Finnish expert report on best available techniques in zinc production
Sigmund Fugleberg

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Foreword


One of the activities included in the Directive concerns the production of non-ferrous metals, according to the definition of category 2.5 (a) in Annex I: “Installations for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes”. These installations are part of the industrial sectors to be studied in 1998.

Within the above mentioned framework, the Finnish Environment Institute and Outokumpu Technology Oy have decided to contribute to the exchange of information in the European Union by making a study on Best Available Techniques for the primary production of non-ferrous metals. Outokumpu Research Oy has been requested to perform this study. The responsible leader of the work has been Raimo Rantanen. Sigmund Fugleberg from Outokumpu Zinc Oy has acted as technical expert in zinc production. Marja Riekkola-Vanhanen has edited the report.

Primary non-ferrous metal production in Finland concerns only copper, nickel, zinc and ferrochromium. Gold and other precious metals are produced as by-products in the copper production. This report describes the primary production of zinc. The productions of primary copper, of nickel and of ferrochromium are described in separate reports.

The main objective of this BAT report is to identify techniques available for the reduction of emissions and energy use of primary zinc production in Finland. Only the hydrometallurgical electrolytic zinc process is in use in Finland to recover zinc from sulphide concentrates and it is described in this report. The information presented is largely based on environmental permit applications, the corporate environmental programme and permit regulations concerning Outokumpu. Additional information concerning general issues of zinc production and comparisons of processing methods has been obtained from literature available.

The project has been guided by a steering group that provided comments on the draft reports and offered a platform for discussion on the scope, themes and results of the study. The steering group members represented the following organisations: Finnish Environmental Institute, Southwest Finland Regional Environment Centre, West Finland Regional Environment Centre, Outokumpu Oyj, Outokumpu Technology Oy and Outokumpu Harjavalta Metals Oy, Outokumpu Chrome Oy and Outokumpu Zinc Oy.
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General Information

1.1 Zinc metal; properties and uses

Zinc is a grey white metal with a specific gravity of 7.14 g/cm³ and a melting point of 419.5 °C.

In nature it occurs mostly as sulphide, but, in certain areas oxide, carbonate and silicate minerals are significant. The concentration ranges from 2 to 30 % zinc in commercial ores.

Metallic zinc is produced principally by two routes, hydrometallurgically by electrolytic deposition from aqueous solution or pyrometallurgically by reduction to metallic form at a temperature so high that the metal is distilled off and subsequently recovered by condensation.

The most important property of zinc is its ability to react with iron so that a thin adherent layer can be applied onto the surface of iron objects. The zinc coating considerably prolongs the lifespan of steel constructions, thus saving energy and other natural resources like iron ore and more rare and expensive metals like nickel and molybdenum as alloying materials in steel, which would be an alternative choice.

Zinc alloys can easily be cast into very complicated forms which are used extensively in household goods and automotive equipment, building and construction utilities.

It is also an essential element for all living organisms; the human body contains 2 to 3 g of zinc compared to not more than 6 to 7 g of iron, and it is therefore used in pharmaceuticals, fertilisers and animal feed.

Other important areas are brass, batteries, tyres and other rubber goods /1/.

1.2 Zinc production and consumption in 1997

Table 1 shows that America and Asia/Pacific are the concentrate exporting areas and Europe the importing one. Production and consumption of metal are again quite equally distributed.

<table>
<thead>
<tr>
<th>Region</th>
<th>Metal Production</th>
<th>Consumption</th>
<th>Mine Production</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,000 t/a</td>
<td>%</td>
<td>1,000 t/a</td>
</tr>
<tr>
<td>Europe</td>
<td>2,668</td>
<td>34.5</td>
<td>2,461</td>
</tr>
<tr>
<td>Asia/Pacific</td>
<td>3,235</td>
<td>41.8</td>
<td>3,150</td>
</tr>
<tr>
<td>Africa</td>
<td>138</td>
<td>1.8</td>
<td>158</td>
</tr>
<tr>
<td>Americas</td>
<td>1,692</td>
<td>21.9</td>
<td>1,954</td>
</tr>
<tr>
<td>World</td>
<td>7,733</td>
<td>7,723</td>
<td>7,162</td>
</tr>
</tbody>
</table>

In Europe the distribution of mining, metal production and consumption, which is shown in Table 2, mostly reflects historical industrial development with some influence of energy cost.
Table 2. Production of zinc in Europe by countries in 1997 in tonnes of metal /1/.

<table>
<thead>
<tr>
<th>Country</th>
<th>Production</th>
<th>Consumption</th>
<th>Mine Production</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,000 t/a</td>
<td>%</td>
<td>1,000 t/a</td>
</tr>
<tr>
<td>Belgium</td>
<td>214</td>
<td>8.0</td>
<td>240</td>
</tr>
<tr>
<td>Finland</td>
<td>177</td>
<td>6.6</td>
<td>37</td>
</tr>
<tr>
<td>France</td>
<td>317</td>
<td>11.9</td>
<td>255</td>
</tr>
<tr>
<td>Germany</td>
<td>318</td>
<td>11.9</td>
<td>485</td>
</tr>
<tr>
<td>Italy</td>
<td>267</td>
<td>10.0</td>
<td>340</td>
</tr>
<tr>
<td>Netherlands</td>
<td>201</td>
<td>7.5</td>
<td>93</td>
</tr>
<tr>
<td>Norway</td>
<td>145</td>
<td>5.4</td>
<td>14</td>
</tr>
<tr>
<td>Poland</td>
<td>169</td>
<td>6.3</td>
<td>110</td>
</tr>
<tr>
<td>Russia</td>
<td>180</td>
<td>6.7</td>
<td>142</td>
</tr>
<tr>
<td>Spain</td>
<td>373</td>
<td>14</td>
<td>150</td>
</tr>
<tr>
<td>Un.Kingdom</td>
<td>97</td>
<td>3.6</td>
<td>226</td>
</tr>
<tr>
<td>Others</td>
<td>210</td>
<td>7.9</td>
<td>139</td>
</tr>
<tr>
<td>Europe</td>
<td>2,668</td>
<td>1,953</td>
<td>965</td>
</tr>
</tbody>
</table>

Most of the zinc is produced in plants with a capacity of 100,000 to 300,000 t/a. A list of the biggest plants is given in Table 3.

Table 3. Capacity of the world’s ten biggest zinc plants /1/.

<table>
<thead>
<tr>
<th>Location</th>
<th>Smelter</th>
<th>Company</th>
<th>Capacity, t/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spain</td>
<td>Aviles</td>
<td>Asturiana de Zinc</td>
<td>320,000</td>
</tr>
<tr>
<td>Canada</td>
<td>Trail</td>
<td>Cominco</td>
<td>272,000</td>
</tr>
<tr>
<td>China</td>
<td>Zhuzhou</td>
<td>Zhuzhou Lead-Zinc</td>
<td>250,000</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>Ust-Kamenogorsk</td>
<td>U-K Int.Lead-Zinc Works</td>
<td>240,000</td>
</tr>
<tr>
<td>Canada</td>
<td>Valleyfield</td>
<td>Canadien Electrolytic Zinc</td>
<td>230,000</td>
</tr>
<tr>
<td>Finland</td>
<td>Kokkola</td>
<td>Outokumpu Zinc (1998)</td>
<td>225,000 x)</td>
</tr>
<tr>
<td>Australia</td>
<td>Risdon</td>
<td>Pasminco</td>
<td>220,000</td>
</tr>
<tr>
<td>Korea</td>
<td>Onsan</td>
<td>Korea Zinc</td>
<td>220,000</td>
</tr>
<tr>
<td>France</td>
<td>Auby</td>
<td>Union Minière</td>
<td>215,000</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Budel</td>
<td>Budel Zinc</td>
<td>205,000</td>
</tr>
</tbody>
</table>

1.3 Economic importance of the zinc industry

From 1950 to 1973 the growth in metal production was very rapid, from 1.5 Mmt/a to about 6 Mmt/a. Growth has since been much slower, and world production is now about 7.7 Mmt/a. In tonnes, most of the increase has come from electrolytic production, representing more than 80% of world current production. The blast furnace process, Imperial Smelting, was also developed during this time and it represents now about 13%, whereas earlier methods have lost their importance.

Like most other metals, zinc has also been subjected to substantial fluctuations in price, mostly triggered by an imbalance of supply and demand. As the price of zinc is quoted in US$, the fluctuations have been more severe outside the dollar area, with the fluctuation in the dollar quotation of local currencies added to the price quoting. The price of zinc in 1998 terms has fluctuated around 1,100 US$/mt from 1960 to 1997, with two exceptions, in 1972–74 and 1989–90, when it was considerably higher /1/. This means that on average the volume of the industry is about 8 to 9 billion US$/a worldwide. This value is divided more or less equally between the mines and the metallurgical works.

The production rate of primary zinc metal in Finland, being 225,000 t/a (end of 1998) at a value of about 1.5 billion FIM, represents about 0.3% of the Gross
National Product and 0.8% of exports, is relatively more important than its value worldwide. All primary zinc in Finland is produced by Outokumpu Zinc Oy in Kokkola.
2

Applied Techniques

Zinc is produced principally by two different methods:
1. Hydrometallurgically where zinc is brought into solution which is then purified and pure zinc is deposited electrolytically from the solution.
2. Pyrometallurgically where oxide is reduced to metallic vapour by coke at a high temperature and the impure metal obtained on condensing is purified by fractional distillation.

In this report only the hydrometallurgical route, The Electrolytic Zinc Process, is described, as this is the only process operated in Finland, and the pyrometallurgical process use somewhat different raw materials and does not directly compete with the electrolytic process.

The most widely used techniques in electrolytic zinc processing are reviewed in this paragraph. The technique employed by Outokumpu Zinc is described separately under each sub-process if this is not a standard used by all producers.

The process operated by electrolytic zinc plants is fairly standard. The major equipment and techniques used and the major process steps are common practice world-wide. The major steps are:
1. Roasting of sulphide concentrate to convert the sulphides to acid soluble oxides and utilising the SO₂ gas for acid production.
2. Leaching of the oxides in recycled sulphuric acid solution to produce a zinc sulphate solution.
3. Purification of the zinc solution.
4. Electrowinning of the zinc as cathodes with simultaneous regeneration of sulphuric acid, the so-called spent acid, which is recycled to leaching.
5. Melting and casting of the cathodes to commercial shapes.

Figure 1 is a flow diagram showing the most important main steps and their main function in a typical process. The division of the description is made according to the main steps shown in the figure.
2.1 Raw materials

The dominating raw material, the concentrate, is produced from sulphidic ores by flotation. The composition of the concentrate is determined by the mineralogy of the ore and the concentration of the different elements fluctuates greatly. Besides zinc some other elements; copper, cadmium and sulphur, are almost always recovered to marketable products, whereas others like silver, lead and some minor elements are either recovered or wasted depending on how economical the processes are. The rest of the elements are wasted, either as a solid or in a waste water bleed from the process. Table 4 shows the concentration ranges of the most common elements in commercial concentrates and they are grouped according to how they end up in the process.

Table 4. Concentration range of elements in zinc concentrates and their behaviour in the electrolytic zinc process

<table>
<thead>
<tr>
<th>Marketable products</th>
<th>Products or waste</th>
<th>Solid waste</th>
<th>Liquid waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn 45–60</td>
<td>Ag 0.001–0.05</td>
<td>Fe 2–14</td>
<td>Mg 0.02–0.3</td>
</tr>
<tr>
<td>Cu 0.1–2</td>
<td>Pb 0.2–3</td>
<td>As 0.01–0.4</td>
<td>Cl 0.01–0.03</td>
</tr>
<tr>
<td>Cd 0.1–0.4</td>
<td>Hg 0.001–0.2</td>
<td>SiO₂ 0.5–4</td>
<td>F 0.01–0.03</td>
</tr>
<tr>
<td>S 29–36</td>
<td>Se 0.05–0.3</td>
<td>Al 0.05–1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>Mn 0.1 0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>Ca 0.05–1.5</td>
<td></td>
</tr>
</tbody>
</table>
The main mineral is sphalerite, ZnS, which contains Cd and Fe in solid solution. The minor minerals are CuFeS$_2$, PbS, FeS$_2$, CaCO$_3$ and mixed silicates of Al, Mg, Ca and Na.

In Europe most of the concentrates used are sulphidic, but some oxidic concentrates also occur. Recycled zinc in the form of oxide from the pyrometallurgical pre-treatment of steel, e.g. Waelz oxide, is also used.

Outokumpu Zinc also uses some oxides from brass production and Zn and Cd containing weak acids and dusts from Outokumpu’s copper and nickel smelters.

2.2 Raw materials handling

Raw materials come by ship, rail or road and are transported by covered belt conveyers to enclosed storage buildings. Here the different concentrates are mixed to give a homogeneous feed. The mix is transported by belt conveyers via day-bins (silos) to the roasting furnace.

2.3 Roasting

Nowadays roasting furnaces are of fluidised bed-type. Combustion air is blown through tuyeres in a grid at the bottom of the furnace and further through the fluid bed of material being roasted on the grid. The concentrate is fed onto the top of the bed. The oxygen reacts with the sulphides in the bed to produce oxides, the so-called calcine, and SO$_2$ gas at about 900–1000°C. The ZnS will form zinc oxide, ZnO, whereas practically all of the iron is combined with zinc to give zinc ferrite, ZnOFe$_2$O$_3$, which, with iron contents in the raw materials as shown in table 4, uses up about 2 to 15% of the zinc content:

$$\text{ZnS} + 1.5 \text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2 \quad (1)$$

$$\text{ZnS} + 2\text{FeS} + 3.5 \text{O}_2 \rightarrow \text{ZnOFe}_2\text{O}_3 + 2\text{SO}_2 \quad (2)$$

The roasting also removes some minor impurities like Cl, F, Se and Hg into the gas phase.

2.4 Gas cleaning and heat recovery

The hot SO$_2$ gas, containing part of the calcine as dust, is first cooled in a waste heat boiler where part of the dust is collected. After cooling the rest of the dust in the gas is reduced to less than 100 mg/m$^3$ in cyclones and electrostatic precipitators. All dusts and the calcine taken out of the furnace are mixed, cooled and pneumatically transported to storage silos.

The heat evolved in the roasting is recovered as steam by cooling coils in the bed and in the waste heat boiler. Utilisation of the steam may vary somewhat depending on the need at the plant site, but part of it is always used for heating in the process.

At Outokumpu Zinc the high pressure steam is sold to an electric power plant and the secondary low pressure steam for heating in the process is bought back. The rest of the energy is sold as electric power and district heat by the power plant.
2.5 Mercury removal

The SO₂ gas from the roaster contains calcine dust, HCl, HF, SeO₂, some SO₃ and metallic mercury. The impurities other than mercury are removed by a first washing and cooling step in the acid plant. This washing step produces the so-called weak acid which contains high levels of chloride and fluoride and cannot as such be used in the zinc plant. Often it is neutralised with lime or limestone and the gypsum is wasted.

The mercury goes through this wash step and needs a separate removal stage. Three different scrubbing processes are available for the removal of the metallic mercury from the SO₂ gas. Processes for removal from the acid are also used, but not frequently in the electrolytic zinc process. All processes produce a sludge which is either stored or used for the production of metallic mercury.

2.5.1 The Boliden-Norzink Process

This removal step is placed after the washing and cooling step in the acid plant, so the gas is dust and SO₃ free and the temperature is about 30°C /2, 4/. The gas is scrubbed in a packed bed tower with a solution containing HgCl₂. This reacts with the metallic mercury in the gas and precipitates it as calomel, Hg₂Cl₂:

\[ \text{HgCl}_2 + \text{Hg} \rightarrow \text{Hg}_2\text{Cl}_2 \]  

(3)

The calomel is removed from the circulating scrubbing solution and partly regenerated by chlorine gas to HgCl₂, which is then recycled to the washing stage. The mercury product bleed is either used for mercury production or stored.

2.5.2 The Bolchem Process

This process step is located in the acid plant as in the Boliden-Norzink process, but the removal is effected by 99 % sulphuric acid. This acid comes from the absorption part of the acid plant and it oxidises the mercury at an ambient temperature. The resulting mercury-containing acid is diluted to 80 % and the mercury is precipitated as sulphide with thiosulphate. After filtering off the mercury sulphide the acid is returned to the absorption. No acid is therefore consumed in the process, it is only in an internal circulation loop.

2.5.3 The Outokumpu Process

In this process the mercury is removed before the washing step in the acid plant /3, 4/. The gas, at about 350 °C, is led through a packed bed tower where it is washed countercurrently with approx. 90 % sulphuric acid at about 190 °C. The acid is formed in situ from the SO₃ in the gas. The mercury is precipitated as a selenium-chloride compound.

The mercury sludge is removed from the cooled acid, filtered and washed and sent to the production of metallic mercury. Part of the acid is then recycled to the scrubbing step.
2.5.4 The thiocyanate-sulphide Process

The SO$_2$ gas is washed with a solution of sodium thiocyanate and the Hg is removed as sulphide /4/:

$$3\text{Hg} + 8\text{SCN}^- + 4\text{H}^+ + \text{SO}_2 = 2[\text{Hg(SCN)}_4]^{2-} + \text{HgS} + 2\text{H}_2\text{O}$$  (4)

2.5.5 Removal from the acid

Potassium iodide is added to the acid, which should be at least 93 %, at a temperature of about 0 °C and mercury iodide, HgI$_2$, is precipitated /4/.

2.6 Mercury refining

Two processes producing marketable metallic mercury from the precipitates obtained in the removal are or have been in operation:

2.6.1 The Outokumpu Process

The precipitate is mixed with lime, heated to 700 °C and the mercury is distilled off as metallic vapour and condensed in a cooler. The resulting gypsum residue contains the selenium, and selenium metal and salts have been produced from it when it was still economical. Outokumpu Zinc is using this process /3/.

2.6.2 The Norzink Process

In the Norzink process part of the precipitate, the calomel, is electrolysed to give metallic mercury and chlorine gas, which is reacted with the rest of the calomel to produce the reagent, HgCl$_2$, used in the scrubbing /2/.

2.7 Leaching of calcine

The calcine is fed by drag and screw conveyors to the first leaching stage where the zinc oxide, ZnO, is leached in agitated tanks at 60 to 80 °C with recycled spent acid solution from the electrolyses and acidic return solutions from the ferrite treatment:

$$\text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O}$$  (5)

This step produces a neutral zinc sulphate solution which is forwarded to purification before the electrowinning. This leaching is standard procedure in every plant /7,9,11,15,17,18/.

The ferrite, as the major component, together with silica, gypsum, lead and silver compounds etc. form the so-called neutral leach residue, which in this report is called the ferrite residue as this is metallurgically more descriptive.
2.8 **Treatment of the ferrite residue**

For this treatment both pyro- and hydrometallurgical routes are available; the latter being the most frequently used and comprising leaching and iron precipitation steps. The different processes used are named after the precipitated iron compound. Figure 2 shows some simplified flowsheets of some of the different options described below.

2.8.1 **Hydrometallurgical processes**

2.8.1.1 **Hot (High) Acid Leach (HAL) of ferrite**

This is the first step in almost every ferrite treatment process regardless of the iron precipitation method used /6,9,15,17/. The zinc in the ferrite is brought into solution in an acid leaching step at close to 100 °C and an acid concentration of above 30 g H₂SO₄/l; the so-called Hot Acid Leach (HAL):

\[
\text{ZnOFe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{ZnSO}_4
\]  

(6)

As this leaching also solubilises the iron, a removal step is needed before the zinc-containing solution can be recycled back to the neutral leach.

---

**Figure 2. Simplified flowsheets for some ferrite treatment options**
Ag and Pb, which stay in the residue, are either recovered or wasted depending on the economy of the process. Recovery of Ag and Pb is done either by smelting, in lead smelters, of the entire acid leach residue, or of Ag(Pb)-concentrate produced by a flotation on the residue. In the case of flotation the tailing is joined with the iron residue, and so is the entire residue if Ag,Pb is not recovered.

Whether the Ag,Pb is recovered or not depends very much on the infrastructure at the plant site; with an adjacent lead smelter transport and separate drying of a very difficult material is avoided and the marginal costs in an existing plant can be justified, whereas a separate treatment process will cost excessively.

For iron precipitation from the HAL solution three different processes are available, i.e. The Jarosite, Goethite and Hematite processes.

### 2.8.1.2 The Jarosite Process

Jarosite, A[Fe₃(SO₄)₂(OH)₆] (where A = NH₄⁺, Na⁺, K⁺, H₃O⁺ etc.), is precipitated directly from the A⁺-ion-containing HAL solution with the iron in ferric, Fe³⁺, form, at about 5 g/l H₂SO₄, which is maintained by neutralising with the zinc oxide in the calcine /11,15/: 

$$3\text{Fe}_2(\text{SO}_4)_3 + (\text{NH}_4)_2\text{SO}_4 + 12\text{H}_2\text{O} + 6\text{ZnO} \rightarrow 2\text{NH}_4[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6] + 6\text{ZnSO}_4$$ (7)

Ammonia is normally used as the source for the A⁺-ion as this is the cheapest and purest chemical available /11/.

The ferrite in the neutralising calcine will stay unleached at the conditions normally used in the precipitation and the corresponding zinc will either be lost with the jarosite, or can be recovered in a subsequent acid leach step of the precipitated jarosite at conditions that will leach the ferrite but leave the jarosite. This is possible because of the high stability of jarosite in acid solutions. Extractions of zinc can thus be raised to 99% even with an iron content of up to 10% in the concentrates /5/.

Outokumpu Zinc operates a simplified process, The Conversion Process /11/, for the treatment of ferrite. It was developed because recovery of Ag,Pb would not be viable with the low Ag in the available feed, and with no lead smelter close by. In this process the leaching of ferrite and the precipitation of iron as jarosite are combined in a single step where the acid content is kept at about 30 g/l by the controlled addition of spent acid:

$$3\text{ZnOFe}_2\text{O}_3 + 6\text{H}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4 + 12\text{H}_2\text{O} \rightarrow 2\text{NH}_4[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6] + 3\text{ZnSO}_4$$ (8)

In the process the jarosite is precipitated at conditions where ferrite is leached and thus it acts as a neutralising agent, therefore no neutralising calcine is needed. This ensures high recovery in a technically simple process which actually combine the 3 steps of HAL, jarosite precipitation and acid leach of the jarosite.

From 1998 the slurry from the Conversion, still having some ferric iron in solution, is led to an atmospheric leach of concentrate. Earlier the solution was recycled to the neutral leach.

### 2.8.1.3 The Goethite Process

Precipitation of goethite, FeOOH, is mostly done with the iron in ferrous, Fe²⁺, form by neutralising with calcine, and oxygen or air for oxidation of the iron at a pH of about 3 /17/:

$$6\text{FeSO}_4 + 1.5\text{O}_2 + 3\text{H}_2\text{O} + 6\text{ZnO} \rightarrow 6\text{FeOOH} + 6\text{ZnSO}_4$$ (9)
The ferrous iron has been formed by reduction of the acid leach solution with concentrate,

$$\text{ZnOFe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4 + \text{ZnS} \rightarrow 2\text{FeSO}_4 + 2\text{ZnSO}_4 + \text{S} + 4\text{H}_2\text{O} \quad (10)$$

The goethite will be leached at conditions where ferrite is leached, and accordingly a re-leach of the ferrite in the neutralising calcine from the goethite is not possible as it is with jarosite. Consequently, similar recoveries to those obtained with jarosite are possible only by using zinc oxide or calcines with very low iron for neutralisation.

![Goethite precipitation graph](image)

**Figure 3. Extraction loss from ferrite in goethite precipitation.**

Figure 3 shows the influence on extraction of the loss of zinc with the ferrite as a function of the iron content in the concentrate used for production of the neutralising calcine. The calculations are based on precipitation according to reaction 9 from a pre-neutralised solution and 52% Zn in the concentrate. Also the recovery of ZnO in the neutralising calcine is taken to be 100%; this may not be the case as the pH in the precipitation is rather high.

### 2.8.1.4 The Hematite Process

The leaching in the Hematite, Fe$_2$O$_3$, process is similar to the one used in the Goethite process, but the precipitation of iron is made in an autoclave at 180 to 200 °C without neutralisation /7,18/:

$$6\text{FeSO}_4 + 1.5\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Fe}_2\text{O}_3 + 6\text{H}_2\text{SO}_4 \quad (11)$$

High extraction, up to 99.5%, is obtained as no neutralising calcine is needed. The hematite has been used as a pigment in the cement industry but the impurity level is too high for it to be generally accepted, and the impurity level also excludes it as a feed to the iron blast furnace.

Generally the processes get very complicated if Ag, Pb is recovered and high recoveries both for these elements and for zinc are sought /18/. To justify the cost of such a process the revenue from Ag and Pb must be substantial and high contents, in the concentrates are needed, especially of Ag.
2.8.2 Pyrometallurgical Processes

2.8.2.1 Waelz treatment

Only the oxide is leached from the calcine and the ferrite residue is filtered, washed, dried and heated with coke in a rotary furnace. The zinc is reduced and fumed off as metallic vapour, reoxidised and collected as an oxide in bag filters and normally leached in a separate step. Part of the Pb and Ag is recovered and the iron is contained in the slag.

2.8.2.2 Residue to Lead Smelting

The lead and silver are recovered in the lead bullion and the zinc, as an oxide fume, is recycled to the zinc leaching /20/. The iron is contained in a slag.

2.8.2.3 Ausmelt

This is a two step bath smelting process where the reagents, coal and air or oxygen are fed with a lance into the molten slag. In the first furnace (or step) the melting of the feed material is performed and in the second the conditions are kept more reducive to remove Zn, Pb and other volatile elements and to obtain an acceptable slag. One plant uses this method for smelting goethite /9/. The slag contains 2.4 % Zn.

2.9 Leaching of concentrates

Roasting and acid production call for high investment and operating cost and, if the market for sulphuric acid is absent, direct leaching of concentrate offers an alternative solution in zinc production, especially when expanding the capacity of existing plants or for new plants in remote areas. Roasting and removing of the sulphur as gypsum would be both very expensive and produce very high quantities of gypsum (about 3 t per ton of zinc).

The concentrates are oxidised by oxygen in a sulphuric acid solution containing iron to produce zinc sulphate solution and elemental sulphur,

\[
2\text{ZnS} + 2\text{H}_2\text{SO}_4 + \text{O}_2 \rightarrow 2\text{ZnSO}_4 + 2\text{S} + 2\text{H}_2\text{O}
\]  

This leaching is performed both at elevated pressure in autoclaves at about 150 °C and at atmospheric pressure at 100 °C.

In most leaching processes the iron is simultaneously precipitated; in the autoclave as hematite and jarosite and in the atmospheric leach as jarosite. In one plant (Korea Zinc) using atmospheric leach the iron is left in solution during the leaching and precipitated in a separate step as goethite.

The elemental sulphur is removed by flotation. It is normally stored because the marketing is problematic due to selenium, which will not be removed in a normal acid plant designed for elemental sulphur. One plant (Cominco) /20/ sells the sulphur to an acid plant.

2.9.1 Pressure leaching

The concentrate is fed to an autoclave and leached with oxygen and spent acid at 150 °C in the presence of iron in the solution. The heat needed for raising the tem-
perature is obtained from the heat of the reaction. The iron is precipitated as a mixture of hematite and jarosite. Reported extractions for Zn are from 97 to 99+%; the latter figure being for a two step process /21/.

### 2.9.2 Atmospheric leaching

Two applications are known, i.e. at Korea Zinc and Outokumpu Zinc. At Korea Zinc the iron is left in solution during leaching and precipitated in a separate step as goethite, whereas at Outokumpu the iron is precipitated as jarosite simultaneously with the leaching of the sulphides /9,14,13/.

**Outokumpu Zinc.**

The concentrate together with the slurry from the Conversion Process and acid from the electrolysis are fed to the reactors where the leaching takes place by sparging oxygen into the slurry. The rest of the dissolved iron in the solution from the conversion and the iron dissolved from the concentrate are precipitated as jarosite:

\[
3\text{ZnS} + 6\text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O} + 4.5\text{O}_2 = 2\text{NH}_4\text{[Fe}_3\text{(SO}_4)_2\text{(OH)}_6] + 3\text{ZnSO}_4 + 3\text{S} \quad (13)
\]

A sulphur concentrate is separated from the slurry by flotation and stored separately from the jarosite residue.

The equipment used in the process is much the same as conventionally used in zinc hydrometallurgy.

Extraction of Zn well above 98% can be reached with a number of available concentrates /13/. A flowsheet of the process as run at Outokumpu Zinc is shown in Figure 4.

![Flowsheet showing the present leach circuit at Outokumpu Zinc.](image)

### 2.10 Residue handling

Most of the components making up the solid residues from any of the leaching processes are very stable, but, as the solid is separated from a concentrated metal sulphate solution, even with thorough washing, some soluble heavy metals will still be left. Consequently the handling of the water-soluble metals is a critical point in the disposal of the leach residues. Different methods are used to handle these soluble metals:

1. Thorough washing.
2. Neutralisation and precipitation of the rest as hydroxides.
3. Precipitation as sulphides.
4. Storing of the residue isolated from ground water.
5. Fixation as other insoluble compounds with cement or phosphate and lime.

Washing is in many plants nowadays performed on horizontal belt filters, which is more effective than in the formerly used drum filters. The water-soluble zinc can be lowered to one tenth of earlier levels. Good washing presupposes availability...
of sufficient water, and the water balance of any plant is always a problem, therefore a higher bleed of dilute solutions through the waste water treatment will ensure a thorough wash of the residues. This will increase the waste water bleed and produce extra gypsum.

Recycling of any water from the storage area to the process or to waste water treatment is normal practice.

Outokumpu Zinc.
All solid residues, except the sulphur concentrate, are combined with the iron residue and filtered on horizontal belt filters. The filter cake is treated with Na₂S to precipitate the soluble metals.

The residue is pumped to the top of the terraced residue area where the solids settle and the pumping water flows downwards via lower sections to a point from where it is recycled to the pumping.

The sulphur concentrate is filtered and washed on horizontal membrane filter presses and pumped to a lined pond within the residue area.

The residue area was built in 1973 and was not lined with plastic cloth, therefore it is surrounded by a seepage ditch from where pumping keeps the ground water flow towards the dikes. The ground water is monitored by observation tubes around the whole area. /10/

2.11 Solution purification

This stage is primarily for removing impurities which will interfere in the electrolysis, either by contaminating the zinc or reducing the current efficiency. Secondly, the valuable metals, copper and cadmium, should be recovered with high selectivity into separate products and in a form that makes refining to end products easy and economical. The dominant reaction is cementation with zinc dust:

\[
\text{MeSO}_4 + \text{Zn} \rightarrow \text{Me} + \text{ZnSO}_4
\]

Two principally different purification systems are used; the difference being in the method for cobalt and nickel removal, where special reagents, As₂O₃ and Sb₂O₃, are needed, otherwise the only reagent is metallic Zn dust. Depending on the copper level, the first step in any purification system can be a copper cementation, where part of the copper is cementated with zinc dust to produce a high grade copper precipitate, which is sold to copper smelters.

2.11.1 Cobalt and Nickel with As₂O₃

In this process Co and Ni are precipitated as arsenides, CoAs and NiAs, using zinc dust and arsenic trioxide.

\[
2\text{CoSO}_4 + \text{As}_2\text{O}_3 + 5\text{Zn} + 3\text{H}_2\text{O} = \rightarrow 2\text{CoAs} + 2\text{ZnSO}_4 + 3\text{Zn(OH)}_2
\]

The process is often referred to as “Hot arsenic zinc dust” purification as it is normally performed at a temperature of 90–95°C. With this process a high grade copper cement with low cadmium content can be produced. At the same time a concentrated cadmium cement which is low in impurities is also produced. This is advantageous in cadmium production.
Arsenic in the Cu, Co, Ni precipitate can be releached and recycled to the process, so the leached product can easily be fed to copper smelters. Some arsine gas is evolved in the Co removal step.

*Outokumpu Zinc* operates its own development, a three step variant of this process. Most of the copper is precipitated as a clean copper product in the first step; in the second step the rest of the Cu plus Co and Ni are precipitated at 70–75 °C, and in the last step Cd is removed using a fluidised bed system /12/.

The process is characterised by low zinc dust and energy consumption as no heating is required. The obtained precipitates, Cu cake, Co cake and Cd cake, are high grade with a minimum of cross contamination. The low content of Cd in the Cu cake is especially an advantage in copper smelting. Both the copper and the cobalt cakes are fed to Outokumpu’s copper smelter in Harjavalta. The Cd is processed to metal at the zinc plant.

Due to the low Zn dust consumption no releach of the cakes from the purification is needed.

### 2.11.2 Cobalt and Nickel with Sb₂O₃

Cobalt and nickel are precipitated as a metallic alloy using zinc dust and antimony trioxide as catalysts.

All impurities, copper, cadmium, cobalt and nickel, are in most applications obtained as a mixed residue with high zinc content. An elaborate releach operation, including a final cobalt and nickel precipitation using As₂O₃, is often required to obtain a satisfying copper product.

The temperature should be 90°C, so heating is required. Stibine gas is evolved, but to a lesser extent than arsine in the As₂O₃ purification. A modified process is used by Pasminco /22/ where a high temperature is not needed. Here all copper is precipitated in the first step and the rest of the metals in the second one.

### 2.12 Cadmium production

Metallic cadmium is produced by two principally different processes, melt refining or electrolysis. The Cd-containing precipitate from the purification is leached in sulphuric acid, and if copper is present it remains unleached and is filtered off and sent to copper production. The solution is purified for copper and lead by Zn dust addition. Then a second Cd precipitate, where the only major impurity is Zn, about 1 % Zn, is produced. The precipitate is either briquetted and melted to a marketable product with sodium hydroxide which removes the zinc, or is releached in spent cadmium electrolyte. The leach solution is purified and sent to electrolytic production of cadmium. The melt-refined cadmium is in some cases also further refined through vacuum distillation. The pure cadmium is cast to sticks or balls using different techniques.

*Outokumpu Zinc*

The raw material is the metallic precipitate from the cadmium removal in the Zn circuit. It contains 85–90 % Cd, most of the rest is Zn with minor amounts, 0.1–0.5 %, of Cu, Ni, Pb, Tl.

The process comprises leaching, solution purification, precipitation of metallic cadmium with Zn dust, briquetting of the precipitate, melt refining with sodium hydroxide and casting of Cd sticks.

All impurities coming into the process have an outlet in the Zn circuit and therefore all impurities are bled back to the same.
Leaching of the precipitate is performed in agitated tanks with a sulphuric acid solution. To prevent fumes coming to the working area the tanks are equipped with forced ventilation which keep a slight under pressure in the tanks. Each stack for the vent air is equipped with a scrubber which removes droplets of solution ripped off the solution surface. The solution obtained in the scrubbers is bled back to the tank. The collection efficiency is about 98 %.

The solution is filtered and the residue is returned to leaching in the Zn plant and the solution goes to purification.

The temperature is about 90 °C and the acid content about 5 g/l at the end.

The solution is purified in the first step where copper and lead are removed by adding cadmium dust and Ba(OH)₂. Copper is precipitated as metallic powder and lead as a mixed Ba,Pb-sulphate. The solution is filtered, the residue is returned to leaching in the Zn plant and the solution goes to nickel removal.

Nickel is precipitated with dimethyl glyoxime and NaOH for neutralising. The solution is filtered, the residue is returned to leaching in the Zn plant and the solution goes to cadmium precipitation. The temperature is about 90 °C.

Zn dust is added to the solution and cadmium precipitates as metallic powder, cadmium sponge. The sponge is settled on the bottom of the tank and the solution is pumped to the Zn plant leach where thallium is precipitated as an insoluble mixed compound with iron, Tl[Fe₃(SO₄)₂(OH)₆] and zinc and eventual cadmium are recovered through the normal route.

The temperature is about 90 °C and the acid content about 5 g/l at the end.

The sponge is briquetted to a density of about 6 g/cm³ to remove the solution and to facilitate the succeeding melting stage.

The only significant impurity, zinc at about 1 %, is removed from the cadmium in the melting stage by NaOH which forms Na₂ZnO₂, sodium zincate, forming a slag on the top of the melt cadmium. The melting is done in an electrically heated furnace equipped with agitation at a temperature of about 400 °C. The cadmium metal under-flows by gravity to a second furnace from where it is cast.

The slag is then removed and leached in water. Eventual cadmium metal stays unleached and is returned to melting whereas the solution with the zinc and NaOH is sent to the Zn circuit where sodium acts as a reagent in the iron precipitation.

For the casting a so-called upward casting technique is used. The metal is cast as a continuous rod drawn upwards through a mould on the surface of the molten metal. The rod is cut into sticks which are packed and despatched. This part of the process is performed in an enclosed area with forced ventilation and the vent air is fed to the roaster where eventual cadmium fumes are recovered. The operation is also highly automated and the need for operators intervention is very minor in the area /23/.

### 2.13 Electrolysis

The pure zinc solution is pumped to the cell house where zinc is electrowon onto aluminium cathode sheets placed in cells. An equivalent amount of oxygen gas and acid, the so-called spent acid, is produced at the lead anode. The overall reaction taking place is:

\[
\text{ZnSO}_4 + \text{H}_2\text{O} \rightarrow \text{Zn} + 0.5\text{O}_2 + \text{H}_2\text{SO}_4
\]

The spent acid produced is returned to leaching. The oxygen bubbles, when bursting at the solution surface, disperse acid mist into the air and to maintain acceptable working conditions a froth layer is maintained on the surface of the cell by
the addition of certain chemicals (glue). Zinc is stripped off the aluminium sheet every 24 to 72 hours depending on whether a high (650 A/m²) or low (400 A/m²) current density is used. The zinc cathode sheets are washed and sent to the casting department.

The cells are made of concrete lined with lead or from synthetic resin-based materials.

About half the electric energy consumed in electrowinning is converted to heat absorbed by the solution and this heat is removed by circulating the solution through cooling towers, where the heat is removed through evaporation. This evaporation represents more than half the water removed from the process and is very important for maintaining the water balance in the plant and thus allows for good washing of residues.

*At Outokumpu Zinc* the current density is 570 A/m² and the stripping cycle is about 35 h.

### 2.14 Casting

The zinc cathodes are melted in induction furnaces and the metal is cast to different shapes and sent to the consumers. Ammonium chloride is used as a fluxing agent. The dross, mainly zinc oxide and small amounts of zinc chloride, is recycled to the roaster. The zinc dust needed in the purification is also produced in this department by atomising molten zinc with air.

*At Outokumpu Zinc* both the air from the zinc dust production and the gas from the smelting furnace are combined and cleaned in bag-filters and the dust is returned to the roaster.

### 2.15 Auxiliary systems

#### 2.15.1 Cooling water systems

All cooling systems are normally closed to save fresh water. The bleed from systems even with no risk of contamination are routed to the water treatment or used in the process.

#### 2.15.2 Waste water treatment

All effluents from the process, excess recycled waters from the residue area and excess run-off water from the plant area are treated. The bleed of solution from the process is for controlling of the magnesium concentration in the solution circuit as well as dilute wash solutions which enable the intake of more water for residue washing.

Normal treatment is to precipitate the metals as hydroxides and/or sulphides which are recycled to the process.

*At Outokumpu Zinc* a three step process is used:

The most concentrated solutions are fed to the first step where the pH is raised to about 7 by lime addition to precipitate the most heavy metals while leaving magnesium in solution. The precipitate is filtered off and recycled to leaching for recovery of the metals.

The solution from the first step and less concentrated waste solutions are fed to the second step where the heavy metals are precipitated as sulphides. These
sulphides are recycled to the process and the solution goes through a clear filtration.

The solution from the second step and cooling waters are mixed and the pH increased to precipitate the rest of the metals. It is then run through settling ponds before being let out to the sea. The ponds are dredged and the sludge is sent to the residue area /10/.
3. Present Consumption and Emission Data

3.1 Raw materials, utilities, energy consumption and energy production

3.1.1 Raw material consumption

The main cost items in zinc production are approximately as follows: concentrate 50%, electric energy 10–15%, maintenance 3%, wages 25%, and chemicals 1% of the total cost. The rest is unspecified.

The recovery of zinc is of outmost importance, because the concentrate is by far the most significant cost item. Metallurgically the two decisive factors concerning recovery are the leaching process used and the iron content of the concentrate, but the economical optimum for the individual plants is also influenced by investment and operating cost and thus the effectiveness of a plant is not decided by the recoveries alone.

3.1.2 Electric energy

This is by far the most important commodity and the consumption is in the order of 4,000 kWh per ton of saleable zinc. About 85% is consumed in the electrowinning step, 4% in the melting and casting and the rest is used for transportation of liquids and solids, agitation, illumination etc.

The consumption per ton of saleable zinc in electrowinning is dependent on a number of factors like current density (high productivity on investment), purity of the feed solution, composition of the electrolyte, and the so-called “house-keeping” or mechanical condition of the cell house. These parameters vary somewhat from plant to plant and are determined by historical and local factors. For example high current density, which causes higher energy consumption, is balanced by lower investment costs.

3.1.3 Heat

The second energy commodity is steam, which is used for heating the solution. The steam used is a part (roughly 40–50%) of the steam generated in the roaster. The rest of the steam is used for electric energy production, district heating or other heating purposes.

3.1.4 Chemicals

The main chemicals used are:
1. Ammonia for jarosite precipitation, which amounts to 50–70 kg NH₃ per tonne of iron in the feed.
2. Lime or limestone for magnesium removal and neutralisation of the residue. The quantity depends on the magnesium in the feed and water-soluble zinc left in the residue, and if an additional sulphate bleed is needed.

3. \( \text{As}_2\text{O}_3 \) or \( \text{Sb}_2\text{O}_3 \) which depends on the quantity of cobalt and nickel; normal values are about 1 kg and 0.05 kg per tonne of zinc respectively.

Table 5 gives some typical consumption and production figures as well as some other parameters from Outokumpu Zinc. It can be seen that due to the need for district heating in the area, the utilisation rate for heat produced is over 80%. Some ranges for the industry are also given as far as they have been available.

<table>
<thead>
<tr>
<th>Heat balance</th>
<th>MWh/t Zn</th>
<th>Industry, MWh/t Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam production</td>
<td>1.55</td>
<td>1.4–2.5 /6/</td>
</tr>
<tr>
<td>Steam consumption in plant</td>
<td>0.88</td>
<td>0.7–1.0</td>
</tr>
<tr>
<td>Electric energy produced</td>
<td></td>
<td></td>
</tr>
<tr>
<td>District heat</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Losses</td>
<td>19 %</td>
<td></td>
</tr>
<tr>
<td>Recoveries %</td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>Zn</td>
<td>98</td>
<td>96–99 /6/</td>
</tr>
<tr>
<td>S as ( \text{SO}_2 )</td>
<td>72</td>
<td>0–92</td>
</tr>
<tr>
<td>S as elemental sulphur</td>
<td>22</td>
<td>0–100</td>
</tr>
<tr>
<td>S in calcine</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Electric energy consump.</td>
<td>MWh/t Zn</td>
<td>MWh/t Zn</td>
</tr>
<tr>
<td>Total</td>
<td>3,800</td>
<td></td>
</tr>
<tr>
<td>Electrolysis</td>
<td>3,300</td>
<td>2950–3400 /6/</td>
</tr>
<tr>
<td>Rest of the plant</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Residue to residue area</td>
<td>t/t Zn</td>
<td></td>
</tr>
<tr>
<td>Jarosite (Pure compound)</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Silicates, ( \text{Pb, MnO}_2 ), etc</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Sulphur concentrate</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.83</td>
<td></td>
</tr>
</tbody>
</table>

The residue quantities in Table 5 refer to the present capacity of the plant of 225,000 t/a. With hematite or goethite the gypsum would be about 40,000 t/a.

Table 6 shows a more detailed, but still approximate, composition of the residues from Outokumpu Zinc.
### Table 6. Composition of Outokumpu Zinc’s residues.

#### JAROSITE

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>t/tZn</th>
<th>Minerals/Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>21–23</td>
<td>0.13</td>
<td>Jarosite, minor components Hematite</td>
</tr>
<tr>
<td>Zn</td>
<td>2.5–3</td>
<td>0.01</td>
<td>Ferrite ZnOFe₂O₄, Sulphide ZnS</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1–0.2</td>
<td>0</td>
<td>Ferrite CuOFe₂O₄, Sulphide CuS</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 0.1</td>
<td>&lt; 0.001</td>
<td>Ferrite CdOFe₂O₄, Sulphide CdS</td>
</tr>
<tr>
<td>Pb</td>
<td>2–6</td>
<td>0.02</td>
<td>Jarosite Pb₆(Fe₃O₇)(OH)₁₂(SO₄)₆, Sulphate PbSO₄</td>
</tr>
<tr>
<td>Ca</td>
<td>3–5</td>
<td></td>
<td>Gypsum CaSO₄·2H₂O</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.8</td>
<td>0</td>
<td>Jarosite NH₄[Fe₃(SO₄)(AsO₄)(OH)₆], Ferriarsenate FeAsO₄</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0.01</td>
<td></td>
<td>Ferrite CoOFe₂O₄</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.01</td>
<td></td>
<td>Ferrite NiOFe₂O₄</td>
</tr>
</tbody>
</table>

#### SULPHUR CONCENTRATE

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>t/a</th>
<th>Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2–15</td>
<td>2,500</td>
<td>Pyrite, FeS₂</td>
</tr>
<tr>
<td>Zn</td>
<td>2–10</td>
<td>1,500</td>
<td>Zn sulphide, ZnS</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01–0.2</td>
<td>50</td>
<td>Cu sulphide, CuS</td>
</tr>
<tr>
<td>Cd</td>
<td>0.01–0.05</td>
<td>10</td>
<td>Cd sulphide, CdS</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1–3</td>
<td>100</td>
<td>Na</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt; 0.01–0.05</td>
<td>3</td>
<td>Sulphide, Ag₂S</td>
</tr>
<tr>
<td>As</td>
<td>0.01–0.5</td>
<td>50</td>
<td>Gypsum, CaSO₄·2H₂O</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0.02</td>
<td>1</td>
<td>Elemental, sulphides</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.02</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.01–0.2</td>
<td>0</td>
<td>Silica, SiO₂, Silicates</td>
</tr>
<tr>
<td>Zn</td>
<td>35–85</td>
<td>33,000</td>
<td></td>
</tr>
</tbody>
</table>

### 3.2 Legislation

Finland has no single environmental law at the moment. Environmental legislation is composed of a number of individual acts /27/. A new Environmental Protection Act is currently under preparation and will combine the environmental acts according to the requirements of the Council Directive 96/61/EC of September 1996 concerning integrated pollution prevention and control (IPPC).

Presently, the integrated approach is included in the two separate permit procedures: the environmental permit procedure according to the Environmental Permit Procedure Act (735/1991) and Decree (772/1992) and the water discharge permit procedure according to the Water Act (264/1961) and Decree (282/1962).

The Environmental Permit Procedures Act combines the permit procedures of the Air Pollution Control Act and Decree, the Waste Act and Decree, the Health Protection Act and Decree and the Adjoining Properties Act. For larger projects an Environmental Impact Assessment has to be completed before the permit procedure is started. The competent authority in environmental permit matters is, depending on the line of activities, either the Regional Environment Centre or the local environmental board.

When discharging waste waters, the Regional Environment Centre must be notified in advance regarding any plans for the discharge of wastewater in the cases listed in the Prior Notification Decree. The Centre assesses the notification and judges whether the activity will cause water pollution. If the pollution is unavoidable, the polluter must apply for a permit from the Water Court or from the local environmental board. Substantial polluters send their applications directly to the
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Water Court. Polluting of groundwater is totally forbidden; this means that no permit can be granted for discharging pollutants into the groundwater.

In the metallurgical industry, an environmental permit granted by the Regional Environment Centre and a water discharge permit granted by the Water Court are needed.

Although the environmental legislation is based on a sectoral approach, the permit system in each sector follows certain uniform lines including the following elements (both in environmental and water permit matters):

- An application describing the activity and its environmental effects is to be submitted to the competent authority. The data and information that the operator of an industrial plant (the applicant) has to submit in the form of an application to the authority is prescribed in the above mentioned Acts and Decrees.
- The documents are public and the persons and organisations affected by the project have a right to comment on them.
- The competent authority makes a decision including emission limits and other permit conditions.
- Those concerned have a right to appeal against the decision.
- A revision of the decisions and permit conditions is made by a certain deadline stipulated in the permit (3–10 years when wastewater discharges are concerned) or when there are significant changes in operation or emissions or when unexpected effects are detected.

Right at the preliminary stage of planning a new establishment, the necessary permits and environmental aspects are to be surveyed. The enterprise is expected to recognise that the environmental criteria may affect siting as well as other economic and technical decisions. Even in the case of changing the production, raw materials or technical devices at an existing plant, the authorities must be informed as soon as these decisions are made, and negotiations shall be initiated to survey the possible need for renewing the permits.

The legislation is based on the Polluter Pays Principle in the sense that the polluter pays all pollution abatement costs, which include also the monitoring costs. In addition, polluters of watercourses are obliged to pay indemnities to the owners of water and shore areas as well as to professional fishermen for any damage caused. A typical feature of the permit procedure is the case-by-case consideration of applications and tailor-making of the permit conditions. The permit conditions are expressed as emission limits and compulsory measures and not as technical standards.

3.3 Emission to water from Outokumpu Zinc

The emissions to the sea from the Kokkola industrial area in 1997 are given in Table 7. The figures include all bleed waters, including cooling waters, from Outokumpu Zinc, OMG Kokkola Chemicals, Fortum Power Plant and are measured at the outlet point. This practise dates back to the time when all 3 plants were owned by Outokumpu. The permit in force was granted by the Water Court in 1995. At present renewing of the permit, separate for each plant, is in process.

The principle for monitoring is:

1. Flow of water measured on a continuous basis.
2. Automatic, continuous sampling. A daily composite sample is analysed at the company’s analytical laboratory.
3. The analyses comprise both soluble and suspended components.
The monitoring of the emissions to water follows standard procedures according to a quality control system. The authorities also supervise through occasional control samples.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Limit&lt;sup&gt;1&lt;/sup&gt; kg/a</th>
<th>Actual release kg/a</th>
<th>Actual release mg/l</th>
<th>g/t Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>5,090,000 m³/a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>5,000</td>
<td>1,300</td>
<td>0.26</td>
<td>7.43</td>
</tr>
<tr>
<td>Cd</td>
<td>100</td>
<td>40</td>
<td>0.0079</td>
<td>0.23</td>
</tr>
<tr>
<td>Cu</td>
<td>700</td>
<td>170</td>
<td>0.033</td>
<td>0.97</td>
</tr>
<tr>
<td>As</td>
<td>50</td>
<td>70</td>
<td>0.014</td>
<td>0.4</td>
</tr>
<tr>
<td>Fe</td>
<td>100,000</td>
<td>32,600</td>
<td>6.4</td>
<td>186</td>
</tr>
<tr>
<td>Hg</td>
<td>5</td>
<td>3</td>
<td>0.001</td>
<td>0.02</td>
</tr>
<tr>
<td>Co + Ni</td>
<td>15,000</td>
<td>6,900</td>
<td>2.95</td>
<td>39</td>
</tr>
<tr>
<td>N</td>
<td>350,000</td>
<td>192,000</td>
<td>70</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<sup>1</sup> Maximum for one month is 15 % of the permit for the year.

Zinc, cadmium and mercury originate mostly and the nitrogen partly from the zinc plant, whereas most of the rest are from the other plants.

### 3.4 Emission to air from Outokumpu Zinc

The figures given in Table 8 include:

1. Dust from the mechanical and pneumatic handling of concentrates, calcine and zinc dust.
2. Gas emission from roasting equipment, with SO₂ as the major constituent, during all, (also emergency and unscheduled) start-ups and shutdowns of the roaster.
3. Vent air from ventilation, cooling and evaporation in the hydrometallurgical part of the process.
4. Vent air from all process buildings.

Principle for monitoring:

1. Automatic, continuous dust measurement after the filters in the roasting area.
2. In other areas the emission with and without the abatement equipment in operation is determined on a predetermined time schedule.
3. The on-time of the abatement equipment is automatically registered and the emission can be calculated.

The surveillance of the emissions is performed according to a detailed monitoring schedule approved by the authorities. The checking of the monitoring programme is done either by independent experts or according to the ISO 14000 Quality Management System.
Table 8. Emissions to air in 1997.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Limit$^1$</th>
<th>Actual release</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/a</td>
<td>kg/a</td>
</tr>
<tr>
<td>Zn</td>
<td>30,000</td>
<td>33,100</td>
</tr>
<tr>
<td>Cd</td>
<td>130</td>
<td>86</td>
</tr>
<tr>
<td>Pb</td>
<td>320</td>
<td>0.0066</td>
</tr>
<tr>
<td>As</td>
<td>1,400</td>
<td>1,300</td>
</tr>
<tr>
<td>S/SO$_4$</td>
<td>14,300</td>
<td>0.30</td>
</tr>
<tr>
<td>S/SO$_2$</td>
<td>7,500</td>
<td>0.16</td>
</tr>
<tr>
<td>Dust</td>
<td>19,000</td>
<td>0.41</td>
</tr>
</tbody>
</table>

$^1$ in force from 1.1. 1999.

Most of the SO$_2$ gas and a substantial part of the dust and heavy metals emissions occur in connection with unscheduled shut-downs of the roaster. In normal operation these emissions are small.

The emission of As almost completely originates from solution purification.

Table 9 gives the chemical composition of the different compounds emitted from the different sources of the plant.

Table 9. Composition and sources of emissions from Outokumpu Zinc.

<table>
<thead>
<tr>
<th>Process step / Source</th>
<th>Physical state</th>
<th>Main elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate handling</td>
<td>Solid. Dust</td>
<td>Zn, Fe, Cu, Cd, Hg, sulphides</td>
</tr>
<tr>
<td>Roasting</td>
<td>Solid. Dust</td>
<td>Zn, Fe, Cu, Cd, Hg, oxides</td>
</tr>
<tr>
<td>Roasting</td>
<td>Gas</td>
<td>SO$_2$</td>
</tr>
<tr>
<td>Leaching, Neutral.</td>
<td>Solid. Dust</td>
<td>Zn, Fe, Cu, Cd, oxides</td>
</tr>
<tr>
<td>Leach, purification, Cd plant</td>
<td>Aerosol. Liquid</td>
<td>Zn, Cu, Cd, sulphates</td>
</tr>
<tr>
<td>Waste water</td>
<td>Solution</td>
<td>Zn, Cu, Cd, Hg sulphates</td>
</tr>
<tr>
<td>Electrolyses</td>
<td>Aerosol. Liquid</td>
<td>ZnSO$_4$, H$_2$SO$_4$</td>
</tr>
<tr>
<td>Melting, casting</td>
<td>Solid. Dust</td>
<td>Zn, ZnCl$_2$, NH$_3$, Cl</td>
</tr>
</tbody>
</table>
4.1 Available techniques

The abatement techniques employed are grouped as follows: dust emission, mercury handling, raw material utilisation and waste minimisation, energy minimisation, solution mist emission to air, emission to sewer and solid waste management.

Figure 5 shows the major abatement operations which are used at Outokumpu Zinc.

4.1.1 Dust emission abatement techniques

Dust emission occur in connection with transport and handling of concentrates and calcine and in melting and casting of zinc, cadmium, lead anodes and distillation of mercury.

Different abatement techniques are used at the sources of emission:

Concentrate handling:
Transport is made with covered or enclosed means; normally belt conveyers. Storing takes place in special storage buildings. Certain dusty operations like mixing of the feed and conveyer transfer points are enclosed and kept at underpressure and the vent air is run through fabric filters to remove the dust.

Roasting and gas cleaning:
The equipment in this operation, including that for mercury removal, is kept at underpressure and no gas emission occurs in normal operation.

Calcine transport:
Calcine is transported pneumatically from the roaster to the storage silos. The transport air is cleaned in fabric filters on the top of the silos. The dust back-flows down into the silo.

Calcine leaching:
From the silos the calcine is fed by different types of conveyers to the leaching tanks. Dusting will occur at the feed point and the vent air from the tanks will contain calcine dust. This dust is removed from the air by wet scrubbing with an acidic solution, like spent acid. The wash slurry flows back to the same reactor.

Melting of zinc cathodes.
The melting furnaces are kept at under pressure and the vent air can be run through bag filters to remove the dust. The dust is recycled to the roaster.
Cadmium melting, anode casting and mercury distillation:
The vent air from these areas can be used as feed air to the roaster and the small quantities of dust are contained in the calcine. The vent air can also be cleaned with bag filters (except mercury) or by wet scrubbing, thus there is no emission from these areas.

The performance of dry cleaning equipment for dust is mostly dependent on the filter media used. At Outokumpu Zinc most of the filters are specified to let through less than 1 mg/m³ dust.

No defined emission data from other plants has been available. The emission data from Outokumpu Zinc, together with the principle for the determination procedure, are given in Chapter 3.

As there are no specified overall techniques used in this area, it has not been possible to compare different techniques either on emission- or on economical grounds.

**4.1.2 Mercury emission abatement techniques**

No standard for mercury in acid exists, so it has to be produced according to the buyer’s specification; for Outokumpu Zinc the buyer of the acid has specified 0.1 mg Hg/l in the acid which corresponds to about 0.02 mg/Nm³ in the gas.

The three processes described in Chapter 2, Boliden-Nor Zinc, Outokumpu and Bolchem are, as reported, able to obtain 0.1 ppm Hg at least in most of the acid production. It has not been possible to make a subsequent rating based on removal efficiency.
Some cost data published indicate that the Boliden-Norzink process (and probably also the Bolchem process) has lower investment costs (200,000 $US for about 200,000 t/a acid in 1972–1975 /2/) than the Outokumpu process (4.70 $US/t of acid/a 1978 /3/). This can be expected from the much milder conditions in the two former options, which allows the use of less expensive materials like fibreglass. The operating costs published, Outokumpu 0.16 $US per ton of acid (1978) /3/ and 0.5 DEM/ ton for the Boliden-Norzink process (1985) /2/ does not, however, give a clear basis for a rating.

This means that Boliden-Norzink and Bolchem are BAT whereas Outokumpu due to high investment costs is a question mark.

4.1.3 Raw material utilisation and solid waste minimisation

The relative economic value of the different elements in the calcine is on average as follows: Zn 85 %, S 6 %, Cd 0.5 %, Cu 1 %, Ag 1.5 %, Pb 1.5 % and on top of this, thermal energy 4 %. The recovery of these values is determined mostly in the roasting and in the leaching, i.e. is more specific in ferrite treatment, but the solution purification also plays a role, especially concerning copper and cadmium recovery to marketable products.

Both factors in the heading are mainly determined by:
1. Primarily the composition of the concentrate (see Table 4).
2. The composition of the iron compound formed, or, in other words, the process applied.
3. Whether silver and lead are recovered or not.
4. Sulphate sulphur in the calcine (see Roasting), as this has to be removed.

Items 1. 2. and 3. are determined by the ferrite treatment process used, and 4. by roasting.

4.1.3.1 Roasting

Two techniques are used in Europe:
1. In the Lurgi system, which is by far the most common, the concentrate is fed as such to the furnace.
2. In the system used by Union Miniere concentrate is micropelletised before being fed to the furnace.
3. Especially in Japan the concentrate is fed as a slurry to the furnace.

In the Lurgi system the sulphate sulphur is about 2 % in the calcine or about 40 kg/t zinc. If this is removed as gypsum this represents about 200 kg CaSO₄*2H₂O/t Zn which in most cases has to be wasted. Part of this sulphate has a “natural” outlet in the magnesium bleed, which is necessarily performed in every plant, whereas the surplus has to be removed by other means.

In the Union Miniere process the sulphate sulphur is lower.

Sulphur recovery to the gas and the heat recovery rates should be very much the same for the two first processes, whereas the steam production with slurry feed will be lower.

Reported heat recovered measured in tonnes of steam per tonne of calcine varies between 0.7 to 1.3. /6/

Outokumpu Zinc

The Lurgi system is employed and the production of steam is about 1.3 t/t calcine and the sulphate sulphur in the calcine is about 2 %.
4.1.3.2 Processes for ferrite treatment

From the technical point of view the following process options are available for the treatment of the ferrite residue:

1. Jarosite
2. Goethite
3. Hematite
4. Smelting processes

As shown in Chapter 2 the hematite and jarosite processes will give higher recoveries from a homogeneous feed than the goethite process. As low-iron concentrates are available and can be used for goethite precipitation the recoveries may be raised to almost the same level as in the two other processes.

The hematite process will give the highest recoveries for zinc and silver and lead, but the difference to the jarosite is small: < 0.5 % for zinc and about 20 % for silver and lead. The extra revenue from these values does not justify such a sophisticated and expensive process, especially as the hematite would, at most sites be wasted. The iron content of precipitated hematite is reported to be 55 % /7/ compared to 70 % for the stoechiometric Fe₂O₃, which shows that it is far from a pure product.

The excess sulphate sulphur (over the quantity for magnesium removal) coming with the calcine will be utilised in the jarosite precipitation, as sulphate is a part of the compound. There is no outlet for sulphate with goethite or hematite so the excess sulphate would in most cases end up as gypsum. The quantity of jarosite will in fact only be about 80 % of the equivalent amount of iron and sulphate as goethite respective gypsum.

Therefore the difference in total residue quantity between the processes will not be very substantial, and especially if SO₂ is used for iron reduction in High Acid Leaching /7/. In this case the total residue will be higher than that for the jarosite process.

The jarosite process normally needs additional acid. This enables the utilisation of acids containing metals to be recovered in a zinc plant, like weak acid from acid plants after zinc roasters or copper and nickel smelters.

*Outukumpu Zinc* uses the weak acid from Outokumpu’s smelters in Harjavalta (copper and nickel), and utilises both the acid and the contained zinc and cadmium, thus recovering a product that would otherwise have been neutralised and wasted.

Decreasing the amount of residue by using only low-iron concentrates is possible only for an individual plant as the availability of such concentrates is limited /24/. The weighted iron content of the world’s concentrates is about 7 % /5/ and a more general thriving for this solution to a residue problem will rapidly increase the residue fallout from other plants.

Smelting processes will reduce the quantity of residue, at least compared to jarosite as the iron content in the slag can be held in the range of 40 %, compared to 34% in the jarosite compound.

Low iron in the feed will also favour a smelting of a neutral leach residue or a goethite to produce a slag, as the quantity to smelt will be low. Metallurgically, however, smelting to recover zinc means that the oxide is reduced to the metallic vapour state, re-oxidised, re-leached and again reduced in the electrowinning. This means that the metal is produced twice. From both the energy consumption and the investment point of view this is a very costly route for producing zinc. Economically, it can only be justified by the recovery of silver and lead and minor elements like germanium which will be fumed with the zinc. On the other hand germanium is a very detrimental element in the electrolytic zinc process and will need very strict control in the leaching so as not to upset the electrolysis. Also the
emission into the air in the pyrometallurgical process will be in addition to the emission of the hydrometallurgical plant as this will not decrease to any noticeably extent.

The recovery in a smelting process will not exceed the recovery obtained with jarosite; one reported slag show 2.4% Zn, corresponding to about 99% extraction /9/.

It can be concluded that the total performance of the described processes is very much dependent on the raw materials available and on the industrial infrastructure at the site, as well as the availability of space for residue storing. Still it seems evident that neither the Hematite Process nor the smelting treatment of ferrite residue generally qualify as BAT processes.

The use of jarosite on the other hand, seems to offer the best solution for an unspecified feed stock as it offers possibilities to obtain high extractions from all concentrates and the ability to utilise heavy metal-containing acids.

4.1.3.3 Waste management

Jarosite will react slowly with zinc hydroxide to give zinc sulphate and iron hydroxide, so the mere neutralisation of the residue to precipitate the water-soluble zinc as hydroxide will not decrease the content of the heavy metals in the moisture left in the residue. Precipitation of the metals as sulphides has shown to considerably improve on this; and the metal content in the moisture can be lowered to a fraction of what it would otherwise be /10/.

Outokumpu Zinc

In the new permit for the expansion of the plant, a solubility of maximum 20, 0.1, 0.1 and 0.05 g/t of residue, according to the CEN Test TC 292, Characterisation of Waste, for respectively Zn, Cd, As and Hg, has to reached by sulphide addition before the residue is transported to the residue area.

4.1.3.4 Solution Purification

All impurities have to be removed from the solution and both systems remove and recover the values (copper, cadmium) to marketable products with about the same efficiency. No major differences in the purity of the solution, which influences the current efficiency and thus the energy consumption in the electrolysis, have been shown to exist between the systems. The two systems must in this respect be regarded to perform equally.

Cost-wise the best reagent in the purification is zinc dust. If excess zinc dust is used it will stay in the cementation products and is normally recovered and recycled in the process by releaching steps. Thus losses are small; but any dust used will correspondingly decrease the output of marketable zinc, thus decreasing the productivity of the plant and increase energy consumption. The dust consumption in plants using Sb₂O₃ seem to be higher than in plants using As₂O₃ /6/; respectively 5.4 % (5 plants average) and 2.8 % (4 plants) on produced zinc.

The cost for other reagents, As₂O₃ or Sb₂O₃, which are the reagents used for Co removal, is only marginal. Energy costs can be noticeable if heating to high temperature is required in any purification step.

It must be concluded that the data discussed above is not sufficient to make a rating of the process options possible.
4.1.4 Energy minimisation

The dominant energy consumption item is electric power in the electrolysis, whereas some steam is used in the leaching and purification.

In electrowinning the energy consumption increases with increasing current density: at 400 A/m² about 3,000 kWh/t Zn is used and 3,400 kWh at 650 A/m² [6]. Energy consumption can therefore be decreased by using low current density. This however is a possible choice only for new electrolyses. Replacement of an operating, high density electrolysis with a new one with lower density will by no means be justified by the saving of energy.

Steam consumption can be lowered by use of heat exchange and processes operating at low temperatures.

Outokumpu Zinc

The plant was built in 1969 when energy was cheap and every plant was built for high current density to keep the investment costs down. Higher energy costs have lead to the use of lower densities in later-built electrolyses, which employ new means to decrease investment cost. New means are, for example, the so-called jumbo cathodes, which means higher cathode surface area per volume unit of building. At Outokumpu the old cell house is still in operation and increased production has been achieved most favourably by utilising the existing one. In 1988 the current density was decreased by enlarging the cathodes, whereas in the latest expansion, 1998, the best economy was obtained by again increasing the current density, thus increased production was reached without investing in new buildings.

4.1.5 Abatement techniques for mist emission to the air

To ensure safe working conditions in the plant, all tanks have to be kept at under pressure. This is carried out by venting either by forced or natural draft or a combination of both. The vent air will always contain some solution mist containing metals in the same proportion as they occur in the solution in the tank.

For the cooling of solutions atmospheric cooling towers are used. Air is blown in at the bottom of the tower and the solution is sprayed in and falls downwards. Mist will be formed in the air flow.

There are two abatement techniques used for emission to the air:
1. Scrubbing with water solution in scrubbing towers producing a dilute solution that should be treated in the waste water treatment.
2. Demisters placed in the ventilation stack or the cooling tower with back flow of the solution to the tank or the tower.

These techniques can be applied in centralised systems as well as in systems with individual abatement equipment as each point source. With decentralised systems the risk for temporary high emission peaks is lower than with centralised ones.

Outokumpu Zinc

Scrubbing is used where dust is present, i.e. in the neutral leach, and for the removal of arsine gas in the Co removal step, where a permanganate solution is used. The solution is recycled to the process.

Demisters are used in all other places. They are placed in the stacks of each individual tank and other emission points. Demisters are also standard in cooling towers in modern zinc plants. The experience with individual demisters has been
very positive and a collecting efficiency of well above 90% for the equipment has been reached.

The operation and supervision of the abatement equipment is connected to the automatic process control and monitoring system.
The conclusions in Chapter 4 show that the differences between the available techniques, concerning both environmental and economic performance, are so small that it is not possible to make a general ranking. The ranking can only be made case by case in which the site-specific play an important role. The best available technique for the production of electrolytic zinc should, however, comprise:

1. Enclosed transport means for concentrates, calcine, zinc dust and other dusting materials, with filtering of ventilation and/or transport air.
2. Mercury removal which, at undisturbed operation, produces an acid with 0.1 mg Hg/l or less.
3. Leach process with precipitation of iron as jarosite or goethite.
4. Silver and eventual lead recovery when feasible.
5. Leaching of concentrates at both atmospheric and elevated pressures.
6. Wash of residues on horizontal filters.
7. Storing of residue in areas isolated from ground water.
8. Treatment of all bleed waters from the plant and plant area which can be contaminated with heavy metals to precipitate the heavy metals and recycle at least most of the precipitate to the process.
9. Use of demisters and/or scrubbers to prevent mist emissions from the ventilation air arising from the reactors and other equipment where mist can occur.
Emerging Techniques

Very few new revolutionary techniques are emerging that will substantially improve on the main factors reviewed in this report; i.e. utilisation of raw material, energy consumption, minimisation of residues and reduction of emissions to air and water, within the hydrometallurgical processing of zinc. It is probable that the development of existing techniques and metallurgy will dominate, at least in the near future. Automation will especially increase, and thus also closer monitoring of emissions and optimisation of processing to maximise recovery and minimise energy consumption.

6.1 Low contaminant jarosite

Precipitation of jarosite from a diluted iron-containing solution without neutralisation has been tested and shown to be technically workable, but it has never been implemented. The jarosite contained about 0.3 % Zn. The extraction of such a process will be the same as for the hematite route /25/.

6.2 Solvent extraction of iron

Different solvents have been tested on the laboratory scale to extract the iron from the contamination solution after the hot acid leach. From here the most promising route is to strip the iron to a chloride solution, concentrate it by evaporation and then decompose it thermally to produce pure hematite. Instability of the extractant, cross contaminations with chloride and excessive cost are the obstacles to solve before this technique could be viable.

6.3 Jarofix

The jarosite is mixed with about 15 % Portland cement to give a concrete-like material. In Quebec, Canada, this material has been approved by the Quebec Ministry of the Environment as inert and can be landfilled. The residue quantity will increase but the cost for disposal will decrease considerably /26/.
Executive Summary

The electrolytic zinc process in Finland operates mostly on sulphide concentrates and comprises the following: roasting of the concentrate to calcine; mercury removal from the SO₂ gas before acid production; precipitation of the iron as jarosite in the leaching of the calcine; production of cadmium by melt refining and a low contaminant copper cake for copper smelting in the purification; conventional electrowinning and melting and casting of the zinc.

Precipitation of iron as jarosite is acid-consuming and the environmental problematic zinc, cadmium and copper-containing weak acids from the copper and nickel smelters in Finland are therefore utilised as reagents. The ability to utilise these acids reduces the total quantity of wastes in Finland compared to precipitation of a sulphate-free iron compound and neutralising of the acids with lime to give gypsum. The high stability of jarosite in acid media also ensures high extraction from all raw materials, which saves natural resources.

Expansion of the capacity of the Kokkola plant by adding a concentrate leach step is being completed. The sulphur is obtained as an elemental sulphur concentrate. Direct leaching was chosen because of the low price of acid and excessive cost for a new roaster and acid plant.

Abatement techniques are used at all significant sources of both dust and solution mist emissions to the air. Also all waters from the plant area go through a waste water treatment plant before being discharged to the sea. Monitoring of all emission point sources is made on a predetermined schedule, and the operation of most of the abatement equipment is automatically registered. The techniques are continuously being developed, especially towards higher reliability.

The emissions for 1997 are given in Table 9. The figures for air emissions also include all operational malfunctions and all cooling waters in the emissions to water.

<table>
<thead>
<tr>
<th>Zinc</th>
<th>Cadmium</th>
<th>Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg/a</td>
<td>g/t Zn</td>
<td>kg/a</td>
</tr>
<tr>
<td>To air</td>
<td>33,100</td>
<td>145</td>
</tr>
<tr>
<td>To water</td>
<td>1,300</td>
<td>7.4</td>
</tr>
</tbody>
</table>

The comparison of different techniques available in the production of electrolytic zinc world-wide did not reveal any generally superior processes or subprocesses. The differences regarding environmental and economic performance are metallurgically and technically so minor that site-specific factors like industrial environment, available raw material, energy cost, etc. will easily compensate for these differences. Therefore the best available technique will easily be site-specific and vary case by case.

The electrolytic zinc process as operated by Outokumpu Zinc represents best available technique because of the following: the ability to obtain high recoveries from high iron concentrates; the availability of space for storing wastes at the plant site and the ability to utilise acids that otherwise would have produced waste at high cost as raw material.
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24. Dutch Notes on BAT for the production of Primary Zinc


Finnish expert report on best available techniques in zinc production

The aim of this BAT report is to identify available techniques for the reduction of emissions and energy use in the primary zinc production in Finland. The electrolytic zinc process used operates mostly on sulphide concentrates and comprises the following: roasting of the concentrate to calcine; mercury removal from the SO2 gas before acid production; precipitation of the iron as jarosite in the leaching of the calcine; production of cadmium by melt refining and a low contaminant copper cake for copper smelting in the purification; conventional electrowinning and melting and casting of the zinc.

Precipitation of iron as jarosite is acid-consuming. The zinc, cadmium and copper containing weak acids from the copper and nickel smelters are utilised as reagents. The ability to utilise these acids reduces the total quantity of wastes in Finland compared to precipitation of a sulphate-free iron compound and neutralising of the acids with lime to give gypsum. The high stability of jarosite in acid media ensures high extraction from all raw materials, which saves natural resources. Liquid effluents from the process result from the cooling water system, the sulphuric acid plant and from the wet gas cleaning system. The main air emissions are SO2 and particulate emissions.

Zinc production, best available technique

Environmental protection

The Finnish Environment 315

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**Målet med den här BAT rapporten är att identifiera tillgänglig teknik för reduktion av emission och energianvändning i primär zink produktion i Finland. Den elektrolytiska zinkprocessen som används för det mesta sulfidiska koncentrat och processen innehåller följande: rostning av koncentratet till kalcine; rening av kvicksilver från svaveldioxidgaser före syratillverkningen; utfällning av järn som jarosit under utlösning av kalcine; produktion av kadmium genom smältraffinering och en lågt kontaminerad kopparkaka för kopparsmältning i raffineringen: konventionell elektrovinning och smältning och gjutning av zinen.**

Finnish expert report on best available techniques in zinc production

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