TYPE OF KILN	PRE-TREATMENT	CAPACITY	START YEAR	COMMENTS
1. Watts Tyre & Rubber Co Lydney	Horsefall incinerator	No	250 kg/h	1964	
2. Standard Tyre Ltd Leyton	Heenan cyclone	No	40 tyres/h	1970	
3. Homerton Tyre Ltd	Heenan cyclone	No		1971	
4. Good Year Tyre & Rubber Co Ltd Wolverhampton	Heenan cyclone	No	450 kg/h	1972	modified to vertical kiln 1975
5. Avon Rubber Co Melksham	Lucas cyclone	No	450 kg/h	1973	
6. Good Year Tyre & Rubber Co Jackson, Michigan	Lucas cyclone	No	1000 kg/h	1974	stopped by EPA in 1978
7. Gummi Mayer KG Landau	Uhde GmbH grate kiln	No	900 kg/h	1973	
8. Colway Tyres Co Durham	Pyrolysis kiln	Yes		1984	partly unsuccessful
9. Michelin, Belfast	Lucas cyclone	No		1984	
10. King Pin Renoulds	Lucas cyclone	No		1984	
11. Michelin, Sropshear	Lucas cyclone	No		1984	
12. Courtaulds, Grimsby	Grate kiln	Yes	3000 kg/h	1984	stopped 1988
13. Gummi-Mayer, Landau	Uhde GmbH grate kiln	No	1400 kg/h	1983	
14. Marangoni, Milano	Eneal	No	1000 kg/h	1984	
15. Pneu Laurent	Air liquid		1500 tonn/y	1981	
16. Pneu Laurent	Seum		3000 tonn/y	1984	
17. Michelin, Spain	Air liquid seum		3000 tonn/y	1984	
18. Wefa AB	Multicyclone	Yes	40 kg/h	1981	powder incineration
19. AB Dala Gummi	Multicyclone	Yes	80 kg/h	1982	powder incineration
20. Anderstorp Gummi Industri	Multicyclone	Yes	80 kg/h	1983	powder incineration
21. Galaxie	Multicyclone	Yes		1984	powder incineration
22. Firestone Decatur, Ill.	Basic Environmental Eng. Inc.	No	1000 kg/h	1983	
23. Firestone Decatur, Ill.	Basic Environmental Eng. Inc.	No	1000 kg/h	1983	
24. Oxford Energi Modesto, CA	Gummi-Mayer grate kiln	No	5500 kg/h	1987	
25. Oxford Energi Sterling, CONN	Gummi-Mayer grate kiln	No	10400 kg/h	1989	
26. SPG, Ahau, Austria Pilot plant	Fluid bed kiln	Yes	60 kg/h		
27. 20 plants in Japan	Nippon	?	25 tyres/h		

4 Waste legislation

The feasibility of the EMPF® process is determined by the positive and the negative value of the treated waste materials. The positive value is determined by the content of zinc, lead, and other metals. The negative value is determined by the disposal or treatment costs. Cost for disposal will change in the future as a result of a stricter legislation. For this reason, a short description of the current developments at EC level regarding legislation is given [1,2,3].

4.1 The Waste Directive

The EC Directive on Waste was originally introduced in 1975 as Directive 75/442/EEC [5]. As time passed, it was considered necessary to update the Directive in the light of experience gained in its implementation and taking as a base a high level of environmental protection. Thus a new Directive amending 75/442/EEC was published in the Official Journal of the European Communities No. L78 on 26 March 1991 and is due to be brought into force in the Member States through the necessary laws, regulations and administrative provision no later than 1 April 1993.

The new Directive on Waste is "Framework Directive" which sets the tone for the whole set of rules in the waste field by laying down the definition of waste. In essence, waste is defined as any substance or object which the holder discards, or which he intends or is required to discard, and which is contained in a list of categories of waste. A number of these categories are of direct relevance to the lead and zinc industries, whether primary or secondary, for example:

- production or consumption residues
- off-specification products
- materials spilled, lost or having undergone other mishap
- unusable parts (e.g. scrap batteries)
- residues of industrial processes (e.g. slags)
- residues from pollution abatement processes (e.g. baghouse dusts)
- machining residues (e.g. lathe turnings).

According to the terms of the Directive, the Commission shall establish a committee comprised of representatives of Member States, which will draw up a comprehensive list of wastes, to be done by 1 April 1993 and reviewed periodically.

Having established the broad principle that all materials unwanted by the originator or holder are wastes, the Directive proceeds to divide wastes into two categories - those which are to be disposed of with no intention for further use, and those which are to be subjected to recovery operations. All industries are likely to produce some wastes in the former category, i.e. for final and permanent disposal. The second category, however, introduces a new concept for the recycling industries in that the recycling and reclamation of metals and metal compounds is now classed as a waste recovery operation and, therefore, becomes subject to the provisions of the Waste Directive and of its various daughter Directives.

Member States are directed to establish a network of disposal installations, with the objectives of making the European Community self-sufficient in waste disposal and of moving towards that situation in the case of individual Member States. One of the purposes of this network is to enable wastes to be disposed of as near as possible to the point of their origin. Operators of both disposal and recycling operations are required to have a permit from the competent authority although exceptions may be possible under specified circumstances for recycling operations.

4.2 The Hazardous Waste Directive

The EC Directive on Toxic and Dangerous Waste was originally introduced in 1978 as Directive 78/319/EEC [6]. However, with the introduction of the amended framework Directive on Waste, with its new definition of waste, it was considered necessary to repeal the 1978 version and introduce a new piece of legislation as a daughter Directive to the newly updated Waste Directive. This new instrument has not yet been adopted by the Commission but it has passed through all the necessary consultation procedures and its adoption is now imminent.

The framework Directive on Waste establishes the basic definition of waste. The term "hazardous" is defined on the basis of a series of Annexes which identify categories or generic types of hazardous waste according to their nature or the activity which generated them and constituents of wastes which render them hazardous when they possess certain properties (for example, explosive, flammable, harmful, irritant, etc.). Lead and lead compounds, and also zinc compounds, are listed amongst the constituents which can render a waste hazardous. Many other metals (notably cadmium), inorganic ions and organic materials are commonly encountered in the lead and zinc industries, either as unwanted arisings or as raw materials for recycling. Examples include metallic dust/powder; liquids or sludges containing metals or metal compounds; residues from pollution control operations (e.g. baghouse dust), batteries, and other electrical cells.

A number of provisions in the Directive will have a direct bearing on the secondary lead and zinc industries. Recycling plants will need to be registered, although the requirement to be granted permits to operate will be at the discretion of Member States. There will be a requirement for periodic inspection of the plants by the competent authorities of the Member State in which the plant is located, and records will need to be kept on quantities, nature, origin, etc. of waste.

Adoption of the Hazardous Waste Directive is expected during the course of 1991. The necessary measures to comply with the Directive must be introduced by Member States within two years of its publication, at which time the old Directive 78/319 will be repealed.

Under the terms of the amended Directive on Waste, provision is made for the creation of specific supplementary rules in order to regulate the management of particular categories of waste. This procedure has been adopted in the case of a category of products of particular relevance to the secondary metals industries, for instance in the form of Directive 91/157/EEC on Batteries and Accumulators Containing Certain Dangerous Substances [7].

(The Battery Directive was adopted on 18 March 1991 and published in the Official Journal of the European Communities No. L78 on 26 March 1991. Measures for compliance must be adopted by Member States by 18 September 1992.)

4.3 International Movements of Waste

The movement of wastes from one country to another is a particularly complicated area since it is currently the subject of regulations or proposals within the jurisdiction of three independent organisations - the European Commission, the United Nations Environmental Programme (UNEP) and the Organisation for Economic Cooperation and Development (OECD).

At one stage, all three of these organisations were engaged in a virtual race to produce rules governing the international movements of waste, the driving force behind their efforts being a spate of incidents involving attempts at uncontrolled dumping of hazardous wastes in developing countries without appropriate facilities for their proper handling. The "race" was won by UNEP which on 22 March 1989 concluded the "Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal", more commonly known as the Basel Convention.

The Basel Convention has so far been ratified by seven countries. It will come into effect when 20 countries have ratified. This is anticipated to occur around the end of 1991/beginning of 1992 when the European Community Member States are expected to ratify. At the time the Convention enters into force, all movements of hazardous waste, whether intended for recycling or not, will be forbidden between countries which have ratified and countries which have not. This additional restriction is expected to introduce its own problems since it could effectively cut off some major supply routes for European metal recycling plants.

4.4 Landfilling of waste

Although it does not pose the same problems with regard to secondary raw materials as the rest of the EC Directives and proposals on waste, a proposed Directive on the landfill of wastes will be of relevance to all companies in the lead and zinc industries which produce true wastes requiring disposal.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

The primary purpose of the proposed Directive is to protect soil and water from pollution resulting from the permanent land disposal of wastes. The proposals are still under discussion and changes are therefore likely but a number of broad principles can be identified. Landfills are divided into three categories - those for hazardous waste, those for inert waste, and those for a broad intermediate category of municipal, nonhazardous and other compatible waste.

As with the whole family of Waste Directives, waste and hazardous waste are defined according to the Directives on these subjects outlined above. Wastes containing lead, zinc and cadmium thus fall into this category. The proposed Directive assesses waste as hazardous or inert on the basis of the amounts of hazardous materials which can be leached from the waste under standard leaching conditions. To qualify as inert, the total concentration of lead, cadmium, zinc, chromium, copper, nickel and mercury in the eluate must be < 5 mg/l [8]. To qualify as hazardous waste pH values are pH = 4 to 13; the eluate concentrations for lead are: 0.4-2 mg/l and for zinc 2-10 mg/l [8]. For eluate concentrations higher than the maximum values fixed, hazardous wastes will have to be treated prior to landfill, unless compatible for disposal with municipal waste, or, if treatment is not possible, destined to a mono-landfill [8].

However, it is unlikely that this proposed directive will be accepted because many countries, like Germany, the Netherlands, and Denmark do not agree with it [2].

4.5 Other waste measures

The programme of EC directives and regulations on waste is already substantial but it is not yet complete. Proposals have already been put forward for Directives on the incineration of waste, on civil liability for damage caused by waste, and on the packaging of waste, and it must be possible that others will follow in the future. Thus the whole wastes field is still evolving and a number of issues will inevitably arise over the next few years with which the lead and zinc industries will have to contend.

4.6 References

- [1] Information from Mr R.H. Donkers, EC, Brussels.
- [2] Information from Mr Th. G. Aalbers, RIVM, National Institute for Public Health and Environmental Protection, The Netherlands.
- [3] Wilson D.N., Recent and prospective developments in regulatory controls in Europe. Paper presented at the symposium "Recycling Lead and Zinc, The Challenge of the 1990s, Rome, 1991.
- [5] Directive 75/442/EEC.
- [6] Directive 78/319/EEC.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

[7] Directive 91/157/EEC.

[8] Proposal for a directive on the landfill of waste, Com (91) 102 final, syn 335, 22 May 1991.

5 Discussion

5.1 Waste materials for the EMPF® process

The different zinc- and lead-containing wastes described in chapter 3 vary in quantity and composition; not all of them are suitable for treatment in the EMPF® process. The following parameters are important for suitability of treatment in the EMPF® process.

Production:

- amount of waste produced
- number of producers

Processability:

- chemical composition
- physical composition

Economy:

- economic value (value of the metals that can be recovered, Pb and Zn)
- negative value (cost of disposal)
- competition in treatment possibilities

These parameters are presented for each kind of waste in Table 54. and have been given a qualification. No weighing factors have been used for the different parameters.

The following qualification is given to the different parameters:

Amount of waste produced:

Arbitrarily, the following discrimination has been made:

0	-	10	tons/year:	-
10	-	100	tons/year:	o
100	-	1000	tons/year:	+
		> 1000	tons/year:	++

Number of producers:

If the produced waste materials are generated at a limited number of producers, the setup of a treatment facility is much easier to accomplish than with a large number of producers. Arbitrarily, the following discrimination has been made for treatment in the EMPF® process:

		> 100	producers:	-
25	-	100	producers:	o
10	-	25	producers:	+
		< 10	producers:	++

Chemical composition:

The processability is mainly determined by the chemical composition of the waste material. In general, it can be stated that if the metals are present in the form of oxides, hydroxides or metals, the qualification is positive (+). Are the metals present as a salt (like chlorides, sulphates or phosphates), the qualification is negative (-).

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Physical composition:

The physical composition of a waste material determines if a pretreatment is required before the high-temperature treatment. This pretreatment can be e.g. dewatering (for sludges or liquids). If pretreatment is necessary, the qualification is negative (-). If no pretreatment is required (for ashes and slags), the qualification is positive (+).

Value of lead and zinc:

If the waste materials contain a high concentration of zinc and/or lead, credits can be expected in the form of Western Grade zinc and/or lead products. The following discrimination has been made:

US\$	0	-	50	/ton:	-
	50	-	100	/ton:	o
	100	-	200	/ton:	+
	>		200	/ton:	++

To calculate the economic value of the waste material, a lead and zinc price of respectively US\$ 750/ton and 1600 US\$/ton has been used (average prices since 1988, [3]).

Negative value:

The negative value of a waste material is the price that a waste producer must pay to dispose of the waste. Generally, the waste producer will choose the lowest-cost option that meets environmental requirements. Options are treatment for recycling purposes and landfilling.

The following qualifications are given, based on the waste producer disposing of the waste:

— Waste has positive value:	-
— Waste has zero value:	o
— Waste has low (< US\$ 50) negative value:	+
— Waste has high (> US\$ 50) negative value:	++

Competition:

The market for treating a waste material is not only dependent on the value of the waste material (negative and value of metals), but also on the competition between the treatment plants. It is difficult to push off the market treatment facilities, which have been established and proven.

The following qualifications are given, based on already operating treatment facilities:

— Established market:	-
— Few treatment options:	+
— No treatment possible:	++

Table 54 gives the waste materials from chapter 3 with their qualifications.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Table 54 Qualification of wastes for the EMPF® process

Description of residue		Production figures		Processability HTWT		Economic value		
No	Waste	Amount Produced	Number of Producers	Chemical	Physical	Value Pb+Zn	Negative value	Competition
I	Blast Furnace dust coarse	++	0	+	+	-	0	+
I	Blast Furnace dust fine	+	0	+	+	0	+	+
I	C-steel Oxygen dust coarse	+	0	+	+	-	0	+
I	C-steel Oxygen dust fine	++	0	+	+	-	0	+
I	EAF-dust C-steel	+	-	+	+	++	++	+
I	EAF-dust stainless steel	0	-	+	+	-	0	+
II	Jarosite	+	++	-	-	0	++	+
II	Goethite	+	++	-	-	++	+	+
II	Hematite	0	++	-	-	-	-	-
IV	Slags direct ZnO process	-	++	+	+	++	+	+
V	Rayon-viscose sludge	0	++	-	-	0	+	+
VI	Thermal metalplating ashes	0	-	+	+	++	-	-
VI	Thermal metalplating dross	0	-	+	+	++	-	-
VI	Therm.mt plt. pickl. acids	+	-	-	-	+	0	+
VII	Electro metal plat. sludge	-	-	-	-	+	++	++
VIII	Cupola dust iron foundries	0	-	+	+	-	++	++
VIII	Brass foundry ashes	0	-	+	+	++	-	-
VIII	Brass foundry slags	0	-	+	+	++	-	-
IX	BF slag	+	++	+	+	+	++	+
IX	ISF slag	+	++	+	+	+	++	+
IX	Kivcet slag	0	++	+	+	0	+	-
IX	Flue dust refining	-	0	+	+	++	++	+
IX	RR-Furnace slag	+	+	+	+	-	++	+
X	Accumulator product. dross	-	0	+	+	++	-	-
XI	Fly ashes MSW-incineration	+	-	+	+	-	+	+
XI	Bottom ashes MSW-incinerat.	++	-	+	+	-	+	+
XI	Scrubber residue	-	0	-	-	-	0	+
XII	Fly ashes HZW-incineration	-	-	-	+	0	++	++
XII	Bottom ashes HZW-incinerat.	+	0	-	+	-	++	++
XIII	Fly ash tyre incinerat.	-	0	+	+	++	?	?

On the basis of this qualification, as summarised in Table 54, the interesting waste materials for the EMPF® process can be given first and second priority for treatment:

First priority:

- Blast Furnace slag from lead production (zinc- and lead-containing)
- ISF slag (containing lead and zinc)
- Blast furnace dust fine from steel production (containing zinc and lead)
- EAF-dust (containing zinc and lead).

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

The most interesting materials are the zinc- and lead-containing materials from primary zinc and lead production (i.e. Blast furnace and ISF melters from primary zinc and lead industry). These waste materials are produced at a limited number of sites. Besides the slags that are currently being produced, large amounts of historical wastes are also present at the factory sites. Probably a large amount of these historical waste materials will have to be cleaned in the future.

Also the primary (blast furnace dusts from steel production) and secondary ferrous industry (EAF dust) produce interesting waste materials.

Secondary priority:

- C-steel oxygen dust fine (containing zinc and lead)
- Jarosite and goethite (containing zinc and lead)
- Reverberatory Rotary (RR-) Furnace slag (containing lead)
- Fly ash from municipal waste incineration (containing zinc and lead).

Treatment of the C-steel oxygen dusts (fine) treatment will not be as economical as the earlier mentioned blast furnace dusts and EAF dust, although the amount of waste is very big. As the zinc content is not so high as the zinc content in EAF-dust, the economic value is less and these dusts are also easier to dispose of.

Treatment of the wastes from the primary (electrolytical) zinc production (jarosite and goethite) are important environmental topics at the moment (Budelco, Metaleurop). Although the processability of these wastes is probably difficult and the economic metal value rather low, the local governments will not allow disposal of residues in the future. From this point of view, the EMPF® process might bring a solution.

A special category is formed by the wastes from municipal waste incineration. Fly ashes from municipal waste incineration might be interesting for treatment in the EMPF® process. No pretreatment is required and disposal is becoming more and more difficult (negative value of US\$ 150/ton). However, the economic value of the ashes is low and processability could give rise to problems because of the metal salts and especially the halides that are present.

Together with the fly ashes, the bottom ashes from municipal waste incineration could be co-processed although they are relatively easy to dispose of, and their economic value is low, compared to the fly ashes.

The following waste streams are not interesting to set up a dedicated EMPF® process. These waste materials might be interesting for co-processing if an EMPF® furnace has been built for one or more other waste streams. The most important reasons for not being interesting for the EMPF® process are:

Ashes and drosses from thermal metalplating, drosses from accumulator production, brass foundry ashes, slags, and hematite have already found their way in the recycling industry and are treated in dedicated plants.

Blast Furnace dust (coarse fraction), C-steel Oxygen dust (coarse fraction) and EAF dust from stainless steel production have a low value (low zinc or lead content and low negative value). The same is probably the case with cupola furnace dusts from iron foundries, because there are no indications about disposal problems in the near future.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Several waste streams are produced in limited amounts, like zinc oxide from the zinc oxide industry, flue dusts from the refining of recycled accumulators, rayon-viscose sludge from the synthetic fibre industry, fly ash from tyre incineration, scrubber residue from municipal waste incineration, fly ashes from hazardous waste incineration, and bottom ashes from hazardous waste incineration. Treatment does not make a dedicated plant economically feasible. Apart from the low quantities, the processability (except for slags from the zinc oxide industry and ashes from tyre incineration) is also bad. The rayon fibre industry will preferably take process-integrated measurements when disposal of the sludges becomes difficult.

Although the value of the slags from the zinc oxide industry is high and their processability good, the amount that is produced and the disposal costs are low (storage at factory site). The same is the case for flue dusts from the lead refining; thus co-processing of this waste material could be considered.

The Kivcet slag has already undergone a kind of zinc-fuming process and is, therefore, not interesting for treatment in the EMPF® process, unless the negative value will rise.

Pickling ashes from thermal metalplating and sludges from the electro-metalplating require a costly pretreatment (drying), and contain a considerable amount of salt (especially chlorides in pickling acids). The electroplating sludges are various in composition and the amount produced per producer is very limited.

5.2 Legislation

Legislations concerning the handling, treatment and disposal of wastes are an important factor concerning the market of waste treatment. Within the scope of the study it was not possible to obtain a complete view of all developments in this complicated field.

At this moment and in the near future, legislation is determined by the national governments of the member states of the EC. Only recently has the European legislation, made at EC level and laid down by means of Directives, been growing in importance. The framework of legislation is described in the "Waste Directive". This directive is accepted and will be brought into force 1 April 1993. All the other Directives are daughter Directives and will be brought into force after this date. The Hazardous Waste Directive has not been adopted yet, but this will probably happen this year. The same is the case with the Directive on the International Movement of Waste.

The directive on Landfilling of Waste is currently under discussion. A proposal has been made, but an agreement is not expected in the near future.

5.3 Comparison between EMPF® process and Waelz process

These are the results of a purely technical evaluation. In practice, a proven technology is essential for the viability of a process.

In the EC, the only process that is in operation for treating zinc containing wastes is the Waelz process. Three plants are in operation in Italy, Spain and Germany and two others are planned in France and Italy.

Applicability of the EMPF® process for treatment of zinc- and/or lead containing wastes

Differences between the Waelz process and the EMPF® process are:

1. The manner of heat generation
2. The form in which flue dusts are charged to the furnace
3. The way in which volatilised nonferrous metals species are recovered in the fume.
4. Environmental emissions of the process.

ad 1: The manner of heat generation

Advantage of this Waelz process in relation to a high temperature process is the relatively low energy cost of the process. The Waelz process uses oil or gas as an energy source; the EMPF® process use electrical energy.

In Table 55, the energy prices of electrical energy for industrial consumers in the EC are shown. The prices are compared to the energy price in Norway, what is 0.1-0.2 NKR/kWh (including tax). From this table, it can be seen that the energy costs in different countries in the EC are not the same. For instance, the energy cost in a plant in the Netherlands would be 60% of the energy costs for a plant in Germany. In some countries, like France, industrial consumers receive considerable discounts, which results in prices less than those in Table 55.

Table 55 *International comparison of electricity prices as per 1 July 1990 for industrial consumers (4,000,000 kWh/year, excl. of VAT)*

Country	Dutch cents Ct/kWh	Norwegian Crowns NKR/kWh	%
Norway		0.15	100
Denmark	11	0.367	245
Netherlands	12.5	0.417	278
France	13.5	0.450	300
Ireland	15.0	0.500	333
Belgium	15.5	0.517	345
Greece	16.0	0.533	355
UK	16.0	0.533	355
Luxemburg	17.25	0.575	383
Portugal	18.0	0.600	400
Spain	20.0	0.667	445
Italy	20.25	0.675	450
Germany	20.5	0.683	455

100 NK = 30.00 HFL

ad 2: The form in which flue dusts are charged to the furnace

The form in which flue dusts are charged to the Waelz kiln is in the form of briquets. This requires a pretreatment of the flue dust.

Charging an EMPF® process does not require such extensive pretreatment, which can be regarded as an important advantage.

- ad 3: The way in which volitised nonferrous metals species are recovered in the fume.

This difference is of considerable interest, from an economic point of view, because the two different zinc phases that can be recovered have a different market value.

In the Waelz kiln, the volitised metals escape from the source material and are collected as a mixed oxide product which contains zinc, lead, cadmium, chlorides, and fluorid, and can be further processed only in an Imperial Smelting Process after it has been agglomerated in a suitable form for charging.

In an EMPF® process, the volitised metals are prevented from being oxidised by using an airtight unit and recovering it as a metal in an ISP type of condenser. The zinc metal that is recovered is of "Prime Western" grade which means that it contains less than 1.6% lead. The other condenser product (lead) has a zinc content of about 2% or less (?) and is also a saleable product. Recovery of the metals from the gas is much easier because the metals are present in a much higher concentration. This is caused by the airtight construction.

- ad 4: Environmental emissions of the process

In the Waelz kiln, temperature conditions are present which favour the generation of harmful dioxines. This will not likely happen in the EMPF® process.

Emissions to the work environment are difficult to control in a Waelz kiln. The waste product of the Waelz kiln is an ash, since it has not been liquid as in the EMPF® process. The leaching characteristics are, therefore, difficult to minimise beneath the required demands.

5.4 References

- [1] Feasibility evaluation of high temperature metals recovery process for a regional EAF-dust processing facility, International Technology Corporation.
- [2] Peek E., Dissolution of reduced zinc ferrite components in ammoniacal-ammonium carbonate solutions. Faculty of Mining and Petroleum Engineering, Delft Technical University, 1991.
- [3] Metal Statistics, Metallgesellschaft AG, 1991.

6 Conclusions

The most interesting materials for treatment in the EMPF® process are the zinc- and lead-containing materials from primary zinc and lead production (i.e. Blast Furnace and ISP smelters). These waste materials are produced at a limited number of sites, their economic value is high, and their processability is good.

Also the wastes from primary (Blast Furnace dusts from steel production) and secondary ferrous industries (EAF dust) have first priority as a result of the amount produced and their processability.

As the economic value of EAF dusts is relatively high, competition for treatment is expected to be considerable.

Several waste materials have secondary priority for treatment in the EMPF® process, e.g. the lead-containing slags from the secondary lead production (Reverberatory Rotary Furnace) and the fine fraction from C-steel production. The amount of these wastes is very big; their chemical and physical processability is good, but their economic value is not high.

Treatment of the wastes from primary (electrolytical) zinc production (jarosite and goethite) also has secondary priority, but is interesting because some producers are under pressure to reduce their waste problem. The processability of these wastes, however, is difficult; pretreatment is required, and their economic (metal) value is low.

Fly ashes from municipal waste incineration might be interesting for treatment in the EMPF® process. In some countries, producers are increasingly confronted with problems in trying to dispose of their waste. However, the economic value of the ashes is low and the (chemical) processability could give rise to problems because of the metal salts and the halides present. Bottom ashes from municipal waste incineration and wastes from hazardous waste incineration could be co-processed.

From an economic point of view, several waste materials, such as slags from zinc oxide production or flue dusts from lead refining, are interesting, but they are produced in a limited amount. These waste materials might be interesting for co-processing if an EMPF® furnace has been built for one or more other waste streams.

Only recently is the European legislation made at EC level becoming more important. So far, only the framework of legislation has been made and will not come into force before 1 April 1993. All the other Directives will come into force after this date. Currently, legislation is determined by the national governments of the Member States, and not by the EC; the same holds for the near future.

7 Authentication

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-

Date upon which, or period in which, the research took place

August 1990 - August 1991

Signature



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