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Amelioration and market strategies for zinc oxide with focus on secondary sources

Christian Doppler Laboratory for Optimization and Biomass Utilization in Heavy Metal Recycling

A thesis submitted in partial fulfilment of the requirements for the degree of a Doctor of Metallurgical and Mining Sciences at the University of Leoben

Presented by Dipl.-Ing. Stefan Steinlechner

May 2013

STATUTORY DECLARATION

I declare in lieu of oath that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

Dipl.-Ing. Stefan Steinlechner
Leoben, May 2013

Acknowledgement

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Rem tene, verba sequentur!
Behalte die Sache im Auge, die Worte stellen sich dann von selber ein!
(Marcus Porcius Cato, 234-149 v. Chr.)

Acronyms

SHG	Special high grade
SHG-zinc	Special high grade zinc
CTL	Coal to liquid
SDHL	Process named after its inventors: Saage, Dittrich, Hasche and Langbein
HP	High purity
EAF	Electric arc furnace
EAFD	Electric arc furnace dust
EDX	Energy dispersive X-ray spectroscopy
SEM	Scanning electron microscopy
XRD	X-ray diffraction
PET	Petroleum
BET	Brunauer, Emmett, Teller
CAPEX	CAPital EXpenditure
OPEX	OPerational EXpenditure
DSC	Dust settling chamber
WOX	Waelz oxide
CWOX	Crude waelz oxide
IZA	International Zinc Association
ESR	Electroslag remelting
EDTA	Ethylenediaminetetraacetic acid
NPK	Nitrogen phosphorus potassium
RCRA	The Resource Conservation and Recovery Act
D_2EHPA	Di-(2-ethylhexyl)phosphoric acid
EBT	Earnings before taxes

Verbesserung der Produktqualität und Marktstrategien für Zinkoxide mit Fokus auf sekundäre Ausgangsstoffe

Die Arbeit befasst sich mit der Erhöhung der Produktqualität von Zinkoxiden aus Recyclingverfahren. Hintergrund ist die mögliche Wertsteigerung im Falle einer Vermeidung des momentanen Einsatzes als Konzentrat-Ersatz in der primären Zinkgewinnung und der alternativen Verwertung als für hochqualitatives Zinkoxid oder Zinkverbindungen wie Zinksulfat. Hierzu sind gezielte metallurgische Prozessschritte nötig, welche die Produktqualität der Zinkoxide heben.

Basierend auf der dominierenden Stellung des Wälz-Verfahrens im Recycling von Stahlwerksstäuben in Europa, wurde im Speziellen das Wälzoxid auf dessen Eignung hin untersucht. Ausgehend von einer detaillierten Charakterisierung und der Ermittlung chemischer sowie physikalischer Eigenschaften der enthaltenen Komponenten, wie auch der Anforderungen der Zielmärkte, wurde ein hydrometallurgisches Verfahren zur Zinksulfat-Herstellung sowie ein pyrometallurgisches Verfahren zur selektiven Verflüchtigung von Störkomponenten untersucht.

Im ersten Prozess, der selektiven Verflüchtigung von Verunreinigungen konnte basierend auf thermodynamischen Berechnungen sowie Versuchen gezeigt werden, dass gewisse Halogenverbindungen mit den Hauptkomponenten wechselwirken und diese Reaktionen gezielt für eine positivere Prozessführung nutzbar sind. Dies kann sich in niedrigeren Prozesstemperaturen, Verweilzeiten oder höheren Ausbringen wiederspiegeln.

Das zweite betrachtete Verfahren ist die Zinksulfat-Herstellung. Es konnte durch Adaptierung von hydrometallurgischen Prozessschritten, wie Zementation, Fällung bzw. selektive Laugung, eine effektive Abtrennung der Störelemente erfolgen. Dies führte zu der Produktion von reinem Zinksulfat sowie der angestrebten Wertsteigerung. Zusätzlich kann durch die Umwandlung in Zinksulfat dem Wälzrohrbetreiber ein weiterer zukunftsträchtiger Markt eröffnet werden, wodurch ein breiteres Kundenfeld erreichbar ist und damit mehr Absatzsicherheit vorherrscht.

Amelioration and market strategies for zinc oxide with focus on secondary sources

The present PhD thesis investigates the quality upgrade of zinc oxides obtained from steel mill dust recycling processes. The driving force is the possibility to get a product with added value by avoiding the usage as substitute for primary zinc concentrates and alternatively utilize it in the high purity zinc oxide market or alternative areas, like the zinc chemicals market in case of zinc sulphate. Therefore, specified metallurgical processes are required to ameliorate the quality of such zinc oxides.

Due to the dominance of the waelz process in the recycling of steel mill dusts in Europe, especially the waelz oxide was investigated. Based on a detailed characterization and evaluation of physical and chemical properties of the constituent parts as well as the requirements of the target markets, a hydrometallurgical concept for the production of zinc sulphate and a pyrometallurgical concept for the selective vaporization of impurities of waelz oxide were studied.

Thermochemical calculations showed next to detailed experimental work that within the first process concept, the selective vaporization, interaction reactions of halides with the main compounds occur and that those reactions can be utilized to enhance the upgrade process. This can lead to lower required treatment temperatures, shorter retention times or higher vaporization yields of disturbing compounds.

The second upgrade process was a hydrometallurgical concept for zinc sulphate production. Based on an adaption of hydrometallurgical process steps such as cementation, precipitation and selective leaching regarding the input material, it was shown that impurities could be effectively separated. An upgraded product, clean zinc sulphate, was produced and an added value was realized. With this, the possibility of breaking into new seminal markets with a possible second product line for waelz kiln operators can be realized and additionally offers a field of new customers.

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1. Introduction

Nowadays, a steady increase in the demand for zinc products can be recognized. The reasons for this are emerging markets like India, China, Russia as well as South America. Based on the main utilization area of zinc as corrosion protection, especially the automotive and construction industries influence the demand. In addition to this, the consumption of other zinc products like zinc oxides or zinc sulphates are growing once again. The best example which presents this circumstance descriptively is the tyre industry. Linked to the steadily growing automotive market, the rubber consumption for tyre production continuously grows, as well. Due to the demand for high purity zinc oxide as an additive for the vulcanization process in tyre production, this market is also growing steadily and can be forecasted to further expand in the upcoming decades.

As a result of these dramatically fast growing markets, the mining industry is subject to more and more pressure to supply the metallurgical plants with raw material to cover the zinc demand. International organizations like the IZA (International Zinc Association) are forecasting a bottleneck in the supply chain within the next years due to the fact that the mining industry cannot adapt their production as fast as it would be necessary to cope with the undersupply. Moreover, the startup of new mines takes several years based on time for prospection, financing and preparing the required operations.

Therefore, based on the increased consumption of zinc and zinc products, also residues or secondary materials which are high in zinc are increasing and moving more and more into the focus of concern, based on the idea to close this supply gap. In some areas, such as the treatment of EAFD (electric arc furnace dust), recycling is already being carried out and several processes are applied industrially. The concept of sustainability has even become part of the law in different European countries; other concepts to treat zinc-bearing materials, like leaching residues, lead slags, residues from artificial silk production or others are evolving too.

Nevertheless, one main problem that most of these recycling concepts of zinc-bearing residues have in common is that a zinc product with very low purity is produced.

As a result of the huge amount of steel produced, the amount of EAFD arising from steel scrap recycling is significantly higher compared to the amounts of zinc-bearing residues from the nonferrous industry. Therefore it is obvious why most of the secondary zinc oxide obtained from low quality raw materials (like hazardous wastes) arises from the recycling of steel mill dust. This big potential is the reason why the focus within this work lies on such zinc oxides from electric arc furnace dust recycling. Beside some non-relevant hydrometallurgical methods, the dominating one, which is also “best available technology,” is the pyrometallurgical waelz technology. Worldwide, more than 80 % [1] of the recycled material is processed in the waelz process.

Figure 1-1 shows the general recycling loop of zinc. The main application area of zinc is the galvanization of steel products for corrosion protection. After the life cycle of zinc coated steel products e.g. in the automotive or building industry is over, the product turns to scrap which is collected and utilized as raw material in electric arc furnace steel making. Due to the volatile character of metallic zinc, it is vaporized and oxidized in the off gas stream, which leads to a high zinc content in the filter dust. Aside from zinc, other volatile compounds, like halides originating from charged plastics or fluxes from steel making, also follow the zinc vapour into the filter dust. As a result of these impurities beside other volatile heavy metals like in case of lead most of the time lead(II) oxide, cadmium compounds, etc. the steel mill dust is declared as hazardous waste and has to be treated in recycling processes, like the waelz kiln, or is alternatively landfilled after a stabilization step.

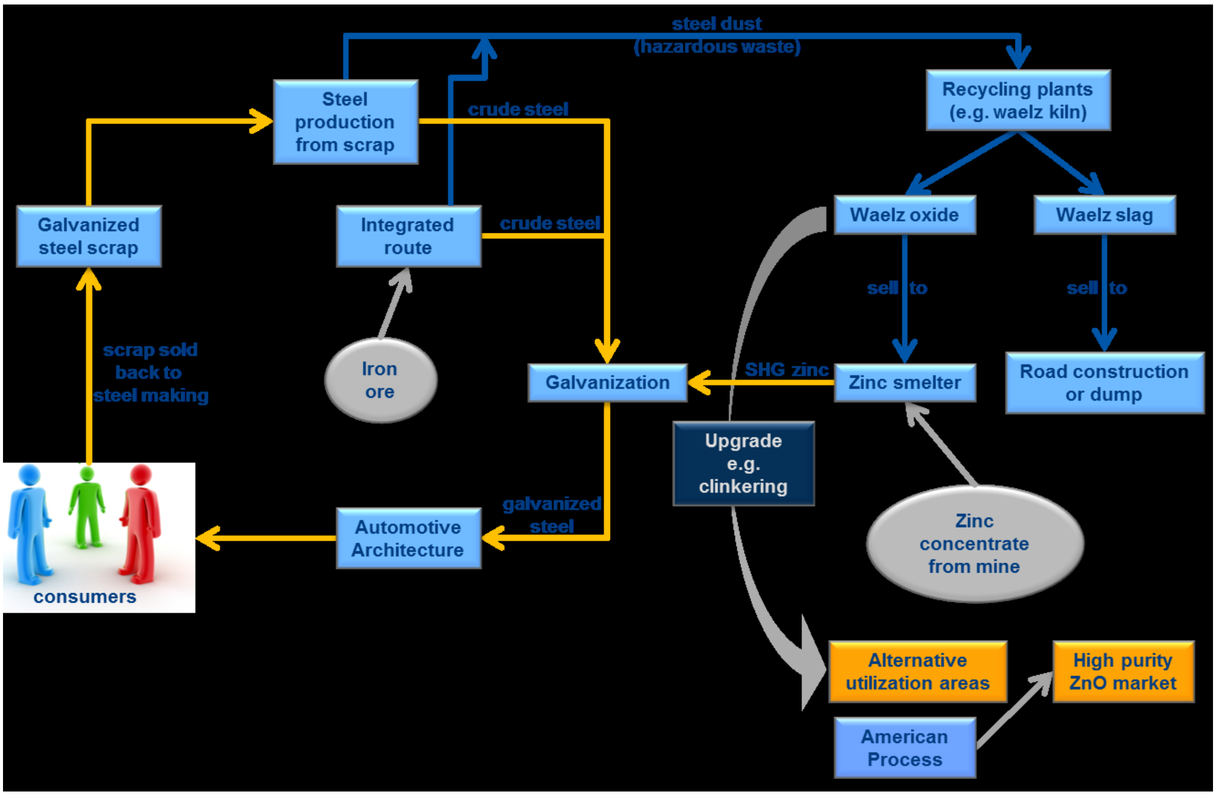


Figure 1-1: Schematic drawing showing the recycling loop of zinc

Due to the high zinc content in the material, in Europe a huge part of the EAFD as well as other steel mill dusts from integrated routes or foundry dusts, are recycled in waelz kilns.

The metallurgical background of the waelz kiln is described in a subsequent chapter, which is the reason why only the two main products are mentioned at this point. The waelz kiln recovers an impure zinc oxide, also called waelz oxide, which similar to steel mill dust is high in its amount of impurities. The other product is the waelz slag, with a relative amount of 650-

700 kg per ton of charged material. In Western Europe, its utilization as a product is only allowed in Spain and Italy as yet, where it is used as road construction material. Everywhere else, the slag has to be dumped.

The waelz oxide is generally utilized in the primary zinc industry as an ore substitute. Due to different critical factors, which are described in detail in a following chapter, the amount of substituted concentrate in primary industry by waelz oxide is limited to a certain amount, in the case of the common roasting-leaching-electro-winning route. Therefore, the main problematic impurities are the different halides and the lead oxide in the waelz oxide.

As a result of the only possible utilization in primary industry, the revenue is also limited and by far lower than achievable ones in alternative markets, like zinc sulphate or high purity zinc oxide applications. These aspects as well as the high energy consumption in the primary zinc industry, due to the electro winning process, led to the present investigations with the target of an upgrade process to prevent the energy and cost intensive primary industry.

As a result, strategies for an upgrade are evaluated, with the above-mentioned aim of avoiding the primary industry and instead, breaking into new markets and areas of utilization.

For this, a detailed characterization of the initial material is necessary, determining the starting conditions as well as possible utilization markets for an upgraded product and their required product qualities and linked critical elements in the target market. The focus in particular is on the achievable product quality. A literature survey on existing concepts dealing with the halide problem as well as the behaviour of the disturbing compounds under different conditions forms the basis for the upgrade experiments carried out.

2. Difficulties in waelz oxide utilization as concentrate substitute

As mentioned in the introduction, secondary zinc oxide (waelz oxide) is typically used in the hydrometallurgical zinc winning route of the primary zinc industry. Initially a soda-leaching is carried out, especially in Europe, in most of the cases in order to reduce the amount of halides. As a result of an efficient solubility of such salts, they can be washed out with hot water. The addition of soda (Na_2CO_3) avoids an unwanted zinc loss based on its precipitation as a carbonate, which is characterized by its low solubility. A disadvantage of soda leaching is that lead is not removed and remains in the waelz oxide. As shown in Figure 2-1 the preliminary washed waelz oxide is charged into the roaster of the plant. This step is necessary because the washing step is not efficient enough to remove all halides and remaining ones can cause problems in the electro-winning. Especially fluorine compounds, like present CaF_2 are hardly removable as a result of their low solubility. This is well known from waste water treatment where lime milk is used for fluorine removal by precipitation of CaF_2.

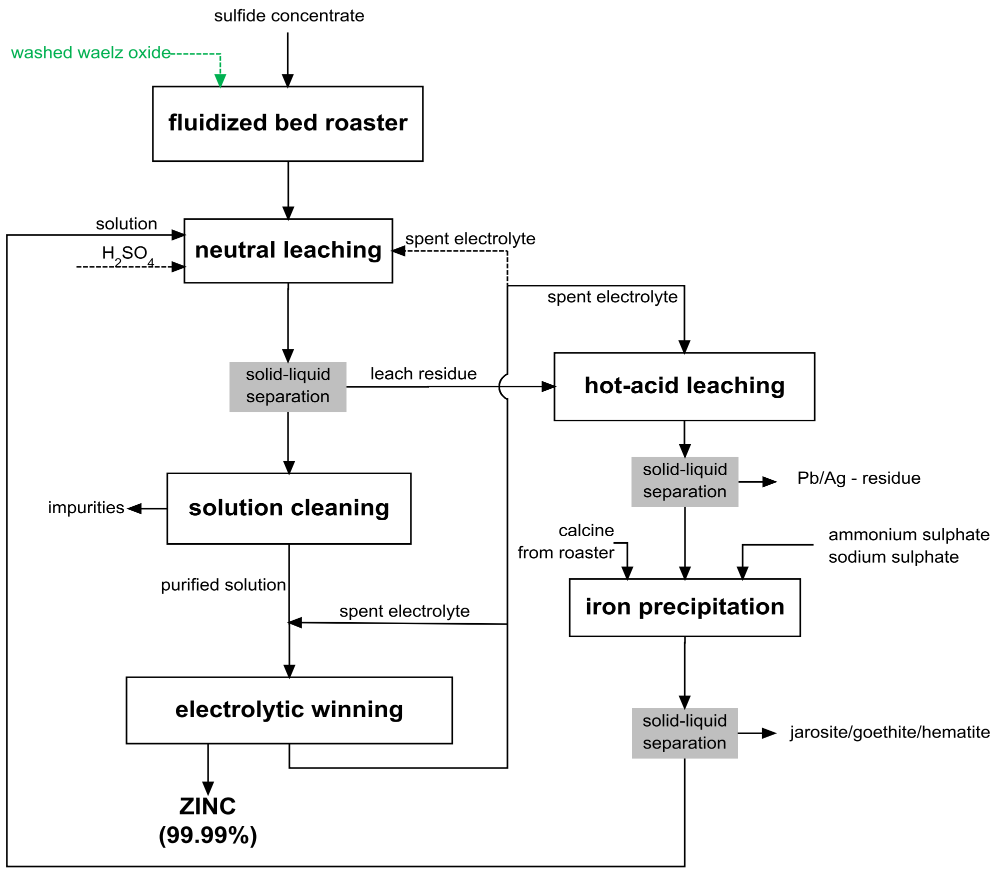


Figure 2-1: Process flow sheet of a conventional primary zinc plant with roasting-leaching-electro-winning

The difficulties which can be experienced during the electrolytic zinc winning in the case of dissolved halogens in the electrolyte are:

Chlorine increases the corrosion addiction of the lead-silver anodes. Furthermore, the formation of chlorine gas can negatively influence the operational safety as well as the physical health of the workers. The maximum concentration of chlorine in the electrolyte mentioned in literature is between 30 and 200 mg/l while most frequently a value lower than 100 mg/l is mentioned [2, 3, 4, 5].

If the fluorine value in the electrolyte is too high, a strong sticking of the zinc layer on the aluminum cathode can occur, causing problems during stripping. The reason for this is the formation of a ZnF^+-complex, which due to its positive charge, reacts on the cathode followed by the formation of HF according to equation 2-1.

$$ZnF^+ + H^+ + 2e^- \leftrightarrow Zn + HF \qquad \text{Equ. 2-1}$$

Owing to the strong acidity of HF, the protection layer of the aluminium cathode (Al_2O_3 layer) is attacked. This allows the zinc to form a direct connection with the aluminium and as a result problems during the stripping process arise. The maximum concentration of fluorine in the solution is 10 to 50 mg/l. Higher values are only acceptable if the plant uses washing steps for the cathodes. Depending on the hydrometallurgical process, the maximum allowed content of chlorine and fluorine in the electrolyte is different. The reason for this is that, for instance, a jarosite precipitation, which is an iron removal step, acts as a natural chlorine and fluorine sink [2, 3, 4, 5].

As mentioned above, to minimize the input of disturbing compounds in the leaching solution, the material is charged into the roaster. This leads to a possible formation of hydrochloric and hydrofluoric acid, which is responsible for increased corrosion of the roaster as well as corrosion in the off gas system in addition to increased sticking ability of the material. Although it is a good cleaning option for these secondary materials, the capacity in the roaster is limited to 10-15 % [6] of the overall charged material. The reason for this is on the one hand because of the halides which are responsible for the mentioned problems, but far more important, on the other hand because of introduced lead and the oxidic characteristic of the material. The energy input in the roaster to achieve temperatures around 950 °C is ensured by the oxidation of sulphur and therefore the waelz oxide works as a cooling agent, which once more limits the charged amount. Additionally, the lead and copper input into the roaster is limited to a total of 3 % [6] of the overall amount. Based on contents of up to 10 % of lead oxide in the waelz oxides, this is also a reason for limited capacity because otherwise the fluidized bed cannot be kept stable [6].

3. Production of zinc oxide

Commercial grades of zinc oxide can be found depending on their quality in a wide range of utilization areas, starting from specialities such as the semi-conductor industry in case of high purity products, its usage in everyday situations like sun creams or in the case of low quality, zinc oxides as a concentrate substitute for zinc production. Based on its diversity, different qualities for each market can be found linked to a variety of different production processes. Aside from the product quality, properties like specific surface area, coatings or individual customer requirements are important, as well.

It can be split roughly into the production routes for high purity zinc oxides, using high quality raw materials and the zinc oxides obtained from low quality input material, which is typically utilized as a concentrate substitute in the primary zinc industry. Both areas are described in the following chapters.

3.1 High quality zinc oxides

The following chapter summarizes the production possibilities of high purity zinc oxides.

3.1.1 State of the art processes from high quality input materials

Figure 3-1 shows a summary of production processes and related utilization areas of high purity ZnO.

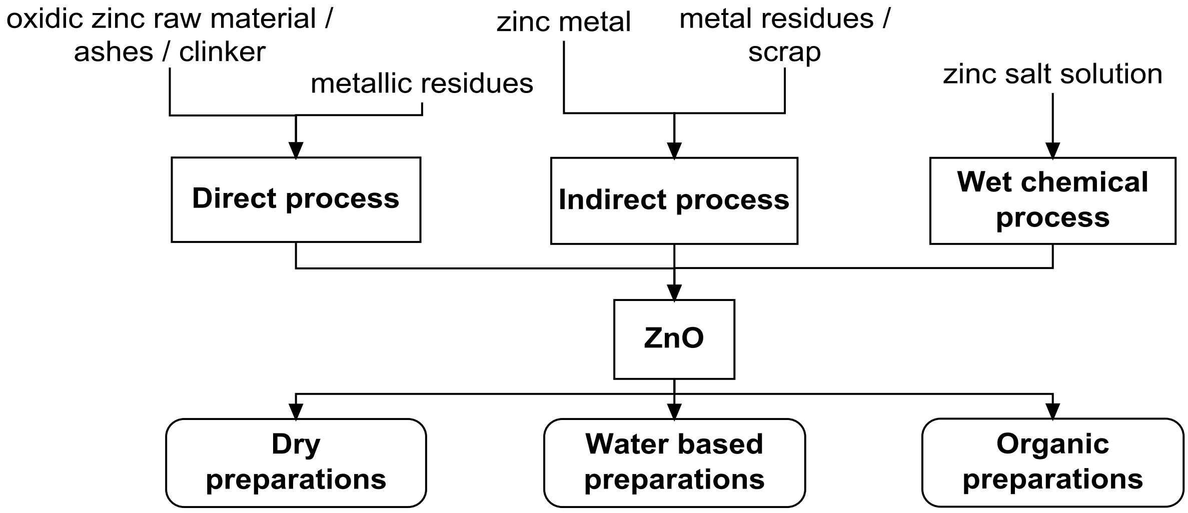


Fig. 3-1: Overview of production and usage of ZnO [7]

Within the high purity zinc oxide production, the following distinction can be made for the main processes used:

- Direct process
- Indirect process
- Wet chemical process

The way the production of zinc oxide is carried out today was developed by Le Claire in France in 1840, by burning metallic zinc in air – the so-called "French process." The zinc oxide was used as a substitute for lead carbonate pigments for around 100 years, since titanium dioxide partly replaced it because of its superior opacity.

In America a different production route was developed – the so-called "American" or "Direct" process. The name originated from the possibility to directly make use of oxidic ore. In both the French (indirect) and American (direct) processes, air is used as a cooling and oxidation agent for the vaporized zinc. Furthermore, the excess air works as a transportation medium for the zinc oxide particles to the filter house.

The third method used for ZnO production is a hydrometallurgical one which is based on zinc hydroxide or zinc carbonate production as a semi-finished product. This semi-finished product is further processed to ZnO by way of thermal treatment.

Compared by weight, most of the high purity ZnO produced is manufactured by the French process, showing a market share of around 60 %. In the following section, each process is described in detail [7].

3.1.2 French process

Over several years different routes of this process have been developed but all of them adhere to the same concept, consisting of the following three parts:

- Combustion
- Evaporation with an air flow to control the particle size after re-oxidation
- Collection

Usually metallic zinc is melted and vaporized at temperatures above 907 °C – typically around 1000 °C. Due to an excess amount of air the metallic zinc immediately reacts to ZnO in an exothermic reaction and a bright luminescence. The air further transports the particles and allows an agglomeration; while by the same token, cooling occurs.

Attributable to that a purification can be achieved within the production process. Critical elements are those with similar high or higher values, like cadmium, bismuth, magnesium or manganese.

There are no significant differences in principle but different equipment can be found. Table 3-1 summarizes old and new technologies for heating and the related energy consumption.

Table 3-1: Combustion systems of indirect methods (old and new technologies) [8]

Type of Combustion	Coal	Heavy Oil	CTL	Clean Coal Gas	Natural Gas	
Heating method	direct burning	regular heat exchange			regular heat exchange	New type of heat exchange
Advantage	simple equipment, lower investment	easy to control the temperature, more environmentally friendly				
Shortcoming	high energy consumption, high pollution	high energy consumption	high energy consumption, unstable gas making equipment	high energy consumption		high investment for equip.
Energy consumption per unit production	0.5-0.7	0.3-0.4	0.4-0.6	0.3-0.4	0.3-0.4	0.15-0.2

The inventor, Le Claire, used horizontal retorts while in the UK vertical crucibles (retorts) were developed in the 1920's. Different heating systems were obtained; while coal was used at first, later they were modified to use heavy oils or gases. The US muffle furnaces were used with upper and lower rooms. While the upper room is fired the heat is transferred to the compartment below where the liquid zinc can be found. While the UK version is semi-continuous, the US muffle furnace works continuously. The remaining amount of non-volatile compounds can be tapped from time to time. Another method from the US is the zinc distillation column. In these columns it is possible to use zinc with high lead and cadmium contents, which are not suitable for a French or American process. Therefore, the lead and cadmium columns are in series and the zinc vapour on top of the lead column is oxidized instead of condensed to SHG zinc [9].

Rotary furnaces are also used for zinc oxide production. Because of the possible utilization of the energy from the exothermic zinc oxidation, the energy consumption can be decreased. This process works continuously, like the US muffle, but needs, compared to not continuously charging in the muffle, a continuous feed of raw material [9].

Typically, the product has a specific surface area in the range of around 2.5 m^2/g to 12 m^2/g [9].

3.1.3 American Process

Approximately 40 % of zinc oxide is produced in the so-called American process. As raw material, oxidic ore or oxidized sulphidic ore can be used as well as other oxidic raw materials, such as hot dip galvanization ashes, brass ashes or ashes from the French process. The raw material is mixed with coal and fired. The carbon monoxide and metallic zinc are expelled as vapour and afterwards combusted to zinc oxide and carbon dioxide. The zinc oxide obtained from the direct process has different physical properties compared to the French process and is therefore preferred for some applications, but in most cases, the lack of product quality and fine control has put it at a disadvantage compared to the French process. The product quality is mainly influenced by the raw material utilized and as a result of the more impure material used, compared to the French process, especially cadmium, lead, iron, copper, sulphur, carbon and manganese limit the application of direct ZnO. For example, these impurities would influence the production process of the rubber industry harmfully [9].

3.1.4 Larvik furnace

Alternatively to the mentioned three possible processes for high purity zinc oxide production a fourth speciality, the Larvik furnace, can be mentioned. The Larvik furnace can be split into three zones, as follows:

- Melting
- Vaporization
- Separation zone

The input material is, similar to that in the French process, metallic. One special difference of the material compared to others is the higher possible limit of impurities, like lead, iron, etc. Possible materials are bottom dross, crude skimming or grinded skimming. The required melting heat is provided by the enthalpy of the off gas in the vaporization zone. Non-meltable components are removed from the liquid metal surface in the melting zone. The general advantage is that more impure material can be utilized.

The vaporization zone acts like a heat exchanger. The metal bath surface is heated by the counter current flow of the zinc vapour bearing off gas stream, which is formed in the separation zone.

The zinc vapour is continuously transported from the vapour zone to a post combustion zone, where zinc oxide is formed, or alternatively to a condensation unit for forming zinc metal pigments. In the case of metallic zinc pigments, a cooling with nitrogen is carried out.

The main influencing parameter for the pigment size and shape is the temperature, adjusted by the nitrogen amount used for cooling.

Special attention is given to aluminium in the input material, due to the fact that a skin on the zinc metal surface can be formed by aluminium oxide, preventing continuous vaporization. Regarding cracks in the slag layer, an impulsive vaporization occurs, which can dramatically increase the pressure in the system, which is unwanted.

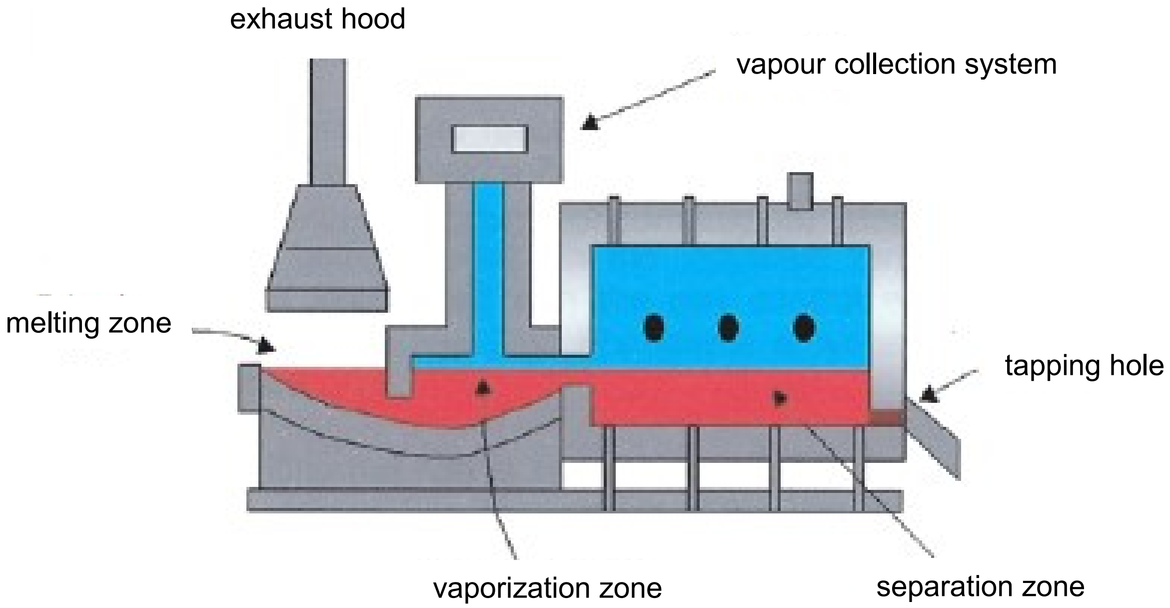


Figure 3-1: Schematic figure showing a Larvik furnace

The change into the gas phase of the zinc bath takes place in the separation zone. There, typical graphite electrodes provide the necessary energy. The recharging of molten zinc is ensured by the melting and vaporization zone.

A cut-off for the furnace atmosphere from the ambient air is given by a refractory plate, which is immerged into the zinc bath but at the same time enables the liquid zinc to pass by. This sealing is necessary to prevent an oxidation of the zinc vapour.

The operation temperature lies at 1500 °C, which is higher than in the French process. The reason for this is the different raw material used, due to the iron present. A phosphor addition is necessary to form an eutectic alloy with iron with the aim of a low liquidus temperature (lower than 1500 °C). This offers the opportunity for a continuous separation of the iron. The advantage is an additional product, the iron alloy, next to lower required temperatures and with that less attack of the lining. The disadvantages are the low quality of the iron alloy and the increased refractory lining attack by phosphorus.

The iron alloy sinks to the bottom as a result of the higher density and is collected in the casting area. The same occurs with the lead present, forming a third liquid metal layer in the furnace, due again to a higher density than iron as well as zinc. With this a separation during the casting process is possible, forming two separate alloys. This is positively influenced by the low solubility of lead for iron.

The gaseous zinc accompanied by impurities has to pass through a kind of labyrinth, with the aim of also condensing vaporized lead. This metallic lead can be collected separately, forming a lead bullion.

For the production of high purity zinc oxide for the pharmaceutical industry, the input material has to be of high quality, which is why in this case, for instance, SHG zinc is used, similar to the French process.

3.1.5 Hydrometallurgical route

Only a small amount of zinc oxide is industrially produced through the wet process. Typically it starts with an aqueous solution of purified zinc salt. The most common method uses a synthesized zinc hydrosulfite ($H_2O_4S_2^{2-}$ and Zn^{2+}) in aqueous solution. The addition of sodium hydroxide precipitates zinc oxide, which is then filtered and dried.

Other concepts use sodium carbonate or sodium hydroxide to precipitate zinc carbonate or a zinc hydroxide. The typical surface area is 25 m²/g. With special drying steps, surfaces up to 100 m²/g are possible (e.g. by Brüggemann Chemicals). As a result of the very high specific surface area, the field of application lies in the desulphurization and as a vulcanization agent in the rubber industry. Typically these high surface area zinc oxides are called “active” [9].

3.2 Low quality zinc oxides from secondary sources

Approximately 50 to 60 % of the zinc produced annually is used in the form of zinc layers on steel sheets for corrosion protection reasons, mainly utilized in the automotive and building industries. After their life cycle, these galvanized steel sheets are recycled in electric arc furnaces, generating a residue called electric arc furnace dust.

Beside brasses, zinc sheets, galvanization residues, etc. which can be remelted or act as input material for the high purity zinc oxide production, the before mentioned hazardous residue (electric arc furnace dust – EAFD) is responsible for the biggest amount of secondary low quality zinc oxides. That is the reason why different recycling concepts for such materials are available and in development.

3.2.1 Methods to treat steel mill dusts

The list below summarizes the industrially applied treatment methods as well as the concepts in development:

- Waelz technology (In Europe more than 80 % of EAFD are processed by waelz technology) [1]
- Other pyrometallurgical processes (less than 20 %) [1]
    - Rotary hearth furnace (ZincOx, Kobelco and Inmetco)
    - Shaft furnace (Cupola furnace - OxiCup, IS Zinc smelter, Mitsui)
    - Multiple hearth furnace, PRIMUS technology (Paul Wurth)
    - Melting cyclone (VAI, HRD)
    - Plasma furnace (ErasMetal, ScanDust, Mintek)
    - Electrothermal (Toho)
- Hydrometallurgical processes (minor utilization) [1]
    - NH_4Cl leaching, Ezinex process (HST)
    - H_2SO_4 leaching (Recupac, HydroMet, ZincOx)
    - NaOH leaching (Zimaval)

Consequently, more or less only pyrometallurgical processes are industrially applied and thereof the waelz process has a market share of more than 80 %, which is the reason why the main focus lies on the waelz kiln technology in this chapter.

The main characterization attribute of the low quality zinc oxides is their utilization as an ore substitute in the primary zinc industry.

3.2.2 Waelz process

As mentioned above, the waelz technology is mainly used to recycle EAFD but in praxis also other zinc-bearing secondaries, like waste water treatment sludges, filter cakes from zinc smelters or cupola furnace dusts are used as input material [10].

The key equipment is a horizontal, slightly tilted, rotary kiln operating in a counter current flow. A self-reducing mixture is charged at the top head of the rotary kiln while the off gas flow is in the opposite direction. A principle drawing of a waelz kiln can be found in the following figure. The two areas, separated vertically, are called the freeboard and the solid material areas, which are more or less independent reaction areas. Horizontally, the pyrometallurgical reactor can be split into 5 main zones, which are described in detail below.

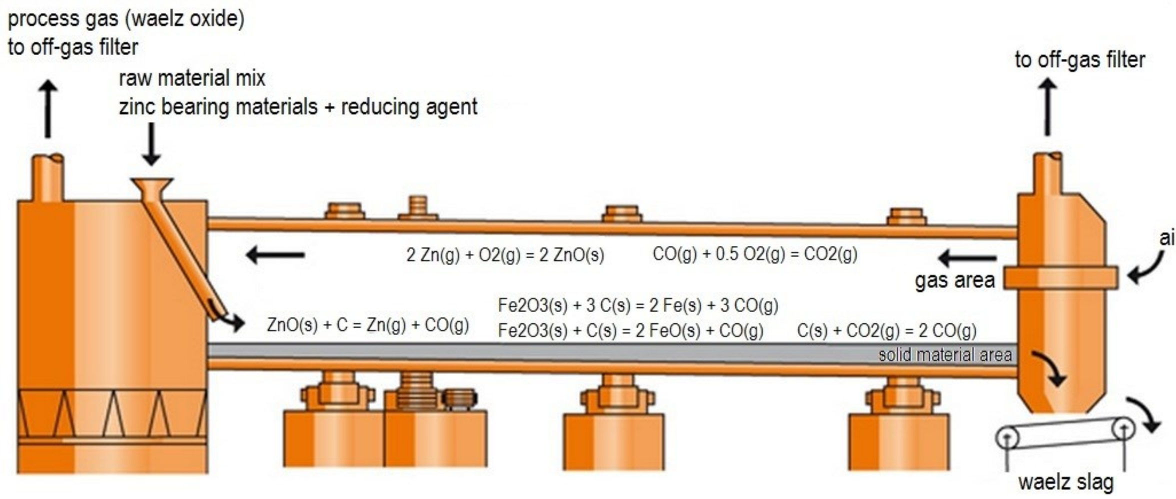


Figure 3-2: Schematic drawing of a waelz kiln [11]

The mixture, consisting of a reducing agent, slag forming additives and zinc-bearing material (most of the time EAFD) is charged as so-called self-reducing micro pellets. In the process a small amount of water is used for agglomeration. Figure 3-3 shows the waelz kiln separated in its different zones, which are described in the following.

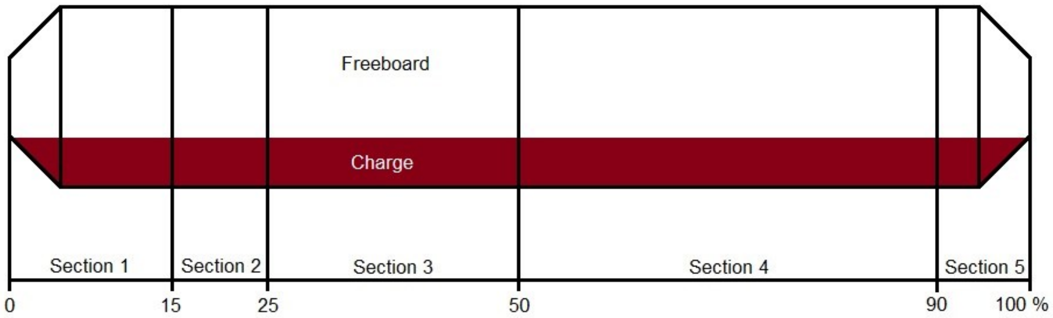


Figure 3-3: Schematic drawing of waelz kiln sections

The first zone (drying zone) of the kiln dries the green pellets by removing the moisture as well as partly crystalline water before the pre-heating zone follows. In the pre-heating zone the feedstock is heated up in addition to a partial combustion of the coke. The third zone can be named the pre-reaction zone. Within section 3 first volatile oxides are vaporized and some oxides, like high-valent iron oxides, start to get reduced. The temperature is between 500 and 900 °C. In the main reaction zone the reduction of zinc oxide to metallic zinc occurs. This leads to a zinc metal vapour which leaves the solid feedstock and moves to the freeboard. Also remaining iron oxides, like wuestite, are reduced partly to metallic iron. In some waelz kilns this metallic iron is reoxidized at the end of the kiln before leaving the furnace due to energy recovery reasons. This concept is called the SDHL process and is carried out in the fifth section. The typical temperature in this section is 1200 °C. Here, an oxygen carrier, which can be pure oxygen, air or enriched air, is blown on top of the solid material area (waelz slag) to reoxidize the metallic iron to iron oxide. This reoxidation is an exothermic reaction and therefore minimizes the necessary heat supplied by the combustion of coke.

The off-gas is conducted in counter flow. While the solid board is under reducing conditions the freeboard is oxidizing and with this the zinc vapour is oxidized to ZnO and forms a dust load of the off-gas stream, which is separated in the filter houses. The flow of the off-gas is described below.

The following table summarizes the sections and the occurring reactions in the solid area as well as in the freeboard of a waelz kiln.

Table 3-2: Summary of chemical reactions in the different areas of a waelz kiln [1]

Horizontal zone	Vertical zone	Reactions	Temp. in [°C]	
			freeboard	charge
Section 1	Charge	$H_2O_{(l)} \leftrightarrow H_2O_{(g)}$ $CaSO_4 \cdot H_2O \leftrightarrow CaSO_4 + H_2O_{(g)}$ $Ca(OH)_2 \leftrightarrow CaO + H_2O_{(g)}$	720-1000	20-150
	Freeboard	No reactions		
Section 2	Charge	$C + \frac{1}{2} O_{2(g)} \leftrightarrow CO_{(g)}$	900-1100	150-500
	Freeboard	$CO_{(g)} + \frac{1}{2} O_{2(g)} \leftrightarrow CO_{2(g)}$		
Section 3	Charge	$CaCO_3 \leftrightarrow CaO + CO_{2(g)}$ $CdO + CO_{(g)} \leftrightarrow Cd_{(g)} + CO_{2(g)}$ $CuO + CO_{(g)} \leftrightarrow Cu + CO_{2(g)}$ $Fe_2O_3 + CO_{(g)} \leftrightarrow 2\,FeO + CO_{2(g)}$ $Fe_3O_4 + CO_{(g)} \leftrightarrow 3\,FeO + CO_{2(g)}$ $C + CO_{2(g)} \leftrightarrow 2\,CO_{(g)}$	1100-1300	500-900
	Freeboard	$CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$		
Section 4	Charge	$ZnO + CO_{(g)} \leftrightarrow Zn_{(g)} + CO_{2(g)}$ $FeO + CO_{(g)} \leftrightarrow Fe + CO_{2(g)}$ $C + CO_{2(g)} \leftrightarrow 2\,CO_{(g)}$ $ZnO \cdot Fe_2O_3 + CO_{(g)} \leftrightarrow 2\,FeO + ZnO + CO_{2(g)}$ $ZnO \cdot SiO_2 + CO_{(g)} \leftrightarrow Zn_{(g)} + SiO_2 + CO_{2(g)}$	1300-1000	900-1200 (1300)
	Freeboard	$Zn_{(g)} + \frac{1}{2} O_{2(g)} \leftrightarrow ZnO$ $CO_{(g)} + \frac{1}{2} O_{2(g)} \leftrightarrow CO_{2(g)}$		
Section 5	Charge	$Fe + \frac{1}{2} O_{2(g)} \leftrightarrow FeO$	1000-800	1150-1000
	Freeboard	Burner: $CH_{4(g)} + 2\,O_{2(g)} \leftrightarrow CO_{2(g)} + 2\,H_2O_{(g)}$		

The zinc oxide bearing off-gas is collected together with ambient air in the dust settling chamber. Within this chamber the heavy particles, mainly carryover, are settled and collected. Typically the temperature is 700-900 °C. When temperature peaks occur, water is sprayed additionally for cooling. Depending on the operation site, the dust from the settling chamber (DSC) is recharged into the waelz kiln or alternatively in small amounts mixed with the waelz oxide obtained in the bag house filters. After a first cooling with ambient air, the off-gas is cooled down in a heat exchanger from 300 °C to around 120 °C, producing electrical power [74].

The first bag filters collect the zinc oxide at a temperature of around 120 °C (product filter) before active carbon is added into the filtered off-gas stream to clean it of volatile metals (e.g. Hg, Cd, As) as well as cyclic organic compounds. With this second filter stage the impurity level can be lowered to fulfil the necessary requirements for the off-gas. The cleaned off-gas leaves the plant through the chimney. Typically the active carbon is, after having been used, injected preliminary to the first filter stage and therefore forms an impurity in the waelz oxide product. As a result of its typical utilization in the primary zinc industry, this is not problematic, due to the fact that the impurities are removed within the zinc winning process. But as mentioned as a result of impure input material also the recovered zinc oxide bears a lot of impurities. Not only volatile heavy metals such as lead or cadmium, but also halides can be found due to their volatile character. This is the reason why after almost every European waelz kiln a washing is carried out to remove soluble slats, like halides. Nevertheless, the achieved purity is only high enough for limited utilization as a substitute in the primary zinc industry.

Because of the rotation and the angle of the waelz kiln the second product, the generated waelz slag, is continuously removed from the furnace. After leaving the furnace it is cooled down in a water bath. This partly removes remaining halides. In general it contains low remaining values of zinc and lead oxide but is still too high due to the leachability of these and other heavy metals. Based on obtained information of waelz kiln operators from different Western European countries, the only places where the waelz slag is not landfilled are Spain and Italy. Here it is allowed to be used as filler in road construction.

4. Characterization of waelz oxide

To develop possible concepts for an upgrade of secondary zinc oxides, first of all a characterization of such materials was carried out. The following chapter summarizes the results of the characterization of three different crude waelz oxides from the company Befesa in Bilbao, Freiberg and Duisburg. The aim was to identify the main impurities in the product to have the basis for investigations, with e.g. synthetic mixtures or also samples from the industry. The main focus was on lead and halogen compounds.

4.1 Element analysis

The following table shows the chemical analyses of waelz oxide from the Befesa plants in Duisburg, Freiberg and Bilbao.

Table 4-1: Chemical analysis of waelz oxide from the waelz kilns: Duisburg, Freiberg and Bilbao

Crude zinc oxide (unwashed)				
Element/ Compound [%]	origin			
	Duisburg	Freiberg	Bilbao	Analysis method
C	0.10	0.82	0.27	DIN EN ISO 15350
S	0.61	0.51	0.24	DIN EN ISO 15350
F	0.07	0.09	0.12	AM_NL.10.01
Cl	5.24	5.32	8.52	AM_NL.15.02
Zn	62.80	62.50	57.20	DIN EN ISO 11885
Pb	4.01	4.08	5.22	DIN EN ISO 11885
Fe	1.22	1.38	1.35	DIN EN ISO 11885
Cr	0.033	0.015	0.023	DIN EN ISO 11885
Cu	0.048	0.04	0.045	DIN EN ISO 11885
Ca	0.61	0.67	1.19	DIN EN ISO 11885
K	2.55	2.99	3.94	DIN EN ISO 11885
Na	1.96	1.95	3.22	DIN EN ISO 11885
Cd	0.11	0.18	0.13	DIN EN ISO 11885
SiO_2	0.19	0.21	0.26	DIN EN ISO 11885
MnO	0.20	0.14	0.13	DIN EN ISO 11885
MgO	0.14	0.17	0.16	DIN EN ISO 11885
Al_2O_3	0.06	0.05	0.07	DIN EN ISO 11885

The chemical analysis builds the basis for further characterization up to the theoretical calculation of a possible phase distribution.

The sulphur is partly fixed (physically) to the carbon, which comes from charged petroleum coke (PET coke); the rest is bound in other compounds. The usual content of sulphur in petroleum coke is approximately 4 % at a carbon content of approximately 90 %, which means that per 1 % carbon 0.045 % S coexists.

Carbon as well as oxide compounds of manganese, magnesium, silica, iron, alumina and calcium are found in the product because of carry over. This is related to the rotation of the waelz kiln, which causes a dust movement into the off-gas in comparable high amounts leading to impurities in the obtained product. Other process concepts where the material does not move show a typical lower carry over.

Due to its volatile character lead can be present as oxide or chloride compound, which typically follows the zinc oxide. Chlorine is relatively high with 5-8 % of the overall amount. The reason for this is that chlorine compounds in the raw material follow the zinc, due to their volatile character similar to lead oxide.

4.2 Phase analysis

XRD is a method which uses X-rays to determine the angle of the crystals in a material. As a result of the diffracted beams and their intensity the chemical bonds, their disorder and various other information can be determined. Since a lot of materials have a crystalline structure, XRD is the main method to determine the characteristic structure and with that the phases or compounds of the investigated material. Figures 4-1, 4-2 and 4-3 are XRD plots of waelz oxide from Freiberg, Duisburg and Bilbao, showing the main compounds in the samples.

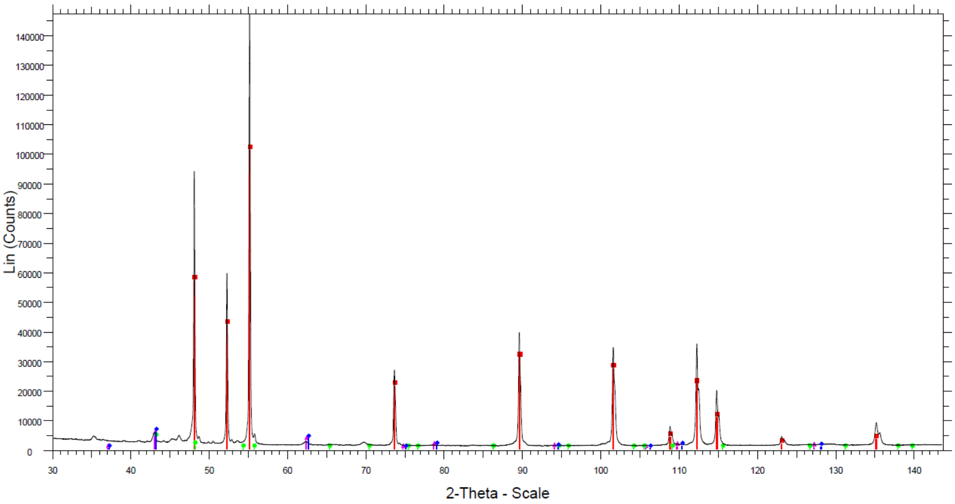


Figure 4-1: XRD of WOX (Freiberg) (■ ZnO, ▲ KCl, ◆ NaCl, ● PbO)

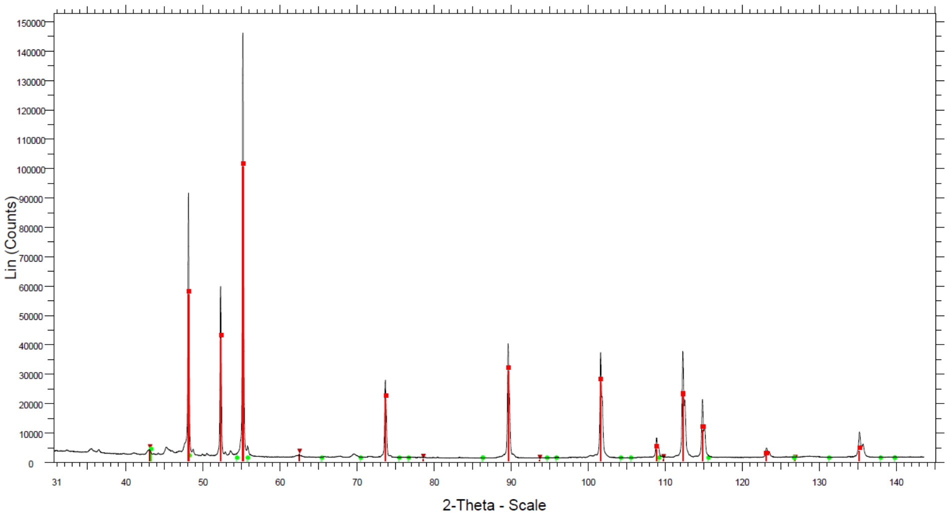


Figure 4-2: XRD of WOX (Duisburg) (■ ZnO, ▼ KCl, ● PbO)

A typical disadvantage of such materials is that especially when only a small amount of an interesting compound is present, the determination of it is very difficult, going hand in hand with a high uncertainty, or is completely impossible. The reason for this is that the area under the curve is related to the amount in the sample. If the amount is too low it is not separable from the background noise (“underground”) generated by the analysis method.

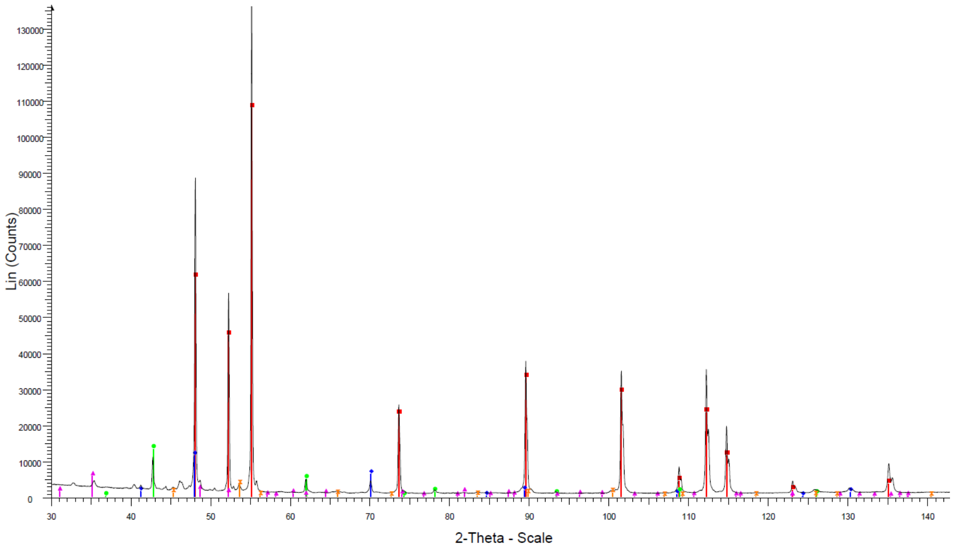


Figure 4-3: XRD of WOX (Bilbao) (■ ZnO, ◆ NaCl, ● KCl, ▲ $ZnPbF_6$, ⧗ $ZnFe_2O_4$)

It is shown that in all samples the main peaks indicate zinc oxide (ZnO), lead oxide (PbO), potassium chloride (KCl) and sodium chloride (NaCl). Other compounds with low concentrations, like other halides or also carry-over are not detected with this analysis method. In case of lead it was shown that lead(II) oxide is the most frequent one from possible other valence states, like Pb_2O_3, Pb_3O_4, etc. Therefore, for further investigations, like thermochemical calculations or trials with synthetic mixture lead was always assumed to be present as dioxide.

Based on these findings, it was expected that chlorine first of all is bound to sodium and potassium and secondly to zinc and lead. Therefore, for the following phase distribution calculation, it was assumed that 40 % of the chlorine is bound as NaCl, another 40 % as KCl and 10 % respectively occurs in the form of $PbCl_2$ and $ZnCl_2$. In the industry samples it is possible that other chlorine compounds such as $CaCl_2$, $FeCl_2$, $FeCl_3$, etc. are present in small amounts.

4.3 Thermogravimetry

The following figures show a thermo gravimetric analysis of the samples under oxidizing (air) and inert (argon) atmosphere.

The sample was heated with a rate of 5 °C per minute up to a temperature of 1200 °C, which was then kept constant for 1 hour. During this thermal treatment, the mass loss was measured.

Figures 4-4, 4-5 and 4-6 show the mass loss in percent (y-axis) in relation to the time and with that in relation to the present temperature (x-axis).

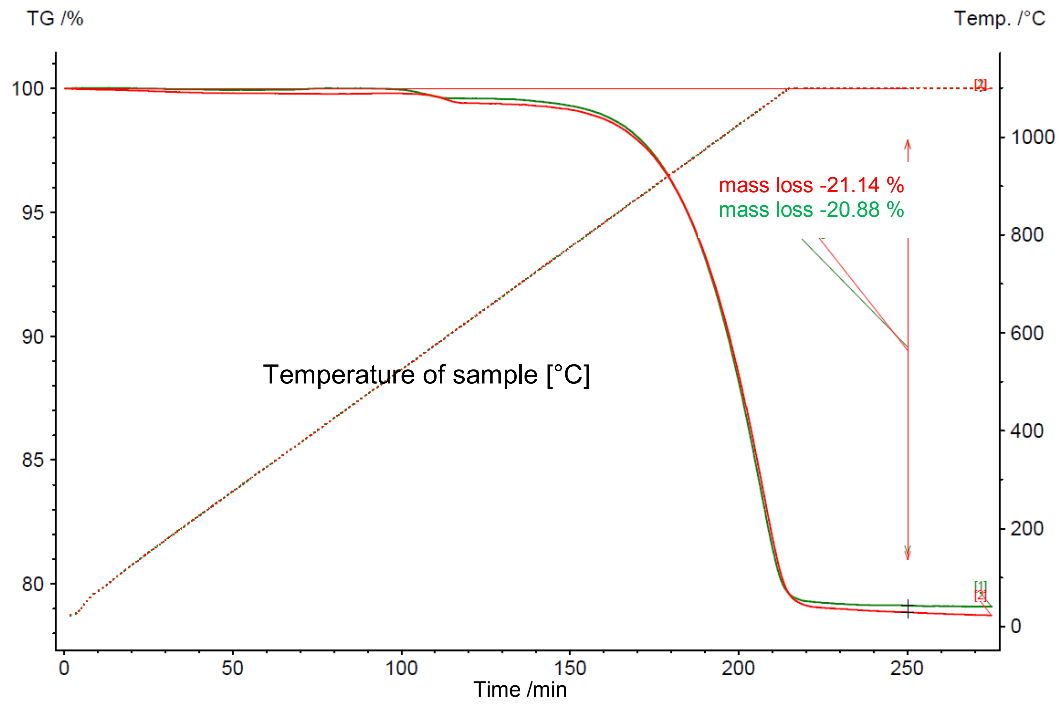


Figure 4-4: Thermo gravimetric analysis (Bilbao) (red = argon; green = air)

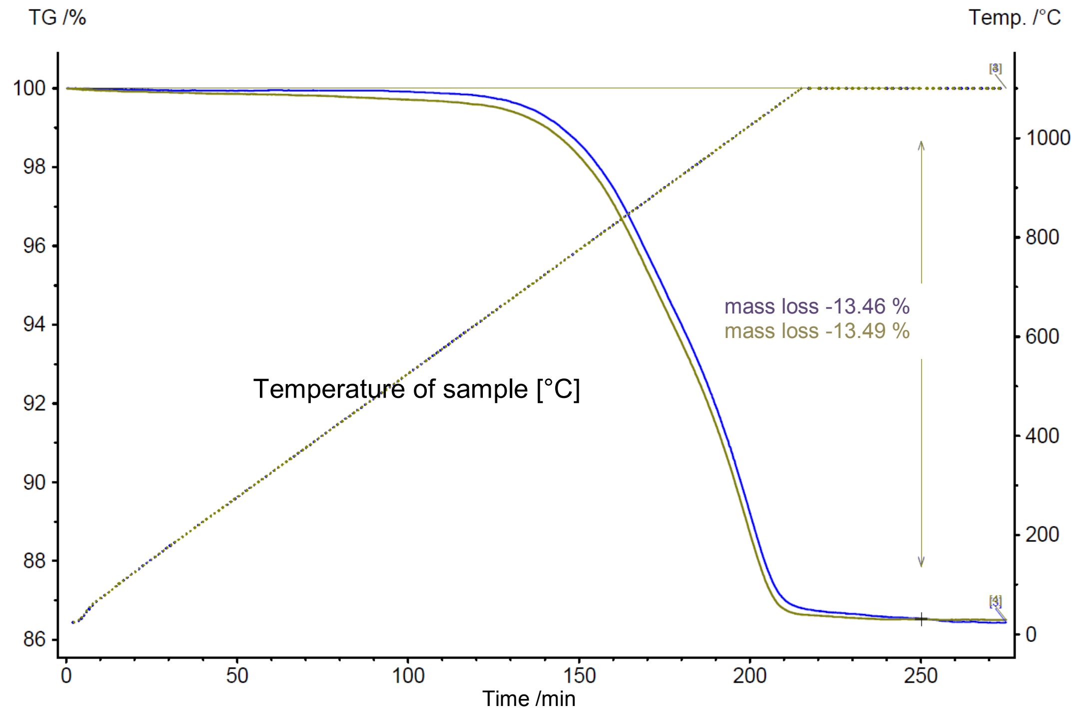


Figure 4-5: Thermo gravimetric analysis (Duisburg) (blue = argon; green = air)

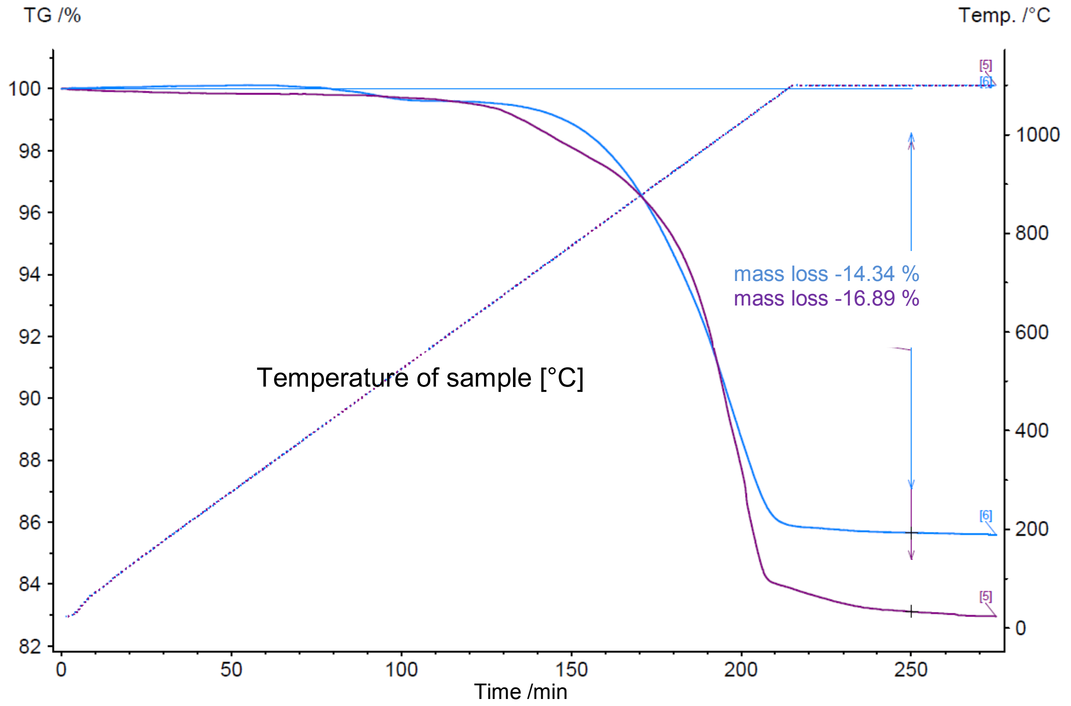


Figure 4-6: Thermo gravimetric analysis (Freiberg) (violet = argon; blue = air)

Table 4-2 summarizes the mass losses of each sample after 250 minutes retention time. It is shown that under inert as well as under oxidizing atmosphere nearly the same mass loss occurs. The Freiberg sample has a larger delta (~2.6 %) between air and argon, which most probably arises from the higher carbon content. As a result of the reducing agent present, oxides like ZnO can be reduced and probably be vaporized. Not only that; a reduction of iron oxide can also occur. So on the one hand carbon is removed and on the other hand metallic zinc is vaporized. In the case of oxidizing conditions (air), a part is oxidized again and remains in the sample, which leads to a smaller overall mass loss.

As mentioned, iron oxide is also a possible example for such behaviour (only reduction in argon atmosphere and reduction followed by an oxidation under air). In this case the oxidation stage of iron and iron oxide respectively is changed, which minimizes the mass loss under air atmosphere.

Table 4-2: Summary of TG results (mass loss after 250 minutes treatment)

[%]	Duisburg	Freiberg	Bilbao
air	13.49	14.34	20.88
argon	13.46	16.89	21.14

Table 4-3 shows the sum of volatile compounds (halides, oxides and sulphates) in the theoretically calculated phase distribution (see Table 4-5).

If the recognized mass loss in the thermo gravimetric analysis (see Table 4-2) is compared with the calculated volatile compounds in Table 4-3, it can be seen that the measured values fit very well to the calculated ones.

Table 4-3: Sum of volatile compounds in the samples
(based on chemical analysis and calculated phase distribution)

[%]	Duisburg	Freiberg	Bilbao
$PbSO_4$	0.29	0.22	0.11
PbO	2.46	2.56	2.86
KCl	4.41	4.47	7.17
NaCl	3.46	3.51	5.62
$PbCl_2$	2.06	2.09	3.34
$ZnCl_2$	1.01	1.02	1.64
K_2O	0.29	0.77	0.22
Total	13.96	14.65	20.95

This circumstance and furthermore the fact that the sum of calculated compounds (see Table 4-5 - total) shows a value close to 100 % gives a satisfying result and for this a likely composition and phase distribution of the investigated material.

4.4 Specific surface

An important parameter, when considering zinc oxides from the recycling of residues for the high purity areas or other possible utilization areas, is the specific surface of the product. BET analysis is a calculation model used for measuring the adsorption isotherm. It represents the equilibrium between adsorption and desorption on a surface and is based on following equation.

$$\frac{1}{W\left(\left(\frac{P}{P_0}\right)-1\right)} = \frac{1}{W_m * C} + \frac{C-1}{W_m * C} * \left(\frac{P}{P_0}\right) \qquad \text{Equ. 4-1}$$

Figures 4-7 to 4-9 show the BET-plots of investigated waelz oxide materials.

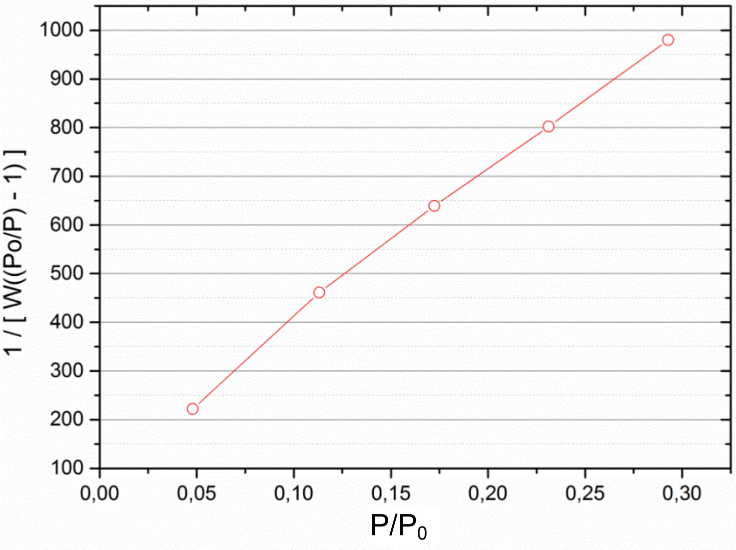


Figure 4-7: BET-plot of WOX (Bilbao)

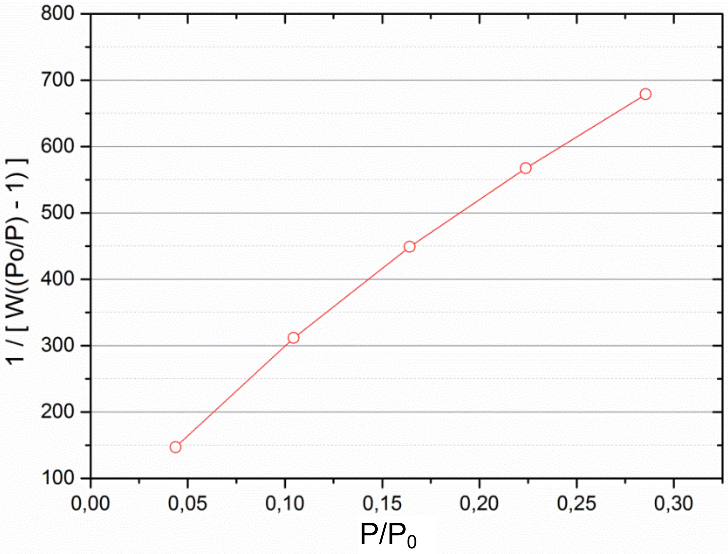


Figure 4-8: BET-plot of WOX (Duisburg)

Regarding surface measurements the aspect of adsorption is used to calculate the specific surface of a porous material.

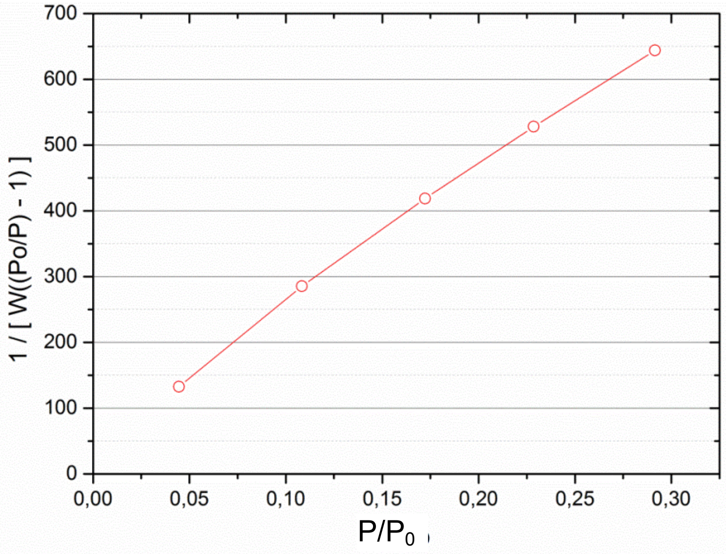


Figure 4-9: BET-plot of WOX (Freiberg)

Table 4-4 summarizes the results of the Quantachrome-BET analysis. It shows the slope, intercept, correlation coefficient and constant of the isotherm. The X-axis shows the relative pressure in the measurement facility of the gas used for analysis, which is the relation of P/P_0. The Y-axis shows the part of the BET equation which is corresponding with the adsorbed weight of the gas on the investigated sample. Based on that, the surface area, which is the main key-figure of the investigated samples, can be calculated.

Table 4-4: Summary of Quantachrome BET-analysis

BET summary	Duisburg	Freiberg	Bilbao
slope	2188.31	2062.08	3139.77
intercept	7.10E+01	5.31E+01	9.56E+01
correlation coefficient, r	0.996519	0.998569	0.998648
C constant	31.802	39.852	33.84
Surface Area [m²/g]	1.541	1.646	1.076

For the typical utilization of waelz oxide in the primary industry (to produce SHG zinc), the surface area is not as important as in other application areas, especially in the field of high quality zinc oxides (e.g. tyre industry as vulcanization agent or others). Nevertheless, it can be said that also in the primary industry, this figure has an influence on the dissolution speed of the material.

Depending on the utilization of high purity ZnO, the following specific surface areas are common:

- Depending on the furnace configuration the surface area of commercial ZnO is in the limits of around 2.5 to 12 m²/g. The standard for a long time has been 5 m²/g as a result of the maximum opacity (corresponding to the particle size) and the utilization in the paint industry. In the rubber and tyre industry 4 to 6 m²/g are common.
- For special applications a higher surface area is used, especially when the transparency is more important than the opacity.
- Special production processes based on hydrometallurgical methods are able to produce specific surface areas up to 50-100 m²/g, which is then called active zinc oxide and has special utilization areas, like in catalysts and latex rubber.

It is shown that waelz oxide has a lower surface area than products for the high purity market. This results from the furnace configuration, which is totally different from the common facilities in high purity zinc oxide production, which use geometry and air flow to control the particle size and with that also the surface area to produce a high quality product.

In case of the waelz kiln the oxidation takes place in the kiln itself, therefore making it difficult to achieve a predefined particle size and with that a defined specific surface area, due to very low possibilities of control. However, this is not that important because the utilization of waelz oxide in a market segment where the specific surface area plays a role is not possible without further treatment to upgrade the quality. Furthermore, an adjustment of some physical properties like surface area, particle size, etc. would be necessary.

Table 4-4 shows that Freiberg and Duisburg are similar in their surface area (around 1.5 m²/g), while Bilbao has only 1 m²/g. A possible reason for that could be the different lengths of the furnaces. While in Freiberg and Duisburg the furnaces are around 40 metres long, the plant in Bilbao has a 60-metre waelz kiln. This results in a longer retention time, which is a possible reason for further agglomeration and different properties of the oxide compared to shorter kilns.

4.5 Morphology

In addition to the characterization methods already described, samples of each product (Befesa, Duisburg and Bilbao) were scanned with an EDX detector (energy dispersive X-ray spectroscopy) on the scanning electron microscope. For the emission of characteristic X-rays from a sample, a high energy beam is required. This can be a beam of charged particles (electrons or protons) or also X-rays. The high energetic beam is then focused on the sample and ejects an electron from an inner atom shell. As a result an electron from an outer shell (higher in its energy) fills the hole and releases the difference in energy between these discrete energy levels. This emitted X-rays can be detected by an energy-dispersive spectrometer. As the energy of the X-ray is specific, the elemental composition of the sample is measured.

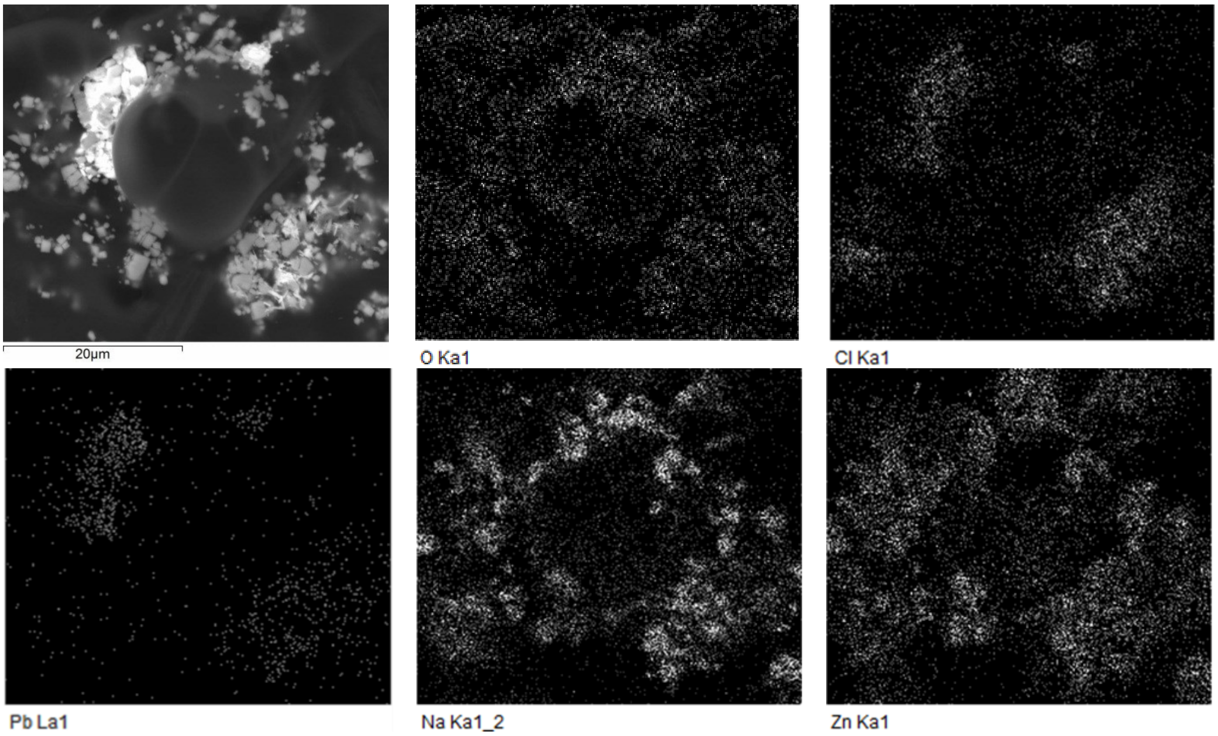


Figure 4-10: EDX-mapping of waelz oxide from Bilbao

The main aim was to verify with the EDX the assumptions for the calculated phase distribution. Figure 4-10 shows the mapping of a crude waelz oxide sample from Bilbao. It is clearly shown that especially sodium, lead, zinc and chlorine are present in the same areas, which underlines the assumption that NaCl should be found in the product in addition to lead and zinc chloride. Moreover, fluorine and calcium can be found in the same regions but with relatively low concentration. Oxygen is present in the areas of zinc and sodium, as well. This allows the assumption that not only chloride, but also sodium oxide can be found.

Figure 4-11 (mapping of crude waelz oxide from Duisburg) shows a lot of small zinc oxide particles (white) and one bigger one (grey) in the right bottom corner. In the same area (white particles) sodium is high in its content, which can be NaCl but is more likely to be Na_2O. The same is shown in the previous figure. The grey one is most probably a result of carry-over from the waelz kiln and shows high contents of fluorine and calcium, which makes it highly likely that this is a CaF_2 particle.

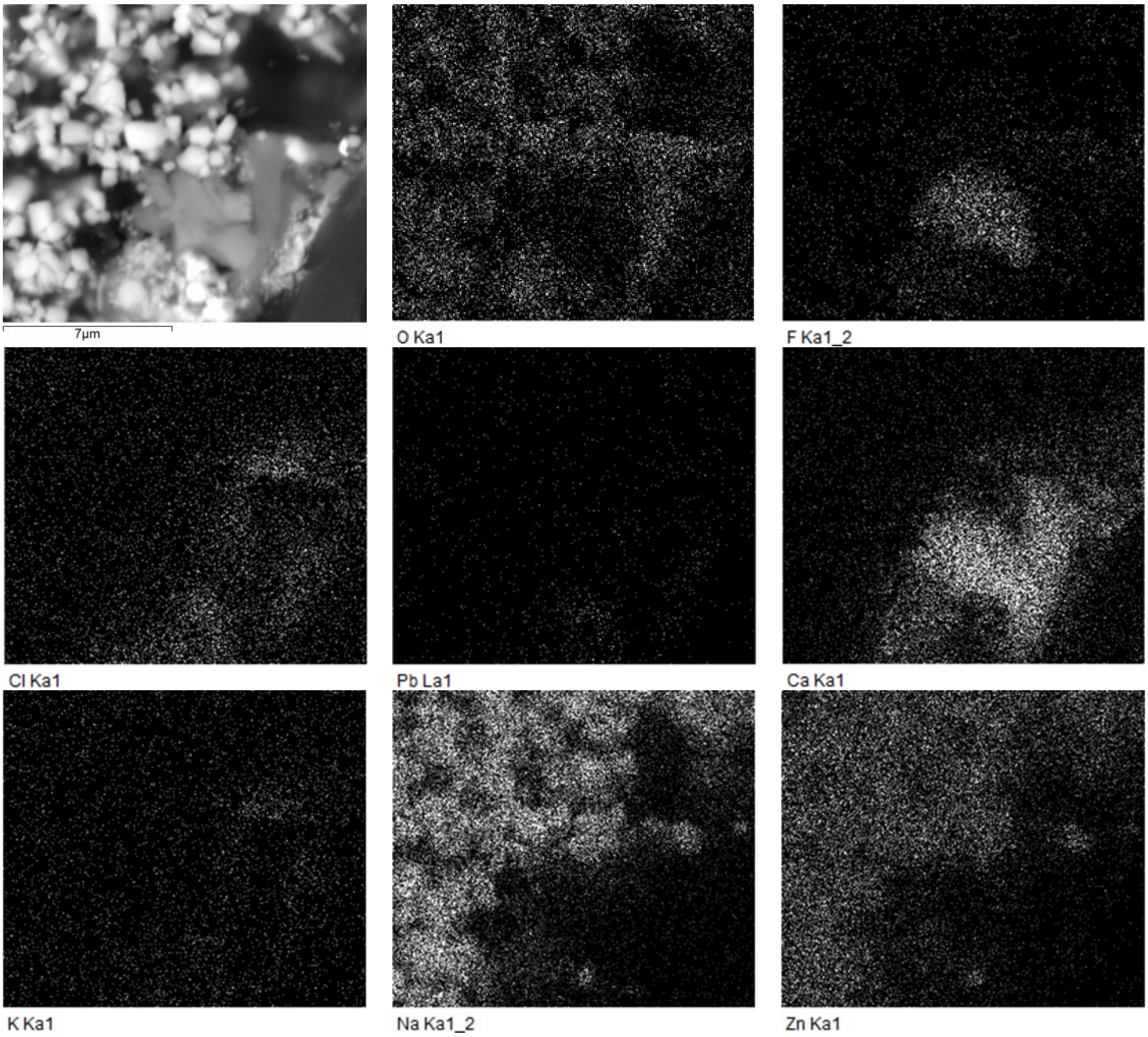


Figure 4-11: EDX-mapping of waelz oxide from Duisburg

Figure 4-12 shows an element mapping of the Freiberg sample. As a result of the high zinc content in all of the supported samples, it is difficult to differ between sodium, potassium and zinc areas/compounds (dark grey areas show the matrix). This, especially in combination with chlorine, makes it difficult to determine how exactly chlorine is found in compounds with sodium and potassium or zinc as well as lead. In any case, based on the carried out XRD and the previously described findings, sodium and potassium are most likely bound to chlorine, as described before as a result of the active character. Moreover, zinc chloride and lead chloride can be found in addition to their oxides (Na_2O, K_2O, ZnO and PbO).

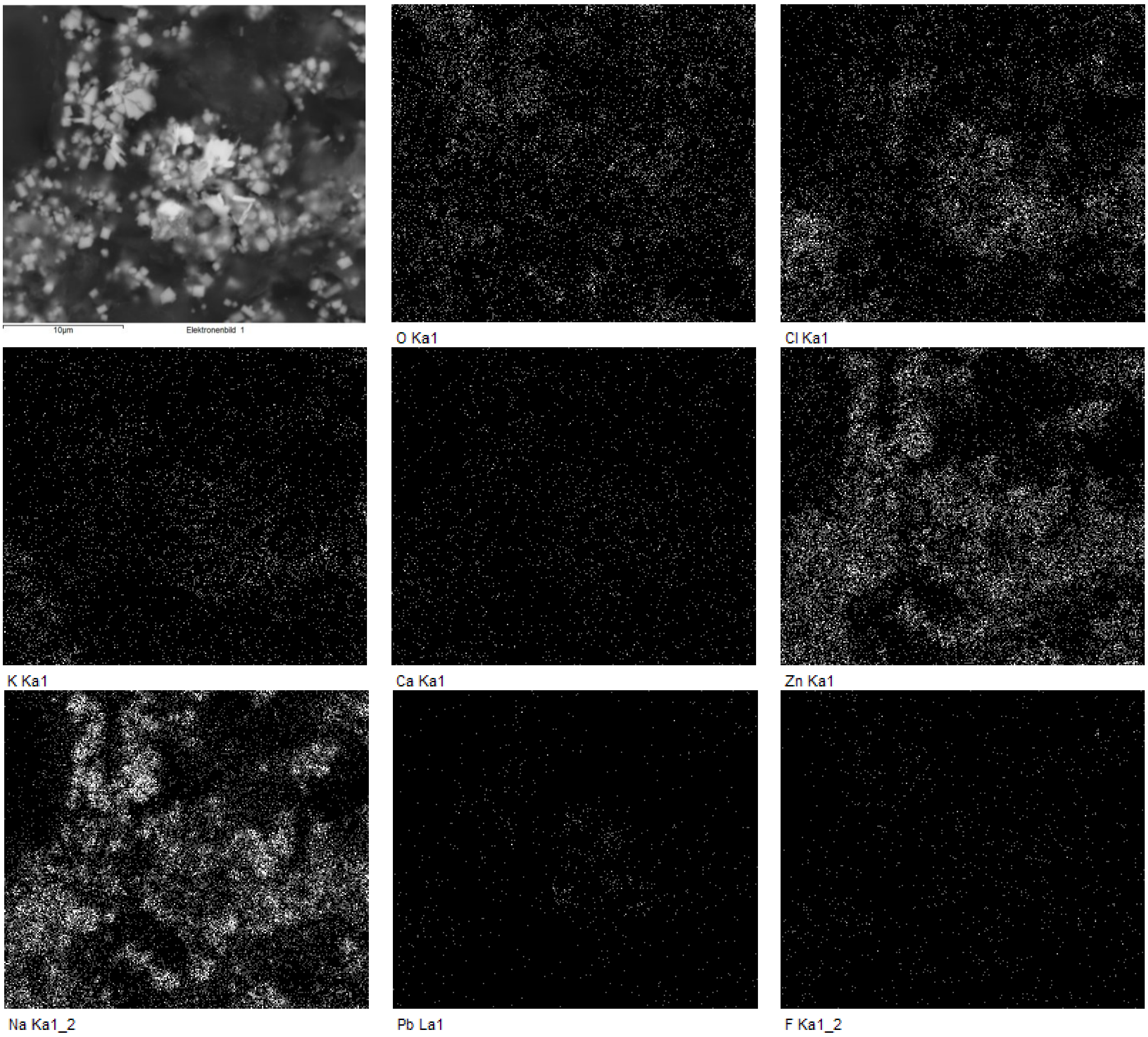


Figure 4-12: EDX-mapping of waelz oxide from Freiberg

4.6 Theoretically calculated phase distribution

Based on the characterization and the chemical analysis, the main compounds were identified. Furthermore, a phase distribution was calculated and is shown in Table 4-5. A part of the sulphur (0.045 % per 1 % carbon) was assumed to be linked to the carbon, as a result of the petroleum coke used in the recycling facility. This is the same ratio of S/C, which is present in commonly used petroleum coke for metallurgical processes. It was assumed, as well, that the remaining sulphur is split into lead sulphate and zinc sulphate in the same ratio as zinc oxide to lead oxide is present in the sample.

Table 4-5: Theoretically calculated phase analysis

[%]	Duisburg	Freiberg	Bilbao
ZnO	76.106	76.041	69.670
PbO	2.459	2.555	2.862
C	0.100	0.820	0.270
S in C	0.004	0.036	0.012
$PbSO_4$	0.286	0.224	0.108
$ZnSO_4$	2.897	2.267	1.091
$ZnCl_2$	1.007	1.023	1.638
$PbCl_2$	2.055	2.087	3.342
NaCl	3.455	3.508	5.618
KCl	4.408	4.475	7.166
Na_2O	0.810	0.768	1.362
K_2O	0.287	0.775	0.219
Cr_2O_3	0.048	0.022	0.034
Cd	0.110	0.180	0.130
CaF_2	0.144	0.185	0.247
CaO	0.750	0.805	1.488
CuO	0.060	0.050	0.056
SiO_2	0.190	0.210	0.260
MnO	0.200	0.140	0.130
MgO	0.140	0.170	0.160
Al_2O_3	0.060	0.050	0.070
Fe_2O_3	1.744	1.973	1.930
Total	**97.322**	**98.364**	**97.861**

The chlorine is mainly bound to sodium and potassium. Owing to the fact that it is not possible to identify the exact amount of chlorine compounds, it was necessary to make assumptions. Therefore, based on the thermo gravimetric analysis, the XRD, and the findings from the EDX the main amount of chlorine is bound to sodium (40 %), potassium (40 %) and two times 10 % in lead and zinc chloride, as stated in one of the previous chapters.

As mentioned above, the sum is close to 100 % and therefore gives a satisfying result and for this a composition and phase distribution of the investigated material, which can be seen as realistic.

4.7 Summary of characterization

The aim of the carried out characterization was to identify the main compounds of typical crude zinc oxide produced by Befesa. In doing so, samples from Freiberg, Duisburg and Bilbao were investigated. The difference between these waelz kilns are on the one hand the length and on the other hand the composition of the charge. This is the reason why the waelz oxides differ in their impurity amount, carry-over amount (e.g. carbon content and slag compounds), as well as their specific surface area.

Based on the characterization performed, the main compounds in crude waelz oxide were classified as zinc oxide, lead oxide, carry-over (slag compounds) and halides, which are mainly sodium and potassium chloride as well as zinc and lead chloride.

Fluorine:

The XRD was not able to detect the relevant fluorine compound, due to the low amount. As a result, further investigations using scanning electron microscopy with an energy dispersive detector were done, showing that the fluorine can mainly be detected in the same areas as calcium, which leads to the conclusion that calcium fluoride is present in the investigated samples. Its origin is from fluxes for slags used in steel plants. Furthermore, it could theoretically be formed during the waelz process by the reaction of CaO with other fluorides. Although the main part seems to be as calcium fluoride, it is not excluded that also other small amounts of fluorides can be present (like zinc, lead, potassium fluoride, etc.).

Carry-over:

Oxides, like MgO, MnO, Al_2O_3, Fe_2O_3, CaO, etc. are generally not volatile and are therefore a result of the rotation of the recycling facility (waelz kiln), which is responsible for carry-over. This is the reason for small amounts of carbon in the product, which is charged as a reducing agent in the waelz process. On average the amount is between 2.9 and 3.9 % of the provided samples. The iron oxide can also be present partly as zinc ferrite because of carry-over or the combination with gaseous zinc vapour. The other slag forming compounds are usually not in their separated form, either; moreover, they form compounds with each other, like $xCaO \cdot ySiO_2$, with different molar factors. Due to their more or less inert behaviour, their exact molar ratio is not of major importance.

Chlorine:

Based on the chemical analysis and the theoretically calculated phase distribution, which is based on the carried out XRD, it was shown that chlorine is bound first of all to sodium and potassium, secondly to zinc and lead. The detection of zinc and lead chloride is difficult because of the huge amount of matrix material, which is mainly zinc oxide and lead compounds.

As a result of the formation process of crude zinc oxide (via the vapour phase) it is very likely that zinc chloride is also present.

Sulphur:

The sulphur is fixed to the carbon in small amounts but as a result of the high amounts in relation to the carbon or even higher values than the carbon itself, the sulphur has to be bound additionally to some other elements, like zinc and lead. The most probable compounds are, as mentioned, lead sulphide or zinc sulphide, which have a low vapour pressure and therefore vaporize. These sulphides are very likely oxidized during their way through the oxidizing off gas system of the waelz kiln and forming sulphates. Again it is difficult to verify this thesis by means of scanning electron microscopy because the sulphur and lead have a similar characteristic radiation. Also the XRD does not deliver reliable results due to the low amount. However, based on thermochemical calculations, it was assumed that zinc and lead sulphate are most probably the compounds present in the samples.

Surface area:

As mentioned in the report, the surface area results from the furnace configuration. In case of the waelz kiln it is totally different from the common facilities used in high purity zinc oxide production (American and French process). With the waelz kiln, lower surface areas are the result. As a fact of the different utilization areas, this is of minor importance.

In the case of an upgrade to higher qualities and the aim of a different application area, this property is gaining influence and has to be considered.

The difference in the measured surface area of the provided samples most probably arise from the furnace length, which influences the particle formation and with that also the measured surface area. It was shown that Duisburg and Freiberg have similar values, while Bilbao has a lower one. This fits with the furnace length; the Bilbao kiln is 65 metres long, while the other two are approximately 40 metres.

5. Zinc products with focus on zinc oxide and zinc sulphate

The following chapter gives an introduction into the zinc oxide and zinc sulphate market concerning their different possible utilization areas and typical required qualities. This forms the basis for an appraisal of the obtained qualities of the investigated upgrade concepts.

5.1 High purity zinc oxide

Due to the versatility of zinc oxide based on its positive properties in many different fields, its area of utilization is wide and fragmented. In the following section, the main application areas are described.

5.1.1 Tyres and rubber

Because the tyre and rubber industry is the biggest application area for technical zinc oxides, with around 61 % worldwide [12], a brief historical abstract of the evolution of this sector is given.

5.1.1.1 History

In the 18th century Charles Goodyear discovered today's common way of producing rubber by pure chance.

Before the vulcanization invention took place, caoutchouc (the base material for today's rubber industry) was used to seal clothes and textiles. In the process, caoutchouc was dissolved in turpentine and ether and with that the textiles were sealed. The problem was that under low temperatures it was very stiff and under higher temperatures it started to stick.

The inventor of the modern rubber production technology, Charles Goodyear, tried to improve the properties by adding chemicals to the rubber and during trials with sulphur, a small part of the mixture fell onto the iron stove by accident. The heat and the sulphur transformed the caoutchouc into rubber by vulcanization. From that time on, the vulcanization process was used in the rubber and tyre industry.

5.1.1.2 Usage and properties

Originally, the vulcanization process was only carried out with sulphur. Nowadays, the most common method is with the usage of sulphur, as well, although the mechanism is still not completely clear. The addition of metal oxides, like ZnO, is used when the polymer chains carry reactive functional groups, like carboxy or halide groups. As a result of the chemical and physical properties of zinc oxide, for more than 100 years now, the tyre and rubber industry has been one of the main application areas of high grade ZnO. Because of high temperatures during the usage of tyres, one necessary property is heat conductivity. This can be achieved if the vulcanization process is carried out with a mixture of zinc oxide and stearin, which is why approximately 2-5 % ZnO is added during the mixture preparation.

Further properties of ZnO used in this application area are mentioned subsequently.

ZnO can be used as an activator, to improve the effectiveness of the vulcanization process; the activated ZnO (related to the surface area) is much more powerful than the normal one which is used for the production of translucent vulcanization products. For the production process it is important to use an exact amount of ZnO, because of improved properties (e.g. mechanical fatigue). Due to numerous additional advantages for the usage of ZnO in rubber production, a summary follows as a short list:

- It increases the reaction velocity of the vulcanization process,
- improves the durability and acts as a blocker for fungus growth in the product,
- increases the abrasion resistance,
- increases the temperature creep resistance and delays the de-vulcanization,
- works as a pigment → white colour and
- adds protection against UV rays.

Table 5-1 shows an example of a mixture for truck tyres. It illustrates that 30 g of red seal zinc oxide quality (typically from the French process) is used as an ingredient for a mixture of approximately 1400 g, which is 2.2 % of the total amount.

Table 5-1: Example of a mixture for truck tyres [13]

Compound/Chemical	Density [g/cm³]	Volume	Mass [g]
Buna CB 30 (cis-BR)	0.91	75.4	411
Buna 1712 (SBR)	0.95	52.6	300
Ruß Corax N 220	1.77	45.2	480
Naftolen ZD (aromat. oil)	1.02	19.6	118
Stearin acid	0.92	2.2	12
ZnO, “Rotsiegel”	5.6	0.89	30
Cumaronharz (optional)	1.1	2.73	(18)
Paraffin wax	0.9	1.11	6
Antiageing agent 4010 NA	1.29	0.78	6
Vulkacit Thiuram	1.3	0.78	3.6
Vulkacit CZ	1.31	0.79	3.6
Sulphur	2.0	0.80	9.6
Total	**1.15**	**202.88**	**1397.8**

5.1.1.3 Required standard

Technical requirements for the tyre industry are much stricter than those for the ceramics industry and indirect production ZnO is almost exclusively required by tyre producers worldwide. Examples for the standard of zinc oxide utilization in the tyre industry are e.g the *“ASTM D4315 - 94(2006) Standard Test Methods for Rubber Compounding Material-Zinc Oxide”* or the *“ISO 9298:1995 Rubber compounding ingredients -- Zinc oxide -- Test methods.”* Within these norms, typical chemical and physical tests for zinc oxide that are considered to be used in rubber compounds are described.

Important parameters are:

- Surface area
- Zinc oxide content
- Heat loss
- Sulphur in zinc oxide
- Lead and cadmium content
- Sieve residue

An example for a guideline of a ZnO producer for tyre grade can be seen in the following list:

- Loss during drying (105 °C): max. 0.5 %
- Ignition residue (950 °C): min. 99.0 %
- Sieve residue (0.045 mm): max. 0.05 %
- ZnO content: min. 99.0 %
- Cadmium content: max. 300 mg/kg
- Copper content: max. 10 mg/kg
- Lead content: max. 0.4 %
- Manganese content: max. 10 mg/kg
- Sulphur content: max. 0.02 %
- Nitrogen surface (BET): min. 5 m^2/g

Furthermore, it can be stated that breaking into the tyre market as a new supplier is quite difficult. Tyre producers generally impose very stringent testing procedures before providing supplier status to an oxide producer.

This testing phase can take up to one and a half years to complete, including samples for lab testing and larger deliveries for production line testing. Especially the consistencies as well as specific qualities (including particle size, surface area, dispersion rates, etc.) are required in a special range.

5.1.2 Glass and ceramics

In the ceramics as well as in the glass industry ZnO offers the opportunity to give the products unique properties; the decrease of thermal dilation, increase of mechanical resistance or also the ability to give brightness to the products can be mentioned.

A special field is the production of varistor elements, which are electrical resistors varying their height of resistance depending on the voltage. The application ranges from lower 5 V to high voltage applications and the interesting thing, from the electro technical and material properties point of view is that in all cases the same modified ZnO in combination with SiC can be used for the production process [14].

5.1.2.1 Varistor elements - a speciality of ceramics

The function of this electrical element is based on the varistor effect. During a sintering of ZnO crystals empty atomic oxygen places arise, which forms a non-linear conductor. Additional compounds like Bi, Co, Mn, Sb and Cr regulate the sintering process and influence the non-linear conductive properties. During sintering a new polycrystalline structure is established and while cooling down, isolating crystal boundaries are formed. These boundaries are the reason for the varistor effect [14].

5.1.2.2 Glass industry

In both glass and ceramics, zinc oxide improves the resistance to thermal and mechanical shock, but more notably in glass; up to 2-3 % in transparent glazes is mentioned in literature. It also works as an opacifier or whitener of the products and enhances colour and clarity in frit production. The high refractive index is the reason for its utilization in optical glass manufacturing.

5.1.2.3 Requirements - ceramic industry

In general there are no special quality issues for zinc oxide used in the ceramics industry. This is a very price-sensitive business and lower quality oxide will be used if the price difference between lower quality and higher quality is wide enough. For example in the late 1990's, directly produced ZnO from concentrates was imported heavily into Spain and Italy and in 2000 from China before anti-dumping duties were imposed by the European Union. These imports were solely into the ceramic business in these two countries.

Although the general requirements are not as strict as in the tyre and rubber industry, depending on the area of usage (medical technology, machine building, wear protection, electrotechnology, etc.), higher requirements in the ceramics industry can also be found.

Very often, the main points are sieving residue due to unwanted big particles which could form a non-smooth surface on the product as well as impurities which can influence the colour of the white zinc oxide, such as copper oxide, iron oxide, etc., which are highly undesirable.

5.1.3 Pharmaceuticals

In this industry, zinc oxide is used to manufacture different chemical compounds and additives. Some of them are summarized in the following list:

- Zinc dispersions for vulcanization
- Zinc salts used in the production of plastics
- Zinc borate and chloride used as flame retardant
- Zinc diacrylate used in golf ball production as a key ingredient
- Dissolved ZnO in phosphoric acid used for coating and metal priming
- Anticorrosion material (e.g. chromate)

The pharmaceutical usages of ZnO are again based on its physical properties, like the adsorption ability of UV rays. Some examples of where ZnO is used are provided below:

- Ingredient in lotions, sun creams and diaper rash prevention
- UV adsorbent in creams
- Ingredient of dietary supplements

In the pharma industry very strict standards are commonly present for the usage of chemicals. Widely used pharmaceutical monographs are the British Pharmacopoeia BP2009, the European Pharmacopoeia EP5.0 or EP6.0 and the U.S. Pharmacopoeia USP30. Typically, they describe the necessary quality and carried out tests for the usage of ZnO (CAS:1314-13-2) in pharma products.

EP6.0, the European guideline, defines the ZnO content after ignition with 99.0 to 100.5 %. The characteristic appearance has to be soft, white or faintly yellowish-white. Additionally, it has to be an amorphous powder and free of gritty particles. The powder has to be virtually insoluble in water and ethanol (96 %).

The maximum content of arsenic is mentioned with 5 ppm, cadmium with 10 ppm, iron with 200 ppm and lead with 50 ppm. The methods and directives/instructions used for determining the content are described in detail in the above-mentioned EP6.0 [15].

Referring to a discussion with a main European ZnO producer, generally the process to achieve supplier status in the pharma-industry can take up to 3 years with constant adaption of their own production processes and standards.

5.1.4 Pigments for paints

During the last decades ZnO was used in paints and coatings due to its positive chemical, physical and optical properties.

The durability of oil paints can be increased by the additive of active pigments which are based on zinc. Another positive effect is that it protects against fungus, mildew and mould growth. In recent years, due to the development of nanotechnology (< 35 nm particle size) in the paint and coatings industry, positive effects of oxide nanopowder concerning its electrical, scratch, abrasive and impact resistance have been discovered.

ZnO is applied in water as well as solvent based formulas to make use of its positive effects. In addition to its usage as a pigment, it works as a brightener and can absorb UV rays to extend the colour retention [9].

5.1.5 Agricultural fertilizer and animal feed

Zinc is very often a deficient micronutrient in agriculture; for that reason, fertilizers are used to increase the growth and yield of the crops and soils. Generally three kinds of fertilizers are common, which differ in their zinc content and price:

- Inorganic sources, like zinc sulphate, zinc oxide, zinc carbonate and also zinc nitrate as well as chloride
- Synthetic chelates, what are special complex micronutrients formed by e.g. EDTA (ethylenediaminetetraacetic acid and a metal ion; in this case zinc (recent research showed that $ZnSO_4$ is cheaper and better than ZnEDTA)
- Natural organic complexes, which are manufactured by mixing zinc and organic products like lignosulphonates from paper production

Table 5-2 shows a typical chemical analysis of a zinc oxide used in the area of agriculture as animal feed additives and with that gives an overview concerning allowed impurity contents, such as lead, cadmium, arsenic and other impurity content.

Table 5-2: Chemical analysis of a typical ZnO used as animal feed grade [16]

Element/compound	Content [%]
ZnO	89.00
CaO	4.00
Fe	3.00
SiO_2	1.50
Mn	0.30
S	0.30
MgO	0.15
Cu	0.05
Pb	0.05
Cd	0.01
As	0.01
Moisture	0.10

What is especially interesting is the high content of CaO allowed, which for example can also be present in lower grade zinc oxide and might be difficult to be separated.

5.1.6 Other application areas

Around 3 % [12] can be summarized as miscellaneous application areas such as:

- Coatings for paper industry
- Semiconductor technology
- Additive in lubricants for thermal engines
- Improvement of properties of lubricant grease
- Desulphurization processes
- Fire retardant
- Blocker for growth of fungi
- Additive in cement production (colour, stability, strength, etc.)

Depending on the area, special grades are utilized, like for instance zinc oxides with very high specific surface, also called activated zinc oxide, which can be found, for example, in desulphurization processes.

5.2 Zinc sulphate

Next to zinc chloride and zinc oxide, zinc sulphate is the technically most important and most used zinc compound. The areas of application are multifaceted. As shown in Figure 5-1, the commonly used raw materials for zinc sulphate production are of high quality, with typically low impurity levels.

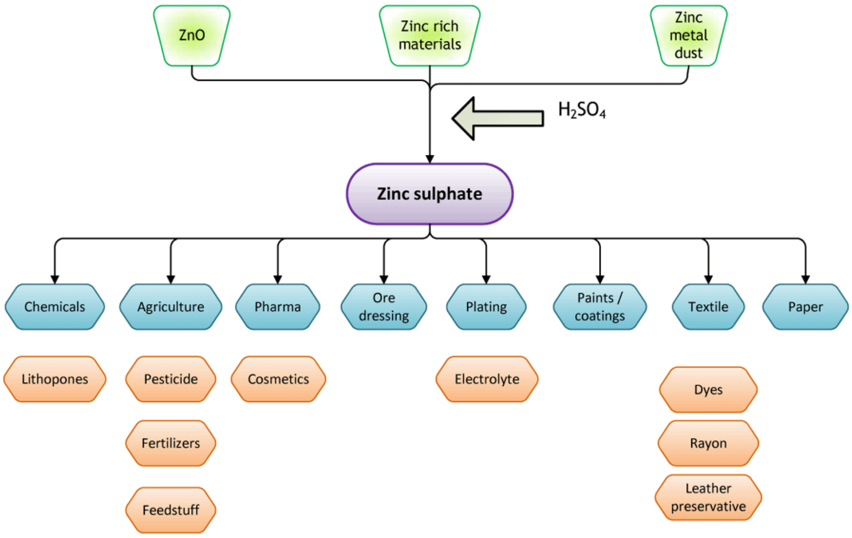


Figure 5-1: Overview of used raw materials and typical application areas of zinc sulphate [17]

Figure 5-2 shows the percentage breakdown in the main utilization areas of zinc sulphate.

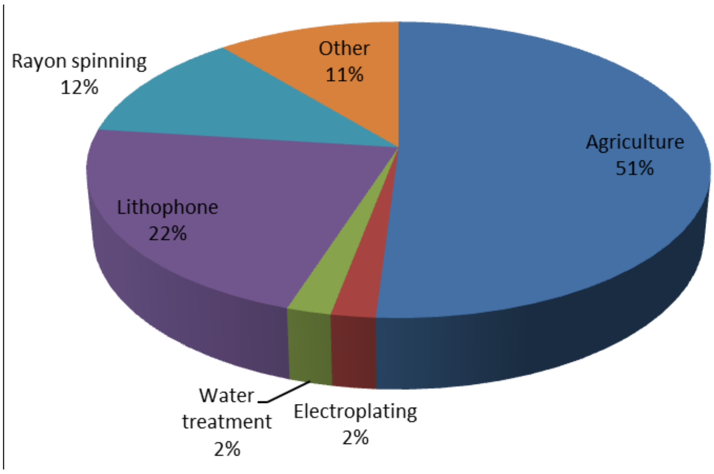


Figure 5-2: Zinc sulphate usage split into utilization areas [12]

The FAO (food and agriculture organization) determined that zinc is the most commonly deficient micronutrient in agricultural soils. Going hand in hand with that, humans and animals are also affected by zinc deficiency, especially in developing countries. Micronutrients are very important to plant health and contribute greatly to yield, which is the main concern for a big field of the agricultural industry. Zinc is one of the most important micronutrients. Zinc deficient soils can be found throughout the world and are normally associated with low soil organic matter and a soil pH higher than 7.0. Zinc deficiencies are corrected in most cases by applying a granular zinc fertilizer or applying it with the macronutrient (NPK) fertilizer either as a coating or incorporated into the macronutrient granule.

International organizations like the IZA (International Zinc Association) try to fight against that by increased fertilizer usage. Due to the fact that presently more than 50 % usage can be found in agriculture and this area is expected to grow further, it was studied in detail because the biggest potential is present in this area [12].

5.2.1 Zinc fertilizer types

Three different compounds are used in zinc fertilizers, which vary in their zinc content, price and effectiveness [17, 18].

1. Inorganic sources [18]:
    - Zinc sulphate ($ZnSO_4$) – most commonly used worldwide
    - Zinc oxide (ZnO)
    - Zinc carbonate ($ZnCO_3$)
    - Zinc nitrate ($Zn(NO_3)_2$)
    - Zinc chloride ($ZnCl_2$)

2. Synthetic chelates [18]:
   Metal ions combined with EDTA (ethylenediaminetetraacetic acid)
   It is indicated in literature that zinc sulphate is better and cheaper.

3. Natural organic complexes are produced by the reaction of zinc salts with citrates or with organic substances from e.g. paper pulp manufacturing (lignosulphonates, phenols and poly flavonoids). They are generally cheaper than chelates but less effective [18].

Historically zinc sulphate has been the most applied zinc source but there are several other alternatives. Tables 5-3 and 5-4 shows the full range of materials used as zinc fertilizer and their typical zinc content.

Table 5-3: Organic compounds used as zinc fertilizer and their typical zinc content [17, 18]

Organic compounds	Formula	Zinc content [%]
Disodium zinc EDTA	$Na_2ZnEDTA$	8-14
Sodium zinc HEDTA	NaZnHEDTA	6-10
Sodium zinc EDTA	NaZnEDTA	9-13
Zinc polyflavonoid	-	5-10
Zinc lignosulphonate	-	5-8

Table 5-4: Inorganic compounds used as zinc fertilizer and their typical zinc content [17, 18]

Inorganic compounds	Formula	Zinc content [%]
Zinc sulphate monohydrate	$ZnSO_4 \cdot H_2O$	36
Zinc sulphate heptahydrate	$ZnSO_4 \cdot 7H_2O$	22
Zinc oxysulphate	$ZnO \cdot ZnSO_4$	20-50
Basic zinc sulphate	$ZnSO_4 \cdot 4Zn(OH)_2$	55
Zinc oxide	ZnO	50-80
Zinc carbonate	$ZnCO_3$	50-56
Zinc chloride	$ZnCl_2$	50
Zinc nitrate	$Zn(NO_3)_2 \cdot 3H_2O$	23
Zinc phosphate	$Zn_3(PO_4)_2$	50
Zinc frits	Fritted glass	10-30
Ammoniated zinc sulphate solution	$Zn(NH_3)_4SO_4$	

5.2.1.1 Production and usage of main types of zinc fertilizers

Residues and by-products of processes using zinc as raw material are typically used as raw material for zinc fertilizer production. After purification, it is chemically altered to produce a compound which is bioavailable to crops. This means that a water-soluble compound is required so that a plant can absorb the zinc with the water from the soil. In future the zinc fertilizer market will increase and primary metal will probably have to be used to meet the requirements for the high zinc demand for production [17, 18].

Zinc sulphate:

Typically $ZnSO_4 \cdot H_2O$ is produced by dissolving zinc oxide in H_2SO_4, followed by dehydration. During this process, also other hydrates can be produced with lower zinc content and higher water content. Typically, at least 98 % of the zinc is water-soluble.

Zinc oxide:

Zinc oxide is produced in several industrial processes but in general it is less water-soluble than zinc sulphate.

Zinc EDTA:

This zinc chelate is typically a liquid zinc fertilizer (~9 % Zn) and can be added during other fertilizer formation. Zinc EDTA is 100 % water-soluble.

Zinc oxysulphates:

Zinc oxysulphates (ZnO_x) are produced by adding H_2SO_4 to a feedstock material. Depending on the amount of added acid, the sulphate content varies as well as the water solubility.

Zinc lignosulphonate:

Zinc lignosulphonate is a complex organic fertilizer formed by the reaction of sucrose-type materials (e.g. sugar molasses) with zinc oxide.

Normally zinc deficiencies are corrected by soil application of zinc but also foliar sprays are common for fruit trees and grapevines as well as field crops. The amount of zinc fertilizer applied depends on the crop to be grown, the fertilizer type itself and the local soil conditions.

Typically 4.5-34.0 kg zinc-equivalent per hectare (typically as zinc sulphate) are applied.

Based on research results and extended field trials, zinc fertilizers are also used to increase the positive effect of other fertilizers (e.g. NPK). Typically 1-2 %wt zinc is added [17, 18].

5.2.1.2 Usage of residues for fertilizer production

In the manufacturing of inorganic fertilizers, industrial wastes and by-products play an important role. Especially in the production of micronutrient fertilizers (e.g. zinc fertilizers) such recycling practices are common. Different feedstock materials can be mentioned here:

- EAFD (electric arc furnace dust), also called K061 (it is the RCRA waste code)
- Brass foundry dust
- Tyre ash (typically, ash from the burning of tyres for energy recovery)
- Galvanizing residues

EAFD is regulated as a listed hazardous material because it can contain significant amounts of cadmium and lead. Brass foundry dust and tyre ash are typically listed as hazardous material, as well, while the galvanization residues typically do not exhibit dangerous amounts of heavy metals.

Also non-waste feedstock materials, like refined ores from lead mining, can often have concentrations of non-nutritive metals comparable to those of waste feedstock material.

The amount of metal contaminants in the fertilizer product is strongly dependent on how the material is treated and less on what kind of raw material is used.

Further residues applicable to fertilizer production, which are not regulated by the RCRA as hazardous wastes, are:

- CKD (cement kiln dust)
- Mining wastes (tailings)
- Gypsum
- Ash from wood burning
- Pulp and paper sludges (soil amendments)

5.2.2 Required product quality

For the production of fertilizers from residues, regulations describing the limits of impurities in the product exist [19].

Table 5-5 presents the limits of five metal contaminants in zinc fertilizers that are made out of hazardous secondary materials (like electric arc furnace dust), which are described in a federally registered environmental document from the US Environmental Protection Agency. The maximum allowable metal constituent concentration is per 1 % zinc content in the fertilizer and with this an absolute value. This is because the zinc content in fertilizers varies widely.

Depending on the area of utilization, different legislation is applicable. As an example, Canada has its own regulations, as does the European Union.

Table 5-5: Limits on metal contaminants [19]

Element	Content [ppm]
Arsenic	0.3
Cadmium	1.4
Chromium	0.6
Lead	2.8
Mercury	0.3

6. Critical aspects for secondary zinc oxides to meet the high quality market

Next to different physical properties, like specific surface, sieving residue, insoluble compounds, etc. mainly the purity of the zinc oxides is significant. Due to that, the physical requirements were described in preceding chapters; this chapter focuses on disturbing compounds in concern of product quality. They are volatile, similar to the metallic zinc vapour, and therefore form in most of secondary zinc oxides from recycling processes, the same impurities. These compounds are mainly halogens and heavy metals - especially lead oxide - which cannot clearly be separated due to possible compounds between halogens with for instance lead, like $PbCl_2$ or PbF_2. The main focus in this chapter lies on the halides and their properties as well as behaviour.

6.1 Halides

Chapter 6.1 summarizes the origin of halides in secondary zinc oxides, their properties and behaviour.

6.1.1 Origin

To describe where the halides in secondary zinc oxides originate from, it is necessary to start from the very beginning of the process chain. The origin can be found in the steel mills, where the raw material for the zinc recycling in waelz kilns, the hazardous steel mill dusts, is generated. They may originate either from integrated steel mills or from electric arc furnace steel making.

In both cases the zinc bearing dust is generated by the usage of galvanized steel scrap as raw material or as a cooling agent. In doing so, zinc is introduced and forms a main component of the generated process dust. Additionally, plastics are partly charged with the scrap as a result of ineffective or not economically realizable separation. This leads to the input of chlorine-containing material in the process chain.

The fluorine content is related to the utilization of fluxes in the secondary metallurgy of the steel plant or in an electroslag remelting process (ESR). In both cases the dust can carry CaF_2.

Due to the aforementioned circumstances, the raw material for the recycling processes, like the waelz process, already carries relatively huge amounts of halides. Based on the volatile character of most of the halides, they vaporize at increased temperatures. As a result of the typical recovery of zinc via the vapour phase, the halides again represent impurities in the obtained zinc oxide product. One exception is formed by CaF_2, which should not be volatile at temperatures below 1300 °C. Nevertheless, it can be found in the waelz oxide as a fluorine carrier.

The presence can be explained by two mechanisms: First of all, the rotation of the waelz kiln leads to carry-over of the treated material. Owing to already present CaF_2 in the raw material, it can also be found in the product. Secondly, other volatile fluorine compounds, like PbF_2, ZnF_2, etc. can form CaF_2 with calcium oxide again.

6.1.2 Properties

This chapter summarizes facts concerning different halides under different conditions. As a result of the vast amount of information available, only the relevant data was extracted. This also includes some facts on the behaviour in aqueous solutions or other solvents in case those theses could be of interest for a pre or post step and forms the basic knowledge for the development of such a cleaning step.

6.1.2.1 Fluoride compounds

Fluorine is the most electronegative element and thus has a very strong affinity to other atoms, which is the reason why fluorine alone can be seen as a radical. Most of the common metals are not attacked by F_2 at room temperature and form a fluoride protection layer but at higher temperatures more or less all metals react with fluorine to a metal fluoride. Generally most of the compounds, like phosphates, carbonates, chlorides or also sulphates decompose under the formation of fluorides.

If halide compounds (chlorides, fluorides) are compared concerning their melting point, fluorides have the highest most of the time and are less volatile.

The differences among the metal fluorides can be found in their volatility and are related to the metal in the compound. In case of highly volatile metals also the fluorine compound is more volatile than those with very stable metals (low vapour pressure). The boundary where a significant increase in their volatility can be found is represented by BeF_2, AlF_3, TiF_4, SnF_4 and BiF_3. On the one hand, there are very hard to vaporize heteropolar compounds and on the other, compounds with homopolar bonding can be found (high vapour pressure).

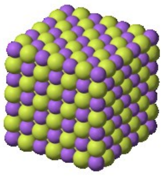
Fluorine compounds with alkaline metals (Li to Cs) show an increasing solubility, which means that with increasing ion radius and decreasing hydrophilic properties of the positive ion the solubility increases. Bivalent hydrophilic alkaline earth metal have a minimum in their solubility at CaF_2.

Generally, fluorides are very stable when heated in the absence of air. If hydrated fluorides are present, oxyfluorides or oxides are formed accompanied by a separation of hydrofluoric acid (HF). Another property of alkali fluorides is that they can easily be split by water steam and most of them react intensively with carbon. The best temperature for this reaction is above 700 °C.

Concentrated hydrosulphuric acid or nitric acid split most of the metal fluorides accompanied by an HF formation. One exception is given by lead fluoride PbF_2, which is not split completely, instead forming a fluoric sulphate compound. Nitric acid is not able to split CaF_2 and therefore no HF is set free. Gaseous hydrochloric acid is able to split NaF and CaF_2.

Fluorides have an affinity to absorb molecules, like H_2O, NH_3, HF or others and form very stable complexes; especially trivalent fluorides behave in this way. Alkaline metals tend to form hydrofluorides, while heavy metal fluorides very often form more or less complex hydrofluoric acids with HF [20, 21].

6.1.2.1.1 Sodium fluoride NaF

Density	2.56 g/cm³	
Melting point	993 °C	
Boiling point	1695 °C	
Crystal structure	cubic	

Sodium fluoride is a colourless solid material and has a cubic crystal structure. Furthermore, it’s not hygroscopic. The vaporization in the flame is 8.04 times faster than in the case of its chlorine salt (NaCl).

In the presence of water steam (H_2O), no complete hydrolysis of NaF takes place. Potassium fluoride (KF) is more sensitive during hydrolysis processes, like other sodium halides. During a temperature treatment above 1000 °C and some moisture, the following reaction is possible [22, 23]:

$$NaF + H_2O \leftrightarrow NaOH + HF \qquad \text{Equ. 6-1}$$

In general the pyrohydrolysis is very slow. After 1 hour only 8 % of NaF are hydrolyzed. With the addition of Al_2O_3 (active component) a complete hydrolysis would occur in the same time. Also TiO_2 can be used, which decreases the time to 30 minutes.

At temperatures above 500-800 °C possible reactions with oxides such as Ca, Sr and Ba as well as zinc oxide, are mentioned in literature [22, 23].

$$3\ NaF + ZnO \leftrightarrow Na_2O + NaZnF_3 \qquad \text{Equ. 6-2}$$

NaF is soluble in both cold and hot water, with no big differences. Compared to NaCl the sodium fluoride does not form a hydrate and with this is less soluble. The following table gives an overview of the solubility in NaOH solutions [22, 23].

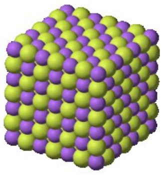
Table 6-1: Solubility of NaF in NaOH solutions with different ratios of NaF/NaOH

NaOH\NaF	0 °C	20 °C	40 °C	80 °C	94 °C
0.00	3.99	4.10	4.47	4.48	4.73
0.81	3.49	3.40	3.51	3.56	3.47
2.71	2.37	2.45	2.70	2.84	2.78
18.40	-	0.38	-	-	-

A annealing in concentrated H_2SO_4, $SiOH_4$, H_3BO_3 and H_2MoO_4 leads to a complete splitting of NaF under the formation of HF.

A further possible reaction could be with gaseous HCl, which leads to the formation of NaCl. Reactions with $CaCO_3$, Na_2CO_3 and CaF_2 are also possible [24, 25].

6.1.2.1.2 Potassium fluoride KF

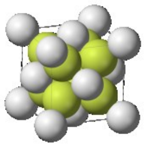
Density	2.48 g/cm³	
Melting point	858 °C	
Boiling point	1502 °C	
Crystal structure	cubic	

Potassium fluoride is soluble in water as well as in hydrofluoric acid (HF) but insoluble in alcohol. Moreover, it is strongly hygroscopic and easily decomposable by water.

At temperatures above 1180 °C increased vaporization is recognizable under the formation of acidic reacting gases. The sublimation of KF starts at 1140 °C. The ratio of volatility compared to NaCl is 0.36/1 [26].

KF is relative easy soluble in water and forms crystalline hydrates ($KF \cdot 4H_2O$ or $KF \cdot 2H_2O$). Solutions of potassium fluoride are decomposable by diluted acids. In this case, also the CO_2 from atmosphere can be absorbed under the formation of HF [26].

6.1.2.1.3 Calcium fluoride CaF_2

Density	3.18 g/cm³	
Melting point	1418 °C	
Boiling point	2533 °C	
Crystal structure	cubic	

The crystal structure of CaF_2 is cubic and it has a melting point of 1418 °C. Calcium fluoride is insoluble in acetone and slightly soluble in acids (HCl, HNO_3, NH_3). In aqueous solutions NaF and KF form the reaction product calcium fluoride (CaF_2) with $CaCl_2$, which is more stable. The same happens when melting these compounds [27].

Concentrated sulphuric acid leads to the following reaction above 40 °C:

$H_2SO_4 + CaF_2 \leftrightarrow CaSO_4 + 2\,HF$ Equ. 6-3

The solubility of CaF_2 in water at 26 °C is approximately 17 mg/l.

Hydrogen alone as a reducing agent has no influence although high temperatures are present but the impact of water steam and/or SiO_2 split CaF_2 – this process is known as pyrohydrolysis [27].

$CaF_2 + H_2O \leftrightarrow 2\,HF + CaO$ Equ. 6-4

The following table shows the vaporization rate of fluorine depending on different test conditions. In trial A, CaF_2 with water steam was treated, trial B used a mixture of calcium fluoride and SiO_2 in water steam carrying atmosphere and trial C was with dry air. Each trial was 30 minutes long.

Table 6-2: Vaporization of fluorine from CaF_2 [27]

Temperature [°C]	800	900	1000	1100	1200	1300	1400
Trial A	-	-	8.9	16.7	31.5	92.1	-
Trial B	11.3	31.5	38.2	54.5	84.5	90.5	84.8
Trial C	-	-	3	3.1	12.2	52.9	-

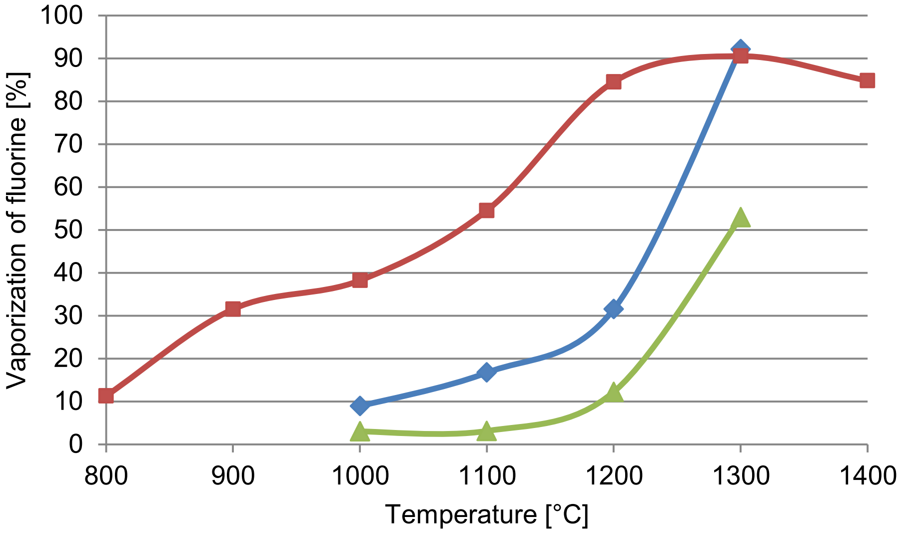
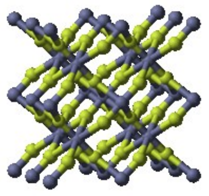


Figure 6-1: Vaporization of fluorine from CaF_2 (— trial A, — trial B, — trial C) [27]

It can be seen (from comparing trials A, B and C) that the influence of water steam in the treatment atmosphere is significant. The addition of SiO_2 has an impact if the temperature is lower than 1300 °C. The influence decreases with increasing temperature and it can be seen that at 1300 °C the trials with or without SiO_2 addition deliver the same yield [27].

6.1.2.1.4 Zinc fluoride ZnF_2

Density	4.95 g/cm³	
Melting point	872 °C	
Boiling point	1500 °C (splitting)	
Crystal structure	tetragonal	

Zinc fluoride is hardly soluble in water, but soluble in HCl, HNO_3, H_2SO_4 and its solubility rises with increasing temperature. The reason for the bad solubility of ZnF_2 in water compared to the other zinc halides is the rutile crystal structure. This leads to an ionic bonding. It hydrolyzes in hot water to zinc hydroxyl fluoride (Zn(OH)F). In liquid NH_3 ZnF_2 is insoluble [28, 29].

If moisture is present the hydrate form of zinc fluoride can also be present ($ZnF_2 \cdot 4H_2O$). The hydrate starts to react to a water free compound at 100 °C and reacts further to ZnO above 300 °C [28].

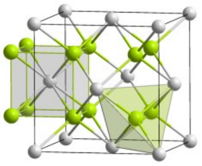
In the basic area of aqueous solutions, alkaline zinc hydroxyl fluoride is also stable ($ZnF \cdot 3Zn(OH)_2$) and can be formed by precipitation of $ZnF_{2(aq)}$ with NaOH.

Pure ZnF_2 is very stable thermally. If air is present (with humidity) during a temperature treatment it can react to ZnO. Also the contact with gaseous HCl leads to the formation of $ZnCl_2$ [28, 29].

The subsequent reactions can occur:

$ZnF_2 + H_{2(g)} \leftrightarrow Zn_{(l)} + 2\ HF_{(g)}$ Equ. 6-5
$ZnF_2 + H_2O_{(g)} \leftrightarrow ZnO + 2\ HF_{(g)}$ Equ. 6-6
$ZnF_2 + 2\ HCl_{(g)} \leftrightarrow ZnCl_{2(l)} + 2\ HF_{(g)}$ Equ. 6-7

6.1.2.1.5 Lead fluoride PbF_2

Density	8.45 g/cm³ (orthorhombic) 7.75 g/cm³ (cubic)	
Melting point	824 °C	
Boiling point	1293 °C	
Crystal structure	cubic / orthorhombic	

Lead fluoride is soluble in nitric acid (HNO_3) as well as diluted HCl and insoluble in acetone, ammonia and diluted HF. It is hardly soluble in water (at 20 °C the solubility is 0.064 g/l). In literature some hints can be found that hydrolyses can happen while diluting saturated solutions [30].

In general, lead forms complexes of low stability with halogens ($F^- << Cl^- < Br^- < J$).

Lead fluoride has two modifications; the beta form, which is the high temperature cubic structure, and the low temperature alpha form. The theoretical transformation is between 220-280 °C but practically does not take place, although it was shown that through very fine grinding the alpha form can be formed [30].

In air with as well as without humidity, PbF_2 crystals are stable. At higher temperatures PbF_2 can be split by CO_2. In H_2 atmosphere PbF_2 can be split before a glowing of the compound ("red heat") is reached [30]:

$PbF_2 + H_{2(g)} \leftrightarrow Pb + 2\ HF_{(g)}$ Equ. 6-8

A temperature treatment with O_2 typically leads to no reactions but during a treatment with water steam, the following reaction takes place:

$$PbF_2 + H_2O_{(g)} \leftrightarrow PbO + 2\,HF_{(g)} \qquad \text{Equ. 6-9}$$

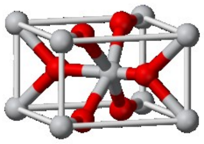
The composition of the HF-H_2O-steam stream can be seen in the following table at treatment temperatures of 500 to 750 °C. It is extrapolated to a gas velocity of zero [30] and based on that the equilibrium constant K_p of equation 6-9 is shown.

Table 6-3: H_2O-HF-steam composition at varying temperatures depending on the gas velocity [30]

Temp. [°C]	500	600	650	700	750
HF [Vol.-%]	2.8	9.5	16.5	26	38
$-\lg K_p$	2.09355	2.00098	1.48673	1.03940	0.63382

In aqueous salt solutions the solubility of PbF_2 at 25 °C decreases with increasing NaF content and decreasing KF concentration [30].

6.1.2.1.6 Iron fluoride FeF_2

Density	4.09 g/cm³	
Melting point	970 °C	
Boiling point	1100 °C	
Crystal structure	tetragonal	

A further possible modification next to iron(II)fluoride is FeF_3. FeF_2 is a green solid with a boiling point of 1100 °C and a melting point of 970 °C [31].

A treatment with H_2 leads to the formation of metallic iron and HF. Also the contact with water steam causes an HF and iron oxide formation. Gaseous HCl forms iron chloride and again HF. A treatment in pure oxygen has no effect, while the treatment with moist air leads to the formation of an oxide (Fe_2O_3) [31].

In case of a melting in the presence of alkaline carbonates, again iron oxide and an alkali fluoride are formed.

FeF_2 is insoluble in ethanol and ether while it dissolves in HF. It dissolves slowly in water and dissociates in the same way as iron chloride ($FeCl_2$). The green solution of FeF_2 oxidizes in air and precipitates, due to the oxidation, as iron hydroxide ($Fe(OH)_3$) [31].

6.1.2.2 Chlorine compounds

Chlorine is a very active element. Metal oxides tend to transform to chlorides or oxychlorides in a Cl_2 gas stream accompanied by an oxygen separation. The following table shows the heat of formation for different halides:

Table 6-4: Formation heat of typical chloride compounds

Compound	Formation heat [kcal]
NaCl	-97
KCl	-104
$CaCl_2$	-191
$ZnCl_2$	-97
$PbCl_2$	-85
$FeCl_2$	-82

The oxidized compounds of sodium, potassium, calcium and zinc react during a temperature treatment in a Cl_2 stream to the corresponding chlorides ($ZnCl_2$, NaCl, KCl, $CaCl_2$). Lead oxide is transformed to $PbCl_2$ during the heating up process. Iron oxide forms $FeCl_3$ or $FeCl_2$. Metal chlorides are more volatile than the contained metals. It can be said that the volatility increases with the chlorine content in the compound (loading of metal ion). Chlorides from the alkaline metals increase their volatility with their atom weight. Most of the (simple) metal chlorides are soluble in water. $PbCl_2$ is only soluble in hot water. Solutions of the alkaline metals and alkaline earth metals react in a neutral way; all others react in an acidic way.

The treatment in a hydrogen stream typically leads to the equilibrium of the following reaction:

$$MeCl_2 + H_{2(g)} \leftrightarrow Me + 2\,HCl_{(g)} \qquad \text{Equ. 6-10}$$

Oxygen has no influence on NaCl and KCl but slowly oxidizes $PbCl_2$ to PbO. A treatment with H_2O leads to the split of HCl – known from pyrohydrolysis processes. For example $CaCl_2$ reacts with water steam to HCl and CaO, while the chlorine compounds of sodium and potassium (KCl, NaCl) do not get oxidized.

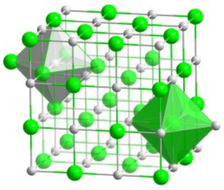
Below are the possible cases which can happen if liquid water meets chlorine compounds:

- Ionization
- Hydrolysis:

  $MeCl + H_2O \leftrightarrow MeOH + HCl$ or Equ. 6-11

  $MeCl + H_2O \leftrightarrow MeH + HClO$ (Me … Na, K, Ca, etc.) Equ. 6-12
- No chemical reaction

6.1.2.2.1 Sodium chloride NaCl

Density	2.17 g/cm^3	
Melting point	801 °C	
Boiling point	1413 °C	
Crystal structure	Cubic face centred	

NaCl is slightly hygroscopic. It reacts with water steam to sodium hydroxide and hydro chloric acid (NaOH and HCl). The reaction with water steam stops when a ratio of 8 mol NaCl to 1 mol NaOH is reached [32, 33, 34].

NaCl can react with hydrogen to metallic sodium and hydrochloric acid (HCl). Fluorine reacts with NaCl forming NaF [33].

The solubility of sodium chloride in different solvents can be found in the following table:

Table 6-5: Solubility of NaCl in different solvents [35]

Solubility of NaCl in various solvents (g NaCl / 1 kg of solvent at 25 °C)	
H_2O	360
Formamide	94
Glycerin	83
Propylene glycol	71
Formic acid	52
Liquid ammonia	30.2
Methanol	14
Ethanol	0.65
Dimethylformamide	0.4
1-propanol	0.124
Sulpholane	0.05
1-butanol	0.05
2-propanol	0.03
1-pentanol	0.018
Acetonitrile	0.003
Acetone	0.00042

In case of a temperature treatment under carbon addition (or carbon containing compounds) a reduction takes place. With carbon monoxide the following reaction occurs:

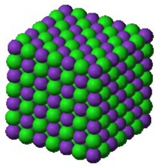
$2\ NaCl + CO \leftrightarrow Na_2O + 2\ Cl + C$ Equ. 6-13

Metallic iron can also react with sodium chloride (starting at temperatures of 800 °C):

$Fe + 2\ NaCl \leftrightarrow FeCl_2 + 2\ Na$ Equ. 6-14

Hydrogen sulphide (H_2S) splits NaCl completely by forming HCl and Na_2S. The reaction is supported by present water steam. Without the influence of H_2O steam, NaCl does not split in the range of 407-878 °C. At temperatures of 1000 °C it vaporizes completely without splitting [33, 34].

6.1.2.2.2 Potassium chloride KCl

Density	1.98 g/cm³	
Melting point	770 °C	
Boiling point	1420 °C	
Crystal structure	Face centred cubic	

The metal halide salt potassium chloride has a melting point of 770 °C and a boiling point of 1420 °C. The crystalline structure is cubic face centred. A common utilization is as fertilizer and it is also known as "potash" [36].

KCl is soluble in glycerol, alkalis, slightly soluble in alcohol and insoluble in ether. The table that follows shows the solubility in different solvents [36].

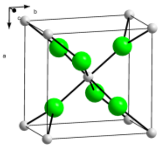
In water KCl dissolves easily and increases its maximum concentration with the temperature (281 g/l (0 °C); 344 g/l (20 °C); 567 g/l (100 °C)). At normal temperatures (room temperature) KCl is less hygroscopic than NaCl. Above 100 °C it is vice versa. Potassium chloride is relatively volatile at temperatures of 200 to 250 °C. The ratio in comparison to NaCl is 1.3:1. The vaporization of KCl is respectable at temperatures above 980 °C under the formation of acidic gases [36].

Table 6-6: Solubility of KCl in different solvents [37]

Solubility of KCl in various solvents (g KCl / 1 kg of solvent at 25 °C)	
H_2O	360
Liquid ammonia	0.4
Liquid sulfur dioxide	0.41
Methanol	5.3
Formic acid	192
Sulpholane	0.04
Acetonitrile	0.024
Acetone	0.00091
Formamide	62
Acetamide	24.5
Dimethylformamide	0.17-0.5

Compared to NaCl the thermal split of KCl can be determined to be less. The separation in water steam atmosphere to KOH and HCl also needs increased temperatures [36].

6.1.2.2.3 Calcium chloride $CaCl_2$

Density	2.16 g/cm³ (anhydrous) 1.85 g/cm³ (dihydrate)	
Melting point	782 °C (anhydrous) 176 °C (dihydrate) 35 °C (tetrahydrate)	
Boiling point	1935 °C (anhydrous)	
Crystal structure	Orthorhombic (anhydrous)	

Similar to a lot of other metal halides, different hydrate stages are possible stable compounds [38].

In case of calcium chloride also the dihydrate, tetrahydrate and hexahydrate can be mentioned. $CaCl_2$ is soluble in acetone, acetic acid as well as in water (740 g/l (20 °C); 595 g/l (0 °C)) [38].

$CaCl_2$ is strongly hygroscopic and turns to liquid in moistures air. The vapour pressure is zero at temperatures below 1137 °C. Under the impact of water steam the following reactions can occur (moisture from air) [38]:

$CaCl_2 + H_2O_{(g)} \leftrightarrow CaO + 2\ HCl_{(g)}$ Equ. 6-15

$CaCl_2 + H_2O_{(g)} \leftrightarrow Ca(OH)Cl + HCl_{(g)}$ Equ. 6-16

$2\ Ca(OH)Cl \leftrightarrow Ca_2OCl_2 + H_2O_{(g)}$ Equ. 6-17

This can be the reason for lower mentioned melting points in older literature because of $CaCl_2$ that was not completely dry.

The presence of pure oxygen does not split $CaCl_2$ but with small amounts of water steam the below-mentioned reactions can occur, which can lead to a possible reaction to chlorine gas:

$2\ Ca_2OCl_2 + 2\ H_2O_{(g)} + O_{2(g)} \leftrightarrow 4\ CaO + 2\ Cl_{2(g)} + 2\ H_2O_{(g)}$ Equ. 6-18

This reaction only works well if compounds are present which react with CaO to shift the equilibrium to the right side of the reaction.

A heat treatment under air leads to a kind of sintering at temperatures above 400 °C. Should liquid $CaCl_2$ melt get in contact with oxidizing atmosphere, a split of the compound and an increase of CaO are mentioned in literature. This can be avoided if the access of air or moisture is prevented [38].

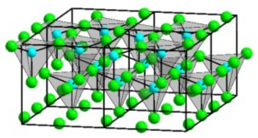
Starting at 425 °C hydrolysis can occur, which is why an air atmosphere saturated with steam is enough to split $CaCl_2$. If SiO_2 is added, the starting temperature can be decreased to approximately 410 °C. As expected, the yield increases with increased process temperature.

$CaCl_2$ also reacts with hydrogen gas at higher temperatures:

$CaCl_2 + 2\ H_{2(g)} \leftrightarrow CaH_2 + 2\ HCl_{(g)}$ Equ. 6-19

This reaction can be supported through catalysis. It is further reported that through CO_2 and an oxidation agent (like e.g. $KMnO_4$), Cl_2 can be emitted [38].

6.1.2.2.4 Zinc chloride $ZnCl_2$

Density	2.91 g/cm^3	
Melting point	292 °C	
Boiling point	756 °C	
Crystal structure	Orthorhombic (anhydrous)	

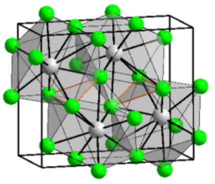
Zinc chloride is hygroscopic and five hydrates are known, while $ZnCl_2$ can occur in four crystalline forms. The anhydrous one is orthorhombic. The hydrate with the highest water content is $ZnCl_2{\cdot}4H_2O$. Next to that, basic hydroxides also exist. The solubility in water at 25 °C is 4320 g/l; furthermore, it can be dissolved in ethanol, glycerol and acetone. The solubility in alcohol is 4300 g/l [39].

Water free $ZnCl_2$ melts and distils without splitting. In the presence of H_2O a formation of HCl can occur [39].

The reduction of $ZnCl_2$ with hydrogen below 600 °C has a low value for the reaction constant, which means that the following equation has its equilibrium on the reactant side and therefore nearly does not take place [39]:

$$ZnCl_2 + H_{2(g)} \leftrightarrow Zn_{(g)} + 2\ HCl_{(g)} \qquad \text{Equ. 6-20}$$

6.1.2.2.5 Lead chloride $PbCl_2$

Density	5.85 g/cm^3	
Melting point	501 °C (beta)	
Boiling point	950 °C	
Crystal structure	orthorhombic	

Lead chloride is slightly soluble in water (6.73 g/l (0 °C); 9.9 g/l (20 °C); 33.4 g/l (100 °C)), in dilute HCl, ammonia and is insoluble in alcohol. Lead chloride is one of four commonly insoluble chlorides ($PbCl_2$, AgCl, CuCl and Hg_2Cl_2). In water, hydrolysis takes place to lead hydroxide or oxychloride [40].

$PbCl_2$ exists in a high temperature modification (alpha) and a low temperature (beta) modification. In addition to that, also lead monochloride is stable under air.

Lead chloride can be formed if HCl gas is in contact with PbO [40].

The melting point of beta-$PbCl_2$ is 480 °C while alpha-$PbCl_2$ has a melting point of 501 °C. During the heating-up process the white powder turns grey, which most likely comes from dissociation [40].

Under the presence of air and moisture $PbCl_2$ can be split by forming lead oxychloride. At higher temperatures also gaseous chlorine can be emitted. In hydrogen atmosphere it gets reduced to metallic lead and hydrochloric acid [40].

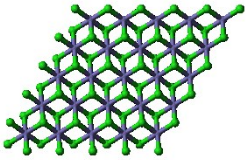
$$PbCl_2 + H_{2(g)} \leftrightarrow Pb + 2\ HCl_{(g)} \qquad \text{Equ. 6-21}$$

In case of high enough temperature and an excess amount of H_2, the $PbCl_2$ can react fast and complete to metallic lead and hydrochloric acid.

For a hydrolysis during a temperature treatment the normal moisture of air is enough.

If carbon monoxide and a temperature of 650 to 750 °C are present, the formation of metallic lead and $COCl_2$ can partly take place [40].

6.1.2.2.6 Iron chloride $FeCl_2$

Density	3.16 g/cm^3 (anhydrous) 2.30 g/cm^3 (dihydrate) 1.39 g/cm^3 (tetrahydrate)	
Melting point	677 °C (anhydrous)	
Boiling point	1023 °C (anhydrous)	
Crystal structure	monoclinic	

There are two possible chlorides: $FeCl_3$ and $FeCl_2$. The dichloride is less hygroscopic than the trichloride [41].

There are also hydrates evident, like the iron(II)chloride tetrahydrate. It is not possible to dehydrate this compound by a temperature treatment because it splits during such a treatment and forms an iron oxide [41].

Gaseous HCl can react with iron oxides as well as metallic iron to iron chloride:

$$2\ HCl_{(g)} + Fe \leftrightarrow FeCl_2 + H_{2(g)} \qquad \text{Equ. 6-22}$$

The other direction is also possible in case of iron(III)chloride, which can be reduced to iron(II) chloride [41]:

$$FeCl_3 + 0.5\ H_{2(g)} \leftrightarrow HCl_{(g)} + FeCl_2 \qquad \text{Equ. 6-23}$$

At high temperatures also $FeCl_2$ can be reduced with H_2.

A treatment with a mixture of steam and air leads to diluted HCl and nearly chloride-free iron oxide (Fe_2O_3) after 1 to 1.5 hours at 250 °C. A treatment at dry air or pure oxygen leads to the reaction below [41]:

$$6\ FeCl_2 + 3/2\ O_{2(g)} \leftrightarrow 4\ FeCl_3 + Fe_2O_3 \qquad \text{Equ. 6-24}$$

The formation of gaseous chlorine cannot be avoided and the oxidation of $FeCl_2$ cannot be carried out without the formation of $FeCl_3$.

Zinc vapour can reduce $FeCl_2$ to metallic iron and zinc chloride in the presence of carbon:

$$Zn_{(g)} + FeCl_2 \leftrightarrow ZnCl_2 + Fe \qquad \text{Equ. 6-25}$$

Iron chloride has a good solubility in water (685 g/l at 20 °C; 1057 g/l at 100 °C) [41].

6.2 Heavy metal oxides

In addition to the discussed halides, which already form partial compounds with heavy metals, other volatile or also non-volatile compounds form impurities. Next to various other oxides, which are non-volatile, the most important in this context is lead oxide.

6.2.1 Lead oxide

A typical companion compound in secondary zinc oxide is lead oxide. Similar to the description in the halides chapter, it is introduced by scrap in the steelmaking route and with that into the steel mill dusts, which are used as raw material for the recycling of zinc.

Although the lead is more noble than iron and would be collected in the melt, under oxidizing conditions it can be removed as lead oxide in the same way as halides.

There are several possibilities how lead oxide is introduced in the system. It is possible that batteries are overlooked and charged with the raw material. Several steel sheets are painted with anticorrosion paints which can carry lead as pigments. Not only that; also zinc coatings, also for corrosion protection, can have lead added as an alloying element due to the fact that it decreases the crystal size and with this leads to a more appealing surface. Other possible sources are free machining alloys, which have added lead to achieve a short chip, because of shear pins formed by lead droplets next to possible present solder, which also uses lead as alloying element [42].

6.2.2 Slag compounds

Other compounds forming impurities can be summarized as mainly non-volatile oxides like typical slag compounds (SiO_2, Al_2O_3, MgO, MnO) but also iron oxides (FeO, Fe_2O_3, Fe_3O_4). They are already present in the raw material itself or are added as slag forming additives, like CaO, for the process. Nevertheless, based on their non-volatile character the presence in the product is a result of carry-over.

7. Options for the improvement of secondary zinc oxide

Generally, pyro- and hydro-metallurgical ways for treating residues for a dehalogenation are possible, but not all are suitable for simultaneously removing other heavy metals. Over the past ten years little new literature concerning this topic has been published, whereat most of it investigates the improvement of already existing treatment methods. One major problem is that mostly only the chlorine removal is discussed, while the more critical fluorine removal is seldom mentioned. The most sustainable solution would be in the field of the process where the halogen-contaminated residues arise - in the scrap-charging steel industry itself. Due to very low investigations in this field, the main part of literature deals with the treatment of the already enriched products (residues, flue dusts) from these processes.

The following chapters are split into pyrometallurgical concepts, hydrometallurgical ones as well as methods carried out in the waelz kiln due to the fact that the raw material chosen to be investigated for an upgrade was waelz oxide, related to its market dominance.

7.1 Methods within the waelz process

Firstly, methods in literature for an improved waelz oxide through variations in operation mode of a waelz kiln were studied.

7.1.1 Agglomeration of EAFD in the waelz kiln

As already mentioned, a substantial part of the fluorine in the waelz oxide is determined to be CaF_2. Due to its thermochemical stability, the occurrence is supposed to be caused by means of carry-over. Thus, a possible precaution is a pelletizing of the input material to decrease the carry-over and hand in hand decrease the fluorine content in the oxide itself. For that a micro pellet can be enough. A literature survey showed that a decrease of 50 % F content in the oxide can be achieved through such a treatment [43].

7.1.2 Optimization of waelz oxide by the addition of MnO

This method is based on the idea of stabilizing the fluorine by an addition of MnO, which forms a stable fluoride. This compound isn’t volatile and therefore stays in the slag. Based on the assumption that the fluorine, which isn’t bound as CaF_2, is in a compound with zinc or lead, equation 7-1 supposedly occurs.

$MeF_2 + MnO + C \leftrightarrow MnF_2 + CO + Me$ (Me = Pb, Zn) Equ. 7-1

The stabilization of the fluorine is effective when the Mn concentration is at a level of approximately 4 % in the dust or in the charged material. Also a good contact between MnO and fluorine is assumed to be necessary to guarantee a reaction in an appropriate retention time and reaction temperature of approx. 950-1000 °C. In case of a temperature increase before a completed reaction, evaporation of PbF_2 and ZnF_2 is the consequence.

To sum up, the described fluorine stabilization only works efficiently when a Mn content of approximately 4 %, a good mixture and contact between fluorine compounds and MnO are achievable and enough time for a complete reaction is available. This is supported by the fusion of PbF_2 at a temperature of 830 °C and ZnF_2 at 947 °C, the consequence of which is that the formation of MnF_2 most likely happens in the temperature range of 950-1000 °C. As a result it is necessary that the waelz kiln charge remains in this range long enough to prevent an unwanted evaporation of PbF_2 and ZnF_2.

In the corresponding literature no quantification for the effectiveness of such investigation was found; it was only mentioned that a small amount of MnF_2 in the waelz slag was present [43, 44].

In this special case it has to be mentioned that this reaction cannot substitute a dehalogenation step of the waelz oxide, but rather it supports or discharges such a step.

To date, there is no known facility which uses such a stabilization method, most likely because of the following disadvantages:

- Slow reaction between fluorine and MnO
- Necessary excess amount of MnO

7.2 Pyrometallurgical methods

In the last three decades a lot of concepts for zinc winning from flue dusts have been investigated, but only a few have exceeded lab scale size. The dominating treatment method for EAF dusts has been the waelz kiln process so far [45]. For dehalogenation the only accomplished pyrometallurgical treatment method is the clinkering process, while other methods like sulphatisation, pyrohydrolysis and the treatment in DC arc furnaces are still in development.

7.2.1 Clinkering

Clinkering is a treatment method for the removal of halogens after the zinc enrichment step. Thereby a waelz oxide contaminated with Pb, Cd, F and Cl is treated in a temperature range of 900-1100 °C in a rotary kiln. To avoid the reduction of zinc oxide, the furnace atmosphere is neutral to slightly oxidizing. As a result only the halogen compounds as well as cadmium and lead are removed. These compounds (oxides, sulphides, sulphates or chlorines) can be found in the off-gas phase, whereby a product high in its zinc value and with low contaminants can be achieved next to a lead-cadmium-halogen flue dust. A typical analysis for such products can be seen in Table 7-1. At an average 800-850 kg oxide clinker and 150-200 kg lead-cadmium dust are generated when 1 ton of waelz oxide is treated [46].

The advantage is a simple process technology as well as a high yield of impurities, whereby the product could be used, for example, in electrolysis.

The necessary high temperatures are the main disadvantage of such a process. As a result of the fuels needed for such treatment, the costs are comparably high.

Table 7-1: Example of an analysis of an oxide clinker and a lead-cadmium-dust [46]

	oxide clinker	lead-cadmium-dust
Zn	55-66 %	5-20 %
Pb	0.5-1.5 %	35-50 %
Cd	0.1 %	1-2 %
Cl	0.1 %	15-25 %
F	0.15 %	1-5 %

7.2.2 Pyrohydrolysis

Pyrohydrolysis represents a process used for a selective removal of fluorine and chlorine from EAF dusts. This treatment is, like the aforementioned clinkering process, a pre-step to the main reduction step, where the zinc oxide content is enriched.

The following equations describe the main reactions of such a pyrohydrolysis. The halogen compounds get in touch with a huge amount of water steam in a temperature range between 850 and 900 °C. The halogen compounds are split (Equations 7-2 and 7-3) and bound to hydrogen, forming HF and HCl, which can then be found in the off-gas, leaving the furnace.

$$MeCl_2 + H_2O_{(g)} \leftrightarrow MeO + 2\ HCl_{(g)} \qquad (Me = Ca, Zn, Pb) \qquad \text{Equ. 7-2}$$

$$MeF_2 + H_2O_{(g)} \leftrightarrow MeO + 2\ HF_{(g)} \qquad \text{Equ. 7-3}$$

The calculated partial pressure of water steam at a temperature of 850 °C concerning the mentioned reaction is $0.75 \cdot 10^5$ Pa (assumption: Me = Ca), and the partial pressure of HCl and HF are relatively low compared to that. Due to that, a bad yield for fluorine and chlorine is predictable, which is the reason why approximately 20 % SiO_2 or WO_3 is added to the material (Equations 7-4 and 7-5). Under the same circumstances and the addition of such said additives, the partial pressures and along with that the yield for fluorine and chlorine can be increased [47, 48].

$MeCl_2 + H_2O_{(g)} + SiO_2 \leftrightarrow MeSiO_3 + 2\ HCl_{(g)}$ (Me = Ca, Zn, Pb) Equ. 7-4

$MeF_2 + H_2O_{(g)} + SiO_2 \leftrightarrow MeSiO_3 + 2\ HF_{(g)}$ Equ. 7-5

Depending on the concentration of fluorine and chlorine at the beginning, the pyrohydrolysis achieves a reduction of 98 % of chlorine next to a fluorine reduction of approximately 80 %. This means that based on a typical concentration of 1-2 % Cl and 0.5-1.3 % F in EAFD a reduction to 0.15-0.25 % fluorine is possible [47, 48].

Although a good fluorine and chlorine decrease is possible along with very low zinc losses, the serious disadvantages are the long necessary treatment time of approximately 8 hours, the high energy consumption and the high process temperatures. Furthermore, the complex off-gas treatment, caused by the acidic gas, is an intensive cost factor. Similar to clinkering, pyrohydrolysis is an additional process step for halogen removal.

The bad kinetics arises from the slow mass transfer between the solid and gaseous phases. An increase in reaction velocity would be possible if e.g. a fluidized bed reactor would be used as facility.

7.2.3 Sulphatisation

In contrast to clinkering and pyrohydrolysis, which are only for halogen removal, sulphatisation has to be seen as a part of a whole process, which also forms a pre-step for leaching.

The EAF dust is purged through by a mixture of water steam, oxygen and SO_2 resulting in a minimization of the halogen content by forming HF and HCl. Hand in hand a formation of alkali sulphate and a selective sulphatisation of zinc should occur. Due to the solubility of these formed sulphates, a separation of zinc and iron could be performed in an additional leaching step upstream to an electrolytic winning.

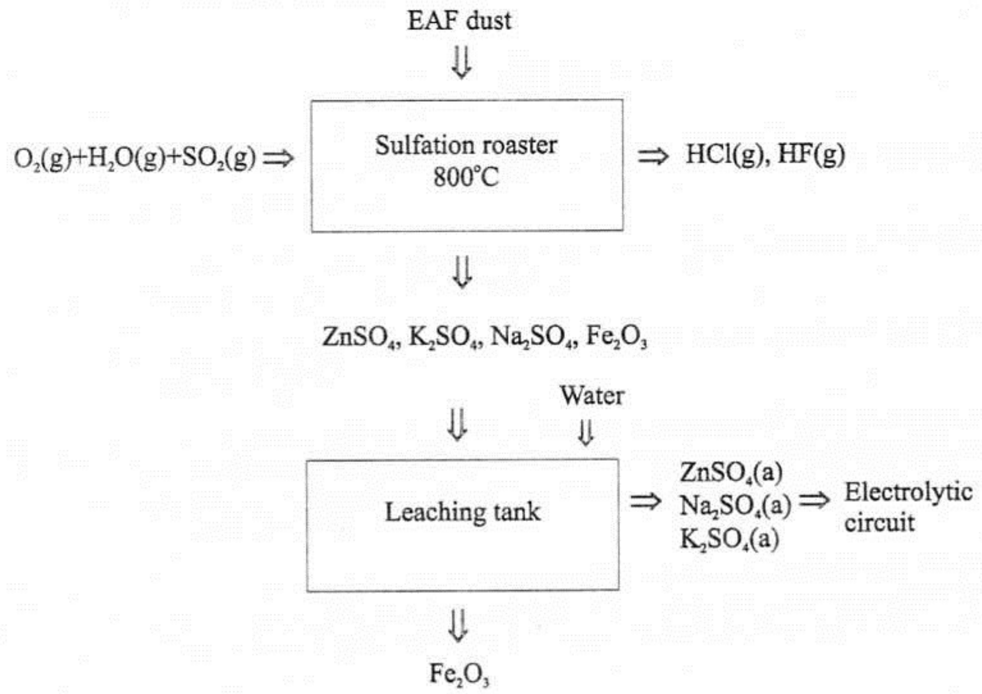


Figure 7-1: Simplified flow sheet of a sulphatisation [49]

An advantage of such a sulphatisation, from the thermodynamic point of view, is that the reaction takes place at lower temperatures compared to a pyrohydrolysis; furthermore, it is exothermic, which is the reason for the low energy consumption.

There are, however, some disadvantages such as bad iron-zinc selectivity, which causes a sulphatisation of iron and with that an increase in the iron content in the electrolyte. That is the reason for enlarged solution purification for Na and K and an additionally necessary iron precipitation. Moreover, the use of SO_2 leads to a high corrosive off-gas, which causes higher efforts concerning the off-gas system next to unsolved problems like selectivity of the zinc- and/or iron-sulphatisation or the cracking of zinc ferrite under the present circumstances for a recovery of zinc from the solution. That probably causes additional zinc losses.

7.3 Hydrometallurgical methods

A typical waelz oxide contains a lot of different contaminants. Due to its extent of ingredients, chlorine and fluorine occur in a number of different compounds [50].

General problems which can occur during hydrometallurgical treatments are the problems concerning wastewater treatment or when carrying out a crystallization, the disposition of the salts. In future, metals like As, Mo, etc. will also become focal points.

7.3.1 Direct leaching with H_2SO_4

At the Chair of Nonferrous Metallurgy, University Leoben, trials concerning a direct leaching of electric arc furnace dust with sulphuric acid were done.

To prevent a high chlorine content in the solution, a neutral leaching with water was done as a pre-step. For a complete dissolving of zinc, acid concentrations higher than 280 g/l and approximately 90 °C were necessary. One interesting aspect of the results was that apparently iron dissolved faster and with a better yield than zinc and that fluorine and chlorine reached their maximum after only 5 minutes. In case of very low iron contents, a modification of such a leaching would be that when using low acid concentrations the main part of zinc would be dissolved while iron and zinc ferrite remain in the solid residue.

The advantage of such a process would be the possibility of a direct input of EAFD in zinc primary metallurgy without a cost-intensive pre-treatment.

The disadvantage clearly can be found in the high halogen content of the solution. Independent of time and temperature, a yield of 80-90 % was realized, which means an absolute amount of 0.9-1.1 g/l, making an electric winning impossible. What is more, high energy consumption caused by the leaching temperature of 90 °C and a bad zinc iron selectivity have to be mentioned [51].

7.3.2 Double leached waelz oxide (DLWO)

Double leaching is used to decrease the halogen content after a waelz process. The goal is a product low enough in halogen content which can be used in the primary zinc winning.

7.3.2.1 Typical process sequence (two step leaching)

In a first step, the crude waelz oxide is leached at 60-80 °C and pH~9 in the filtrate of the second step and under addition of soda (Na_2CO_3). Thereby the alkaline metals and halogens are leached with a yield of approx. 90 %. The addition of soda is necessary for a precipitation of dissolved zinc and lead (Equations 7-6 and 7-7) as indissoluble carbonate.

$$ZnCl_{2(aq)} + Na_2CO_3 \leftrightarrow ZnCO_{3(s)} + NaCl \qquad \text{Equ. 7-6}$$

$$PbCl_{2(aq)} + Na_2CO_3 \leftrightarrow PbCO_{3(s)} + NaCl \qquad \text{Equ. 7-7}$$

After a solid-liquid separation the filter cake, with a remaining chlorine content of approximately 0.5 %, is processed in the second step. There, a second leaching with fresh water at 40-60 °C is carried out. The following solid-liquid separation delivers a filter cake with approx. 17-19 % water content. Due to its thixotropic properties, an additional drying step is required to reduce the moistness to below 13 %. The average content of fluorine in the washed waelz oxide is between 700 ppm and 100 ppm chlorine. The filtrate from the second step is reused in the first step and has to be treated after this leaching step to remove contaminants. Possible methods for this are a crystallisation of salts and a reuse of the condensate as a leaching medium or after a heavy metal precipitation a discharging as wastewater.

With this method the chlorine content can be decreased to acceptable values, while the fluorine content is still relatively high, which only leads to a possible substitution of 15-20 % of primary concentrates in the zinc winning [54]. The double leach process is an additional step to the waelz kiln and in the last years different modifications (like further additional steps) were established, which generate a substantial part of the production costs but don't actually decrease the halogen content significantly [54].

One possible adaption is leaching under pressure in an autoclave like Ruhr-Zink did, and since its shutdown SA Hydrometal does, due to its acquisition of the facility. It has been confirmed by Ruhr-Zink as well as IMN Poland for Boleslaw ZG that fluorine contents of 0.03 % and chlorine contents of 0.01 % can be reached. The relevant patent in this case is EP0834583.

7.3.2.2 Halogen elimination from alkaline solutions

Mishina Olga [55] describes in principle the possibility of a halogen separation of alkaline solutions. The idea is to remove the contaminants from a sodium carbonate solution, which can be found for example after a double leaching of waelz oxide, which can substitute a desalting unit. The solution carries halogens and could be recirculated in the process when the contaminants could be removed. Additionally, this would decrease the sodium carbonate consumption next to a minimization of wastewater and the salt content in it.

The literature survey lists several possibilities how to separate halogens from neutral to acidic solutions and the applicability for alkaline solutions:

- Precipitation
- Adsorption
- Separation as gaseous chlorine
- Liquid/liquid separation (solvent extraction)
- Electrodialysis
- Ion exchange
- Nanofiltration

During the **precipitation** in acidic solution the chlorine is precipitated as CuCl, PbClF or AgCl; the fluorine as CaF_2. In alkaline solution the metal ions, used as a precipitating agent, form hard dissolvable metal hydroxides and/or carbonates instead of metal halogens. That is the reason why this kind of precipitation in alkaline media is not possible.

The **adsorption** at activated alumina and other adsorption agents can separate fluorine from aqueous solutions. The advantage is the very low fluorine value achievable. As a result of that the capacity of the adsorbents is very low the process is not economical when higher fluorine concentrations are present. Additionally, the optimal pH value is around the neutral area.

Through strong oxidation agents, like H_2O_2, H_2SO_5, ozone (O_3) or anodic oxidation chlorine can be **separated as gaseous chlorine**. Due to the formation of chlorates and perchlorates in alkaline solutions, which are easily dissolvable and disturbing in the electrolytic winning, this process is not applicable for such solutions.

The **extraction** of fluorine and chlorine from acidic zinc sulphate solutions is possible through ammonium bases, aliphatic amine and mixtures of trialkylamine and mono carboxylic acid in kerosene. Other impurities such as Sb, As, In, Ti and Cd are also removed. Due to the fact that the organic phase is regenerated through alkaline solutions, an effective separation in alkaline sodium solutions is not possible.

The **electrodialysis** to separate univalent ions, especially for chlorine and fluorine, uses monovalent selective anion- and cation-exchange diaphragms. The optimum pH value is 3.5 to 5.5. An application in alkaline solutions is not possible, due to the instability of an anion-exchange diaphragm in alkaline solutions.

The use of middle to strong alkaline **anion exchangers** to separate chlorine ions at pH levels of 2 to 5 from sulphate solutions is another option. A disadvantage is the low capacity of such exchangers combined with a high consumption of regeneration agent. The fluorine separation is used in drinking water and the semi-conductor industry but is only applicable in neutral to acidic solutions with low salt content, which is the reason why it cannot be used for alkaline zinc solutions.

The **nanofiltration** shows different selectivity concerning ions with varying electric charge, size and deformation. Therefore, the nanofiltration seems to be applicable for chlorine and fluorine separation, although no existing process describing such a separation of carbonates and halogens in alkaline solutions was found. One advantage of such a process would be that no further chemicals, which can lead to environmental pollution, are consumed.

All methods based on acidic solutions for halogen removal seem to be difficult or completely not adaptable for basic solutions. Practical trials showed that weak to strong alkaline anion exchangers, which are normally suitable for halogen removal from solutions with high carbonate content, allow the simultaneous separation of chlorine and fluorine from such solutions. Due to the different selectivity and capacity of the exchanger resins, the capacity of the resins is not fully used, leading to increased resins consumption [55].

7.3.3 High purity Zn/ZnO production from WO or DLWO

This investigation deals with the leaching of WO or DLWO and the production of zinc. The described process is based on a hydrochloric or sulphuric leaching, followed by a purifying step and a finishing (e.g. electro winning). In case of the hydrochloric leaching, an ion exchange between Cl^- and SO_4^{2-} is necessary. Due to the absence of chlorine and lower lead concentrations the sulphuric acid leaching is more suitable [52, 53].

The first purification stage is usually an oxidation of iron by the use of MnO_2, H_2O_2 or air. When using MnO_2 the pH increases and H_2O_2 decreases the pH value. As a result the trials were performed with a mixture of these two chemicals. Afterwards, a cementation of Cu, Pb, Cd with zinc dust was carried out.

The leaching process was described and three possible scenarios

- one-step lixiviation
- two-step lixiviation
- two-step counter-current lixiviation

were investigated. From the economic point of view, there are several problems concerning this process no matter which lixiviation variant is used [52, 53].

First of all, contaminations like Sn and Mn caused by the oxidant, which cannot be separated from the solution, can be found. Furthermore, too high concentrations in chlorine and cadmium for a subsequent electro-winning are present. The author recommended a mixing with clean electrolyte as possible solutions for the Cd content. As a solution to the chlorine problem, it was suggested that double leached waelz oxide could be used as input material.

Another possible way to avoid the electrolytic winning described by the author is a precipitation with NaOH followed by calcination. The questions of major importance are the consumption of chemicals and the recycling of the remaining solution after the ZnO production [52, 53].

7.3.4 Solvent extraction (modified ZINCEX-process)

The former Zincex process was developed by Tecnicas Reunidas and first introduced in a plant in Bilbao, Spain in 1976. The second plant with a capacity of 11,500 t/a was built in 1980 for Quimigal in Lisbon (Portugal). The modified Zincex process is a more developed and simplified Zincex process, especially adapted for oxidic materials or impure sulphate solutions. It offers the possibility without a separated leaching circuit to leach washed and unwashed waelz oxide or dusts without the need to pay attention to the halogen content. One peculiarity is that the leaching is carried out in a sulphate-chloride solution while the electrolysis needs a sulphatic base. This becomes feasible through a chloride barrier formed by a solvent extraction between electrolytic winning and the leaching step (see Figure 7-2). Thereby 99 % zinc is dissolved in addition to some impurities such as Si, Al, Fe, Cd or Cu. The zinc ferrite present cannot be leached under the given conditions. The solvent extraction uses kerosene and D_2EHPA (di-2-ethyl-phosphoric acid) to extract the zinc from the sulphate-chloride solution. Impurities like fluorine and chlorine remain in the solution. Afterwards the organic phase, which carries the zinc, is stripped by the sulphate solution of the electrolytic winning circuit. A small part of the organic phase is regenerated by a treatment with HCl to remove unwanted elements from the solvent extraction phase. From the economical point of view it is important how many extraction circles are necessary and how much organic phase (D_2EHPA) is consumed (or has to be renewed) [56, 57, 58, 59, 60].

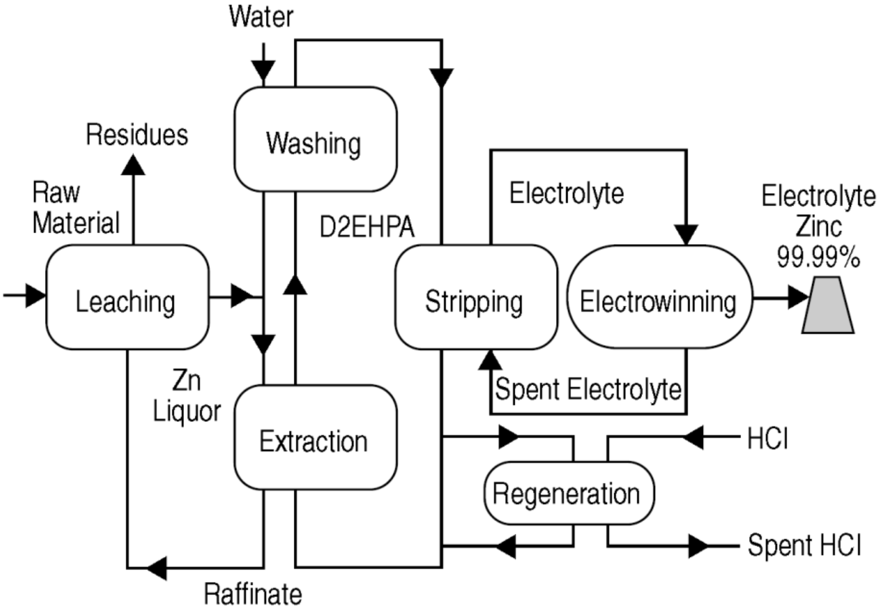


Figure 7-2: General flow sheet of a modified Zincex process [67]

At the moment five places are mentioned where the Zincex process was (Quimigal, Metalquimica), is (Skorpion Zinc in Namibia and Pilagest S.L. in Spain) and will be used:

Skorpion Zinc Refinery (Namibia)	150 000 t/a SGH-Zn	May 2003 - present
Pilagest S.L. (Spain)	400 t/a SGH-Zn	1998 - present
Quimigal at Lisbon (Portugal)	11 500 t/a SGH-Zn	1980 - 1995
Metalquimica (Spain)	8 500 t/a SGH-Zn	1976 - 1992
Alkita Zinc Japan	20 000 t/a SHG-Zn	2010 - present
Glencore Portovesme (Italy) [71]		start-up expected Q1 2013
Horsehead Monaca, PA [71]		start-up expected Q3 2013

The advantage of this process is the possibility to selectively extract only the zinc without any impurities. What's more, there is the opportunity to operate either an electrolytic winning or a zinc sulphate crystallization.

The disadvantage is the consumption of a costly organic phase and it is not exactly declared how many extraction steps are necessary to achieve a satisfying zinc yield. Losses by the indissoluble zinc ferrite which lead to a bad zinc yield are not mentioned in literature, either. Another aspect is the not described wastewater treatment; it is not clear what e.g. happens with the solution from the first leaching step as well as precipitated salts.

7.3.5 Fluor elimination from waelz oxide by NaOH-leaching

The possibility to remove fluorine by the dissolving of waelz oxide in NaOH and a subsequent precipitation of a zinc hydroxide product was investigated at the Chair of Nonferrous Metallurgy at the University of Leoben. It was shown that the NaOH/Zn ratio has to be in a certain stoichiometric proportion; furthermore, a certain absolute concentration of NaOH has to be present for a good Zn yield.

The precipitation trials showed low chlorine and fluorine concentrations after a washing of the precipitate. As a result of the washing, halogen compounds on the surface, which are caused by adhesive process solution, can be removed. A small amount of chemically bound halogens stays in the product. An elimination of these contaminants is hardly possible.

Basically the NaOH leaching seems to be a good possibility combined with a precipitation and a subsequent leaching of the mainly clean product again compared to a cost-intensive pyrometallurgical treatment. Another positive effect is the very low achievable fluorine values. A disadvantage of such a process is the multiplicity of necessary steps and the high leaching temperatures. The fact that zinc is precipitated as a hydroxide instead of a carbonate has to be considered, which increases the NaOH consumption.

7.3.6 Precipitation of F^- with $AlPO_4$ and Cl^- with Cu^+

Two patents (DE2646857 and US4005174) [61] describe a possible process for a chlorine removal from zinc sulphate solution. This is carried out by Cu^+ ions, which can be added in the following three ways (see Equations 7-8 to 7-11):

- Copper sulphate and zinc powder

  $CuSO_4 \leftrightarrow Cu^{2+} + SO_4^{2-}$ Equ. 7-8

  $2\ Cu^{2+} + Zn \leftrightarrow 2\ Cu^{+} + Zn^{2+}$ Equ. 7-9

- Cupric salt and metallic copper
  $Cu^{2+} + Cu \leftrightarrow 2\ Cu^{+}$ Equ. 7-10
- Cuprous salt (e.g. cuprous oxide)
  $Cu_2O + H_2SO_4 \leftrightarrow 2\ Cu^{+} + SO_4^{2-} + H_2O$ Equ. 7-11

After a conversion of Cu^{2+} to 2 Cu^{+} a precipitation to CuCl is carried out. In order to reuse the copper a conversion to copper oxide (Equation 7-12) again follows:

$2\ CuCl + 2\ NaOH \leftrightarrow Cu_2O + 2\ NaCl + H_2O$ Equ. 7-12

The advantage is the recovered copper oxide; the disadvantage is the sodium chloride solution for what no application is suggested for.

The cupric copper left in the excess solution from the chlorine removal procedure is cemented with zinc powder and the obtained product is transferred to metallic copper again. A complete flow sheet of the chlorine removal by copper ions is shown in Figure 7-3.

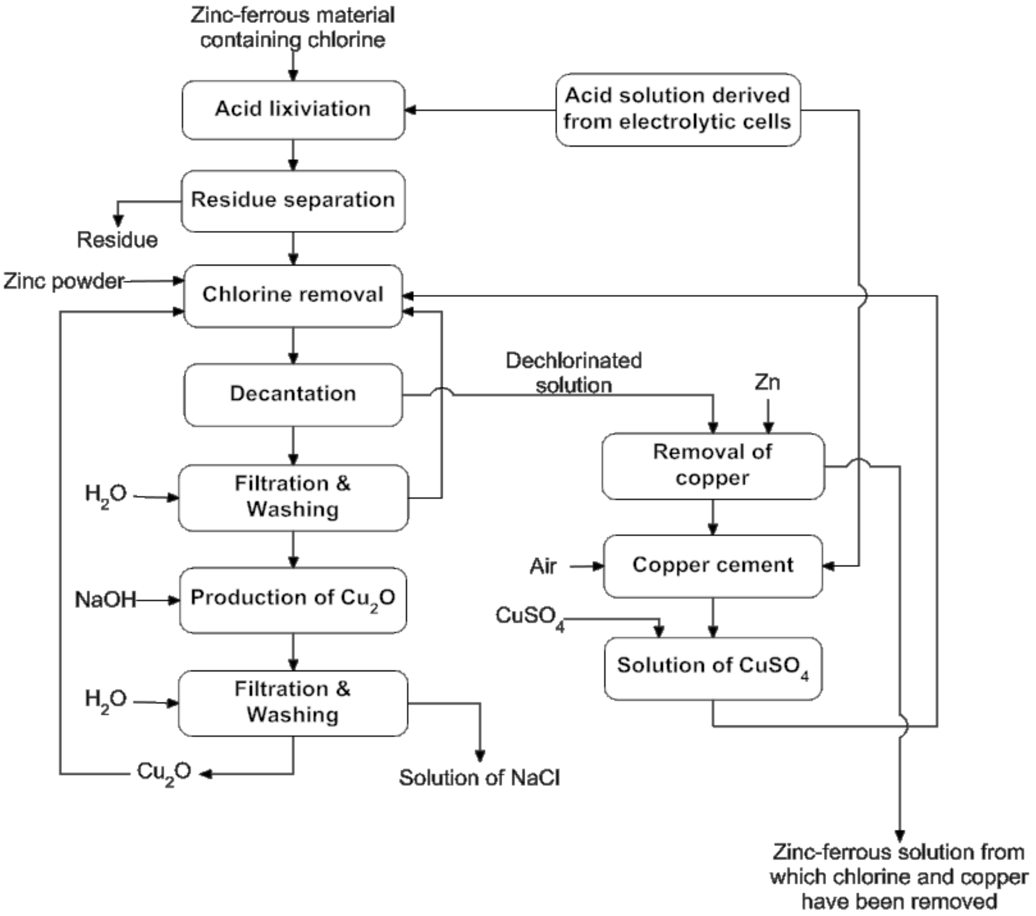


Figure 7-3: Flow sheet of a chlorine removal by Cu^{+} ions [61]

The patents WO2010/072773A1 and MHO EP0132014A2 [62] define a process to remove fluorine and chlorine from waelz oxides and oxides from PRIMUS processes below a level of

50 mg/l fluorine. The first step is a sodium-carbonate washing step to remove Na, K, Cl and F (see Figure 7-4 - Etape 1). After a leaching of the residue (R1) with H_2SO_4 the solid residue (Pb, Zn, Fe, Ag) (R2) is separated from the solution (L2), which is then treated by the addition of Al^{3+} and PO_4^{3-} ions. The residue R2 can be treated in lead plants. To adjust the pH for an optimum process, NaOH, $Ca(OH)_2$ or the previously mentioned residue is used (Etape 3). The residue R3 then carries the main part of fluorine.

The next step (Etape 4), before the solution goes into an electrolytic winning (Etape 5), is purification, which is the same as in the conventional zinc winning route. The mechanism used is a cementation with metallic zinc to remove cadmium, copper, cobalt and nickel. Potentially dissolved Mn^{2+}-ions cannot be removed [62].

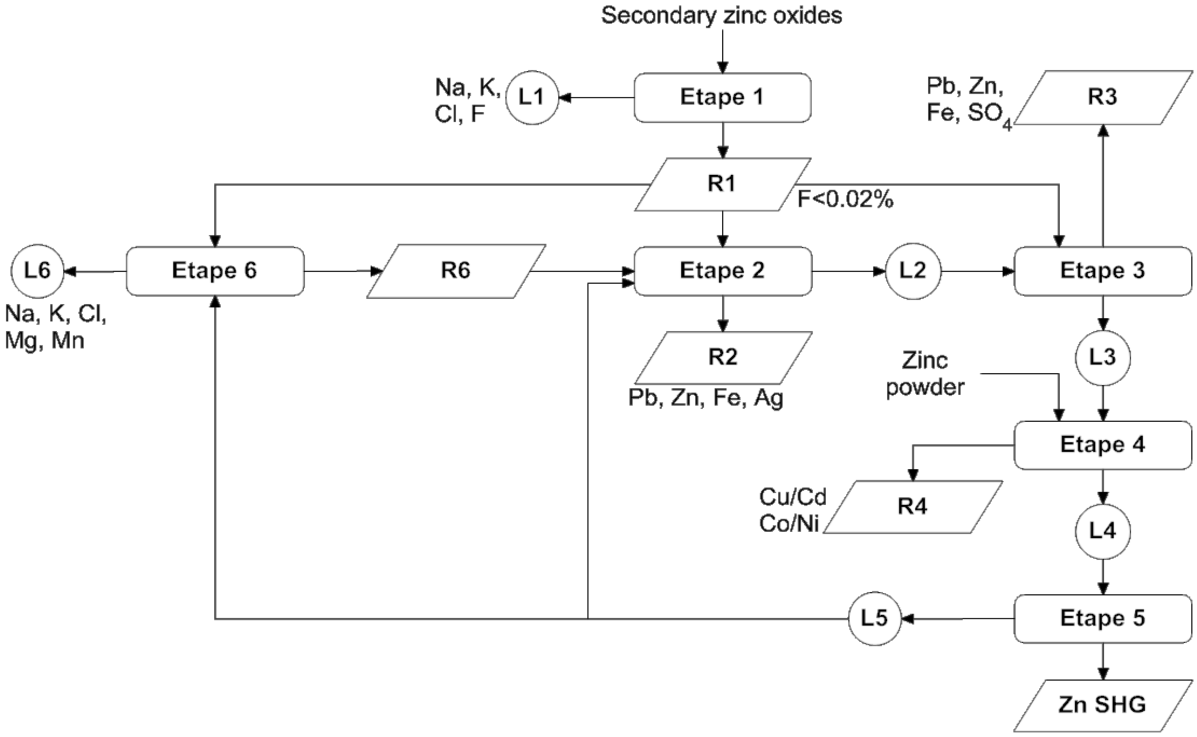


Figure 7-4: Flow sheet of the fluorine removal as described in the patent [62]

The last step is the electrolytic winning, where metallic zinc is deposited as SHG zinc. Generally the opportunity to remove fluorine and chlorine from zinc sulphate solutions in primary zinc metallurgy would be a good process enhancement because secondary raw materials containing halogens would not be limited to 15 % of the input material anymore. Disadvantages are higher efforts due to the additional process steps, the sodium chloride solution which no application is suggested for and the not clarified application area of the newly generated residue R3, where the fluorine is collected in. Also no recovery of $AlPO_4$ is mentioned; therefore, the consumption and the arising costs would be of interest to assess these additional cleaning processes of the zinc sulphate solution [62].

7.3.7 Removal of F with FeOOH (akaganeite)

The author [63] describes a possible process to remove fluorine and chlorine from leaching solutions of secondary zinc oxide.

As shown in Figure 7-5 the first step is a washing of secondary ZnO with NaOH solution, which removes part of the fluorine and most of the chlorine compounds. After a leaching of the washed ZnO with spent electrolyte, the solution has 153 g/l Zn, 0.27 g/l fluorine and 1.6 g/l chlorine. This solution is then forwarded to the fluorine separation, which is carried out by an iron compound FeOOH (akaganeite), which has a hedgehog shape (see Figure 7-6) and is consequently ideal for the use as an adsorbent [63].

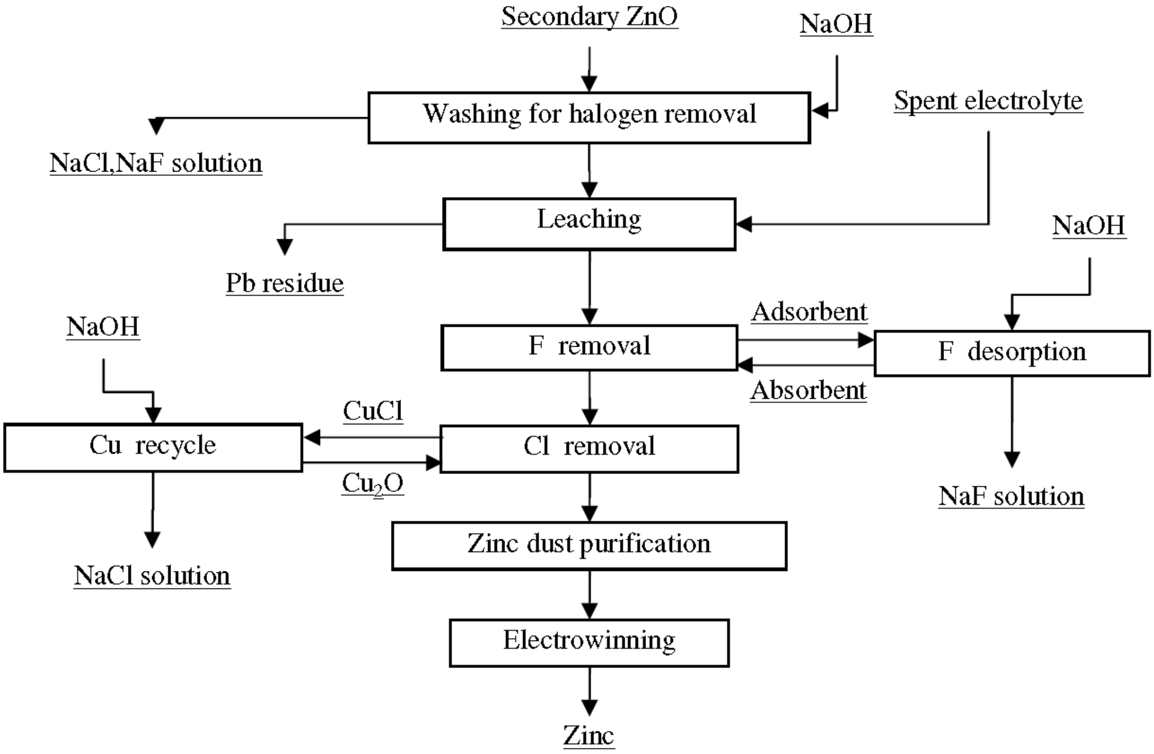


Figure 7-5: Possible process flow for a removal of fluorine and chlorine from leached secondary ZnO solutions [63]

The production of FeOOH was carried out at 80 °C by adding a $FeCl_3$ solution to a Na_2CO_3 solution. The occurring equation is shown below:

$$2\ FeCl_3 + 3\ Na_2CO_3 + H_2O \leftrightarrow 2\ FeOOH + 6\ NaCl + 3\ CO_2 \qquad \text{Equ. 7-13}$$

The fluorine adsorption with this akaganeite was carried out at 60 °C and a pH of 3. The end concentration reached after the treatment was approximately 20 mg/l fluorine, even after 100 performed circles of adsorption and desorption.

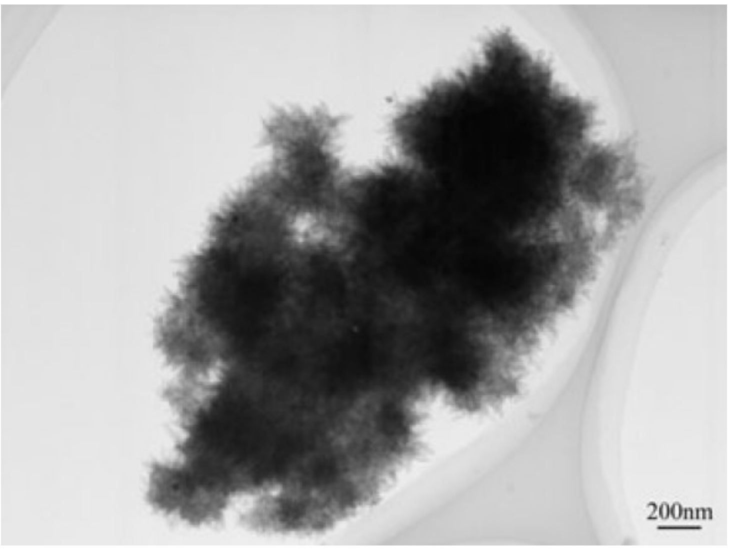


Figure 7-6: TEM photo of the produced akaganite (FeOOH) [63]

After the fluorine adsorption the electrolyte is forwarded to the chlorine removal which is carried out with copper oxide. This process is based on the patent described in detail in Chapter 7.3.6.

7.4 Summary of treatment methods

The realized literature survey showed clearly that little new literature can be found. Concerning the chlorine problem, more papers than those dealing with the fluorine topic are available.

Summing up, the topic is split into three parts; the possibilities within the waelz kiln, the pyrometallurgical methods and the hydrometallurgical methods to remove contaminants from the waelz oxide.

The possibilities of a halogen content reduction in the waelz kiln are the ***agglomeration of EAFD*** by forming pellets. This is already carried out and based on literature, a decrease to 50 % fluorine content can be achieved.

Also the ***addition of MnO*** is discussed but this method is difficult to verify because no quantification for the effectiveness was found.

The second chapter covers the **pyrometallurgical treatment methods**. The following three main methods are described: Clinkering, pyrohydrolysis and sulphatisation. ***Clinkering*** is a method which is used, for instance, by the company Horsehead, to improve their product quality. What is advantageous is the simple process technology. On the other hand, the high necessary temperatures are a disadvantage. Own trials showed that a good fluorine and chlorine yield can be achieved by such a process. Furthermore, ***pyrohydrolysis*** is discussed. It is a process for a selective removal of halogens by forming HF and HCl, which can then be found in the off-gas. The main disadvantages are a long necessary treatment time, a complex off-gas system due to the reaction products, high energy consumption and the need to add SiO_2 or WO_3 for an acceptable fluorine and chlorine yield. The positive point is the selective removal of halogens next to low zinc losses. The last process in this chapter is ***sulphatisation***, which has to be seen as a part of a complete process and forms a pre-step to leaching. The main part is a sulphatisation roaster, which removes the halogens and transforms the zinc oxide into an easily leachable form, $ZnSO_4$. This happens through a gassing with water steam and SO_2. The advantage compared to pyrohydrolysis is the lower necessary temperatures because of the exothermic reactions. The bad selectivity leads to an extended purification of the solution, which again increases the costs. The corrosive off-gas and the unsolved zinc ferrite problem also have to be mentioned.

The last chapter in this paper dealing with the removal of halogens is dedicated to **hydrometallurgical methods**. Consistent with the problem with wastewater or when doing crystallizations, the deposit of salts has to be mentioned, similar to the dust problem in pyrometallurgical processes.

The idea of the ***direct leaching of EAFD with H_2SO_4*** is to have an opportunity to directly process EAFD in zinc metallurgy. The disadvantage and the reason why it is not possible is the high content of halogens, which are dissolved in addition to iron and zinc.

A common method is the ***double leaching of waelz oxide***. The halogens are leached and dissolved, and zinc and lead are precipitated as a result of sodium carbonate (Na_2CO_3) addition. With this leaching method, the chlorine content can be decreased effectively while the fluorine content is very often still too high. That is the reason why the substitution of primary concentrates in zinc smelters is still limited to approximately 15 %.

The University of Bilbao is investigating a process to produce ***zinc from waelz oxide or double leached waelz oxide*** by eliminating the chlorine problem by using either double leached WO or an ion exchange. One important issue is what happens with Sn and Mn if they are in the solution, but the main question in that process is the consumption of chemicals and with that, additional costs has to be covered.

A technical development by Tecnicas Reunidas is the ***modification of the Zincex process***, which results in a specially adapted process for oxidic materials or sulphate solutions. Due to the solvent extraction which works as a chlorine barrier, the input material is variable. What is not mentioned is how many circuits are necessary for a satisfying zinc yield; moreover, the chemical consumption is a question mark, especially of D_2EHPA. Another issue is how high the zinc losses are caused by the indissoluble zinc ferrite and the wastewater treatment, e.g. of the solution from the first leaching step. Next to that, the purification of the organic extraction liquid requires tremendous effort.

A literature survey of Mishina Olga describes in principle the possibility of a ***halogen separation of alkaline solutions***. The base is a sodium carbonate solution from a waelz oxide washing. In case of a possible separation of the halogens from the process solution, a recirculation without crystallizations would be realizable and with that a decrease of sodium carbonate consumption happens. The only two things which seem to be applicable are nanofiltration, but in that case, no industrial examples were mentioned, and the use of weak to strong alkaline anion exchangers, which can simultaneously remove chlorine and fluorine from such solutions but are generally expensive chemicals.

Based on two patents, ***chlorine and fluorine from zinc sulphate solutions with*** $AlPO_4$ ***and*** Cu^+ ***ions*** were described in detail in Chapter 7.3.6.

The possibility to ***remove fluorine by the compound FeOOH***, which is similar to the iron precipitation in primary zinc metallurgy (goethite precipitation) a fluorine-sink, is the last method described. This method seems to be an interesting approach because the author outlined that even after a couple of circulations of the adsorbent, a satisfying fluorine yield can be achieved. But next to that this method is only proved in lab scale and no industrial application is known, the issue again being the effort of treating the effluent from adsorbent regeneration and the related costs. Furthermore, it only removes the fluorine, while the typically higher contents of chlorine are not removed by this concept.

8. Investigation into a selective vaporization of impurities

As a basis for the trials, thermochemical calculations were done regarding the behaviour of different compounds, their vapour pressures and possible interaction reactions.

Figure 8-1 shows the vapour pressure of selected chlorine compounds (also used in synthetic mixtures) as a function of the temperature. The ordinate gives the vapour pressure in Pascal dependent on the present temperature (X-axis).

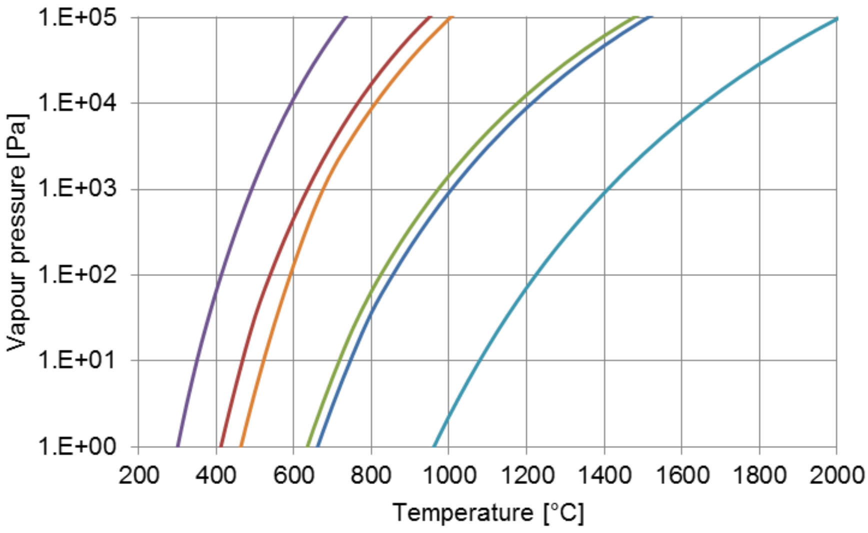


Figure 8-1: Vapour pressure curves of chlorine compounds (— $NaCl \leftrightarrow NaCl_{(g)}$, — $PbCl_2 \leftrightarrow PbCl_{2(g)}$, — $KCl \leftrightarrow KCl_{(g)}$, — $ZnCl_2 \leftrightarrow ZnCl_{2(g)}$, — $CaCl_2 \leftrightarrow CaCl_{2(g)}$, — $FeCl_2 \leftrightarrow FeCl_{2(g)}$)

Figure 8-2 shows the vapour pressure of selected fluorine compounds (also used in the synthetic mixtures) as a function of the temperature, calculated with the thermodynamic software HSC Chemistry version 6.12.

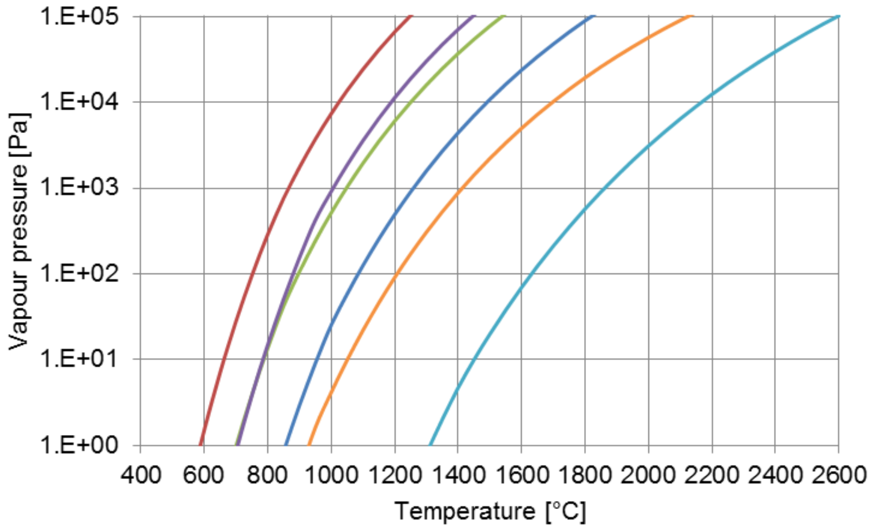


Figure 8-2: Vapour pressure curves of fluorine compounds (— NaF↔$NaF_{(g)}$, — PbF_2↔$PbF_{2(g)}$, — KF↔$KF_{(g)}$, — ZnF_2↔$ZnF_{2(g)}$, — CaF_2↔$CaF_{2(g)}$, — FeF_2↔$FeF_{2(g)}$)

Figure 8-3 gives the vapour pressure of lead oxide, lead sulphide and metallic lead as a function of the temperature.

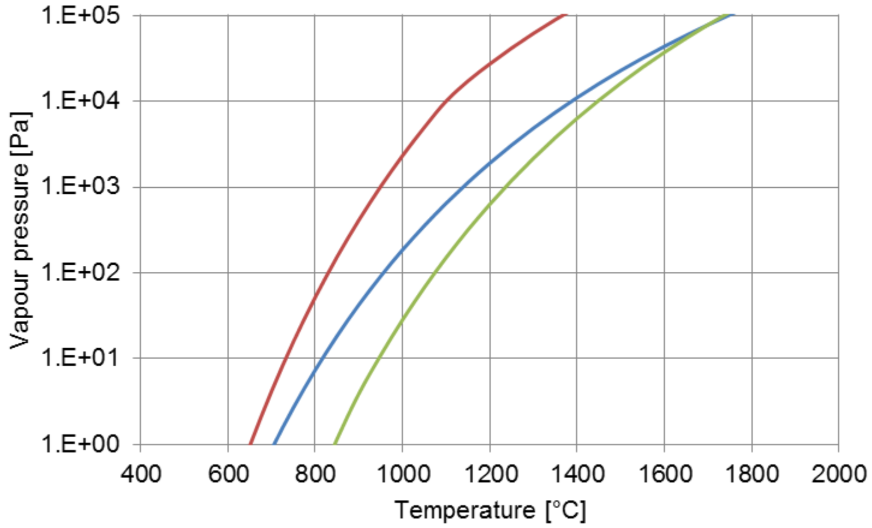


Figure 8-3: Vapour pressure curves for — PbO, — Pb and — PbS

The target process facility to upgrade the zinc oxide by selective vaporization is the rotary kiln, which is typically a counter current working furnace and therefore continuously changes its furnace atmosphere. Relating to the frequency on how often the atmosphere changes and with this the absolute partial pressure of volatiles in the reaction chamber, where the vaporization takes place, also theoretically low vapour pressures can lead to a significant loss of material. The reason for this is a continuous removal of reaction product (gaseous halide) and with this, based on the principle of Le Chatelier, a support of the evaporation. The maximum clinkering temperature on the one hand should not exceed 1400 °C, because at this temperature waelz oxide starts to get an increasing vapour pressure; on the other hand, the aim is to remove as many of the impurities present as fast as possible. Therefore, based on the calculations done (see Figures 8-1 and 8-2) a minimum temperature of 900 °C should be reached to be able to remove most of the halides as well as lead oxide.

The relevant temperature field for the investigation starts at 900 and rises up to 1300 °C. This should make a removal of most of the impurities possible while the zinc loss can be kept low. Because interaction reactions between compounds can also occur, it is possible to get better or worse results than expected from these theoretically calculated vapour pressure curves.

Based on thermochemical calculations only, it is not possible to draw conclusions concerning reaction yields and kinetics. Therefore, the following trials are important to study such interactions as well as the influence of temperature and treatment time.

It was necessary to eliminate as many side effects as possible. Because of this, synthetic mixtures were used, so that only those compounds which were in focus could react. As a matrix ZnO and PbO were used, while at each trial one halide compound was added. This offers the opportunity to study if a reaction with lead oxide or zinc oxide takes place, which is, due to the amount of these matrix compounds, very likely.

In a first step the atmosphere was air without water steam or carbon dioxide. In a second step, trials with an atmosphere like under industrial conditions were carried out. For this, a rotary kiln with heat supply by gas burners was used. As a result the furnace off-gas was exchanged during the trials and offered the opportunity to investigate the influence of atmosphere.

8.1 Investigated materials

In a first step synthetic samples were used to limit the possible on-going reaction between the matrix (ZnO and PbO) and one impurity compound.

8.1.1 Synthetic samples

The aim of these clinkering trials was to identify the compounds which cause problems or influence the vaporization of impurities positively or negatively during a pyrometallurgical treatment of crude zinc oxide.

8.1.1.1 Composition of synthetic material

The following table shows the used chemicals, while Table 8-2 describes the prepared synthetic mixtures.

Table 8-1: Used chemical compounds for sample preparation
(in brackets the supplier of the chemical used)

Matrix:			
Zinc oxide	≥ 99 %	Lead(II)oxide	≥ 99 % (Roth)
Added chemicals - “impurities”:			
Fluorine compounds:		Chlorine compounds:	
NaF	> 99 % (Merck)	NaCl	> 99.5 % (Merck)
KF	> 99 % (Merck)	KCl	≥ 99.5 % (Roth)
CaF_2	99 % (Riedel-de Haën)	$CaCl_2$	pure (Merck)
$Pb(II)F_2$	> 99 % (Fluka)	$Pb(II)Cl_2$	> 98 % (Merck)
ZnF_2	99 % (Sigma-Aldrich)	$ZnCl_2$	≥ 98 % (Roth)
$Fe(II)F_2$	98 % (Aldrich)	$Fe(II)Cl_2 \cdot 4H_2O$	> 99 % (Fluka)

The base of each mixture was ZnO and PbO, while in each trial a different halogen compound was added. So the matrix is very similar to a crude zinc oxide composition, with 85 or 89 % zinc oxide and 8 to 10 % lead oxide, depending on the kind of trial (fluorine or chlorine compound). In case of fluorine trials, each time 1 % of a different compound was added. In the same way 7 % of a chlorine compound was added to 93 % matrix material (ZnO + PbO).

The following table summarizes the prepared synthetic mixture compositions for the thermal trials.

Table 8-2: Synthetic mixtures of investigated samples

	ZnO [%]	PbO [%]	Halogen amount [%]	Added halide [compound]
Chlorine comp.	85	8	7	NaCl, $PbCl_2$, KCl, $ZnCl_2$, $CaCl_2$, $FeCl_2$
Fluorine comp.	89	10	1	NaF, PbF_2, KF, ZnF_2, CaF_2, FeF_2

8.1.1.2 Sample preparation

Due to the usage of synthetic materials, the components had to be mixed intensively prior to the tests to guarantee a homogenous distribution of the investigated compounds.

After weighing the necessary chemicals for the trial, they were mixed in a mortar before filling the ceramic boats with the homogenized material.

8.1.2 Industrial materials

The aim of these trials was on the one hand to investigate a commercial material and its behaviour during a thermal treatment. On the other hand, conditions similar to industrial clinkering were simulated by using a rotary kiln and an atmosphere similar to a gas heated device by using an off-gas generated by a methane oxygen burner.

8.1.2.1 Composition of industrial material

For the trials with industrial samples an impure waelz oxide was investigated as the starting material. With the aim of an economically viable upgrade process, utilization of a cheap raw material is meaningful. A waelz oxide collected in the dust settling chamber was used, which is typically higher in its chlorine and fluorine content. The chemical composition can be seen in the following table.

Table 8-3: Chemical analysis of investigated DSC WOX (rest is oxygen)

Element/ Compound	Content [%]	Element/ Compound	Content [%]	Analysis norm
ZnO	56.634	Na	2.79	DIN EN ISO 11885
CuO	0.089	Cr	0.07	DIN EN ISO 11885
Pb	6.82	As	<0.005	DIN EN ISO 11885
Cd	0.11	Ni	0.015	DIN EN ISO 11885
Fe	4.04	Al_2O_3	1.247	DIN EN ISO 11885
Ca	3.25	MnO	0.852	DIN EN ISO 11885
MgO	0.365	K	5.1	DIN EN ISO 11885
C	0.88	S	0.3	DIN EN ISO 15350
F	0.33	Cl	9.78	DIN 38405 D1-2/Teil 1

It can be observed from the relatively low content of ZnO (56.6 %) that the impurity level is higher compared to normal crude waelz oxide, where ZnO contents of around 75 % are typical.

8.1.2.2 Sample preparation

Due to the fact that the sample was dry and in powder form, no sample preparation was carried out prior to the trials. This means that it was used as it was collected at the end of the waelz kiln in the so-called dust settling chamber.

8.2 Trials

Subsequently, the trials carried out for a product upgrade of waelz oxide by selective vaporization are described, which comprises the trial set-up, experiment procedure and results obtained.

8.2.1 Trials with synthetic materials

In a first step, the possible reactions were limited by the use of synthetic mixtures, allowing for the possibility to study each potential reaction separately.

8.2.1.1 Trial set-up and experiment procedure

For the trials carried out, a “Carbolite Incineration furnace AAF 12 18 1200 °C”, shown in Figure 8-4, was used. The muffle furnace was programmed to the experiment temperature set-up and the sample material was placed in ceramic boats in the middle of the furnace after the temperature was reached.

Figure 8-4: Carbolite incineration furnace AAF 12 18 1200 °C

In order to prevent measuring errors, the first step was to heat up the empty ceramic boats to vaporize possible volatile compounds or moisture. After cooling down again, the boats were filled with the synthetic mixture and charged into the hot muffle furnace at the actual treatment temperature. To eliminate influences of the sample height, only a small thickness of approximately 1 millimetre was chosen and the material was split and placed in several ceramic boats. After the treatment time, the boats were taken out of the furnace and cooled down under air atmosphere.

As a result, the vaporization of the samples was calculated based on their mass loss. Additionally, the lead oxide yield and the halide yield based on the chemical analysis of the clinker were calculated next to the evaluation of possible interaction reactions.

Figure 8-5 (left picture) shows the prepared mixtures before a trial, split and placed in several boats. On the right side a clinkered sample, directly after having been removed from the furnace, is shown. The colour (yellow) comes from the thermochromism property of crystalline zinc oxide. The reason for that is a small loss of oxygen at high temperatures. Due to that, a non-stoichiometric compound is formed which is yellow-coloured.

Figure 8-5: Left: Sample material before treatment (white);
Right: Sample material directly after the treatment at 900 °C (yellow ZnO)

8.2.1.2 Results

The following chapter describes the vaporization yields of the overall samples, the halide compounds and the lead oxide as a function of the treatment temperature and within the second round of trials as a function of the treatment time at a constant temperature of 1100 °C.

The detailed raw data such as:

- sample weights (before and after trial → resulting delta) of trials with temperature variation and trials at different treatment times,
- exact sample composition,
- chemical analysis of clinkered materials,
- calculated values for overall vaporization, lead oxide as well as halide vaporization yield

can be found in the Appendix. In this chapter only the results used for the figures (calculated end results) are summarized in the form of tables and visualized as figures for interpretation.

8.2.1.2.1 Variation of treatment temperature

The variation of treatment temperatures delivered the overall vaporization yields shown in Table 8-4. While the temperature was varied, the retention time was constant with 60 minutes.

Table 8-4: Summary of overall vaporization yield of sample material at a constant treatment time of 60 minutes and varying temperature

Trial/temp.	900 °C	1000 °C	1100 °C	1200 °C	1300 °C
NaF	4.12	12.01	10.85	15.28	12.33
PbF_2	3.77	10.78	10.71	15.87	12.12
KF	4.20	11.00	13.64	12.30	12.32
ZnF_2	4.44	10.29	12.80	11.80	11.03
CaF_2	3.59	7.77	11.07	11.85	10.71
FeF_2	3.39	8.40	10.67	11.89	11.18
Trial/temp.	900 °C	1000 °C	1100 °C	1200 °C	1300 °C
NaCl	10.77	16.17	16.07	18.38	17.15
$PbCl_2$	10.00	15.14	14.52	15.65	16.17
KCl	10.91	15.96	15.83	16.32	16.76
$ZnCl_2$	13.61	14.36	14.08	14.60	15.52
$CaCl_2$	17.57	15.38	15.30	16.45	16.27
$FeCl_2$	12.13	13.13	13.51	13.34	13.78

In Figures 8-6 and 8-7, the above-mentioned results are summarized in the form of a diagram. The achievable vaporization yield is influenced by the treatment temperatures and with that by the present vapour pressure of the halides. Based on the synthetic mixture, an amount of halide plus lead oxide of 15 % is present in the chlorine mixtures and 11 % in the fluorine samples.

At 1200 °C (see Figure 8-6 - fluorine compounds) a mass loss of nearly 16 % is shown (NaF and PbF_2 trials), which seems to be implausible. A dissociation of zinc oxide is very unlikely at such temperatures and would otherwise also occur within the other trials. A possible reason for this is an interaction reaction of the halide with the matrix, which is discussed in a following chapter.

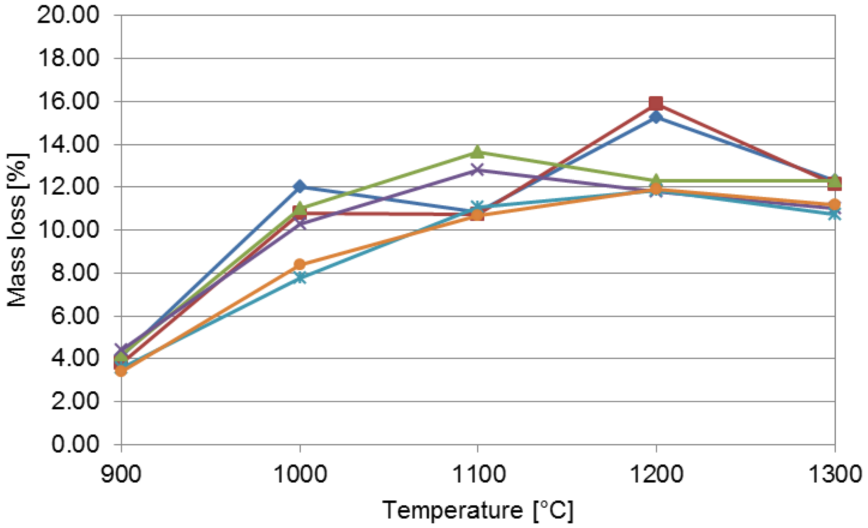


Figure 8-6: Overall vaporization yield for trials investigating the influence of treatment temperature and the influence of fluorine compounds (—◆— NaF, —■— PbF_2, —▲— KF, —×— ZnF_2, —✳— CaF_2, —●— FeF_2)

The chlorine trials (see Figure 8-7) illustrate more or less the same losses independent of the temperature, with the exception of the very first trial at 900 °C. This leads to the conclusion that above 1000 °C a good separation of chlorine compounds as well as lead oxide from zinc oxide should be possible. Moreover, Figure 8-8 underlines clearly that chlorine compounds can be effectively removed with temperatures of 900 °C. The sprinkling at 900 °C (see Figure 8-7) arises from a dissimilar lead oxide yield (see Figure 8-11). The reason for that is a possible interaction between PbO and halide, which is discussed in a later chapter. Above 1000 °C a very similar yield independent of the sample can be achieved.

It can be stated, as well, that above 1100 °C a treatment time of less than 60 minutes should deliver the same results.

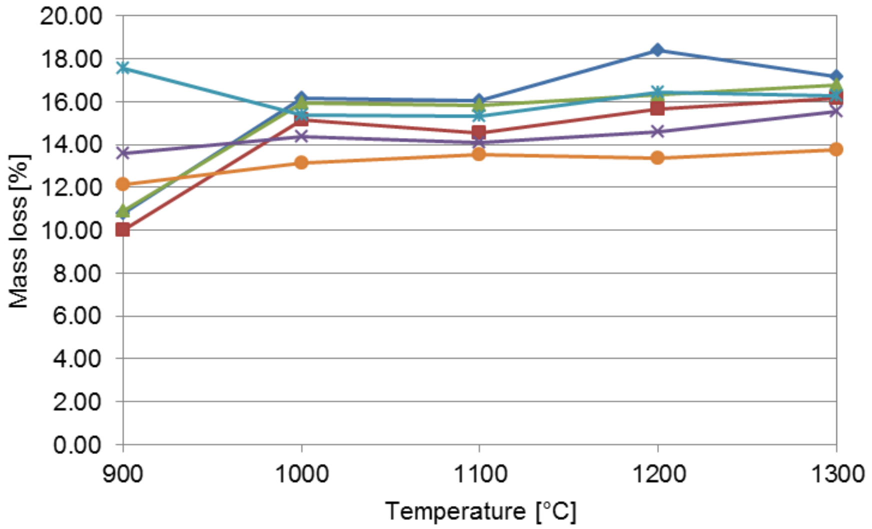


Figure 8-7: Overall vaporization yield for trials investigating the influence of treatment temperature and the influence of chlorine compounds (—◆— NaCl, —■— $PbCl_2$, —▲— KCl, —×— $ZnCl_2$, —✳— $CaCl_2$, —●— $FeCl_2$)

Table 8-5 summarizes the halogen compound yield, which is based on the chemical analysis of the clinkered material.

Table 8-5: Summary of halide vaporization yield (based on chemical analysis of fluorine and chlorine) (influence of temperature at constant treatment time of 60 minutes)

Trial/temp.	900 °C	1000 °C	1100 °C	1200 °C	1300 °C
NaF	62.56	99.81	99.22	97.57	>98.15
PbF_2	98.18	>99.44	97.71	>94.57	26.23
KF	98.28	99.47	98.95	96.86	87.85
ZnF_2	95.18	99.76	99.06	97.65	>97.58
CaF_2	48.68	75.71	61.94	96.99	60.58
FeF_2	96.18	99.55	97.87	97.45	97.64
Trial/temp.	900 °C	1000 °C	1100 °C	1200 °C	1300 °C
NaCl	>97.90	99.98	>98.03	>98.08	>99.84
$PbCl_2$	99.09	99.95	>95.22	>95.30	>95.31
KCl	99.39	99.97	>97.48	>97.49	>97.50
$ZnCl_2$	99.83	99.63	>97.64	>97.66	>97.69
$CaCl_2$	99.67	98.02	>98.11	>98.13	>98.13
$FeCl_2$	>97.75	>97.78	>97.79	>97.78	>97.80

Figures 8-9 and 8-9 show the visualization of the halogen compound yields. It seems that satisfying results can be achieved in the range of 1000 to 1200 °C. Below 1000 °C the vapour pressure is relatively low and as a consequence also the yield. This would cause long treatment times to achieve satisfying results.

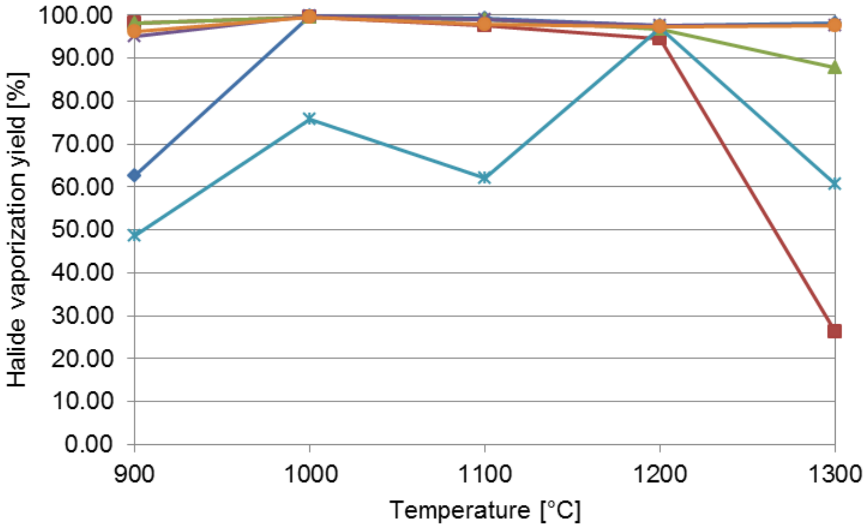


Figure 8-8: Halide vaporization yield for trials investigating the influence of treatment temperature and the influence of fluorine compounds (—◆— NaF, —■— PbF_2, —▲— KF, —×— ZnF_2, —✳— CaF_2, —●— FeF_2)

The chlorine seems to support the lead oxide vaporization, which results in higher lead oxide yields, illustrated in Figure 8-11 (at lower temperatures) compared to the results of the fluorine trials (see Figure 8-10). Actually, fluorine compounds can also support the lead oxide yield but due to the lower content in the synthetic mixtures, this is not as clearly visible as shown in the results of the chlorine trials. It is, however, explicitly demonstrated that the amount of halide compound has an influence on the lead oxide yield.

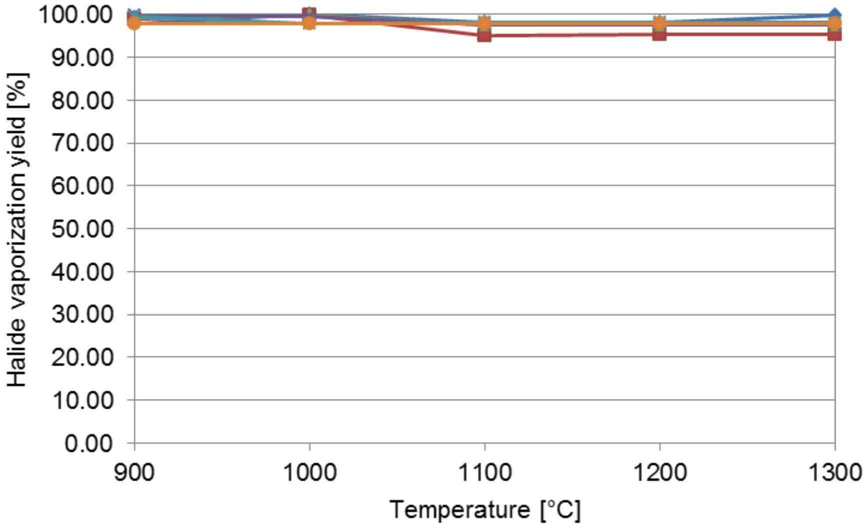


Figure 8-9: Halide vaporization yield for trials investigating the influence of treatment temperature and the influence of chlorine compounds (—◆— NaCl, —■— $PbCl_2$, —▲— KCl, —×— $ZnCl_2$, —✳— $CaCl_2$, —●— $FeCl_2$)

Table 8-6 shows a summary of the lead oxide yields. In case of lead chlorine or lead fluorine as added halide, the yield was determined based on the rest halogen content in the sample and the analysis of lead. This is necessary because of possible remaining lead bound to unreacted lead halogen compound, which is the reason why the lead content was decreased by the lead bound in the remaining lead halide before the PbO yield was calculated.

Table 8-6: Summary of lead oxide vaporization yield (influence of temperature)

Trial/temp.	900 °C	1000 °C	1100 °C	1200 °C	1300 °C
NaF	49.90	54.22	85.94	99.92	>99.95
PbF_2	58.05	85.94	74.49	99.95	>99.95
KF	64.25	89.45	89.95	99.86	>99.95
ZnF_2	60.42	87.01	90.42	99.79	99.94
CaF_2	5.99	85.67	61.94	>99.95	>99.95
FeF_2	21.34	70.70	99.12	>99.95	>99.95
Trial/temp.	900 °C	1000 °C	1100 °C	1200 °C	1300 °C
NaCl	61.03	92.52	97.97	99.80	100.00
$PbCl_2$	55.83	93.77	100.00	99.60	99.93
KCl	53.92	87.63	97.96	99.77	>99.94
$ZnCl_2$	87.87	97.11	98.84	99.71	>99.94
$CaCl_2$	99.46	99.55	99.73	99.88	>99.94
$FeCl_2$	93.41	97.67	99.18	99.90	>99.94

Figures 8-10 and 8-11 illustrate the lead oxide yields, which show increasing values until they reach a maximum at temperatures above 1200 °C in case of fluorine as well as chlorine compounds. As mentioned before, below 1200 °C the lead oxide yield has higher values in case of the chlorine compounds than with the fluorine trials, which leads to the assumption that halides support the evaporation of lead oxide and especially the amount influences the necessary time and achievable yield.

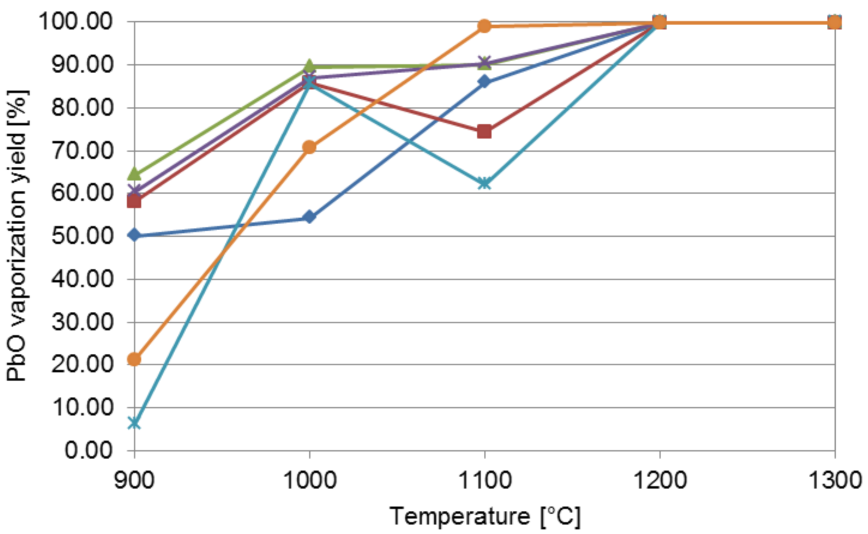


Figure 8-10: PbO vaporization yield for trials investigating the influence of treatment temperature and the influence of fluorine compounds (◆ NaF, ■ PbF_2, ▲ KF, × ZnF_2, ✳ CaF_2, ● FeF_2)

This is underlined by the fact that in the fluorine trials, which have lower amounts of halides compared to the chlorine trials, the lead oxide yield is also lower. In a following chapter this circumstance is discussed in detail, including thermochemical calculations describing possible interaction reactions.

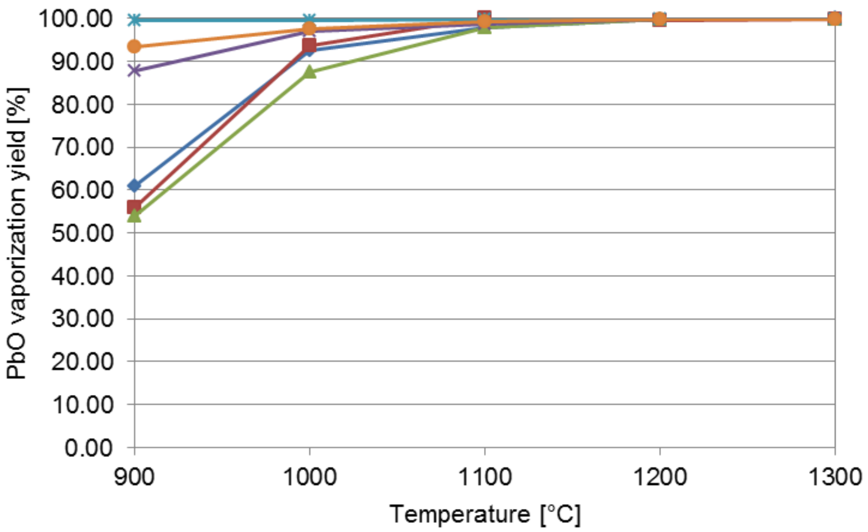


Figure 8-11: PbO vaporization yield for trials investigating the influence of treatment temperature and the influence of chlorine compounds (◆ NaCl, ■ $PbCl_2$, ▲ KCl, × $ZnCl_2$, ✳ $CaCl_2$, ● $FeCl_2$)

8.2.1.2.2 Variation of treatment time

This chapter describes the vaporization results as a function of the treatment time. Here, the temperature was kept constant at 1100 °C, with the same experimental set-up as in the previously described series, investigating the influence of temperature.

In general it can be stated that the mass loss and with that the overall vaporization increase with progressing treatment time (see Table 8-7).

Table 8-7: Summary of overall vaporization yield as a function of the treatment time (influence of treatment time at a constant temperature of 1100 °C) [72]

Time/trial	1 - NaF	2 - PbF_2	3 - KF	4 - ZnF_2	5 - CaF_2	6 - FeF_2
5	3.69	3.59	3.79	4.19	4.61	4.03
10	4.96	5.72	5.39	5.09	4.68	5.44
20	6.78	7.31	6.61	7.27	6.86	6.57
30	8.25	8.39	8.37	8.60	7.79	8.10
60	10.85	10.71	13.64	12.80	11.07	10.67
Time/trial	7 - NaCl	8 - $PbCl_2$	9 - KCl	10 - $ZnCl_2$	11 - $CaCl_2$	12 - $FeCl_2$
5	2.95	10.34	4.32	17.11	8.76	15.60
10	6.08	12.03	9.61	16.50	14.14	15.66
20	11.35	13.37	14.87	16.22	16.97	16.48
30	12.19	14.79	16.52	16.99	17.78	16.70
60	16.07	14.52	15.83	14.08	15.30	13.51

Figure 8-12 shows that at constant temperature (1100 °C) the overall yield of theoretically 11 % volatile compounds (PbO and halide) is reached after approximately 60 minutes. The related results show a steady increase even at the end of the trial. This demonstrates the necessity for longer treatment times, in case of low halide contents in the material, to remove the lead oxide efficiently (see Figure 8-17).

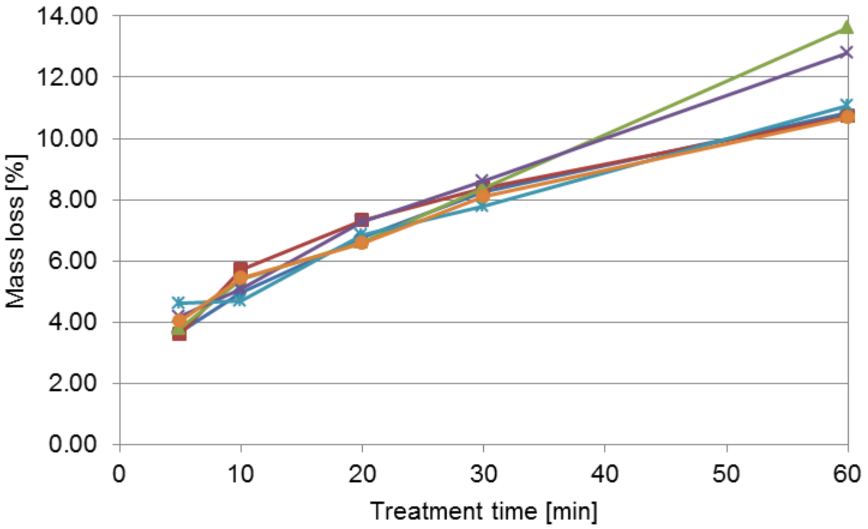


Figure 8-12: Overall vaporization yield for trials investigating the influence of treatment time and the influence of fluorine compounds (—◆— NaF, —■— PbF_2, —▲— KF, —×— ZnF_2, —✳— CaF_2, —●— FeF_2)

In comparison to the fluorine trials, the chlorine trials (see Figure 8-13) show a curve progression. This underlines the fact that either the lead oxide or the halides have no linear vaporization or that the ratio of halide to lead oxide influences the speed of vaporization by, for example, chemical reactions. Attributable to that, in both trials (chlorine and fluorine) nearly the same amount of lead oxide is present; it is unlikely that the lead oxide alone is responsible for that circumstance.

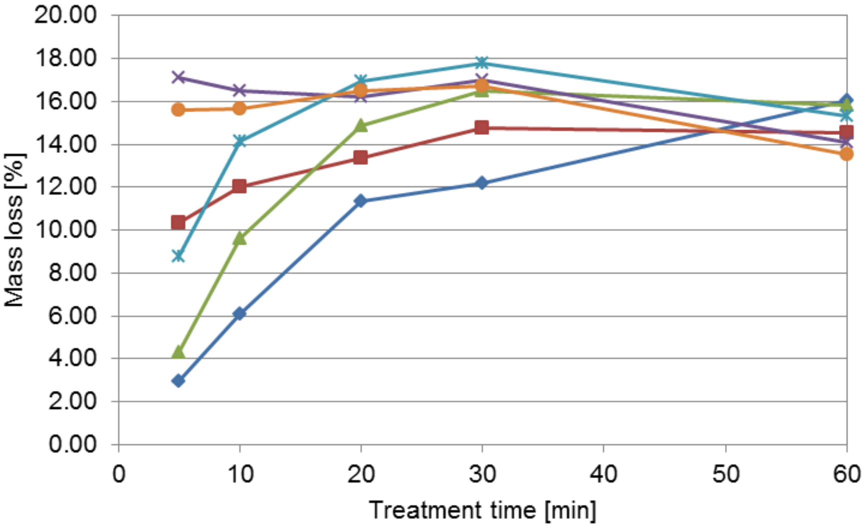


Figure 8-13: Overall vaporization yield for trials investigating the influence of treatment time and the influence of chlorine compounds (—◆— NaCl, —■— $PbCl_2$, —▲— KCl, —×— $ZnCl_2$, —✳— $CaCl_2$, —●— $FeCl_2$)

In most cases the theoretical amount of 15 % volatile compounds is reached earlier (after 20-30 min) compared to the fluorine trials.

The results of the halide vaporization are summarized in Table 8-8.

Table 8-8: Summary of halide vaporization yield depending on treatment time [72]

Time/trial	1 - NaF	2 - PbF_2	3 - KF	4 - ZnF_2	5 - CaF_2	6 - FeF_2
5	26.15	69.15	73.73	84.49	8.63	83.54
10	70.85	95.78	94.26	97.70	18.41	97.68
20	97.96	97.63	98.87	99.00	29.77	99.08
30	99.20	97.66	98.89	99.01	34.23	99.10
60	99.22	97.71	98.95	99.06	61.94	99.12
Time/trial	7 - NaCl	8 - $PbCl_2$	9 - KCl	10 - $ZnCl_2$	11 - $CaCl_2$	12 - $FeCl_2$
5	29.64	80.43	29.65	97.73	38.24	97.84
10	54.48	95.08	76.40	97.71	71.61	97.85
20	97.91	95.15	97.45	97.70	88.50	97.87
30	97.93	95.23	97.49	97.72	90.08	97.87
60	98.03	95.22	97.48	97.64	98.11	97.79

Concerning the fluorine yields (see Figure 8-14), it is illustrated that especially calcium fluoride can cause problems because of the long necessary treatment time to achieve satisfying fluorine removal results. The fluorine yields of the other compounds are above 97 % after 20 minutes. In case of the chlorine compounds, again the calcium compound is the one which is most difficult to vaporize or to interact with lead oxide.

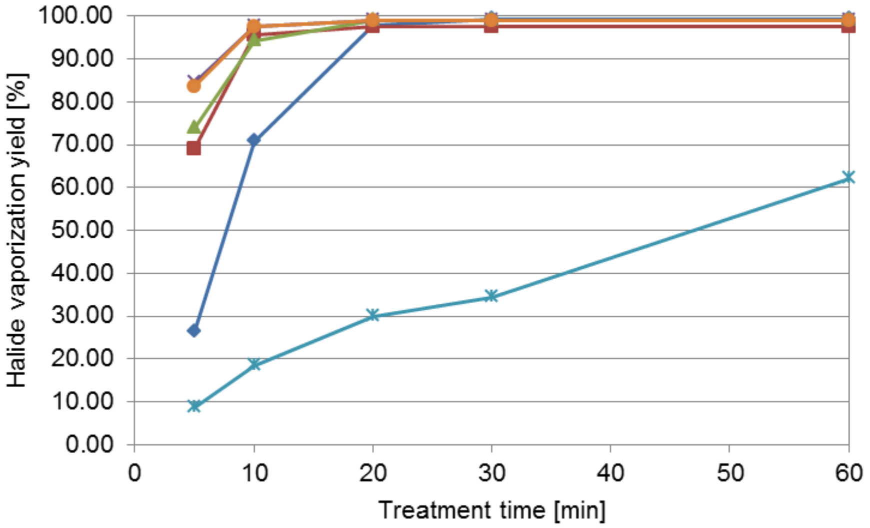


Figure 8-14: Halide vaporization yield for trials investigating the influence of treatment time and the influence of fluorine compounds (—◆— NaF, —■— PbF_2, —▲— KF, —×— ZnF_2, —✳— CaF_2, —●— FeF_2)

Figure 8-15 shows that after 20 minutes good chlorine removal yields can be achieved. Three compounds which are quite difficult to remove are sodium-, potassium- and calcium chloride. It seems that sodium and potassium act in a similar manner, which is underlined by the lead oxide yields of the mentioned trials (see Figure 8-16). It can be seen that calcium chloride supports the lead oxide yield, while sodium and potassium lead to a slower removal of lead.

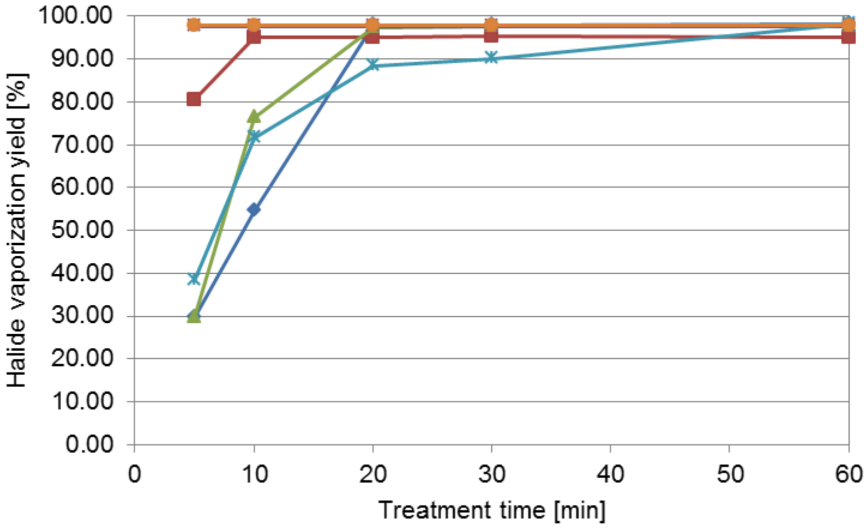


Figure 8-15: Halide vaporization yield for trials investigating the influence of treatment time and the influence of chlorine compounds (◆ NaCl, ■ $PbCl_2$, ▲ KCl, × $ZnCl_2$, ✳ $CaCl_2$, ● $FeCl_2$)

Table 8-9 shows the lead oxide yields for the trials with varying treatment times.

Table 8-9: Summary of lead oxide vaporization yield for the trials with varying treatment times [72]

Time/trial	1 - NaF	2 - PbF_2	3 - KF	4 - ZnF_2	5 - CaF_2	6 - FeF_2
5	7.37	4.97	12.75	12.10	16.49	9.65
10	13.42	24.21	18.69	27.44	22.71	15.49
20	33.51	39.13	42.07	28.81	41.73	38.83
30	48.05	49.13	54.71	62.50	49.26	39.44
60	85.94	74.49	89.95	90.42	74.91	70.76
Time/trial	7 - NaCl	8 - $PbCl_2$	9 - KCl	10 - $ZnCl_2$	11 - $CaCl_2$	12 - $FeCl_2$
5	15.76	20.51	20.58	96.77	41.45	93.87
10	16.49	19.43	19.87	99.21	86.83	97.96
20	41.20	52.25	51.33	99.44	99.22	99.21
30	64.09	61.74	72.82	99.55	99.78	99.55
60	97.97	100.00	97.96	98.84	99.73	99.18

In the following two figures, the lead oxide yields are illustrated. Figure 8-15 shows that corresponding with the vapour pressure curves, zinc and iron chloride are possible to be vaporized very effectively. An interesting aspect is that in both cases, also the lead oxide evaporation shows an increased speed compared to the other compounds. Additionally, the $CaCl_2$ can be removed very effectively although it has the worst vapour pressure compared to the other chlorine compounds investigated. The reason for this most probably can be found in interaction reactions of compounds forming more volatile reaction products, which is described in the next chapter, “Thermochemical considerations”.

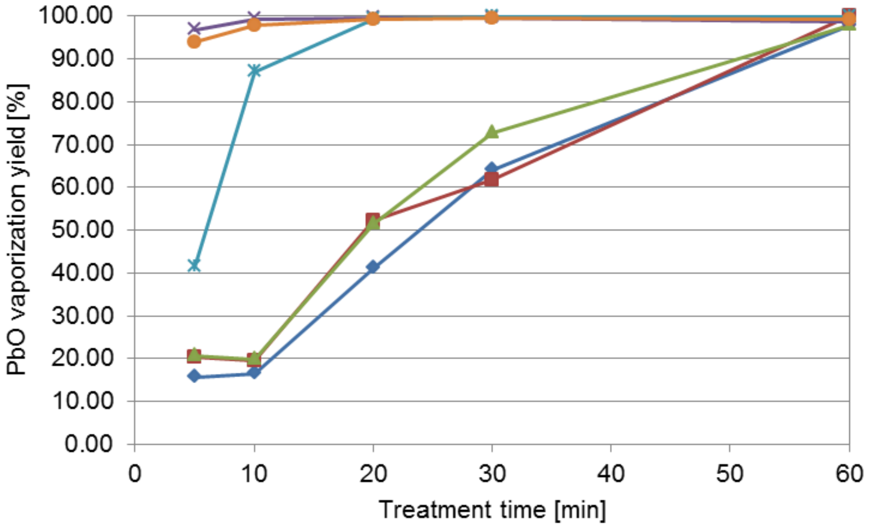


Figure 8-16: PbO vaporization yield for trials investigating the influence of treatment time and the influence of chlorine compounds (—◆— NaCl, —■— $PbCl_2$, —▲— KCl, —×— $ZnCl_2$, —✳— $CaCl_2$, —●— $FeCl_2$)

The lead oxide yield from the fluorine trials (see Figure 8-17) shows a very straight development, especially after 20 minutes treatment time. The reason for this is most likely that after 20-30 minutes, most of the fluorine is vaporized and therefore only the vapour pressure of the remaining lead oxide is responsible for the removal and no interaction reactions can take place.

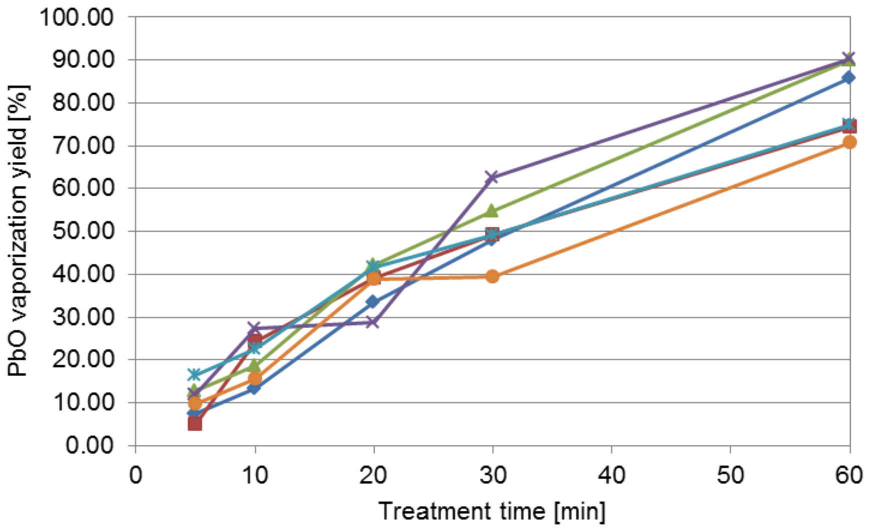


Figure 8-17: PbO vaporization yield for trials investigating the influence of treatment time and the influence of fluorine compounds (—◆— NaF, —■— PbF$_2$, —▲— KF, —×— ZnF$_2$, —✳— CaF$_2$, —●— FeF$_2$)

8.2.1.3 Thermochemical considerations

The previously described results of the selective vaporization trials showed interesting vaporization rates, especially in the case of CaF_2, where the expected elimination was lower than the one achieved as well as very high yields in lead oxide volatilization during the trials with $ZnCl_2$, $FeCl_2$ and $CaCl_2$. This leads to the assumption that interaction reactions occur and support the vaporization of halogen as well as lead.

Thermochemical calculations were carried out with the composition of the synthetic mixtures used in the lab scale trials as calculation base. Table 8-10 shows the initial amount used in kmol. To simulate a furnace atmosphere, an excess amount of air (79 kmol N_2, 21 kmol O_2) was assumed.

Table 8-10: Assumption for thermochemical calculations (based on synthetic mixtures)

Compound [kmol]	Case 1 $FeCl_2$	Case 2 $ZnCl_2$	Case 3 $CaCl_2$	Case 4 CaF_2
ZnO	1.044	1.044	1.044	1.093
PbO	0.036	0.036	0.036	0.045
$FeCl_2$	0.055			
$ZnCl_2$		0.051		
$CaCl_2$			0.063	
CaF_2				0.013

The following figures display the calculated equilibrium amount for four different cases, shown in the table above.

Cases 1 (Figure 8-18) to 3 (Figure 8-20) show a possible formation of volatile compounds in the area of 1100 °C, partly starting at temperatures of 800-900 °C, which are most probably responsible for the high lead oxide and halide yield. As a result of the formation of these compounds with higher vapour pressure ($PbCl_{2(g)}$ and $ZnCl_{2(g)}$) than the investigated halide compounds ($FeCl_2$ and $CaCl_2$), the yield can be increased by a reaction of the investigated halide with the matrix (PbO or ZnO). Possible reactions can be:

$FeCl_2 + ZnO \leftrightarrow ZnCl_{2(g)} + FeO$ Equ. 8-1

$FeCl_2 + PbO_{(g)} \leftrightarrow PbCl_{2(g)} + FeO$ Equ. 8-2

$CaCl_2 + ZnO \leftrightarrow ZnCl_{2(g)} + CaO$ Equ. 8-3

$CaCl_2 + PbO_{(g)} \leftrightarrow PbCl_{2(g)} + CaO$ Equ. 8-4

Although the volatile compound $PbCl_{4(g)}$ is also stable below a temperature of 1000 °C, the more probable reaction is to $PbCl_{2(g)}$ above 1000 °C. The reason for this can be found in reaction kinetics. As a consequence of not gaseous reaction partners present at temperatures lower than 1000 °C, the probability of reacting is less than above, where lead oxide gets volatile and with that offers the opportunity for a solid-gas reaction. The same reason is responsible for, why the reaction to lead dichloride is more probable than to zinc dichloride.

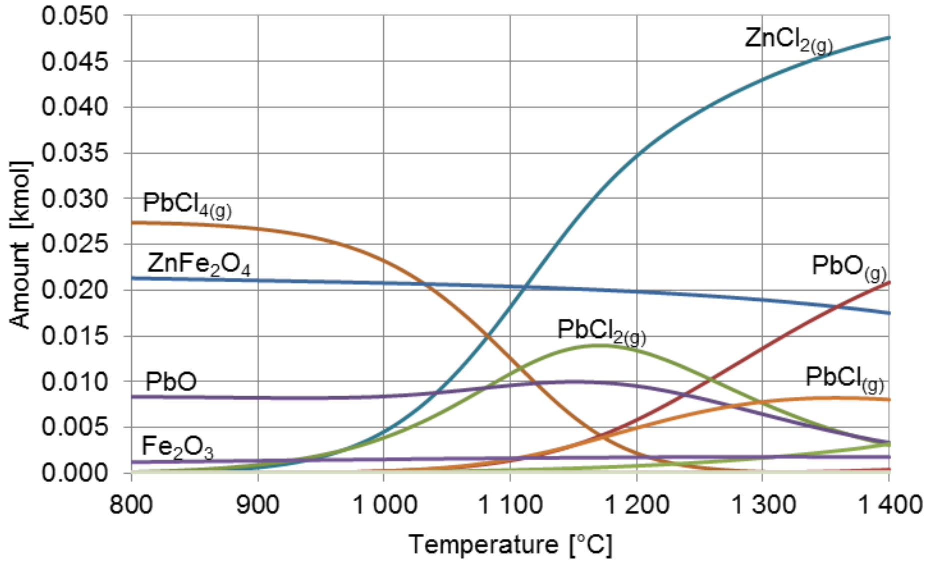


Figure 8-18: Equilibrium amount calculated for case 1 ($FeCl_2$)

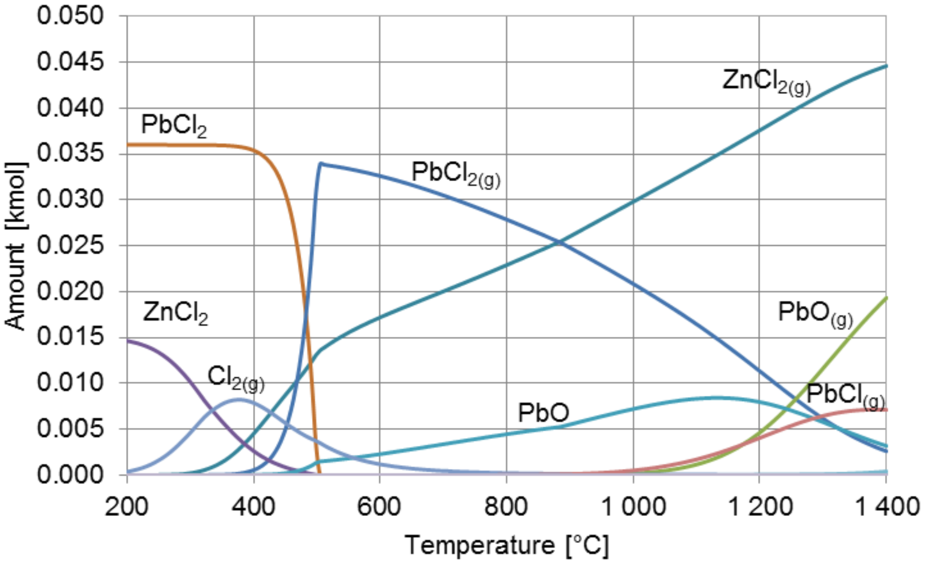


Figure 8-19: Equilibrium amount calculated for case 2 ($ZnCl_2$)

It can be seen in Figure 8-19 that $PbCl_{2(g)}$ and $ZnCl_{2(g)}$ are co-existent next to each other, and based on the volatility shown in the calculated vapour pressure curves, a further possible reaction could be as follows:

$$PbCl_{2(g)} + ZnO \leftrightarrow ZnCl_{2(g)} + PbO_{(g)} \quad \text{Equ. 8-5}$$

This would not really influence the halide and the lead oxide yield but would lead to unwanted losses of zinc.

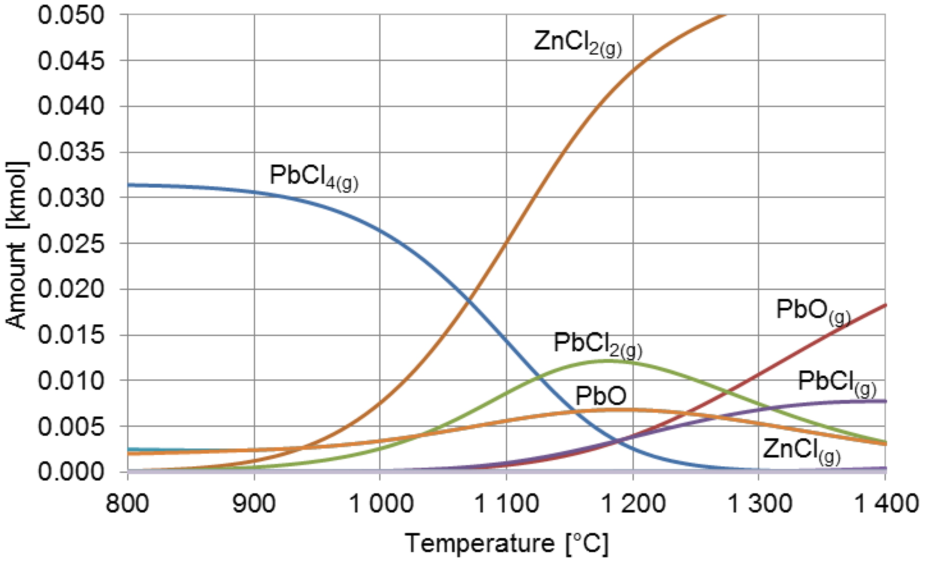


Figure 8-20: Equilibrium amount calculated for case 3 ($CaCl_2$)

Case 4 describes the experiment with CaF_2 as the impurity. It is shown that starting at 700-800 °C a lead(IV) fluoride ($PbF_{4(g)}$) as well as a lead(II) fluoride (starting at 1100 °C) can be formed, which are both volatile. This describes a possible scenario why the fluorine content can be decreased (see Figure 8-14), although the vapour pressure of calcium fluoride at a treatment temperature of 1100 °C is close to zero.

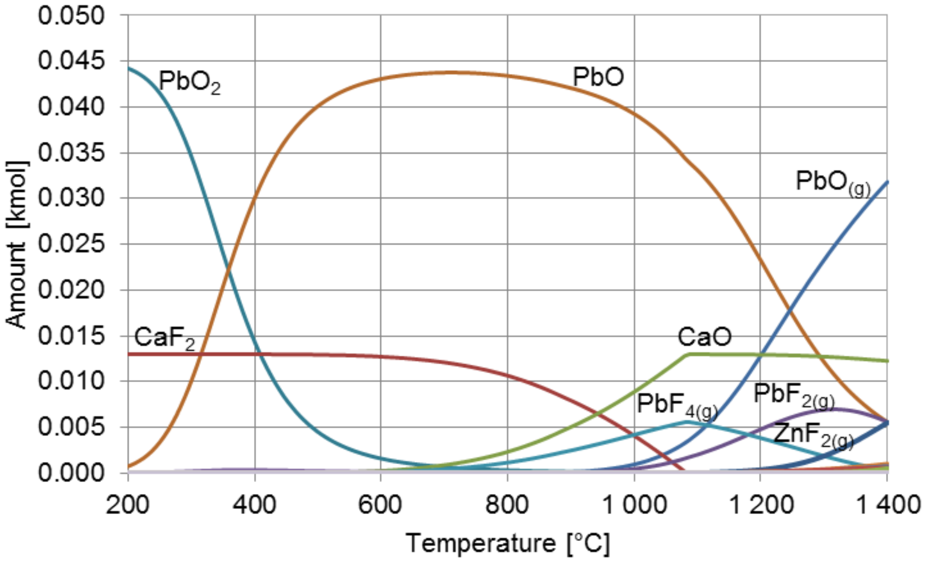


Figure 8-21: Equilibrium amount calculated for case 4 (CaF_2)

8.2.1.4 Discussion

Based on the chemical analysis of the clinkered material (see Appendix), the thesis of interaction reactions can be validated. In the following table, the relevant analysis is summarized for the calculated cases.

Table 8-11: Chemical analysis of selected clinkered synthetic mixtures

Trial	Cl [%]	element [%]	Trial	F [%]	element [%]
$FeCl_2$	<0.1	4.00 Fe	FeF_2	0.004	0.48 Fe
$CaCl_2$	<0.1	2.66 Ca	CaF_2	0.21	0.66 Ca
KCl	<0.1	<0.01 K	KF	0.004	<0.01 K
NaCl	<0.1	<0.01 Na	NaF	0.004	<0.02 Na

It is demonstrated that in trials with iron and calcium chloride, a rest of the metal (Ca, Fe) from the halide can be found in the clinkered sample, although the chlorine content is more or less zero (<0.1 %). For a comparison, the chemical analysis of potassium and sodium trials is also shown in the table above. This also fits to the fact that similar yields of the two stated compounds can be found as well as a remaining metal content (Ca, Fe) from the halide, now bound as oxide. Again this can also be found for KCl and NaCl, where the yield is similar but the rest element content is very low (<0.01 %), which makes it likely that in these cases no interaction reactions occur or a further mechanism has to be considered, which minimizes the remaining amount of reaction products (oxides). A possible explanation for this could be the dissociation of resulting oxides from interaction reactions (Na_2O or K_2O). Thermochemical calculations show that at temperatures above 800-900 °C, a possible separation takes place.

For the other investigated compounds - $ZnCl_2$, $PbCl_2$, PbF_2 and ZnF_2 - it is almost certainly also true that interaction reactions occur but could not be verified as a result of the matrix, which consists of PbO and ZnO (the possible reaction products), although it is very likely.

The practical trials showed that especially in case of present lead oxide as well as halides, different interaction reactions occur which influence the yield of the two reaction partners and lead to wanted or partly unwanted reaction products.

An example is for instance that, although good yields of fluorine and lead can be achieved, a reaction product (typically an oxide) is formed which cannot be removed easily in every case. Calculations showed reaction products like e.g. Na_2O or K_2O, which can split or evaporate and as a consequence no remaining (disturbing) reaction product was found after the trials. Regarding calcium and iron compounds, a rest content of the element (oxide) was detected while on the other hand no halogen remained, which underlines the fact of occurring reactions as well as splitting under oxidizing atmosphere. This was also verified by the thermochemical calculations carried out.

The literature survey also showed that especially in case of iron chloride, nearly no vaporization takes place and a complete reaction with e.g. lead oxide could happen. But also in case of no present lead oxide, the chlorine compound can be split to an oxide if an oxidizing atmosphere (e.g. air) is present. The same behaviour can be found for calcium chloride.

<u>Halide compounds:</u>

Thermochemical calculations showed the viability and the practical trials carried out showed that satisfying yields (>95%) were achieved after 20-30 minutes at constant treatment temperatures of 1100 °C. The most problematic compounds – with the lowest vaporization intensity – are calcium chloride as well as calcium fluoride.

It was shown that also 900 °C and a treatment time of 60 minutes lead to very low rest halogen contents in the clinker.

In case of fluorine compounds it seems that a temperature below 900 °C is problematic and would increase the necessary retention time. Another interesting aspect is that at 1300 °C a worse yield than at 1100 or 1200 °C can be found. One possible reason for this could be that the fluorine yield is related to the lead oxide content, its vaporization speed, etc., which would mean that at very high temperatures, where the lead removal occurs fast, less time for a possible reaction is given and with this the fluorine yield is lower. This is underlined by the lead oxide yields. It can be seen from the figures that the higher the temperature, the better the yield, and with this, the vaporization speed is also increased, leading to less possible reaction time with the halide.

Lead oxide:

The behaviour of lead oxide is easily described. Related to the volatile character of lead oxide, lead chloride and lead fluoride, it is difficult to determine possible interaction reactions based on the lead yield. To verify occurring interaction reactions, the remaining metal content in the clinker from the halide has to be taken into account.

It can be clearly seen that with increasing temperature and treatment time, the yield of lead increases continuously. Trials showed that 1100-1200 °C and a treatment time of 60 minutes lead to a more or less complete removal of lead.

In case of a constant temperature of 1100 °C, the necessary retention time for a satisfying removal was mainly influenced by the amount of present halide as well as the type of halide. As a result of the higher volatility of lead chloride or fluoride compared to lead oxide, higher halide contents increased the lead yield.

Remaining metal content from the halide:

It was shown that especially calcium and iron form reaction products (oxides) which are not volatile and remain in the clinker product. In the case of potassium and sodium chloride, the thermochemical calculations carried out showed that the reaction product (the oxide) also tends to split and evaporate and with this does not remain in the product after the treatment.

8.2.2 Addition of chemicals with the aim of increased lead oxide vaporization

The background idea of the subsequently described investigations is to increase the lead oxide vaporization speed to form a more economical process by reducing the required retention time or to lower the necessary treatment temperature and with this require less energy for the same results.

Due to that, the lead oxide yield varied in the former trials, although the chemical used – lead oxide – was always the same; the fact that with halides, the vaporization yield can be influenced, is obvious. The addition of three different halides (NaCl, $CaCl_2$, $ZnCl_2$) is evaluated to achieve the aforementioned targets.

In the same way as described in the previous chapter, synthetic mixtures were used for these investigations. The aspired reactions of the carried out trials are shown below:

$PbO + ZnCl_2 \leftrightarrow PbCl_2 + ZnO$ Equ. 8-6

$PbO + CaCl_2 \leftrightarrow PbCl_2 + CaO$ Equ. 8-7

$PbO + 2NaCl \leftrightarrow PbCl_2 + Na_2O$ Equ. 8-8

This would add a further advantage to a process concept for product upgrade. It could be summarized as a more complete evaporation of lead oxide, lower necessary treatment temperature as well as shorter retention time.

The reason why only chlorine compounds were evaluated is because in the industrial material, high contents of chlorine compounds are present (mainly NaCl and KCl). So on the one hand no new impurity is introduced, while on the other hand it was already determined that the chlorine removal is possible with satisfying results and therefore no further difficulties are expected with the addition of chlorine compounds. The fluorine content in typical waelz oxide is low and the removal is linked to difficulties, which is the reason for avoiding using them as additives.

8.2.2.1 Trial set-up

The facility used, the “Carbolite incineration furnace,” was the same as in the previous experiments.

8.2.2.2 Sample preparation and experiment procedure

The first step was to prepare the synthetic mixtures. In the process, a base of 92 % zinc oxide and 8 % lead oxide was used.

Depending on the investigated chemical addition (NaCl, $CaCl_2$ or $ZnCl_2$) and the stoichiometry, the following compositions (see Tables 8-12 to 8-14) were used for the experiments:

Table 8-12: Synthetic mixtures used for the trials with $ZnCl_2$ addition

Synthetic mixture/ Stoichiometry	1	2	3
ZnO [%]	87.72	83.81	80.24
PbO [%]	7.63	7.29	6.98
$ZnCl_2$ [%]	4.66	8.90	12.78

Table 8-13: Synthetic mixtures used for the trials with $CaCl_2$ addition

Synthetic mixture/ Stoichiometry	1	2	3
ZnO [%]	88.48	85.22	82.19
PbO [%]	7.69	7.41	7.15
$CaCl_2$ [%]	3.83	7.37	10.66

Table 8-14: Synthetic mixtures used for the trials with NaCl addition

Synthetic mixture/ Stoichiometry	1	2	3
ZnO [%]	88.30	84.89	81.73
PbO [%]	7.68	7.38	7.11
NaCl [%]	4.02	7.73	11.17

So as to prevent measuring errors, the first step was to heat up the empty ceramic boats to vaporize possible volatile compounds or moisture. After cooling down again, the boats were filled with the synthetic mixture and charged into the hot muffle furnace at the treatment temperature of 1000 °C. To eliminate influences of the sample height, only a small thickness of approximately 1 millimetre was chosen and the material was split and placed in several ceramic boats. After the treatment time, varying from 5 to 60 minutes for each synthetic mixture, the boat was taken out of the furnace and cooled down under air atmosphere.

As a result, the vaporization of lead oxide was calculated based on their mass loss. Additionally, the zinc oxide loss and the remaining reaction product were determined.

8.2.2.3 Results

Subsequently, the vaporization yield of lead oxide, the zinc oxide loss as well as the remaining content of reaction product as a function of the treatment time and varying added halide are discussed.

The experiment temperature was constant in all trials, with 1000 °C.

The detailed raw data like:

- Sample weights (before and after trial → resulting delta) of trials as a function of treatment time
- Chemical analysis of clinkered materials
- Calculated values of lead oxide yield as well as zinc oxide loss, etc.

can be found in the Appendix. In this chapter only the values used for the figures (calculated end results) are summarized in the form of tables and visualized as figures for interpretation.

8.2.2.3.1 Clinkering with the addition of NaCl

Figure 8-22 shows the calculated lead oxide yields for the trials with sodium chloride addition with one, two and three times the stoichiometric amount of required halide added as well as the lead oxide evaporation with no halide addition.

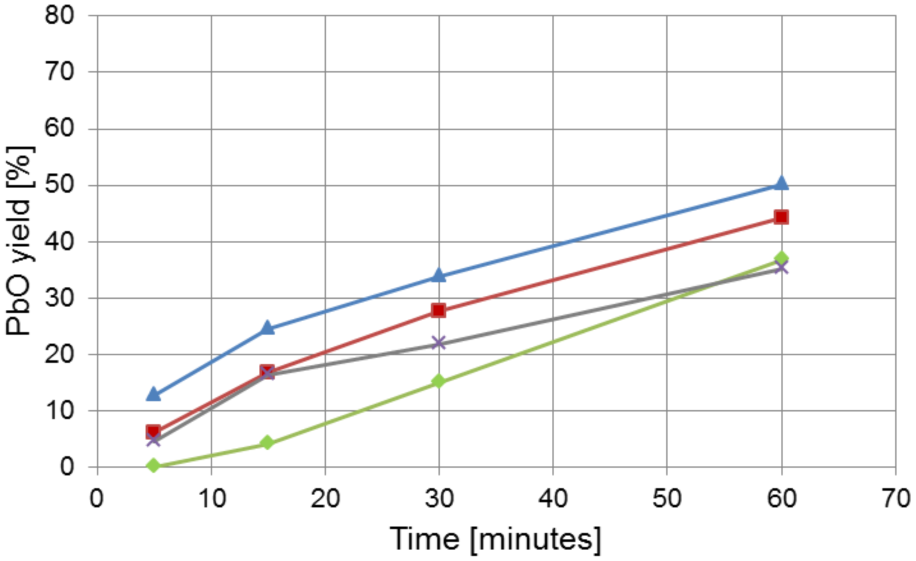


Figure 8-22: PbO-yield of trials with the addition of NaCl as a function of treatment time and varying stoichiometric amount of NaCl (—×— no addition, —◆— 1 time, —■— 2 times, —▲— 3 times)

The diagram shows that the amount of chemical added only has a slight influence on the vaporization of lead oxide. The increase of the theoretically required amount leads, similar to an increased treatment time, to an increased yield. Even in case of three times the addition of the stoichiometric amount needed, the achieved yield after 60 minutes treatment time was only around 50 %.

The lead oxide yield obtained with no halide addition was 35 %, so an increased yield can be determined in case of present sodium chloride.

Table 8-15 shows the calculated zinc oxide losses during the trials. Again they are based on the chemical analysis, responsible for a slight deviation, which is the reason why a negative zinc oxide loss is calculated. This would mean that as a reaction product ZnO is generated, which is impossible in this special case but shows clearly that no significant loss can be expected with the addition of sodium chloride, while at the same time a slight increase of lead oxide was realized.

Table 8-15: Calculated ZnO loss of experiments with NaCl addition

Time [min] / Stoichiometric amount	5	15	30	60
1	1.05	1.02	0.08	0.32
2	0.92	-0.58	-0.70	-0.47
3	1.63	-0.19	-0.46	-0.67

Furthermore, no reaction products (Na_2O) were found in the clinkered material. There are two possible reasons for this:

- No reaction of NaCl and PbO happens or
- the reaction product is volatile itself or split under treatment conditions.

This circumstance will be discussed in one of the following sections.

8.2.2.3.2 Clinkering with the addition of $CaCl_2$

Figure 8-23 shows the calculated lead oxide yields for the trials with calcium chloride addition with one, two or three times the stoichiometric amount of needed halide added.

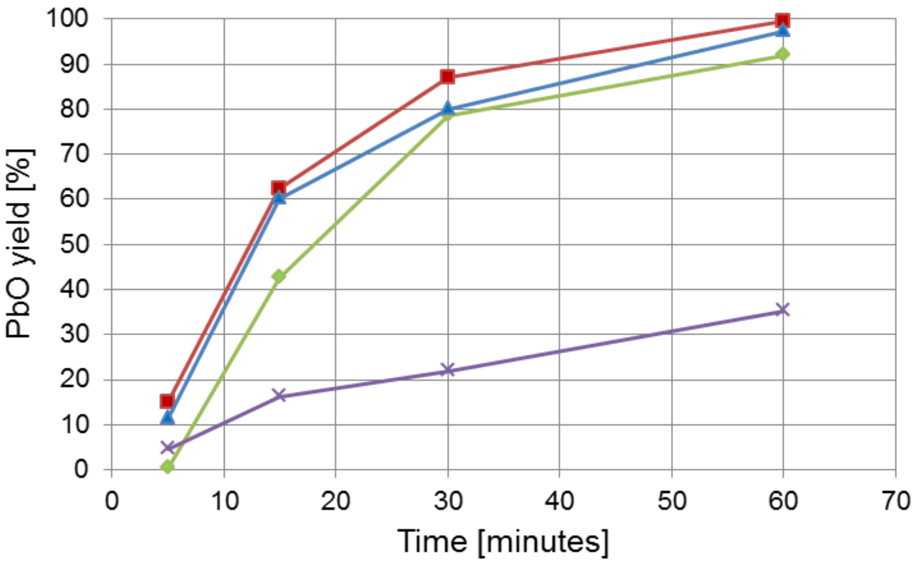


Figure 8-23: PbO-yield of trials with the addition of $CaCl_2$ as a function of treatment time and varying stoichiometric amount of $CaCl_2$ (—×— no addition, —◆— 1 time, —■— 2 times, —▲— 3 times)

The calcium chloride trials show that an increased stoichiometric amount of halide leads to slightly increased lead oxide yields. Although there had been a factor of three in between, only 8 % difference was determined in the final achieved yield after 60 minutes.

The more interesting thing is that the curves show a declining increase compared to the NaCl curves, which have a monotone increase, in the examined time frame. This results in far better yield even after 15 minutes with the $CaCl_2$ addition than after 60 minutes with NaCl.

A disadvantage of the addition of calcium chloride is shown in Table 8-16. With the addition of halide, the zinc oxide loss also increases. So it can be stated that $CaCl_2$ reacts with lead oxide, leading to significantly higher yields than with NaCl, but also leads to unwanted losses of zinc oxide.

Table 8-16: Calculated ZnO loss in experiments with $CaCl_2$ addition

Time [min] / Stoichiometric amount	5	15	30	60
1	2.55	2.71	2.53	2.86
2	2.64	1.90	2.62	3.05
3	0.70	3.38	5.32	5.02

Due to increased PbO yields as well as ZnO losses, as a result of the reaction with calcium chloride to volatile lead chloride or zinc chloride, CaO is obtained as a reaction product. CaO has very stable properties and its non-volatile character leads to the fact that it remains in the product.

8.2.2.3.3 Clinkering with the addition of $ZnCl_2$

Figure 8-24 shows the calculated lead oxide yields for the trials with zinc chloride addition with one, two or three times the stoichiometric amount of the halide.

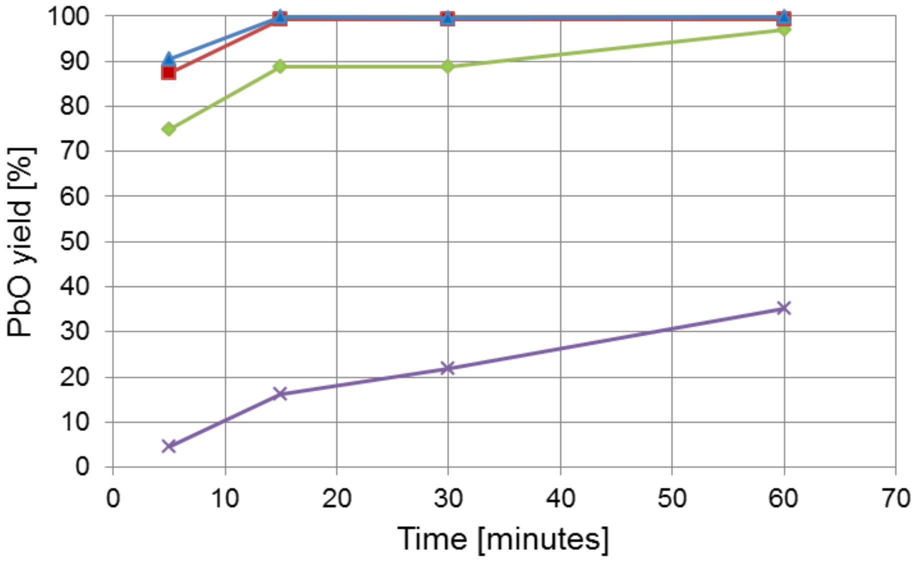


Figure 8-24: PbO-yield of trials with the addition of ZnCl as a function of treatment time and varying stoichiometric amount of $ZnCl_2$ (—×— no addition, —◆— 1 time, —■— 2 times, —▲— 3 times)

First of all, the increased yield of lead oxide even after 15 minutes compared to both other investigated halides (NaCl and $CaCl_2$) is interesting. This leads to very short necessary retention times for a satisfying lead oxide removal in case of a $ZnCl_2$ addition.

As shown in Table 8-17 also the ZnO loss is below zero in case of one and two times the addition of halide.

Table 8-17: Calculated ZnO loss in experiments with $ZnCl_2$ addition

Time [min] / Stoichiometric amount	5	15	30	60
1	-0.83	-0.44	-0.37	-0.80
2	-1.16	-0.44	-0.54	-0.10
3	0.63	0.71	1.11	1.50

In contrast to the NaCl trials, the negative value present in the table above can have two reasons, while one is different from what was originally mentioned:

- Deviation of chemical analysis or more probably
- The presence of the non-volatile reaction product ZnO

Due to the fact that the matrix was also partly zinc oxide, it is difficult to verify if it is an analysis deviation or an obtained reaction product which leads to the “negative” zinc loss.

But, due to the increased lead oxide yield compared to the obtained ones in case of clinkering only the matrix, it seems to be obvious that zinc chloride reacts with lead oxide. This circumstance would inevitably lead to ZnO as a reaction product.

8.2.2.4 Thermochemical calculations

In addition to the trials, equilibrium calculations were carried out with the thermodynamic software HSC Chemistry version 6.12.

In a first step only one mole of lead oxide reacts with one time the amount of the stoichiometric required halide. Once again, based on the analysis of the investigated material it was assumed that lead oxide is mainly present as dioxide and therefore the base for the subsequent calculations. The corresponding reaction equations are shown in the following:

- Addition of NaCl:
  - $PbO + 2\ NaCl \leftrightarrow PbCl_2 + Na_2O$ 0-950 °C Equ. 8-9
  - $PbO + 2\ NaCl \leftrightarrow PbCl_{2(g)} + Na_2O$ 950-1100 °C Equ. 8-10
- Addition of $CaCl_2$:
  - $PbO + CaCl_2 \leftrightarrow PbCl_2 + CaO$ 0-950 °C Equ. 8-11
  - $PbO + CaCl_2 \leftrightarrow PbCl_{2(g)} + CaO$ 950-1100 °C Equ. 8-12
- Addition of $ZnCl_2$:
  - $PbO + ZnCl_2 \leftrightarrow PbCl_2 + ZnO$ 0-730 °C Equ. 8-13
  - $PbO + ZnCl_{2(g)} \leftrightarrow PbCl_2 + ZnO$ 730-950 °C Equ. 8-14
  - $PbO + ZnCl_{2(g)} \leftrightarrow PbCl_{2(g)} + ZnO$ 950-1100 °C Equ. 8-15

It can be seen from the equations that the melting of the compounds is considered in the programme itself, while the changeover of the phase to the gaseous state has to be considered by separate equations.

Figures 8-25, 8-28 and 8-29 show the thermodynamic properties, enthalpy, entropy, Gibbs free energy as well as the corresponding equilibrium constant of the equation of all three investigated reactions.

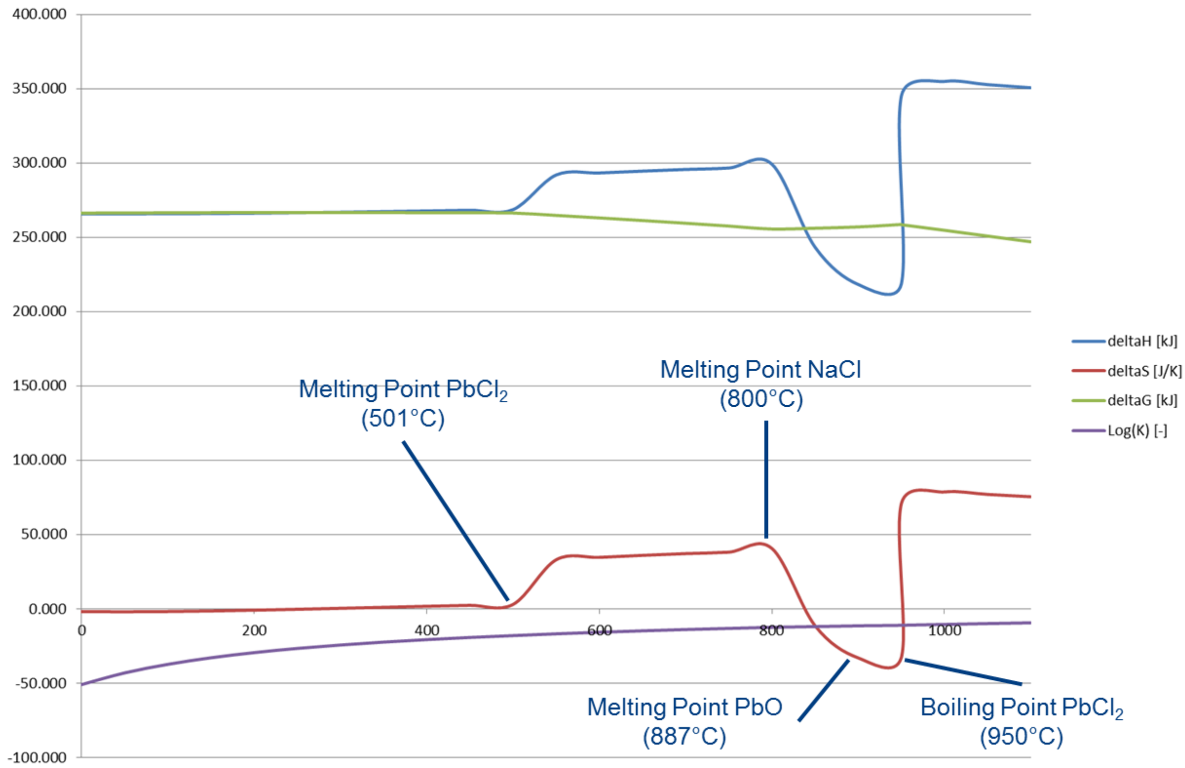


Figure 8-25: Thermodynamic properties of the reaction with NaCl as a function of the temperature for one mole lead oxide (— delta H [kJ], — delta S [J/K], — delta G [kJ], — log(k))

The Gibbs free energy is of special interest, since it is responsible for whether the reaction is thermodynamically autonomous elapsing.

The calculations for one mole of lead oxide show that in case of sodium chloride the Gibbs free energy is highly positive, demonstrating that the reaction does not take place. Below, further calculations simulating an excess amount of atmosphere in a potential furnace are done, influencing the partial pressure of the gaseous compounds. This is the reason why the result shown above differs from the ones obtained during the experiments.

The same mole of reactant as above were assumed but with different volumes of atmosphere in the system. Nitrogen was chosen as the added gas because it does not play a part in the investigated reaction.

Figures 8-26 and 8-27 show the two cases, investigating the influence of present atmosphere and with that the partial pressure of gaseous compounds. The added volume of excess amount of atmosphere was 0.1 mole of nitrogen in case 1 and 790 mole of nitrogen in case 2.

Typically, thermodynamic software needs defined system borders to be able to calculate equilibrium states. Attributable to the fact that it cannot calculate open systems, as it is present in industrial conditions where furnace atmospheres are exchanged continuously during a metallurgical process, the only way of simulating such behaviour is by adding huge excess amounts of inert atmosphere to the system, calculated by the thermodynamic software. With this the partial pressure of gaseuos compounds can be decreased to a low value where the influence on the other reactions of the system is minimized.

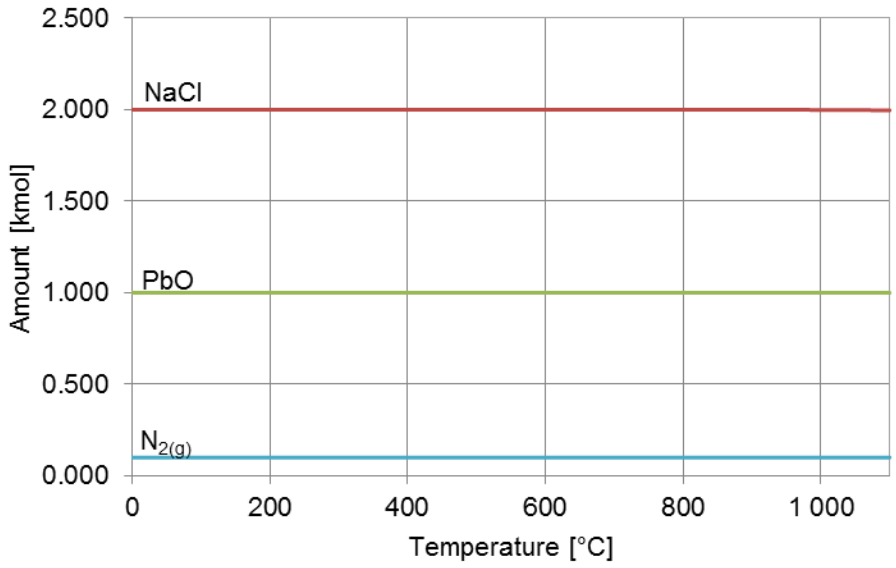


Figure 8-26: Case 1: Reaction of 2 mole NaCl with 1 mole PbO and 0.1 mole nitrogen atmosphere

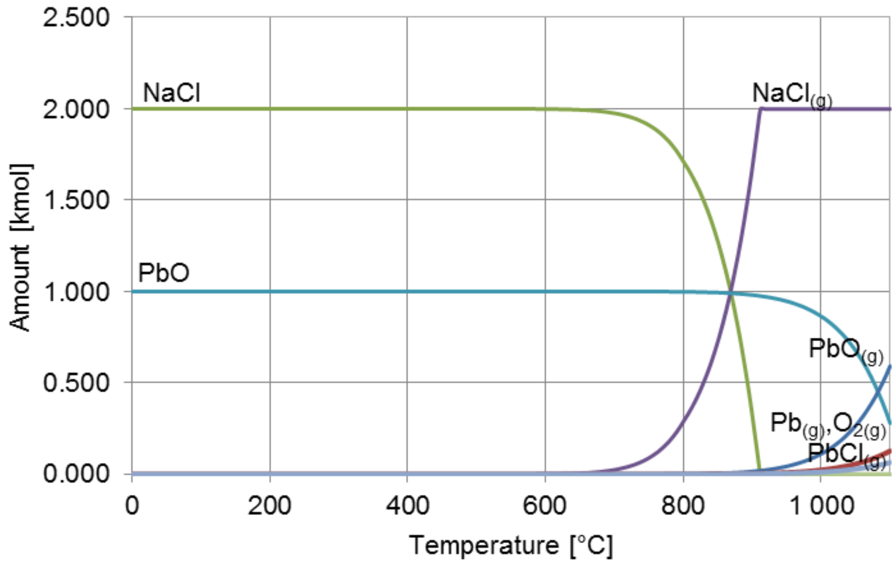


Figure 8-27: Case 2: Reaction of 2 mole NaCl with 1 mole PbO and 790 mole nitrogen atmosphere

It is shown in the equilibrium calculation above that the difference between an open or closed system can influence the results significantly, although case 2 just simulates an open system. Figure 8-27 illustrates clearly that sodium chloride in the gaseous state can be found, although its boiling point is with 1465 °C far above the present temperatures. The same situation is present in the case of lead oxide as well as lead chloride, which is the question answered already as to why the vaporization of lead oxide can be supported by sodium chloride even though the boiling points of reactants are not reached and the equilibrium of the equation lies on the reactant's side.

In case of calcium chloride, up to a value of 1100 °C, the Gibbs free energy is positive and from 1100 °C it becomes increasingly negative. This is the reason why Equation 8-12 runs efficiently above 1100 °C. What is not considered in these calculations is that the partial pressure of formed reaction products also influences the yield. Going hand in hand with a consideration of the partial pressure, it becomes clear why in practice also at temperatures lower than the calculated ones, an evaporation of lead chloride can occur, which is discussed in the next chapter.

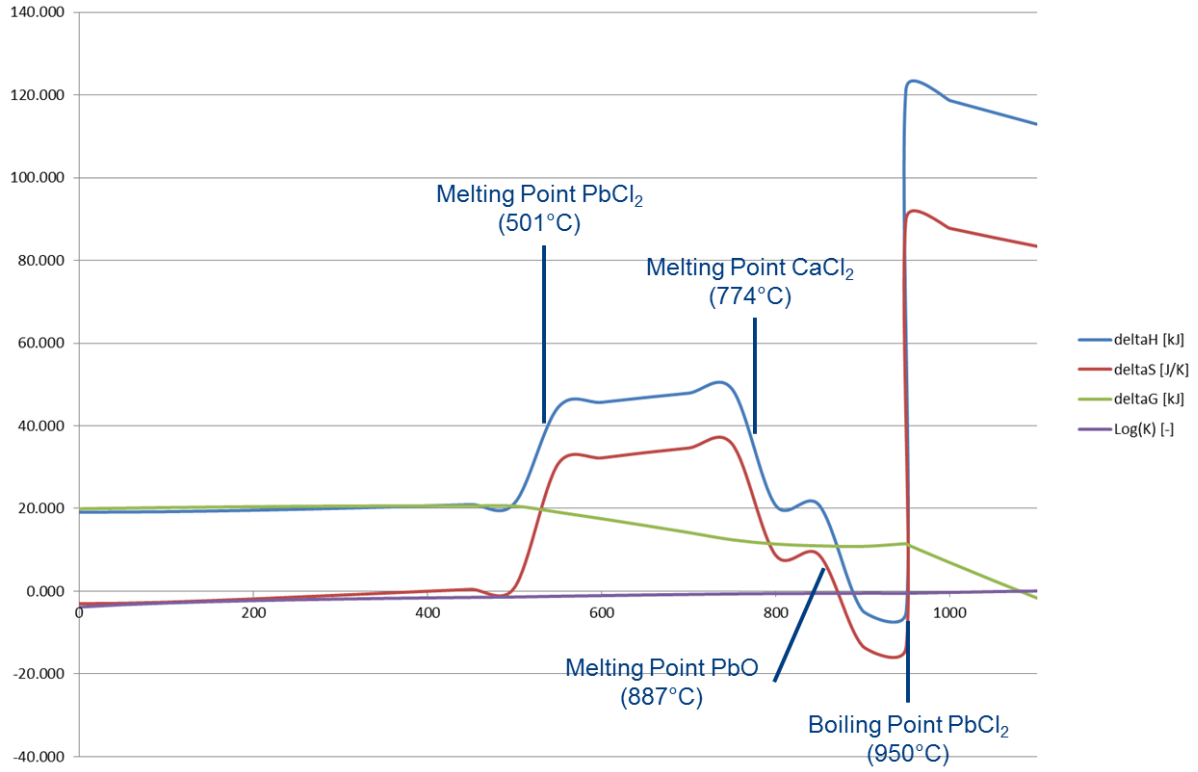


Figure 8-28: Thermodynamic properties of the reaction with $CaCl_2$ as a function of the temperature for one mole lead oxide (— delta H [kJ], — delta S [J/K], — delta G [kJ], — log(k))

Figure 8-29 shows the calculations for the addition of zinc chloride to reach an increased lead oxide yield. It is shown, based on the Gibbs free energy, that in theory, the reaction happens at room temperature. In practice, this does not occur due to kinetic reasons but points out why a satisfying yield within the trials was reached after significantly shorter retention times than with calcium chloride. The reason is the early start of the reaction and with this, the equilibrium constant at treatment temperature is more positive than those of the reactions with calcium chloride or sodium chloride.

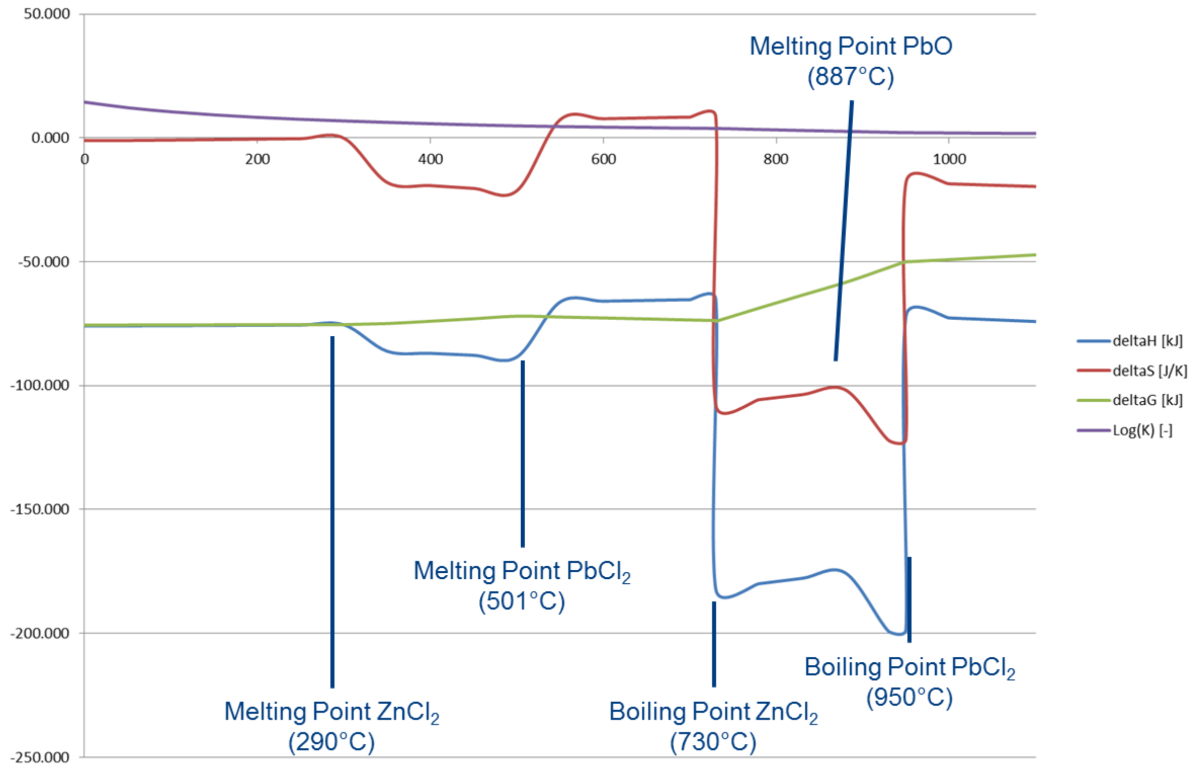


Figure 8-29: Thermodynamic properties of the reaction with $ZnCl_2$ as a function of the temperature for one mole lead oxide (— delta H [kJ], — delta S [J/K], — delta G [kJ], — log(k))

8.2.2.5 Discussion

Summarizing, it can be stated that all three additives (sodium chloride, calcium chloride and zinc chloride) influence the lead vaporization positively. The effect of each additive is summarized and discussed below.

<u>NaCl:</u>

Despite the fact that from the thermochemical point of view it is difficult to support the lead oxide vaporization, with NaCl it was shown that it is possible, taking the partial pressures of the products into account which are low, due to the continuous process, shifting the reaction to the product side according to Le Chatelier's law. This circumstance is underlined by the fact that in the experiments, depending on the added stoichiometric amount of additive, the yield could be increased from no addition (35 %) up to 50 % in case of three times the required amount.

Based on the chemical analysis of the clinkered material, the remaining reaction product was calculated. Considering still present unreacted sodium chloride in all stages, no reaction product could be found. As discussed earlier in this thesis, the reason is that the obtained reaction product would be sodium oxide, which is not stable under clinkering conditions and therefore does not remain in the product.

While the increase in the lead oxide yield is not as high as within the trials with the other two investigated additives, the results obtained are interesting. The reason for this is that typical low quality zinc oxides, like waelz oxide, are mainly contaminated with sodium chloride. So even if the addition of another additive is more meaningful, it is proven that NaCl influences the lead oxide yield positively and does not leave an impurity (reaction product) behind.

$CaCl_2$:

Above 1100 °C thermodynamics show the ability of $CaCl_2$ to support the vaporization of lead oxide by forming lead(II)chloride.

Similar to the case of sodium chloride, the vapour pressure of lead chloride plays a significant role above 950 °C when the boiling point is reached, resulting in satisfying yields also at 1000 °C treatment temperature in the experiments. As previously discussed, this effect can be explained by the continuous change of the atmosphere.

A disadvantage of the usage of $CaCl_2$ compared with the other two additives investigated is that inevitably CaO is formed, which is non-volatile and remains in the product.

$ZnCl_2$:

The addition of zinc chloride has several advantages. First of all, the thermodynamics show a possible reaction also at lower temperatures than 1000 °C, which would lead to economic advantages of a selective vaporization step, due to lower energy consumption. Furthermore, the results were satisfying at very short retention times. Compared to the trials with a calcium chloride addition, where high lead yields were achieved (>99.6 %), the required retention time in case of zinc chloride addition was only a quarter.

Next to that, the reaction product formed is zinc oxide, which is non-volatile and does not form an impurity in the clinkered material. Moreover, it increases the amount of product in the best case by native material. Going hand in hand with that, the zinc oxide loss is almost zero, like in the sodium chloride trials.

Remaining halide content (unreacted additive):

Another key factor is the amount of remaining halide in the product. For this, not only the increased lead oxide vaporization, the zinc oxide loss or possible reaction products are important.

Next to that, the amount of added halide, the necessary treatment time to achieve satisfying lead oxide yields and the kind of used chemical influence the remaining amount of unreacted halide in the clinkered material.

The halide yield was determined, based on the chemical analysis of the generated product. Figure 8-30 shows the results of the trials with all investigated chemical additives for the variation in stoichiometric amount (in brackets behind the additive) and for the treatment times of 30 and 60 minutes.

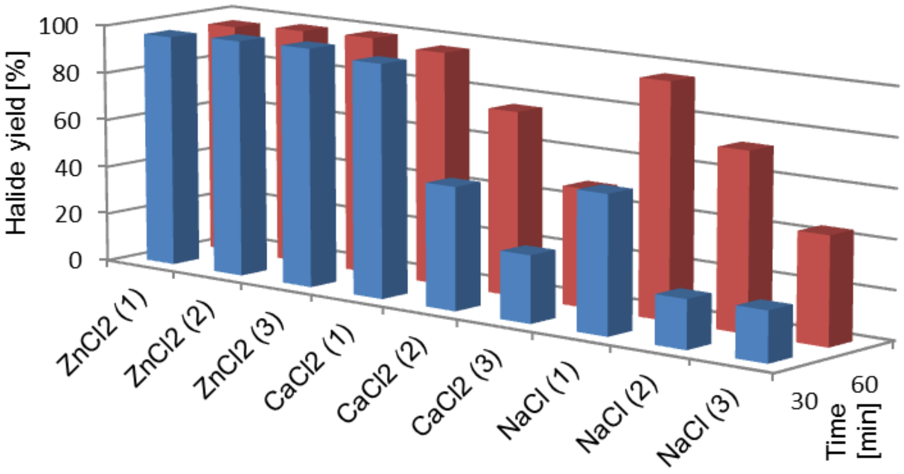


Figure 8-30: Halide yield for the clinkering trials carried out with a retention time of 30 and 60 minutes

From the figure above, it can be seen clearly that the yield of halide in case of sodium chloride and calcium chloride increases with lower stoichiometric addition and with higher treatment time. This means that although the lead oxide yield could be increased with the addition of further halide, the remaining halide in the product increased.

In case of zinc chloride addition, very high halide yields were achieved. More or less all of the compound reacted with lead oxide or vaporized directly, leading to almost no remaining halide in the clinkered material. The reason for this is the low boiling point of zinc chloride, which would cause a complete evaporation regardless of whether a reaction with lead oxide took place or not.

8.2.3 Trials with industrial materials

Along with the previously mentioned trials with synthetic mixtures, investigations with industrial material were carried out. The main aim was to verify the clinkering results and in addition investigate the influence of the industrial atmosphere and furnace conditions.

Especially the influence of $H_2O_{(g)}$ in the furnace atmosphere was of interest, due to the fact that in bigger scale the facilities are not indirectly heated and moreover the common technology based on economic reasons have to be a gas fired facility. The origin of the $H_2O_{(g)}$ present is the combustion of methane or natural gas.

8.2.3.1 Trial set-up

In order to simulate industrial conditions, a rotary kiln was used for the experiments, the objective being to maximize the contact between material and atmosphere. Due to that, the furnace was heated conductively from outside. A combustion box was used for supplying the required atmosphere. This had the advantage that the temperature was easy to control by the electric heating system without having an influence on the atmosphere composition and volume.

Figure 8-31 shows the arrangement of the trial. As it can be seen, the burner is fixed to the combustion box, which has the aim of forming a homogeneous atmosphere before the hot off-gas, carrying the steam and CO_2, is fed by a steel pipe into the ceramic rotary kiln. The second aim of this arrangement is that, in addition to the homogenous off-gas composition, the flame of the burner is not in direct contact with the ceramic kiln, because otherwise, the ceramic can crack due to local thermal expansion, leading to mechanical tension. At the end of the rotary kiln the off-gas, carrying halide vapour and lead compounds, is sucked off by an off-gas system.

Figure 8-31: Experimental set-up for trials investigating industrial furnace conditions

8.2.3.2 Experiment procedure

After preheating the kiln up to the treatment temperature by conductive heating, the burner was regulated to the target gas amount and a lambda higher than one, to prevent unwanted reduction of zinc oxide and with this an unwanted loss. The gas composition was controlled by two mass flow controls linked to a computer. For the trials, a mixture of 30 % of CH_4 and 70 % of oxygen was used to guarantee an oxidizing atmosphere.

The weighted sample material was then charged into the hot furnace, simulating a charging process in industrial scale, where a rapid heat-up phase typically happens.

During the treatment different samples were taken.

8.2.3.3 Thermochemical calculations

The thermochemical calculations were carried out with an excess amount of atmosphere, with the composition of 800 kmol N_2, 100 kmol CO_2, 200 kmol H_2O and 50 kmol O_2. The aim was to verify the possible reactions from the thermodynamic point of view.

Different halides in combination with an industrial type atmosphere were assumed as the starting condition for calculating the equilibrium composition. The excess amount of atmosphere had two tasks, the first was to supply the steam for a possible reaction and the second one was to simulate an exchange of atmosphere in the furnace, which is realized by the huge amount compared to the small halide amount. By doing this, the partial pressure of possible reaction products can be kept low.

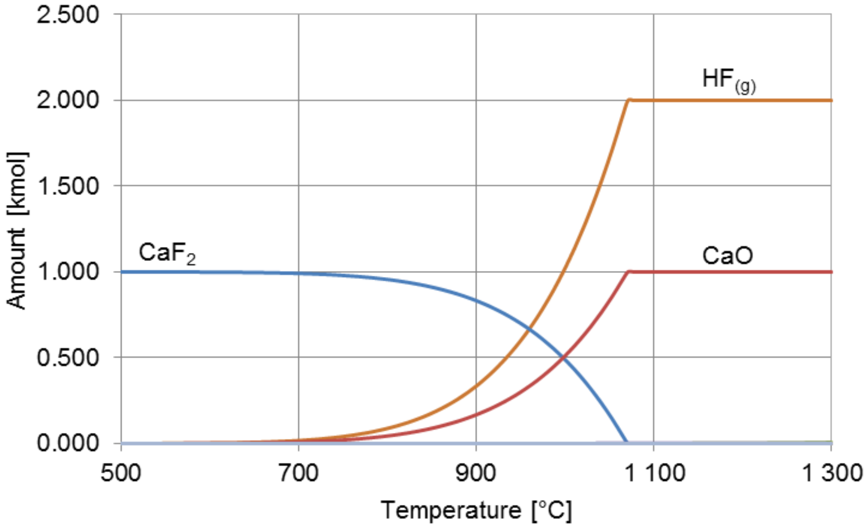


Figure 8-32: Thermochemical calculation on the behaviour of CaF_2 in industrial-like atmosphere as a function of temperature

The main target halides are CaF_2, because it is hard to vaporize and still remains in the clinkered material after long treatment time, as well as NaCl and KCl, based on their main presence in waelz oxide.

Figure 8-32 shows the first equilibrium calculation with 1 kmol CaF_2. It can be seen that, starting at 700 °C, the formation of $HF_{(g)}$ is possible, before a vaporization of CaF_2 occurs. Beside this, CaO as a reaction product is present. Figure 8-33 shows that the main chlorine compounds in waelz oxide are partly affected by $H_2O_{(g)}$. Mainly NaCl reacts with steam to NaOH and HCl, while KCl is vaporized mainly as a halide and only a small portion vaporizes as KOH.

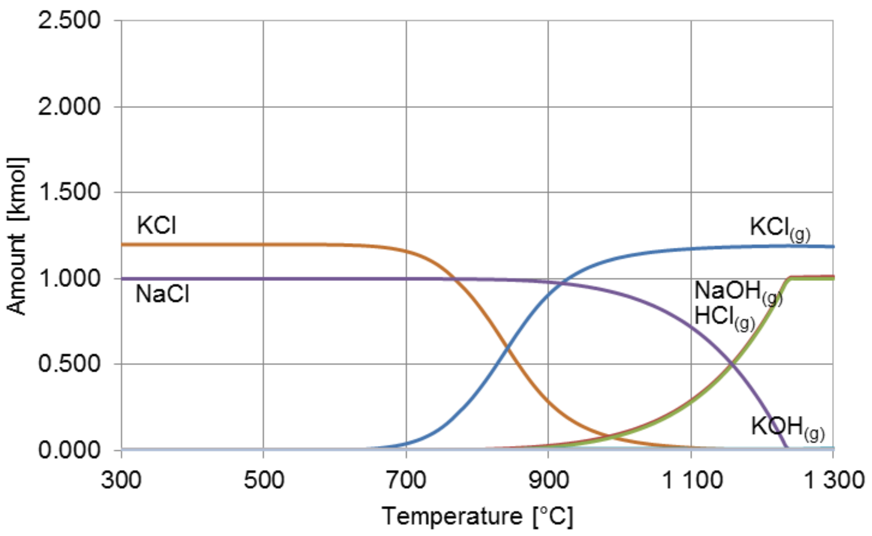


Figure 8-33: Thermochemical calculation on the behaviour of NaCl and KCl in industrial-like atmosphere as a function of temperature

8.2.3.4 Results and discussion

Subsequently, the chemical analysis of the clinkered material under industrial-type conditions is summarized. The following two tables each show two campaigns, one with a gas flow of 1 m³ per hour combusted mixture, 30 % of which had been CH_4 and the rest was oxygen, and the second without gas flow. The one with 0 m³ acts as a reference trial and shows the difference between steam carrying atmosphere and dry air.

It can be seen from Table 8-18 that with elapsing treatment time, the content of chlorine, fluorine as well as lead decreases continuously in the mentioned case of 1100 °C as well as the following one with a treatment temperature of 1200 °C (see Table 8-19).

Table 8-18: Chemical analysis of clinkering trials with steam bearing atmosphere at 1100 °C

	Temp.	Time	Chemical analysis [%]		
Gas	[°C]	[min]	Cl	F	Pb
0 m³/h	1100	5	11.10	0.40	6.57
0 m³/h	1100	15	8.31	0.29	4.06
0 m³/h	1100	25	9.31	0.31	4.74
1 m³/h	1100	5	9.46	0.33	5.75
1 m³/h	1100	15	9.01	0.29	2.17
1 m³/h	1100	25	8.02	0.29	1.17

Below the results of the carried out trials at a treatment temperature of 1200 °C are shown. It can be seen that similar to the results shown above, the steam influences the halide removal positively. Although the same amount of atmosphere was purged through the facility, better results, which mean lower remaining halogen content than in the above mentioned trials at 1100 °C, were obtained, showing the more significant influence of temperature than that of steam.

Table 8-19: Chemical analysis of clinkering trials with steam bearing atmosphere at 1200 °C

	Temp.	Time	Chemical analysis [%]		
Gas	[°C]	[min]	Cl	F	Pb
0 m³/h	1200	5	9.84	0.33	6.96
0 m³/h	1200	15	9.83	0.32	7.07
0 m³/h	1200	25	9.70	0.32	6.60
1 m³/h	1200	5	8.63	0.32	5.98
1 m³/h	1200	15	6.78	0.31	3.14
1 m³/h	1200	25	4.73	0.21	1.53

Due to still too high amounts of lead as well as halogens after 25 minutes, the last carried out trials, shown in the following table, treated the material for one and a half hour.

It can be seen that aside from the temperature, especially the retention time influences the obtained results.

Table 8-20: Chemical analysis of clinkering trials with longer retention time
with steam bearing atmosphere at 1200 °C

	Temp.	Time	Chemical analysis [%]		
Gas	[°C]	[min]	Cl	F	Pb
1 m³/h	1200	30	5.60	0.28	1.80
1 m³/h	1200	60	1.50	0.09	0.70
1 m³/h	1200	90	0.80	0.06	1.10

Summarizing, it can be observed that in case of purging with steam carrying atmosphere, better results were achievable. The reason for this is on the one hand the positive influence of the steam on the other also the higher exchange rate of furnace atmosphere compared to previous trials, which leads to the increased vaporization yields.

9. Zinc sulphate production

The following chapter describes the lab scale trials carried out for zinc sulphate production from low-grade zinc-bearing materials (crude zinc oxide, C-WOX; dust settling chamber zinc oxide, DSC-WOX; and double leached zinc oxide, DL-WOX).

9.1 Background

The aim is to investigate a counterpart to the pyrometallurgical upgrade possibilities, due to the fact that different difficulties present during thermal treatment can be avoided in a hydrometallurgical process, like heavy metal separation, halide removal, etc. This leads to a product higher in quality, concerning for instance its heavy metal content, than after a thermal treatment. Furthermore, the handling of sludge or solutions is generally easier than with metallic vapours or volatile halides.

Another positive aspect is that with the production of zinc sulphate, a waelz plant would be able to increase its array of products. Going hand in hand with that, a new clientele can also be addressed, while no business competition with their present clients (primary zinc plants) would occur, as zinc sulphate is not typically sold by primary zinc smelters.

9.2 Trials

Three different trials investigating the mentioned raw materials were carried out. The materials used, process flow of the trials and results are described and discussed below.

9.2.1 Material

The investigated materials are zinc oxides recovered from electric arc furnace dust in a waelz kiln. The difference lies in the sampling point and pre-treatment. The DSC-WOX is collected directly after the kiln hood in the dust settling chamber, the crude WOX is the generally known and commonly produced product of the waelz kiln, while the double leached WOX is a post-treated material with the main aim of removing disturbing halides prior to the primary zinc plants.

The following table gives the element analysis of all three investigated materials.

Table 9-1: Element analysis of investigated waelz oxide samples

	DL-WOX	DSC-WOX	C-WOX		
ZnO	87.379	56.634	75.803	%	DIN EN ISO 11885
CuO	0.070	0.089	0.056	%	DIN EN ISO 11885
Pb	5.370	6.820	4.100	%	DIN EN ISO 11885
Cd	0.160	0.110	0.130	%	DIN EN ISO 11885
Fe	2.040	4.040	1.630	%	DIN EN ISO 11885
Ca	1.350	3.250	0.930	%	DIN EN ISO 11885
MgO	0.166	0.365	0.116	%	DIN EN ISO 11885
Al_2O_3	0.132	1.247	0.076	%	DIN EN ISO 11885
MnO	0.284	0.852	0.207	%	DIN EN ISO 11885
K	0.100	5.100	4.010	%	DIN EN ISO 11885
Cl	0.150	9.780	7.580	%	DIN 38405 D1-2
C	0.800	0.880	0.260	%	DIN EN ISO 15350
S	0.050	0.300	0.190	%	DIN EN ISO 15350
F	0.170	0.330	0.140	%	DIN 38405 Teil1
Na	0.100	2.790	2.110	%	DIN EN ISO 11885
Cr	0.030	0.070	0.025	%	DIN EN ISO 11885
As	<0.005	<0.005	<0.005	%	DIN EN ISO 11885
Ni	0.004	0.015	0.004	%	DIN EN ISO 11885
Hg	0.001	<0.001	<0.001	%	DIN EN ISO 11885

It can be seen that especially the chlorine and fluorine contents are decreased by the leaching treatment (DL-WOX) as described in Chapter 7.3.2.

9.2.2 Process flow sheet

The following figure gives an overview of the necessary steps to clean the pregnant solution after dissolving (leaching) of the raw material to achieve satisfying zinc sulphate qualities.

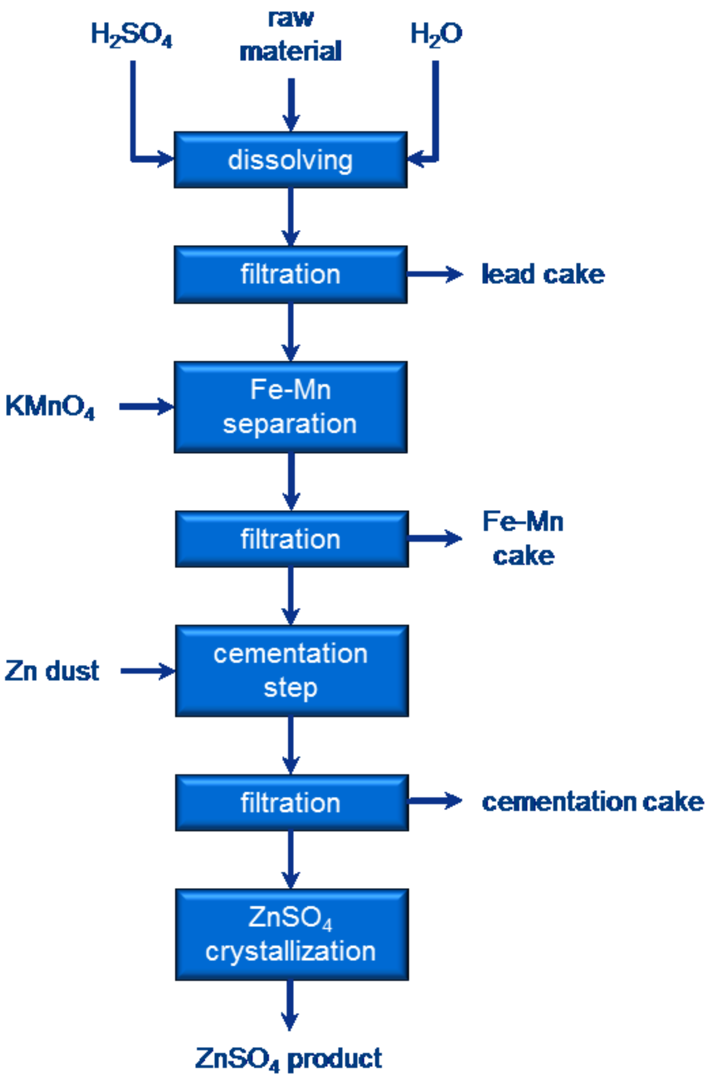


Figure 9-1: Experimental procedure for solution purification during zinc sulphate production

The general process steps can be specified in a dissolving step (leaching), wherein the zinc is dissolved next to salts present (like KCl, NaCl, etc.) as well as other impurities (mainly oxides of lead, copper, nickel, etc.). The residue of this step is typically rich in lead and insoluble components in this acidic media, like SiO_2, CaO, Al_2O_3, etc.

Afterwards, the dissolved iron and manganese have to be precipitated by oxidation with an oxidation agent, like $KMnO_4$. After a filtration, the separation of precipitation residue from the liquid, a solution cleaned from iron and manganese, is further treated in a cementation step to remove less noble elements as zinc, in advance of the crystallisation.

The last step is an evaporation of water to form zinc sulphate crystals.

9.2.3 Lab scale trials

As illustrated in the figure shown above, lab scale trials were carried out to determine the achievable product quality of the different investigated starting materials.

Similar to the flow sheet, the main steps are described in the following.

9.2.3.1 Leaching

The leaching step is the first step and due to the dissolving of zinc in sulphuric acid, highly exothermic. Typically, a target density of the pregnant solution of 1.3 to 1.6 kg/dm³ is the aim. Due to a lot of impurities in the raw material, it was difficult to predict the density which would be achieved by dissolving the right amount of zinc oxide in diluted sulphuric acid. Therefore, as a simplification only zinc sulphate was considered, which is the main compound dissolved and with this has the biggest impact. The following figure shows the density as a function of dissolved $ZnSO_4$ and the temperature of the solution.

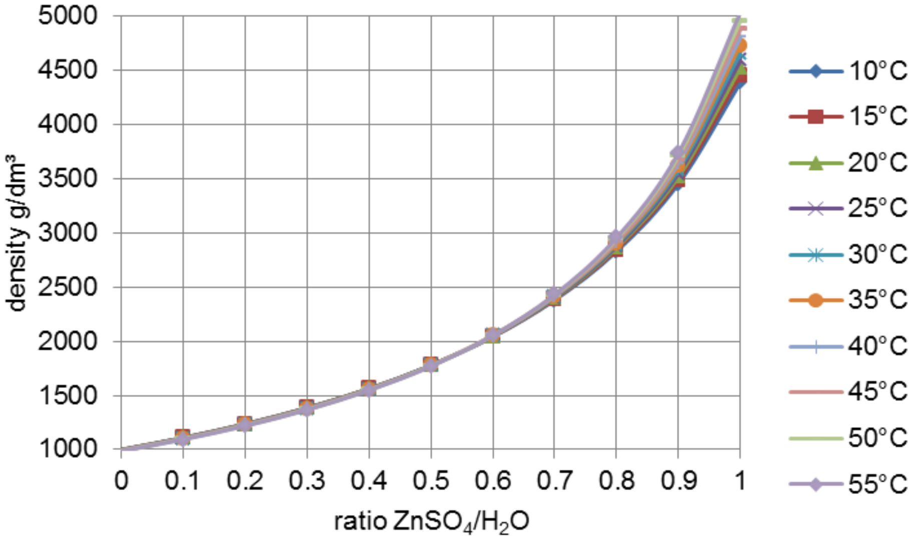


Figure 9-2: Density of $ZnSO_4$-solution depending on temperature and zinc sulphate concentration

It can be seen that the temperature has no significant influence in the area of target density but the density increases with increasing mass fraction of $ZnSO_4$. Due to the target density of the pregnant solution of 1.3-1.6 kg/dm³ (and the selection of 1.5 for the lab scale trials) the relevant area in the above figure for the trials is between 25 and 45 % mass fractions of zinc sulphate. In this area the influence of temperature is a minimum and was therefore not considered further.

After calculating the necessary amount of raw material, the density of the solution as well as the pH were measured and adjusted to a target pH of around 4.5.

Figure 9-3 shows the experimental setup for leaching.

Figure 9-3: Leaching of raw material to dissolve zinc oxide

The following two equations (equ. 9-1 and equ. 9-2) show the dissolving of metal oxides along with the elemental metal. As a result of the mainly oxidic material, the more important equation is the first one.

$MeO + H_2SO_4 \leftrightarrow Me^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + H_2O$ Equ. 9-1

$Me + H_2SO_4 \leftrightarrow Me^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + H_{2(g)}$ Equ. 9-2

After a filtration the first residue (lead cake) can be separated from the now pregnant solution.

Table 9-2 shows the element analysis of the first filtration cakes of the trials. It can be seen that the lead content is enriched and already high, while the zinc content could be further decreased in case of a washing step for the filter cake.

Table 9-2: Element analysis of lead residue (insoluble compounds)

	Pb residue				
	CWO	DSC	DLW		
Al	0.11	0.16	0.13	%	DIN EN ISO 11885
Ca	4.2	6	5.1	%	DIN EN ISO 11885
Cd	0.05	0.05	0.06	%	DIN EN ISO 11885
Cr	0.13	0.11	0.11	%	DIN EN ISO 11885
Cu	0.23	0.11	0.2	%	DIN EN ISO 11885
Fe	6.5	6.7	6.9	%	DIN EN ISO 11885
K	2.4	3.7	0.12	%	DIN EN ISO 11885
Mg	0.13	0.13	0.12	%	DIN EN ISO 11885
Mn	0.35	0.46	0.37	%	DIN EN ISO 11885
Na	0.7	1.1	0.24	%	DIN EN ISO 11885
Ni	0.02	<0.01	<0.01	%	DIN EN ISO 11885
Pb	18.7	10.6	17.9	%	DIN EN ISO 11885
Zn	16.6	18.9	23.9	%	DIN EN ISO 11885
Cl	1.8	3	<0.1	%	DIN 38405 D1-2
F	0.27	0.4	0.11	%	DIN 38405 Teil1
S	11	0.69	0.78	%	DIN EN ISO 15350
C	0.54	12.6	9.5	%	DIN EN ISO 15350

Figure 9-4 shows the lead residue after filtration.

Figure 9-4: Filter cake of lead residue

The residues generated during the process (lead cake, Fe-Mn cake and cementation cake), were dried for 24 hours at 120 °C before they were analysed.

9.2.3.2 Iron manganese precipitation

As a result of the acidic media, impurities such as iron, manganese and others are also dissolved during the first leaching step.

If no removal takes place, these elements will form unwanted impurities in the final product, which is why the second step after removing insoluble compounds is the precipitation of iron and manganese by oxidation with $KMnO_4$. Figure 9-5 shows the solution with already partly precipitated iron and manganese compounds (see Equations 10-3 and 10-4) during the reaction with $KMnO_4$.

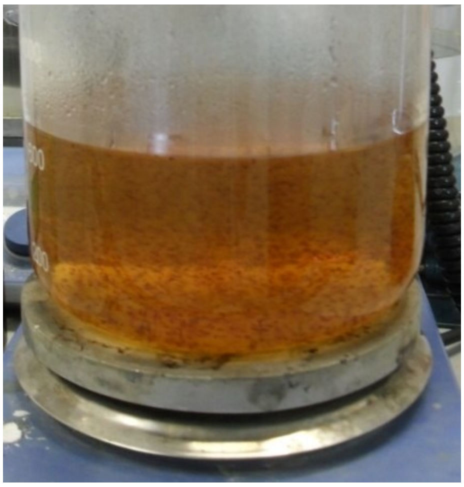


Figure 9-5: Solution with partly reacted $KMnO_4$ (solution with dispersed Fe-Mn precipitate)

As mentioned above, the addition of potassium permanganate precipitates iron hydroxide $Fe(OH)_3$ and MnO_2.

$$2\ KMnO_4 + 6\ FeSO_{4(aq)} + 14\ H_2O \leftrightarrow 2\ MnO_2\downarrow + 6\ Fe(OH)_3\downarrow + K_2SO_{4(aq)} + 5\ H_2SO_4 \quad \text{Equ. 9-3}$$

$$2\ KMnO_4 + 3\ MnSO_{4(aq)} + 2\ H_2O \leftrightarrow 5\ MnO_2\downarrow + K_2SO_{4(aq)} + 2\ H_2SO_4 \quad \text{Equ. 9-4}$$

During the trials the reagent was added as long as no new precipitate was formed and the liquid was coloured slightly purple, which indicates the end of this reaction.

Figure 9-6: Filter cake of Fe-Mn residue

Figure 9-6 shows the filtered iron hydroxide and manganese dioxide cake, while Table 9-3 gives the element analysis of the achieved residues.

Table 9-3: Element analysis of iron manganese residue

	Fe-Mn residue				
	CWO	DSC	DLW		
Fe	3.3	2.9	1.44	%	DIN EN ISO 11885
K	1.8	2.1	0.09	%	DIN EN ISO 11885
Mn	6.1	9.1	7.8	%	DIN EN ISO 11885
Zn	27.0	25.4	29.8	%	DIN EN ISO 11885
S	12.6	11.4	12.7	%	DIN EN ISO 15350

The table shows that an enrichment of Fe and Mn in the cake can be found, although the main compound is zinc. The reason for this is that during the trials, no washing of the filter cakes was carried out. In industrial scale each cake would get washed to minimize the losses of zinc and the gained wash water could then be used for the first leaching step as a water source. This is also advocated in the process concept described in Chapter 10.2.

9.2.3.3 Cementation

While in the previous step (precipitation) the element Mn was also removed, the cementation step removes all elements which are nobler than zinc. As shown in Table 9-4 most of the critical elements in the fertilizer industry (Pb, Cd, Co, Ni, Cu, Hg, etc.) are removed in the last step (every element with a standard electrode potential below zinc can be cemented). As a result, this step is crucial for the achievable product quality.

Table 9-4: Standard electrode potentials

Half-cell reaction	Standard electrode potentials [V]
$MnO_4^- + 8\ H^+ + 5\ e^- \leftrightarrow Mn^{2+} + 4\ H_2O$	1.51
$MnO_2 + 4\ H^+ + 2\ e^- \leftrightarrow Mn^{2+} + 2\ H_2O$	1.23
$Hg^{2+} + 2e^- \leftrightarrow Hg$	0.85
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	0.77
$MnO_4^- + 2\ H_2O + 3\ e^- \leftrightarrow Mn^{2+} + 4\ OH^-$	0.6
$MnO_4^- + e^- \leftrightarrow MnO_4^{2-}$	0.56
$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.34
$H^+ + e^- \leftrightarrow \frac{1}{2} H_2$	±0.000
$Fe^{3+} + 3e^- \leftrightarrow Fe$	-0.04
$Pb^{2+} + 2e^- \leftrightarrow Pb$	-0.13
$Ni^{2+} + 2e^- \leftrightarrow Ni$	-0.23
$Co^{2+} + 2e^- \leftrightarrow Co$	-0.28
$Cd^{2+} + 2e^- \leftrightarrow Cd$	-0.4
$Fe^{2+} + 2e^- \leftrightarrow Fe$	-0.44
$Zn^{2+} + 2e^- \leftrightarrow Zn$	-0.7627
$2\ H_2O + 2e^- \leftrightarrow H_2 + 2\ OH^-$	-0.83
$Mn^{2+} + 2e^- \leftrightarrow Mn$	-1.18
$Al^{3+} + 3e^- \leftrightarrow Al$	-1.66
$Mg^{2+} + 2e^- \leftrightarrow Mg$	-2.37
$Na^+ + e^- \leftrightarrow Na$	-2.71

Equation 9-5 shows the general valid cementation reaction in acidic (diluted sulphuric acid) media.

$$Me^{2+}_{(aq)} + SO_{4\ (aq)}^{2-} + Zn_{(solid)} \leftrightarrow Me_{(solid)} + Zn^{2+}_{(aq)} + SO_{4\ (aq)}^{2-} \qquad \text{Equ. 9-5}$$

It can be seen from the sum of Table 9-2 that almost everything is considered in this analysis. Due to the metallic state of the precipitate, a calculation of phases is not necessary.

Table 9-5: Element analysis of cementation residue

	Cementation residue				
	CWO	DSC	DLW		
As	<0.01	<0.01	<0.01	%	DIN EN ISO 11885
Cd	11.5	5.8	36.1	%	DIN EN ISO 11885
Cr	<0.005	<0.005	<0.005	%	DIN EN ISO 11885
Cu	0.043	0.012	0.020	%	DIN EN ISO 11885
Hg	<0.001	<0.001	<0.001	%	DIN EN ISO 11885
Ni	0.014	0.013	0.032	%	DIN EN ISO 11885
Pb	0.67	0.19	0.27	%	DIN EN ISO 11885
Zn	83.9	92.0	56.7	%	DIN EN ISO 11885
S	0.55	0.59	0.99	%	DIN EN ISO 15350
SUM	**96.69**	**98.62**	**94.13**		

Especially cadmium as well as lead and copper dissolved during the first step are precipitated in this stage. The amount of added zinc powder was calculated based on maximum dissolved Cu, Pb, Ni, etc. from the raw material analysis, plus an additional safety factor. As it can be seen from the rest zinc content, by far not all of the theoretically present impurities in the raw material were dissolved and therefore are not in the pregnant solution after the first two “cleaning” steps. That is the reason for the relatively high zinc content in the cementation cake.

In industrial scale the charged amounts of both the zinc dust and the used chemical $KMnO_4$ in previous Fe-Mn precipitation, are empirical values (lower than the calculated ones) and with this will have a positive impact on the economics of the process.

Table 9-6 shows the element analysis of the pregnant solution after the cementation step. It can be seen from the table that the main ion is zinc, while in the trials with CWO and DSC the main impurities are formed by Na, K and Cl, which arise from the halides present in the raw material.

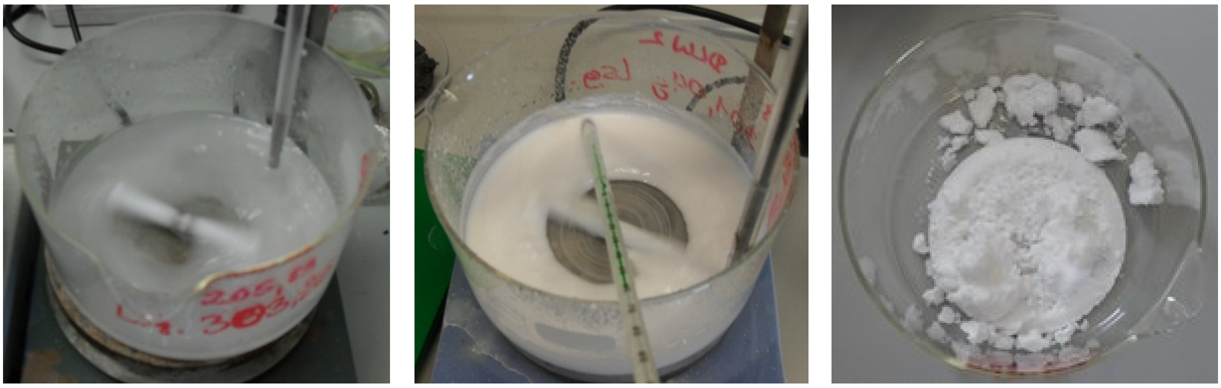
Table 9-6: Element analysis of pregnant solution before crystallization

	$ZnSO_4$ Solution				
	CWO	DSC	DLW		
F	0.020	0.014	0.044	g/l	DIN 38405 Teil1
Cl	17.0	29.6	0.0221	g/l	DIN 38405 D1-2
Al	0.0107	0.0502	0.0544	g/l	DIN EN ISO 15350
Ca	0.3	0.327	0.21	g/l	DIN EN ISO 15350
Fe	0.0469	0.0395	0.0039	g/l	DIN EN ISO 15350
K	8.73	10.90	3.06	g/l	DIN EN ISO 15350
Mg	0.101	0.550	0.142	g/l	DIN EN ISO 15350
Mn	n.a.	0.29	n.a.	g/l	DIN EN ISO 15350
Na	4.73	7.77	0.117	g/l	DIN EN ISO 15350
Zn	164	159	180	g/l	DIN EN ISO 15350
S	76.3	74.3	83.1	g/l	DIN EN ISO 15350

As a rule, the halides are not removed during the cleaning steps due to their anionic character. Therefore, the third raw material, the DLW, was investigated because it runs through a “state-of-the-art” washing step (soda leaching) to remove the disturbing halides. With this a preliminary washing step is simulated and for this reason was not necessary any more in the trials.

9.2.3.4 Crystallisation

The last step is the crystallisation of zinc sulphate hydrate by evaporating water from the pregnant cleaned solution. Figure 9-7 shows the progress during evaporation: (a.) first crystals are formed; (b.) a dispersion is formed, (c.) crystals after filtration.



a) first crystals b) dispersion of particles c) zinc sulphate crystals

Figure 9-7: Crystallisation of zinc sulphate crystals

9.2.4 Results

Table 9-7 shows the element analysis of zinc sulphate crystals (dry). Due to the very high zinc content, which would give more than 100 % in case of pure zinc sulphate, the theoretical crystal composition (see Table 9-8) was calculated, based on the element analysis of the solution before the crystallisation step (see Table 9-6).

The reason for the too high Zn value might be the drying step at 120 °C, or a formation of a different salt (e.g. chloride) instead of zinc sulphate, which makes it difficult to calculate a phase distribution.

Table 9-7: Element analysis of crystallized zinc sulphate

	$ZnSO_4$ crystallized product				
	CWO	DSC	DLW		
Al	0.011	0.012	0.013	%	DIN EN ISO 11885
As	<0.01	<0.01	<0.01	%	DIN EN ISO 11885
Ca	0.084	0.071	0.062	%	DIN EN ISO 11885
Cd	<0.005	<0.005	<0.005	%	DIN EN ISO 11885
Cr	<0.005	<0.005	<0.005	%	DIN EN ISO 11885
Cu	<0.005	<0.005	<0.005	%	DIN EN ISO 11885
Fe	0.10	0.02	0.02	%	DIN EN ISO 11885
Hg	<0.001	<0.001	<0.001	%	DIN EN ISO 11885
K	2.30	2.50	0.12	%	DIN EN ISO 11885
Mg	0.035	0.13	0.04	%	DIN EN ISO 11885
Mn	<0.01	0.076	<0.01	%	DIN EN ISO 11885
Na	1.50	2.30	0.05	%	DIN EN ISO 11885
Ni	<0.01	<0.01	<0.01	%	DIN EN ISO 11885
Pb	<0.005	<0.005	<0.005	%	DIN EN ISO 11885
Zn	35.6	35.0	38.4	%	DIN EN ISO 11885
Cl	4.15	6.77	0.11	%	DIN 38405 D1-2
F	0.03	0.03	0.40	%	DIN 38405 Teil1
S	16.7	15.8	17.6	%	DIN EN ISO 15350

It is shown that a very pure zinc sulphate can be produced (see Table 9-8) in case of using the double leached WOX (99.26 % zinc sulphate hexahydrate).

Table 9-8: Theoretical composition of zinc sulphate based on element analysis of pregnant solution (see Table 9-6)

$ZnSO_4$ solution (→ crystallized)				
	CWO	DSC	DLW	
NaCl	1.76	2.89	0.00	%
KCl	2.43	3.04	0.00	%
$ZnSO_4 \cdot 6H_2O$	93.68	91.43	99.26	%
rest	2.13	2.63	0.73	%

In the other two investigated cases of raw material (CWO, DSC) 93.7 % and 91.4 % zinc sulphate hexahydrate purity was achieved. The main reason for the lower values can be seen in the table below. This is mainly caused by present salts, which could be removed easily and would therefore offer the opportunity to achieve higher product qualities, like in case of the DLW raw material.

The far more important analysis is the content of heavy metals in the products, shown in Table 9-9. Owing to the analysed crystals, which were dried at 120 °C, the comparison with industrially produced monohydrate seems to be the most meaningful and represents the worst case of impurity content. In case of CWO and DSC even lower values can be achieved if a preliminary washing step is carried out. Arsenic, chromium, copper and mercury are all below 1 ppm (*based on chemical analysis of AMCO united samplers*). This is compared with common fertilizers and animal feed grades within the requirements, and shows excellent results considering not optimised trial conditions.

Table 9-9: Detailed element analysis of critical elements in the product

$ZnSO_4$ crystallized product (critical elements)					
	CWO	DSC	DLW		
As	<1	<1	<1	ppm	DIN EN ISO 11885
Cd	<1	<1	17	ppm	DIN EN ISO 11885
Cr	<1	<1	<1	ppm	DIN EN ISO 11885
Cu	<1	<1	<1	ppm	DIN EN ISO 11885
Hg	<1	<1	<1	ppm	DIN EN ISO 11885
Ni	11	53	13	ppm	DIN EN ISO 11885
Pb	17	12	11	ppm	DIN EN ISO 11885
Mn	40	760	21	ppm	DIN EN ISO 11885

Cadmium has its highest value in the trial with double leached WOX (17 ppm). Compared with e.g. monohydrate of Grillo GmbH, the biggest producer of zinc sulphate in Europe, it is only 2 ppm above their maximum content. Based on the results achieved for the other two raw materials investigated, it seems that there is optimization potential for that.

The achieved content of nickel is within the requirements for CWO (11 ppm) and DLW (13 ppm). Compared again with the mentioned quality of monohydrate, they lie below the maximum content of 20 ppm in their zinc sulphate product. In case of the DSC the content needs to be investigated in more detail.

The same circumstance can be found with the manganese content in the DSC trials. The maximum mentioned Mn content in the monohydrate is 50 ppm. So, based on the element analysis of CWO and DLW compared to DSC (see Table 9-9) it seems that there is optimization potential left.

All in all it can be stated that the results of the achieved heavy metal contents after the cementation in the zinc sulphate product are excellent, taking into consideration that no optimization was carried out at this stage.

9.2.5 Discussion

Although the results of the trials are very promising, there is still room for optimization.

To improve the nickel removal, it could be better to increase the temperature again for the cementation step.

The manganese content could be decreased by two methods; firstly by the usage of oxidation agents, which contain no more manganese like H_2O_2 instead of $KMnO_4$ and secondly by an increased time for reaction. It was observed during the trials that the retained samples after the iron manganese precipitation continued reacting and one day later again a small amount of precipitate was recognizable.

To minimize the fluorine and chlorine content, the easiest way is a preliminary washing step because it is detached from the main process. Within the process there are routines described in patents to lower the chlorine content with copper-“one-plus-ions” or alternatively the fluorine with $AlPO_4$, but that would increase the facility effort dramatically.

In the trials there was no pH adjustment carried out at the end of the process. The main advantage of such a step is that the sulphuric acid consumption is minimized and additionally the target pH of the fertilizer is always the same. In case of too much free H_2SO_4 it would get too low in the preliminary dissolving for fertilizer usage. So in industrial production it makes sense to have a pH adjustment at the end, by dissolving further zinc oxide or another compound. In this context zinc carbonate would be a good alternative because it is only soluble under acidic conditions and is therefore the optimum reagent to adjust the pH on a neutral level. In case there are still too high contents of heavy metals in the product, a dilution with high-grade raw material is also possible.

10. Industrial concepts

Based on the pyro- and hydrometallurgical experiments, concepts were developed for a possible implementation in industrial scale.

10.1 Clinkering of waelz oxides in gas-fired facility

The first concept deals with the implementation of the selective vaporization into an existing industrial production process for high grade zinc oxides.

Due to the energy consumption of such a clinkering step, the aim was to minimize the additional energy needed to reach high purity quality. The idea is to use the heating up process employed in common American processes for high purity zinc oxide production, for the treatment of low quality raw materials (waelz oxides). Within this selective vaporization, the disturbing compounds, which are mainly volatile ones, are removed. For this, it is necessary to treat the material during the heating phase under oxidizing conditions, so that only the volatile compounds are removed and the zinc oxide remains. Afterwards, the atmosphere is switched to reducing conditions or the material is charged with reducing agents in a second furnace and the zinc oxide is converted to metallic zinc, which leaves the furnace and is post combusted before it enters the off-gas system, where the high purity product is collected in baghouse filters.

Non-volatile reaction products from the preliminary clinkering remain in the reduction facility as residue.

10.1.1 Mass- and energy balances

Figure 10-1 shows a mass balance for a two-step concept (clinkering – reduction) for an average quality waelz oxide, with 80 % of ZnO and 20 % other compounds, consisting of volatiles (PbO, halides, etc) as well as non-volatiles, like carry over (SiO_2, Fe_2O_3, etc.).

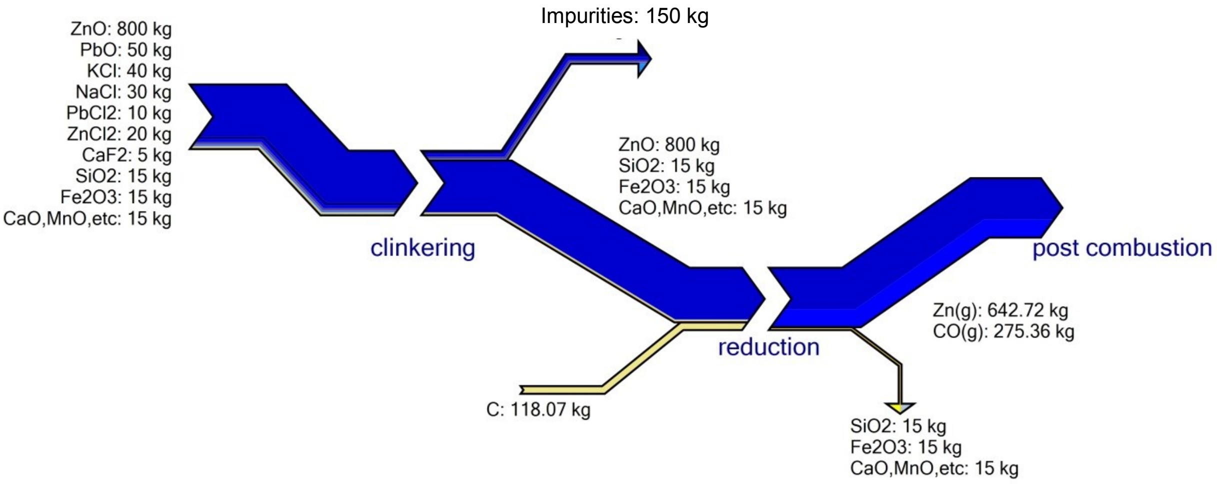


Figure 10-1: Mass balance for a clinkering followed by a reduction step

Based on the mass balance, the following energy consumptions in relation to one kg initial material, which means impure zinc oxide, can be calculated:

Heating up (clinkering):	~1150 kJ/kg initial material (1200 °C)
Facility heat losses :	~350 kJ/kg initial material
Reduction step:	~3550 kJ/kg initial material (1200 °C)
Heating up (reducing agent):	~250 kJ/kg initial material

Due to the high dust load of the off-gas, the post combustion step is not of major interest, because the excess energy is difficult to utilize in, for instance, heat exchange.

It can be seen from the above-listed energy consumptions that the biggest part by far is consumed by the endothermic reduction step of zinc oxide. The heating process together with the heat losses of a rotary kiln is less than the half of the reduction energy.

An average gas burner (methane-air) supplies, if adjusted to a lambda of 1.05, around 15.5 MJ/m³ under norm conditions, which is equal to 4.3 kWh. The overall energy consumption would be roughly 5.3 MJ per kg of waelz oxide, leading to a consumption of 0.35 m³ of methane (combusted with air). If the carbon is substituted by methane, another 0.07 m³ has to be added. Together and with an assumed contingency of 30 %, this leads to a consumption of 0.54 m³ methane per kg of material.

10.1.2 Economic considerations

Based on a natural gas price of 35 € per MWh (3.5 Cent/kWh), the calculated consumption of 0.54 m³ per kg of waelz oxide would lead to costs of around 0.08 € per kg of waelz oxide, which is 81 € for one ton.

To evaluate the potential of such an upgrade step, the delta of the revenue for different zinc oxides was calculated and summarized in the following table.

Table 10-1: Calculated prices for different zinc oxide products

	Price	Zinc content		Amount	Zn content		€/550kg Zn
	[€/t]	[%]	[€/%Zn]	kg	kg	%	
CZO	417	55	7.6	1000	550	55	417
WZO	727	68	10.7	809	550	68	588
SHG Zn	1530	100	15.3	550	550	100	842
HP ZnO	1469	80	18.4	688	550	80	1010

The calculation shown above is based on the LME price of 1530 € per ton of zinc. The first column shows the price based on the LME for one ton of each material. The one in the first row is the investigated crude zinc oxide (CZO) with 417 € per ton. The next two, washed waelz oxide (WZO) and metallic zinc (SHG Zn), are just mentioned because the product from waelz kiln operations normally sold in Europe is washed waelz oxide and one typical raw material for high purity zinc oxide production is metallic zinc, in case of the French process. It is clear that the value of the product increases steadily (grey column) from 7.6 € per percentage of zinc to 18.4 €/%. This shows that downstream the product clearly increases its value.

Due to the fact that during the purification the amount of material is reduced, the calculation assumes a constant zinc content of an absolute amount of 550 kg per ton of material. With this, an evaporation of volatiles is simulated, while the zinc content stays the same and a subsequent reduction step would lead to a high purity product (HP ZnO). Assuming that there are no zinc oxide losses, a delta of around € 600 per ton of crude zinc oxide can be calculated, which can theoretically be used for the costs of an upgrade step.

If it is assumed that the clinkered material is charged in one heat from the clinkering step to the reduction step, only the heat losses during the treatment and the energy consumed by the evaporation of impurities have to be supplied. This would again decrease the costs from 81 € per ton of waelz oxide to somewhat lower. The costs for the reducing agent and the energy for heating up, which are included in the calculated 81 €, would arise in the same way as in the typical stand-alone American process, without a preliminary clinkering step.

Typically treatment charges of 100-300 € per ton of material are common in primary industry for example, treating zinc or lead concentrates. As a result of the highly concentrated raw material in this case, the waelz oxide, even lower treatment costs can be assumed. The better part of the costs in case of an implementation into an existing American process would not be the OPEX side as discussed above, but rather the capital expenditures; with them, the depreciations would account for the main part of the expenses.

What is responsible for the additionally arising investment costs is the need for a separate off-gas system for the clinker dust, due to the fact that the zinc oxide product is typically collected in the baghouse filters and would therefore be contaminated by the clinker flue dust as well as a facility for the clinkering step. This would lead to additional energy consumption because of a second facility as well as inevitable heat losses during the charging process of the clinkered material into the reduction step.

In summary, it can be stated that the possibility to utilize the waelz oxide as a cheap raw material for the American process seems to be an interesting and economic concept,
although different aspects have to be considered in each case, such as

- modified throughput by the adaption to a two-step concept,
- possible change from continuous to discontinuous operation mode,
- additional equipment required,
- additional space,
- required adaption of infrastructure, etc., which can be different from plant to plant;

the high delta between raw material and target product of around 600 € per ton compared to only a delta lower than 300 € in a primary zinc industry, shows the high potential. This is underlined especially by the fact that the primary zinc industry operates economically even though it is a cost-intensive processing from concentrate to metal, owing to the electrolytic winning step.

10.2 Zinc sulphate production from waelz oxide

The second concept is also based on the experiments carried out, which is why this shows a CAPEX and OPEX estimation for an upscale production of zinc sulphate.

10.2.1 Flow sheet

The process flow sheet of zinc oxide to zinc sulphate was already shown in the previous Chapter 9, in Figure 9-1. In industrial scale this schema would be extended by washing circuits to minimize losses, different storage areas, an additional pH adjustment, etc. Such a possible plant layout is shown in the following figure.

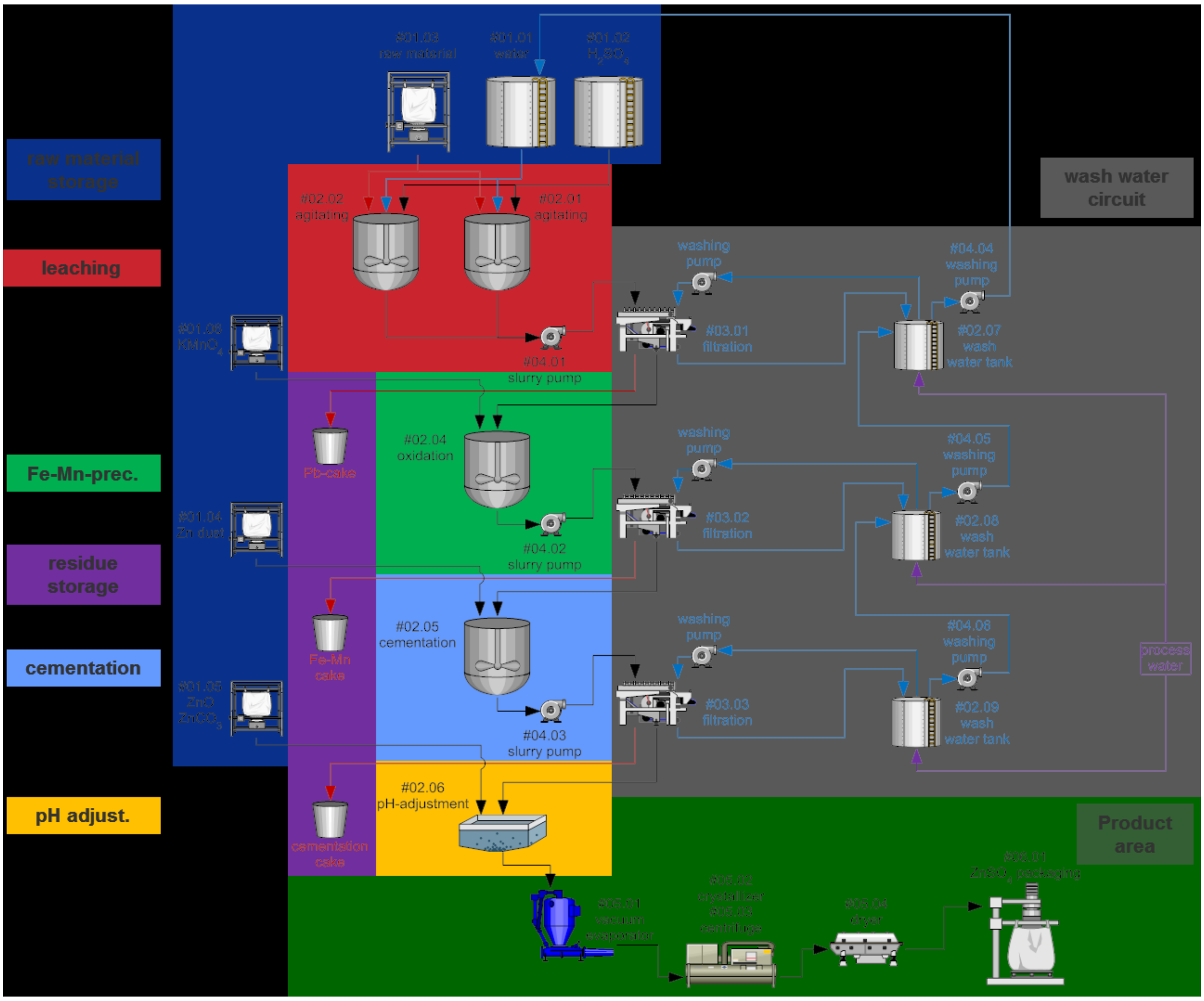


Figure 10-2: Possible plant layout for the production of zinc sulphate

10.2.2 Mass- and energy balances

The basis for the capital expenditure (CAPEX) as well as operational expenditure (OPEX) estimation is formed by a mass balance.

10.2.2.1 Assumptions for the mass balance

In the same way as in the lab scale trials, the calculations were carried out for all three investigated materials.

The assumptions for the mass balance are summarized as follows:

- Precipitation yield in Fe-Mn-step:
  - Fe .... 99 %
  - Mn .... 99 %
- Cementation yield:
  - Cu^{2+} .... 99 %
  - Pb^{2+} .... 99 %
  - Cd^{2+} .... 99 %
  - As^{3+} .... 99 %
  - Cr^{3+} .... 99 %
  - Hg^{2+} .... 99 %
  - Ni^{2+} .... 99 %
  - Fe^{2+} .... 99 %
- Crystallisation as $ZnSO_4 \cdot 6H_2O$

Because the mass balance is for the OPEX estimation the yields of leaching are assumed to be relatively high to form the worst case for the consumption of chemicals needed for solution purification. The achievable product quality was determined in the practical part.
Based on the same chemical reaction as pointed out in the practical part, the consumption of chemicals was calculated, summarized below:

1.) Leaching:

$$MeO + H_2SO_4 \leftrightarrow Me^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + H_2O \qquad \text{Equ. 10-1}$$

$$Me + H_2SO_4 \leftrightarrow Me^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + H_{2(g)} \qquad \text{Equ. 10-2}$$

2.) Fe-Mn-precipitation:

$$2\ KMnO_4 + 3\ MnSO_{4(aq)} + 2\ H_2O \leftrightarrow 5\ MnO_2\downarrow + K_2SO_{4(aq)} + 2\ H_2SO_4 \qquad \text{Equ. 10-3}$$

$$2\ KMnO_4 + 6\ FeSO_{4(aq)} + 14\ H_2O \leftrightarrow$$
$$2\ MnO_2\downarrow + 6\ Fe(OH)_3\downarrow + K_2SO_{4(aq)} + 5\ H_2SO_4 \qquad \text{Equ. 10-4}$$

3.) Cementation:

$$Me^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + Zn_{(solid)} \leftrightarrow Me_{(solid)} + Zn^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \qquad \text{Equ. 10-5}$$

10.2.3 Economic considerations

The economic considerations are based on the calculated consumption of chemicals obtained in the mass balance. Due to there being so many possible variations of parameters, assumptions had to be made.

10.2.3.1 Assumptions for the OPEX calculation

In the following, the necessary assumptions for the calculation of operational costs are given:

- Raw material:

DSC-WOX	350 €/t
C-WOX	450 €/t
DL-WOX	650 €/t

- Chemicals:

H_2SO_4	135 €/t	(incl. transport)
$KMnO_4$	2 520 €/t	(incl. transport)
Zn dust	1 500 €/t	
H_2O	0.06 €/m^3	

- Packaging:

Sack (50 kg)	0.35 €/sack

- Power:

Electricity	80 €/MWh

- Labour:

Manager	63 000 €/year and head
Salesman	28 000 €/year and head
Blue-collar worker	28 000 €/year and head
Shift leader	42 000 €/year and head
Administration	28 000 €/year and head
Logistics	28 000 €/year and head

Based on the assumption of two shifts, 1 manager, 4 blue-collar workers, 2 shift leaders, 1 person in administration as well as sales and 1 for logistics were considered.

- Transportation within the plant:

Raw material	0.5 €/t
Product	0.5 €/t
Residues	0.5 €/t

- Other costs:

Dumping	20 €/t

- Overhead: (insurance, rental, leasing, travelling, etc.)

Overhead costs	35 000 €/year (assumed)

Although it can be expected that the lead cake as well as the cementation cake can be utilized and in the best case sold, it was assumed that a waste dumping fee of 20 € per ton has to be paid for the cementation cake and the iron-manganese cake. For the lead cake, it was assumed that no revenue would be generated. The maintenance of the plant was calculated with 2 % of the total CAPEX (24 226 €/year).

10.2.3.2 Estimation of the CAPEX

The costs for acquiring the needed land as well as the erection of a working hall, including ground work, storage, laboratory and maintenance area were estimated to be 365 500 €. Based on the developed layout, another 845 798 € were estimated for the machinery at the production plant itself, including the following categories:

- Storage area:
    - Water and chemicals .... 183 724 €
- Reactors:
    - Div. tanks (washing, agitating, etc.) .... 222 107 €
- Filter presses:
    - 3 presses, pumps and control .... 209 500 €
- Div. pumps:
    - Water pumps .... 4 500 €
- Crystallisation:
    - Evaporator, crystallizer, centrifuge, dryer .... 47 000 €
- Packaging:
    - Packaging unit .... 18 000 €
- Laboratory:
    - Lab equipment .... 20 000 €

The mentioned data are not based on quotations and mainly estimated based on company information provided by telephone or modified data from similar projects which had already been completed. A contingency on the plant equipment of 20 % was considered.

In total, this would mean an investment of 1 211 298 €.

10.2.3.3 Estimation of the OPEX

Based on the mass balance for each of the raw materials, the previously mentioned estimated CAPEX as well as on the costs of the individual OPEX items, the following running costs (see Table 10-2) per year were calculated:

Table 10-2: Running costs for the three investigated materials

	€ / year		
	C-WOX	DL-WOX	DSC-WOX
PRODUCTION			
raw material	1 303 675	1 909 081	1 173 323
chemicals	580 664	626 595	935 357
fluids	697	739	616
personnel	259 000	259 000	259 000
maintenance	24 226	24 226	24 226
other costs	59 916	61 028	63 972
Sub total	2 228 178	2 880 668	2 456 494
ADMIN			
transport	5 646	5 987	6 127
personnel	56 000	56 000	56 000
overhead	35 000	35 000	35 000
	96 646	96 987	97 127
OTHER COSTS			
energy	76 800	76 800	76 800
	76 800	76 800	76 800
DEPRECIATION (10 years)	36 550	36 550	36 550
DEPRECIATION (5 years)	169 160	169 160	169 160
INTEREST (8%, 30% own cap.)	67 833	67 833	67 833
TOTAL	**2 675 167**	**3 327 997**	**2 903 963**

The depreciation was split into two parts with different periods. The depreciation time for buildings was set at 10 years while for the machinery it was set at 5 years. Furthermore, a 70 % financing by bonded capital was assumed, with an interest rate of 8 % per year.

Estimation of revenues:

Based on a survey a sales price of 600 to 850 USD per ton of sulphate was assumed. Converted, this would mean a sales price of 475 to 670 EUR per ton.

Two cases were calculated, with a low sales price of 450 € (see Table 10-4) and a high one of 650 € (see Table 10-3)

Table 10-3: Revenues based on a sales price of 650 €/t of zinc sulphate hexa-hydrate

650 €/t $ZnSO_4 \cdot 6H_2O$	€ / year		
	C-WOX	DL-WOX	DSC-WOX
Running costs	2 675 167	3 327 997	2 903 963
SALES	5 204 745	5 368 073	5 012 191
EBT	2 529 579	2 040 076	2 108 228

In the table above, the total of the running costs is shown again, beside the calculated revenue of the sales of zinc sulphate. In all three cases, the revenue is higher than the costs, including the depreciation of the machinery and housing. This shows clearly that an economic upgrade of waelz oxide to zinc sulphate is possible. The last line shows the positive EBT value (earnings before taxes), which is the revenue (sales) minus the running costs.

Table 10-4: Revenues based on a sales price of 450 €/t of zinc sulphate hexa-hydrate

450 €/t $ZnSO_4 \cdot 6H_2O$	€ / year		
	C-WOX	DL-WOX	DSC-WOX
Running costs	2 675 167	3 327 997	2 903 963
SALES	3 603 345	3 716 473	3 470 191
EBT	928 179	388 476	566 228

Also the second calculation, with the low sales price of the zinc sulphate product, indicates an economic process concept for all three cases. Although the DL-WOX has the lowest EBT value, it produces the best quality, due to the fact that the other two would need an additional washing step to produce an zinc sulphate as pure as with double leached WOX as the raw material. This leads to the fact that the difference between the EBT of all three cases decreases.

10.2.3.4 Summary

A possible plant layout was designed, which was the basis for the calculation of the capital expenditures.

The CAPEX calculation showed an estimated investment of approximately 1.3 million €. Based on the assumed costs for chemicals, other consumables, etc. the running costs of a zinc sulphate plant were estimated, being in a range of 2.5 to 3.5 million € per year, depending on the raw material used.

To evaluate the economic viability, two cases were investigated, the first with a sales price of 650 € per ton of zinc sulphate, which would be the best case and the second case with 450 € per ton of sold product.

Summing up, it can be stated that in both cases (450 and 650 €/ton), based on the rough CAPEX and OPEX estimation, it seems to be an economical way of upgrading secondary zinc oxides to zinc sulphates.

The most realistic case is the one with washed material, attributable to the fact that too high chlorine contents can also limit the applicability. Alternatively, a washing step has to be considered when using the other two materials.

11. Markets

This chapter deals with possible markets for an upgraded waelz oxide. In this case, if a pyrometallurgical upgrade process were applied along with the discussed hydrometallurgical one, the obtained target products would be on the one hand high purity zinc oxide or on the other hand a zinc sulphate, mainly used in the fertilizer industry.

11.1 Zinc oxide

The estimated global capacity of zinc oxide production was 1 887 000 metric tons per year in 2010. The consumption was 1 326 000 tons worldwide. Figure 11-1 shows the breakdown of the different market segments which utilize high quality ZnO [12].

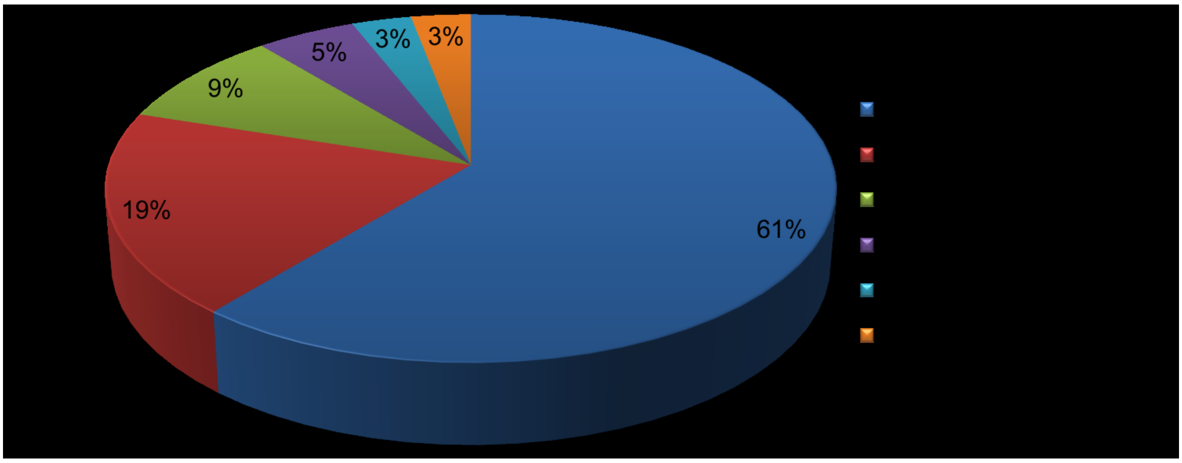


Figure 11-1: Estimated global breakdown of ZnO consumption for different utilization areas [12]

It clearly can be seen that the tyre and rubber industry is the biggest consumer of high quality zinc oxide worldwide, followed by the ceramics and glass industry. As described in an earlier chapter, it is used mainly as a vulcanization agent or as a result of its optical properties [12].

11.1.1 Global ZnO market in different regions

A major player in both production and consumption is China, a significant reason being the increase in automobiles and with that the market for tyres in Asia. Figure 11-2 shows the percentage of the world production capacity of each region, wherein approximately one third of the capacity is covered by China. North America and Europe have nearly the same production capacity with 16 %. The rest – also approximately one third – is split among other areas of the world [12].

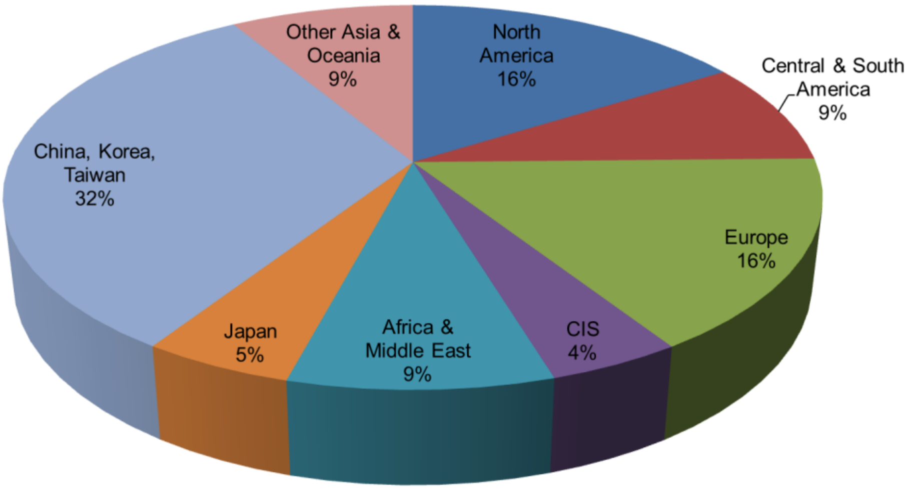


Figure 11-2: Estimated global ZnO production capacity for different regions [12]

The following pie chart (see Figure 11-3) illustrates the real production compared to the production capacity shown in Figure 11-2. Table 11-1 also gives the amount in thousand metric tons capacity as well as the real production amount.

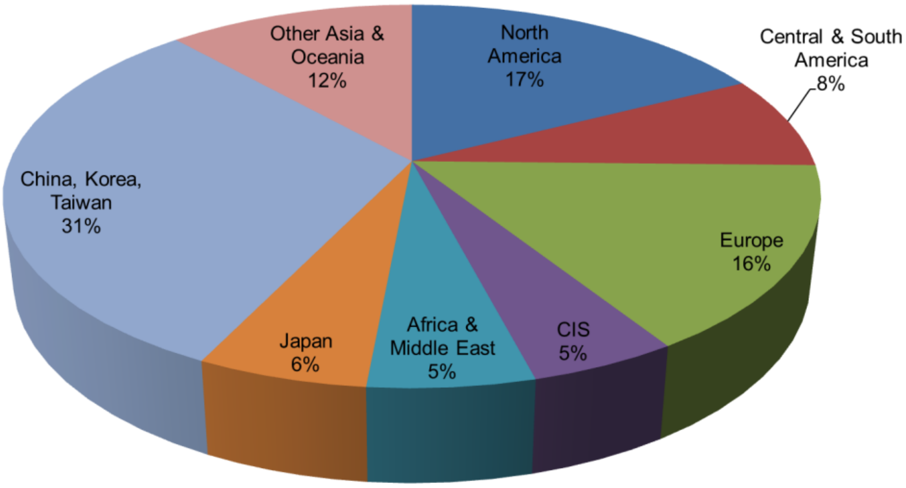


Figure 11-3: Estimated global ZnO production for different regions [12]

Figures 11-4 and 11-5 show the consumption of ZnO. While Figure 11-4 breaks it down into the percentage of the total consumption for each region Figure 11-5 gives the total amount in thousands of metric tons.

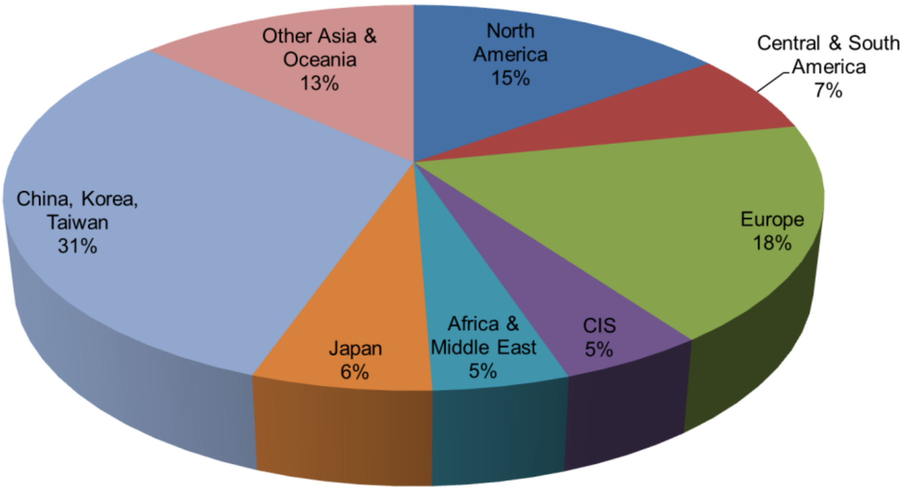


Figure 11-4: Estimated global ZnO consumption for different regions in percentage [12]

Figure 11-5 illustrates the clear domination of China and that the major consumption lies in the tyre industry. Due to the source of data for China [65] compared to the others [12], the tyre and rubber industry has to be seen as a separate utilization area. In this special case of China, the part of the tyre and rubber industry has to be increased, while the amount of the ceramic sector has to be decreased. This is because the rubber, chemical and ceramics industries were one utilization area in the literature [65] dealing with China's ZnO market. What's more, it can be seen that in most of the regions, the tyre industry is responsible for more than 60 % of the consumption, the only two exceptions being Europe and Central and South America, with over 50 %. This is discussed later in the present chapter, where a detailed description of the utilization areas for each region is given.

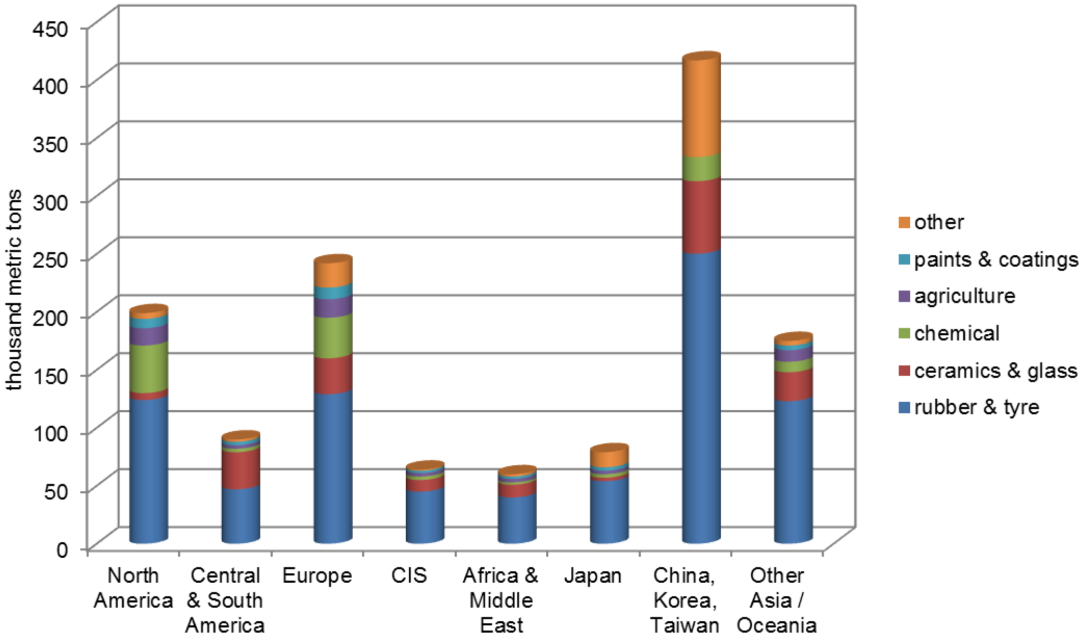


Figure 11-5: Estimated global ZnO consumption for different regions in thousand metric tons [12, 65]

Table 11-1 summarizes again the consumption, capacity and real production amount of different regions. Based on this data, the net exports in thousands of metric tons can be calculated by subtracting the consumption from the production. An interesting fact is that Europe has the highest negative net export although the production capacity is available, the reason perhaps being because of price politics.

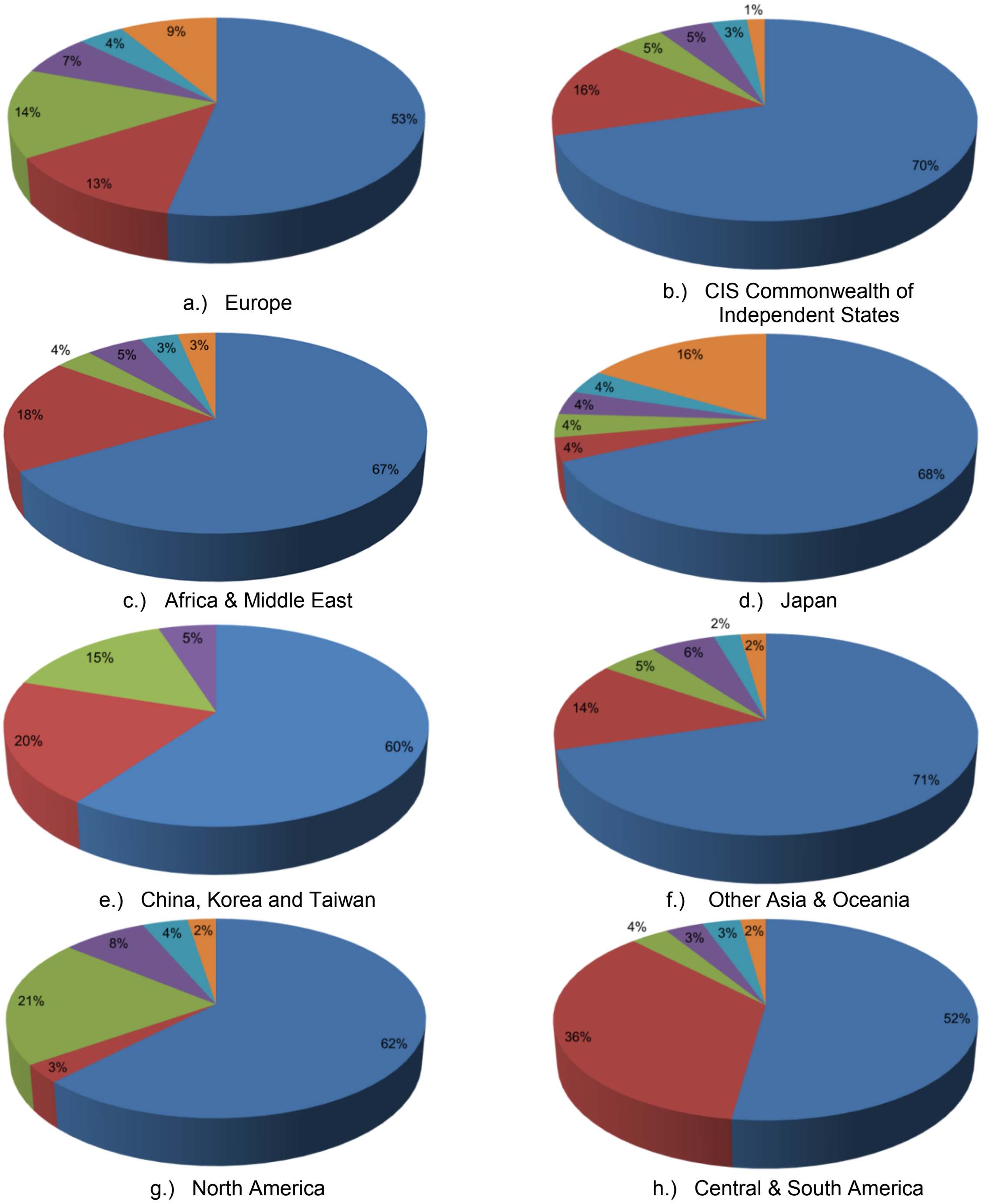
Table 11-1: Summary of ZnO production, capacities and consumption of high quality ZnO [12, 65]

	North America	Central & South America	Europe	CIS	Africa & Middle East	Japan	China, Korea, Taiwan	Other Asia & Oceania
Capacity	306	164	308	85	168	96	613	164
Production	236	106	211	67	75	77	421	157
Consumption	199	90	242	64	60	79	417	175
Net Exports	37	16	-31	3	15	-2	4	-18

11.1.2 Utilization of ZnO in different regions

The following figure summarizes the available data describing each region of the world one by one in pie charts, showing its percentage of ZnO utilization in its different application areas. It again clearly shows that globally, the main consumption of high grade ZnO lies in the rubber and tyre industry (blue part), followed in most of the cases by the ceramics industry (red part).

In each case, the tyre and rubber industry is the dominating sector of usage, while in most of the cases it is followed by the ceramics and glass industry. An exception is formed by North America, where the chemical industry is a huge consumer and Japan, where the ceramics and glass industry is a more or less small consumer.



a.) Europe

b.) CIS Commonwealth of Independent States

c.) Africa & Middle East

d.) Japan

e.) China, Korea and Taiwan

f.) Other Asia & Oceania

g.) North America

h.) Central & South America

Figure 11-6: ZnO consumption in different utilization areas in different regions [12, 65]

🟦 rubber & tire 🟥 ceramics & glass 🟩 chemical 🟪 agriculture 🟦 paintings & coatings 🟧 others

11.2 Zinc sulphate

Zinc sulphate is one out of three main inorganic zinc salts (chloride, oxide and sulphate) used in agriculture. All of them are applied in a variety of areas next to the utilization in the food or agricultural industry. Based on the target market (zinc sulphate), this chapter gives a detailed overview concerning possible zinc sulphate utilization areas, the yearly demand and supply statistics as well as an overview of the main producers.

11.2.1 Statistical data

Figure 11-7 shows the worldwide plants producing zinc sulphate and their accumulated capacities based on data from 2009.

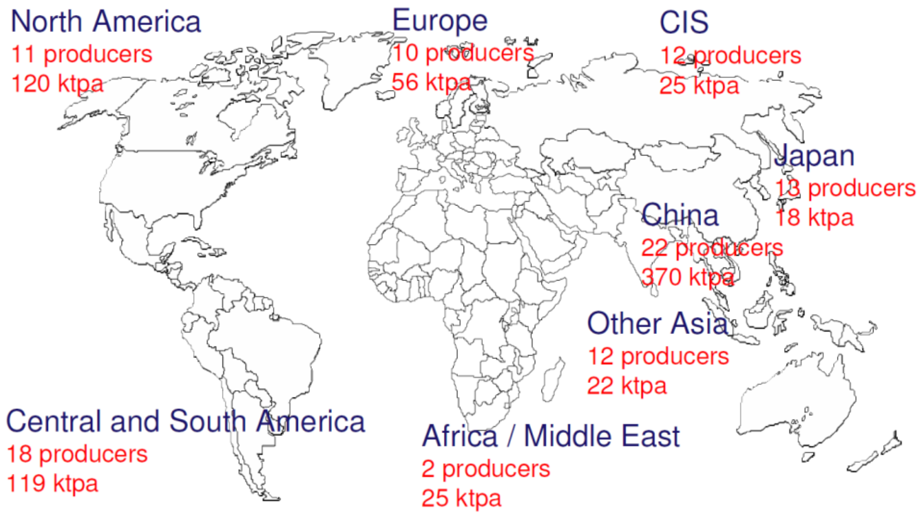


Figure 11-7: Worldwide capacities and number of zinc sulphate producers [12]

Table 11-2 lists the supply and demand data for zinc sulphate production. Based on the real operation rate, the production amount can be calculated. Furthermore, the import and export statistics are of interest. More or less only China exports zinc sulphate, while all others are importers.

Table 11-2: Supply/Demand for zinc sulphate by major regions (2009) in thousands of metric tons of product [12]

(in 1000 tons)	North America	Central & South America	Europe	CIS	Africa & Middle East	Japan	China, Korea, Taiwan	Other Asia & Oceania	Total
Statistical data									
Capacity	120.0	118.8	55.7	25.0	25.0	17.5	370.0	22.0	754.0
Operating rate	79%	35%	59%	16%	76%	27%	64%	64%	59%
Production	94.2	41.2	32.9	4.0	19.0	4.7	235.8	14.0	445.8
Imports	17.3	5.1	8.0	0.6	0.5	2.0	3.6	15.0	52.1
Exports	1.0	1.8	0.4	-	-	0.8	75.4	-	79.4
Consumption	110.5	44.5	40.5	4.6	19.5	5.9	156.8	29.0	411.3
Forecast									
Growth rate 2009-2014	1.9%	2.6%	0.0%	2.4%	3.8%	3.9%	14.4%	41.8%	11.9%
Consumption forecast 2014	121.2	50.6	40.5	5.2	23.5	7.1	307.6	166.0	721.7

The overall growth rate from 2009-2014 is expected to be 11.9 %, which leads to a total consumption of 722 thousand tons. This would cause an additional need in production of 300 thousand tons of zinc sulphate by the end of 2014.

11.2.1.1 General information on fertilizer

On account of the biggest market for zinc sulphate being in the fertilizer industry, this area is discussed more in detail.

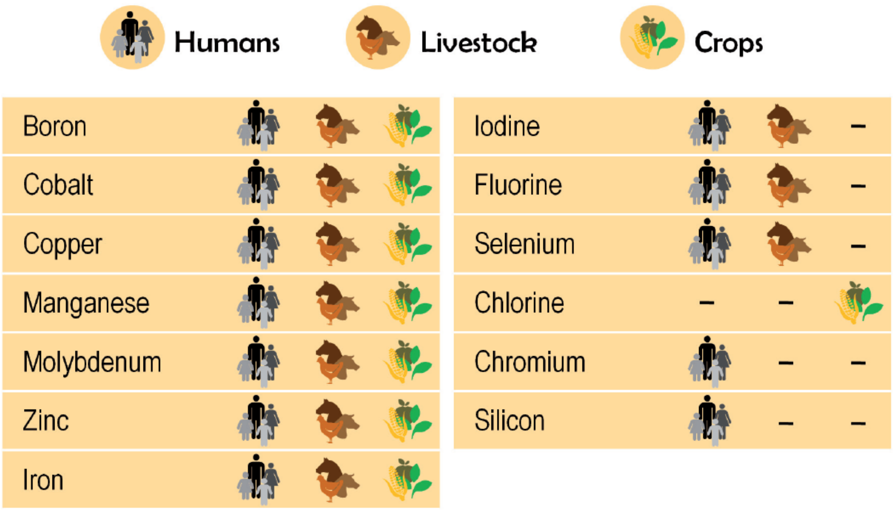
The FAO (food and agriculture organization) determined that zinc is the most commonly deficient micronutrient in agricultural soils. Going hand in hand with that, humans and animals are also affected by zinc deficiency, especially in developing countries.

Beside so-called macronutrients, plants additionally need other elements in smaller amounts (micronutrients) [67], including:

- Boron
- Chlorine
- Copper
- Iron
- Manganese
- Molybdenum
- Zinc

Leguminous crops, such as beans and peas, also need small amounts of cobalt. Water is typically supplied by rain while the atmosphere supplies carbon as CO_2, the oxygen as well as a small part of the nitrogen. But most of the plants obtain the nitrogen from the soil. All other nutrients have to be obtained completely from the soil – (or from what is added to the soil – fertilizers).

The figure below shows in which area (animals, plants or humans), which of the nutrients are important. It can be seen that zinc has a positive effect on each creature and is needed for all kinds of life.



	Humans	Livestock	Crops
Boron	✓	✓	✓
Cobalt	✓	✓	✓
Copper	✓	✓	✓
Manganese	✓	✓	✓
Molybdenum	✓	✓	✓
Zinc	✓	✓	✓
Iron	✓	✓	✓
Iodine	✓	✓	–
Fluorine	✓	✓	–
Selenium	✓	✓	–
Chlorine	–	–	✓
Chromium	✓	–	–
Silicon	✓	–	–

Figure 11-8: Assignment of important nutrients to humans, animals or plants [66]

Field experiments and research showed that the addition of zinc to commonly used fertilizers (e.g. N-P-K fertilizers, urea, etc.) improves the soil fertility, crop quality and yield and with that increases the zinc supply to people and animals.

Applying zinc-containing fertilizers to crops and soils is a fast, cost-effective and sustainable solution to correct deficiencies in soils, crops, animals and humans and with this fight against malnutrition. Especially in developing countries, the combat against malnutrition is of major importance. It has been proven that birth defects are related to malnutrition and can be decreased by supplying sufficient amounts of nutrients like zinc.

Nearly 50 % of cereal-cultivated soils have zinc deficiencies, causing problems with the crop yield and quality. Especially in developing countries, a huge part of the daily caloric needs is supported by cereal-based food [69].

Going hand in hand with a zinc deficiency in soil is the deficiency of zinc in humans (see the following two figures). It can undoubtedly be seen that in both cases, the same areas are affected.

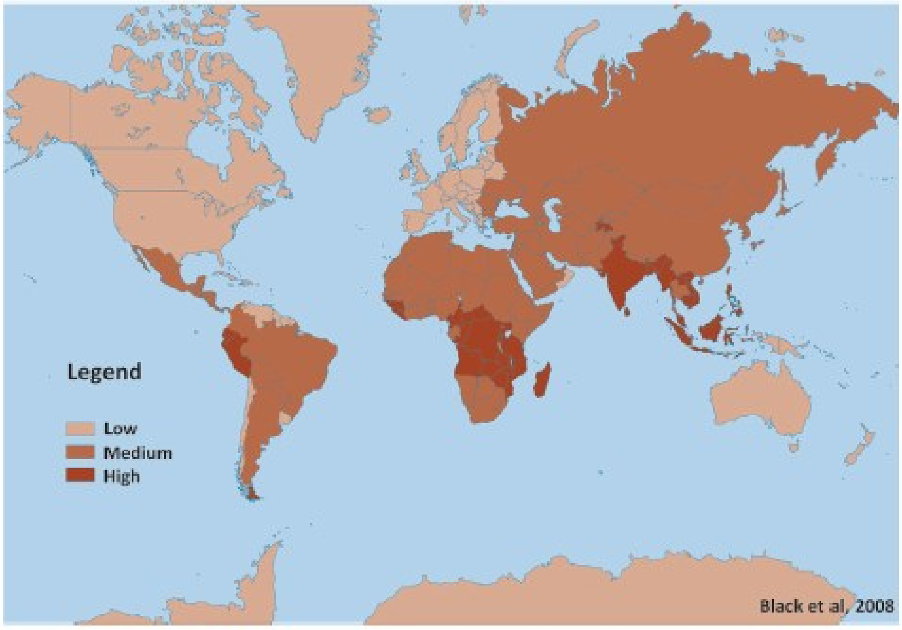


Figure 11-9: Regions with deficiency of zinc in humans [70]

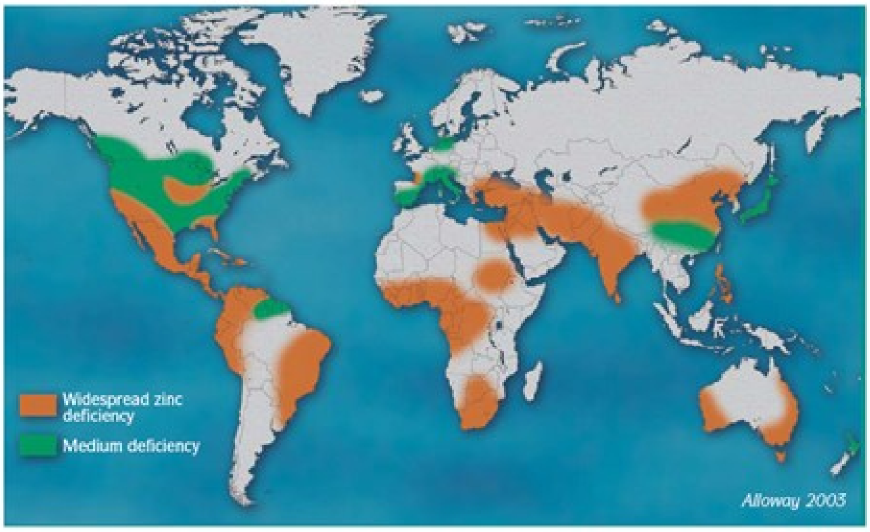


Figure 11-10: Regions with deficiency of zinc in soils [70]

A main focus of international associations like the IZA (International Zinc Association) or IFA (International Fertilizer Industry Association) is the fight against deficiencies of micronutrients in global crop production. Since 2004, the aim has been to increase the use of zinc fertilizers. Countries like China, India and Brazil have shown keen interest and first implementations have already been carried out. Nevertheless, the application of zinc fertilizers alone is not the only way of utilization; it is also used as an additive for other fertilizers. The reason for that is on the one hand an increased yield of other nutrients (nitrogen, etc.) as well as on the other hand a minimization of zinc deficiencies.

General types of fertilizers where zinc can typically be added in amounts of 1-3 % are:

- Multi-nutrient fertilizers (e.g. NPK)
- Nitrogen fertilizers
- Phosphate fertilizers
- Potash fertilizers
- Organic fertilizers

11.2.1.2 Zinc sulphate usage in agriculture

As mentioned before, the biggest utilization of $ZnSO_4$ is in agriculture (51 %), followed by lithopone (pigment) (22 %) and rayon spinning (12 %). Also the usage in water treatment (2 %) and electroplating (2 %) is mentioned next to a huge number of small application areas (in total another 11 %).

In 2009, approximately 445 000 metric tons of zinc sulphates were produced worldwide, while again China, Korea and Taiwan together were responsible for more than 50 % (235 000 tons). The consumption in these regions was lower (156 000 tons); while only a small amount was imported (3 600 tons), a far bigger amount of 75 000 tons per year was exported. These 75 000 tons per year were 35 % of the consumption in the rest of the world. This shows that the biggest producer again is China, like in the high purity ZnO production, and makes it clear why in all other areas of the world the import of this chemical is always higher than the export and with that, also the consumption is higher than the present production.

This is not because the capacity is not available; the reason for that is most probably price politics. As an example, the area Central and South America should be mentioned, where a capacity of 118 000 tons is present. Only 41,200 tons are produced, while the consumption lies at 44 500 tons. This is equivalent to an operation rate of 35 % [6].

As stated above, the utilization of zinc in agriculture is not only limited to zinc sulphate. Also zinc chloride and zinc oxide are partly present. The following figure shows how zinc is utilized in agriculture (calculated as tons zinc equivalent). This means that 75 000 tons of zinc are utilized as zinc sulphate, which further can be monohydrate, hepta-, hexahydrate, etc. But it can be clearly seen that the major utilization of zinc in agriculture is in the form of zinc sulphate.

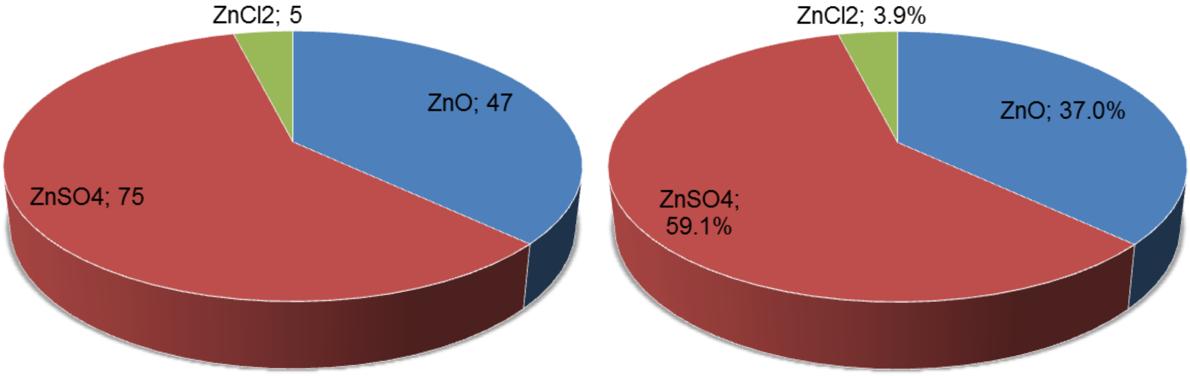


Figure 11-11: Zinc utilization in agriculture (thousand metric tons - zinc equivalent) and in percentages, respectively [12]

The total of zinc utilization (see pie chart above) is 127 000 metric tons zinc equivalent (base 2009 [3]). In the years after 2009 (based on the literature [5]) the total zinc equivalent in zinc sulphate and zinc oxide for agricultural use (excluding chelates, oxysulphates, ammoniated sulphates, etc.) increased to 185 000 tons. In 5 to 10 years, the forecast estimates a zinc equivalent usage of 500 thousand tons in agriculture, which is more than twice the amount utilized at the moment.

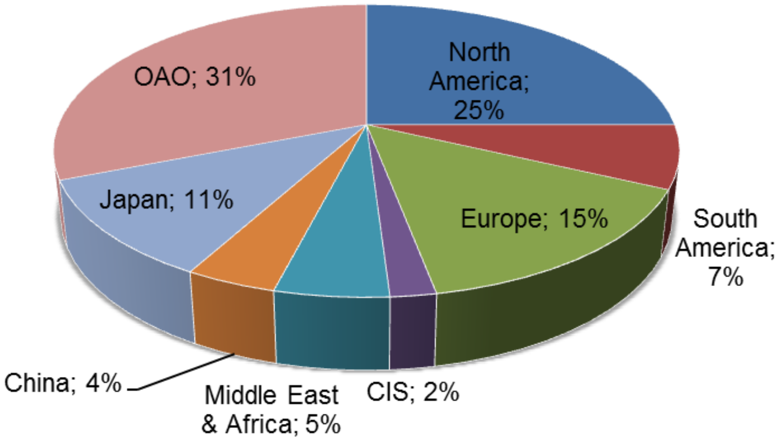


Figure 11-12: Regional breakdown of zinc chemical markets (agriculture use) of $ZnSO_4$ and ZnO [68]

Zinc sulphate utilization in China is clearly not in the field of agriculture, but in the field of paints and coatings as well as in different chemical applications. This underlines that especially China is one main target for improving crop yields and minimizing zinc deficiencies by applying zinc fertilizers in agriculture.

Figure 11-13 shows the breakdown of $ZnSO_4$ and ZnO usage in agriculture. The application of zinc is divided as follows: two thirds zinc sulphate and one third zinc oxide.

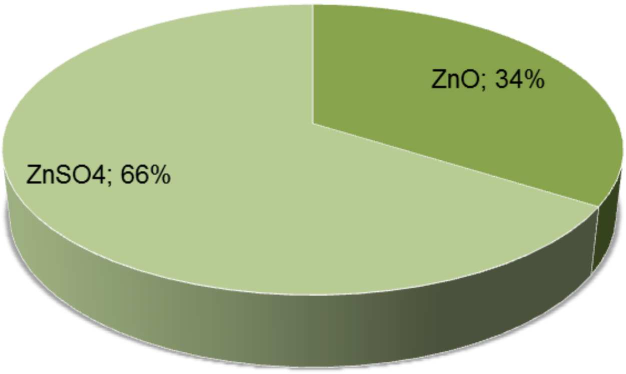


Figure 11-13: Breakdown of agricultural use of zinc in zinc sulphate and zinc oxide [68]

In the area of agricultural use of zinc, a split into animal feed additive and fertilizer can be carried out. Approximately 20 % of the ZnO used is in the fertilizer industry, whereas 75 % of the zinc sulphate is utilized. The remaining percentages, 80 % ZnO and 25 % $ZnSO_{4,}$ are used as animal feed additive [68].

12. Result discussion and conclusions

The overall aim of this thesis was the evaluation of the possibility to generate a product with added value, utilizing waelz oxide as raw material and with this break into new markets, for waelz kiln operators. This chapter recapitulates the obtained quintessence of the key topics of this thesis.

Based on the characterization of the materials and the evaluation of the required target quality, the behaviour of halides under different conditions was studied using databases and literature. Due to the good solubility as well as the opportunity of selective vaporization of halides, the decision to investigate two possible upgrade processes was made. The first is based on the selective vaporization of impurities by clinkering and the second on the production of zinc sulphate fertilizer by a hydrometallurgical concept. Both are discussed in the following section.

The selective vaporization trials were carried out in a temperature range of 900-1300 °C and with retention times up to 60 minutes. Treatment times of 20-30 minutes achieved satisfying results for the halide removal with values above 97 % at temperatures of 1100 °C. Also lower temperatures of 900 °C led to satisfying results but required a longer retention time. The most problematic compounds to be vaporized were calcium chloride and calcium fluoride. Nevertheless, all halides had a positive influence on the lead oxide yield in varying intensity. Owing to the typically low amount of fluorides, the chloride compounds had a significantly higher impact on the PbO removal results. NaCl, KCl and $PbCl_2$ increased the lead oxide yield less than $CaCl_2$, $FeCl_2$ and $ZnCl_2$. Remaining reaction products from fluoride and chloride trials were obtained in the form of oxides in case of investigated calcium and iron compounds.

It was also possible to validate the results from the experiments with obtained partial pressure curves calculated with thermodynamic software. Especially the one from CaF_2 is almost zero even at temperatures around 1300 °C. Nevertheless, fluorine removal rates above 50 % were achieved for this compound, due to a reaction with lead oxide, leaving calcium oxide as reaction product behind.

Attributable to economic reasons, the next step was to carry out the selective vaporization at lowest possible treatment temperature and with maximum possible throughput, which means low retention times and still achieving satisfying results. NaCl, $CaCl_2$ and $ZnCl_2$ as additives for an increased lead oxide yield were evaluated.

It was determined that NaCl is less effective than $CaCl_2$ and $CaCl_2$ less than $ZnCl_2$. Based on these results, NaCl is not the first choice but due to already high amounts present in waelz oxide, it is interesting that it influences the lead oxide yield positively and does not leave any reaction products behind. $CaCl_2$ performed better but had the disadvantage of zinc oxide losses. Furthermore, CaO as a reaction product is formed, which is not directly a disadvantage with regard to the aim of increased PbO yields but in spite of a further utilization directly in a high purity zinc oxide market. The reason is that the zinc oxide content is limited by the presence of non-volatile CaO, which is virtually not removable without further process steps. The utilization of $ZnCl_2$ leads to reduced retention times. Compared to the other two additives investigated, it was only one fourth of the time of calcium chloride and even less regarding NaCl. Another positive effect was that the obtained reaction product is ZnO and therefore does not form an impurity; next to that only a small loss of ZnO can be balanced. Also important for an upgrade process is the fact that NaCl, which is present in high amounts in industrial material, does not lead to significant zinc losses.

Based on thermochemical calculations, it was shown that steam containing furnace atmosphere, like in the case of gas-fired facilities, can have an influence on the halide removal by supporting the formation of volatile acid (HF and HCl). This was investigated in lab scale trials with simulated industrial atmosphere. Results showed that satisfying clinkering results were obtained but due to the small amount of fluorine (0.33 %) present in the samples, it was not possible to determine the effect of steam on the vaporization of fluoride as HF. Rather it seems that the impact of interaction with PbO by forming PbF_2 is higher than that of steam.

As a consequence of the obtained results from the selective vaporization trials, it can be stated that it will not be possible to utilize the upgraded zinc oxide directly in the high purity market. The reason is not only the chemical analysis and with that the achieved purity; the specific surface does not fit and due to a typical agglomeration during clinkering, the particle size does not correspond with the requirements. However, because of the effective removal of volatile compounds, it is perfectly suitable as raw material for the American process. An implementation could be done by carrying out the clinkering process in the heating up phase of the American process, leading to only a small amount of additional required energy. In this case, the additional value for the high purity producer would be the cheaper raw material but it has to be considered that the facility has to be adapted to meet the requirements of the process, like the installation of a separated off-gas system for the clinkering step. Concluding, it can be stated that it is a potential upgrade process but has to be evaluated for each case separately depending on the existing local conditions, infrastructure and possibilities for the adaption of already existing facilities.

The second investigated upgrade process for waelz oxide was the production of zinc sulphate fertilizer. In this case, three waelz oxides, obtained from different process stages in a waelz plant, were processed to zinc sulphate by removing impurities and a subsequent crystallisation. The main difference of the utilized raw materials lies in the quantity of present halides, carryover and with those also in the zinc oxide content, which is reflected in the costs for the raw material. Two of them, the DSC-WOX and the C-WOX, are generated in the waelz plant, while the DL-WOX is an already washed crude waelz oxide (C-WOX), low in its halide content.

The production of zinc sulphate combines four main process steps, including leaching with diluted sulphuric acid, iron-manganese precipitation, cementation and crystallisation.

The achieved purity was 99.3 % zinc sulphate hexahydrate in case of DL-WOX, 93.7 % and 91.4 % zinc sulphate hexahydrate in case of C-WOX and DSC-WOX, respectively. The lower values in the last two cases are caused by salts, which could be removed easily in a washing step and would therefore offer the opportunity to achieve higher product qualities, like in case of the DLW raw material. Arsenic, chromium, copper and mercury were found below 1 ppm in the obtained products. This is compared with common fertilizers and animal feed grades within the requirements, and shows excellent results considering production conditions that have not been optimized yet.

Relating to the chemical composition of the obtained by-products, the lead filter cake should be applicable in the lead industry, the Fe-Mn filter cake might be usable for producing an iron manganese alloy and the cementation cake is relatively high in cadmium and might be used for cadmium production.

With regard to the results of the experiments, a possible plant layout was designed, which was the basis for the calculation of the capital expenditures. The assumed 5 000 tons production capacity of $ZnSO_4$ led to an estimated CAPEX of approximately 1.3 € million . Based on the mass balance, the costs for chemicals, other consumables, etc. the running costs of a zinc sulphate plant were estimated. They are in a range of 2.5 to 3.5 € million per year depending on the raw material used. To evaluate the economic viability, two cases were investigated, with a sales price of 650 € per ton of zinc sulphate and 450 € per ton of sold product.

In summary, it can be stated that in both cases (450 and 650 €/ton), based on the CAPEX and OPEX estimations, it seems to be an economical way of upgrading secondary zinc oxides to zinc sulphates. The most realistic case is the one with washed material, which is more expensive but due to the fact that a too high chlorine content can also limit the applicability, it is meaningful to include a washing step or to purchase material that has already been washed.

13. Summary

The state-of-the-art processes for the recycling of zinc bearing steel mill dusts generate as their main product an impure zinc oxide. The most frequently used technology is the waelz process. The obtained product, the waelz oxide, can only be utilized in the primary zinc industry and even there causes several difficulties, due to disturbing impurities. Although typically the waelz oxide is washed by soda-leaching, the remaining halide content is still too high for a direct input into the leaching circuit because of possible cathode corrosion and possible chlorine gas formation. Therefore, the washed waelz oxide can only be utilized as a concentrate substitute and is charged into the roasting step, also causing difficulties like corrosion and sticking in these facilities.

In contrast to such secondary zinc oxides mainly obtained from waelz kilns, the so-called American and French process produces a high purity zinc oxide by making use of high grade raw materials. They are sold to different application areas, such as the tyre, ceramics or pharmaceutical industry. If the revenue of the two aforementioned zinc oxide qualities, concentrate substitute from steel mill dust recycling and high purity material from for instance the French process, are compared, a delta of up to € 600 would be possible. This high amount of possible additional revenue by upgrading low quality waelz oxide to high purity products justifies the process costs of an upgrade step, which is why the aim of this thesis was the development of an upgrade process, utilizing waelz oxide as raw material.

A detailed characterization of the material was done to generate basic know-how concerning morphology and general behaviour of the material. It clearly showed that a main part of the impurities are halides next to lead oxide. Based on that, a detailed survey on the behaviour of such halides under different conditions and related to those possible available concepts for a possible removal was carried out.

An additional target of this research was to identify utilization areas for such an upgraded waelz oxide and by this break into new markets for waelz kiln operators. For this, the two areas zinc sulphate and high purity zinc oxides were evaluated.

In the course of these investigations, the selective vaporization was studied, varying parameters like treatment temperature or retention time. The results showed satisfying halide and lead oxide vaporization under reasonable treatment conditions. It was affirmed that in case of present iron and calcium halides, non-volatile reaction products are obtained which limit the possibility of utilization in the high purity market.

To form a more economic process, the addition of chemicals was also studied to increase the speed of vaporization, especially that of lead oxide. The results showed that zinc chloride is the most effective additive, due to a four times faster evaporation of lead oxide compared to the others. Additionally, minimal zinc losses next to the formation of not disturbing reaction products were recognized.

Concerning an upgrade to industrial scale, where the heat supply for such a clinker step would most probably be provided by gas burners, industrial-like experiments were carried out, using similar conditions. As a result of steam bearing furnace atmosphere, the formation of hydrofluoric and hydrochloric acid by reaction with the present halide is supported. Due to the enhanced vaporization of fluorine and chlorine as HF and HCl, the efficiency of lead oxide vaporization was increased too because of a likely reaction with the acid vapour. Next to that, the higher exchange rate of furnace atmosphere generally leads to increased vaporization yields as a result of lowered partial pressure of gaseous reaction products.

Based on the obtained quality of clinkered zinc oxide, an industrial implementation was proposed prior to an American process forming a two-step concept. The heating up has to be carried out under oxidizing conditions, removing the impurities from the waelz oxide. Afterwards, a reduction in the same way as it is already done in the common American process follows, producing high purity zinc oxide.

Alternatively to the selective vaporization, a hydrometallurgical upgrade to zinc sulphate was investigated. The main challenge lies in the utilization of low grade starting materials, with critical contents of heavy metals. Particularly based on the utilization as fertilizer and animal feed additive, the attention was focused on the product quality. The production of zinc sulphate combined four main process steps, including leaching with diluted sulphuric acid, iron-manganese precipitation, cementation and crystallisation. The results obtained showed that especially the critical heavy metals, like arsenic, chromium, lead, etc. were removed with satisfying yields and a product quality comparable with commercially available ones was produced. Parallel to the trials, a model based on the chemical reactions of the production process was created, simulating the mass and energy balances for the three raw materials investigated. This allowed a qualified estimation of the consumption of consumables and mass flows, which were further used as a basis for the development of a possible plant design. The calculation of CAPEX as well as OPEX was again based on this mass balance as well as on the results obtained from the experiments.

In general, all three raw materials were successfully processed to a zinc sulphate with satisfying low heavy metal contents and furthermore, the economic viability showed positive results.

In conclusion, it can be said that both investigated processes can be applied for an upgrade of the investigated waelz oxide. Additionally, the market research showed that there is potential in both product areas and the consumption is forecasted to grow steadily, but as discussed, the price politics have a major influence on the possible sale figures, which underlines once more the necessity of cheap raw materials and intelligent process concepts.

14. Recommendations for constitutive work

The focus of this thesis was to evaluate the upgrade of waelz oxide to a product with added value and develop a concept which can be scaled up to industry. Both concepts investigated show high potential and will be further developed together with company partners at the Christian Doppler Laboratory for Optimization and Biomass Utilization in Heavy Metal Recycling. So as to optimize the process concept and due to the fact that during this work, several topics with less significance came up but were considered to be interesting, recommendations for constitutive work are provided below:

- To optimize the selective vaporization concept a utilization of the obtained clinker dust in lead chemicals production is proposed but has to be verified.
- Due to missing available assumption for local conditions of a possible site, the estimation of economy for the clinkering concept was not as precise as the case study for zinc sulphate. To be able to make a more accurate estimation of the economic viability, a detailed study would be meaningful.
- Currently, the mentioned utilization of by-products from the zinc sulphate production was not evaluated in detail. Therefore, it is recommended that the possibilities for utilization are evaluated in detail and alternatives are found.
- In case of lead cake, a flotation for a further enrichment of valuable metal could be carried out, if the valuable metal content is too low for direct utilization.
- The trials for zinc sulphate production showed losses of zinc via the filter cakes. For that reason, a washing circuit was included in the suggested plant layout. The optimum parameters for the washing should be evaluated in separate lab scale trials.
- Further optimization would be possible for the zinc sulphate production steps; the remaining manganese content could be decreased by optimized precipitation parameters, for instance.

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16. Appendix

16.1 Appendix – A1

Synthetic mixture and calculated sample composition for trials investigating the influence of temperature:

Table 16-1: Synthetic mixture [g] and calculated sample composition [%]
for test series at 900 °C for 60 minutes treatment time

Trial	comp.	ZnO [g]	PbO [g]	halog. comp.[g]	[g] F or Cl in compound	ZnO [%]	PbO [%]	halid [%]
13	NaF	3.56	0.401	0.041	0.019	88.956	10.020	1.024
14	PbF_2	3.562	0.401	0.041	0.006	88.961	10.015	1.024
15	KF	3.563	0.4	0.041	0.013	88.986	9.990	1.024
16	ZnF_2	3.561	0.402	0.041	0.015	88.936	10.040	1.024
17	CaF_2	3.561	0.4	0.04	0.019	89.003	9.998	1.000
18	FeF_2	3.561	0.402	0.04	0.016	88.958	10.042	0.999
19	NaCl	3.401	0.321	0.281	0.170	84.961	8.019	7.020
20	$PbCl_2$	3.407	0.321	0.281	0.072	84.984	8.007	7.009
21	KCl	3.4	0.32	0.281	0.134	84.979	7.998	7.023
22	$ZnCl_2$	3.409	0.32	0.28	0.146	85.034	7.982	6.984
23	$CaCl_2$	3.401	0.321	0.282	0.180	84.940	8.017	7.043
24	$FeCl_2$	3.403	0.322	0.28	0.157	84.969	8.040	6.991

Table 16-2: Synthetic mixture [g] and calculated sample composition [%]
for test series at 1000 °C for 60 minutes treatment time

Trial	comp.	ZnO [g]	PbO [g]	halog. comp.[g]	[g] F or Cl in compound	ZnO [%]	PbO [%]	halid [%]
25	NaF	3.56	0.403	0.041	0.019	88.911	10.065	1.024
26	PbF_2	3.565	0.401	0.041	0.006	88.969	10.007	1.023
27	KF	3.561	0.4	0.041	0.013	88.981	9.995	1.024
28	ZnF_2	3.561	0.402	0.041	0.015	88.936	10.040	1.024
29	CaF_2	3.563	0.4	0.04	0.019	89.008	9.993	0.999
30	FeF_2	3.56	0.403	0.04	0.016	88.933	10.067	0.999
31	NaCl	3.401	0.322	0.28	0.170	84.961	8.044	6.995
32	$PbCl_2$	3.4	0.322	0.281	0.072	84.936	8.044	7.020
33	KCl	3.401	0.324	0.28	0.133	84.919	8.090	6.991
34	$ZnCl_2$	3.401	0.322	0.286	0.149	84.834	8.032	7.134
35	$CaCl_2$	3.401	0.325	0.284	0.181	84.813	8.105	7.082
36	$FeCl_2$	3.401	0.321	0.28	0.157	84.983	8.021	6.997

Table 16-3: Synthetic mixture [g] and calculated sample composition [%]
for test series at 1100 °C for 5, 10, 20, 30, 60 minutes treatment time

Trial	comp.	ZnO [g]	PbO [g]	halog. comp. [g]	[g] F or Cl in compound	ZnO [%]	PbO [%]	halid [%]
1	NaF	45.01	5.04	0.51	0.231	89.023	9.968	1.009
2	PbF_2	45.01	5.05	0.51	0.079	89.005	9.986	1.009
3	KF	45.02	5.06	0.51	0.167	88.990	10.002	1.008
4	ZnF_2	45.01	5.06	0.51	0.187	88.988	10.004	1.008
5	CaF_2	45.01	5.06	0.51	0.248	88.988	10.004	1.008
6	FeF_2	45.01	5.06	0.51	0.206	88.988	10.004	1.008
7	NaCl	45	4.24	3.71	2.251	84.986	8.008	7.007
8	$PbCl_2$	45	4.24	3.71	0.946	84.986	8.008	7.007
9	KCl	45	4.24	3.71	1.764	84.986	8.008	7.007
10	$ZnCl_2$	45	4.24	3.71	1.930	84.986	8.008	7.007
11	$CaCl_2$	45	4.24	3.71	2.370	84.986	8.008	7.007
12	$FeCl_2$	45	4.24	3.706	2.073	84.992	8.008	7.000

Table 16-4: Synthetic mixture [g] and calculated sample composition [%]
for test series at 1100 °C for 60 minutes treatment time (only chlorine compounds)

Trial	comp.	ZnO [g]	PbO [g]	halog. comp. [g]	[g] F or Cl in compound	ZnO [%]	PbO [%]	halid [%]
70	NaCl	6.801	0.641	0.561	0.340	84.981	8.009	7.010
71	$PbCl_2$	6.802	0.641	0.561	0.143	84.983	8.008	7.009
72	KCl	6.805	0.641	0.562	0.267	84.978	8.004	7.018
73	$ZnCl_2$	6.803	0.641	0.561	0.292	84.984	8.007	7.008
74	$CaCl_2$	6.801	0.641	0.562	0.359	84.970	8.008	7.021
75	$FeCl_2$	6.801	0.640	0.560	0.313	85.002	7.999	6.999

Table 16-5: Synthetic mixture [g] and calculated sample composition [%]
for test series at 1200 °C for 60 minutes treatment time

Trial	comp.	ZnO [g]	PbO [g]	halog. comp. [g]	[g] F or Cl in compound	ZnO [%]	PbO [%]	halid [%]
37	NaF	3.56	0.401	0.04	0.018	88.978	10.022	1.000
38	PbF_2	3.561	0.402	0.04	0.006	88.958	10.042	0.999
39	KF	3.562	0.4	0.041	0.013	88.983	9.993	1.024
40	ZnF_2	3.561	0.401	0.041	0.015	88.958	10.017	1.024
41	CaF_2	3.561	0.402	0.041	0.020	88.936	10.040	1.024
42	FeF_2	3.561	0.403	0.041	0.017	88.914	10.062	1.024
43	NaCl	3.403	0.322	0.281	0.170	84.948	8.038	7.014
44	$PbCl_2$	3.403	0.322	0.282	0.072	84.926	8.036	7.038
45	KCl	3.401	0.32	0.281	0.134	84.983	7.996	7.021
46	$ZnCl_2$	3.405	0.32	0.281	0.146	84.998	7.988	7.014
47	$CaCl_2$	3.402	0.322	0.28	0.179	84.965	8.042	6.993
48	$FeCl_2$	3.402	0.322	0.28	0.157	84.965	8.042	6.993

Table 16-6: Synthetic mixture [g] and calculated sample composition [%]
for test series at 1300 °C for 60 minutes treatment time

Trial	comp.	ZnO [g]	PbO [g]	halog. comp.[g]	[g] F or Cl in compound	ZnO [%]	PbO [%]	halid [%]
58	NaF	3.562	0.4	0.042	0.019	88.961	9.990	1.049
59	PbF_2	3.562	0.401	0.04	0.006	88.983	10.017	0.999
60	KF	3.562	0.401	0.046	0.015	88.850	10.002	1.147
61	ZnF_2	3.561	0.4	0.04	0.015	89.003	9.998	1.000
62	CaF_2	3.562	0.401	0.041	0.020	88.961	10.015	1.024
63	FeF_2	3.56	0.402	0.041	0.017	88.933	10.042	1.024
64	NaCl	0.29	0.321	3.414	2.071	7.205	7.975	84.820
65	$PbCl_2$	3.405	0.324	0.281	0.072	84.913	8.080	7.007
66	KCl	3.401	0.32	0.28	0.133	85.004	7.998	6.998
67	$ZnCl_2$	3.405	0.32	0.281	0.146	84.998	7.988	7.014
68	$CaCl_2$	3.402	0.322	0.28	0.179	84.965	8.042	6.993
69	$FeCl_2$	3.402	0.32	0.280	0.157	85.010	7.996	6.993

16.2 Appendix – A2

Synthetic mixture and calculated sample composition for trials investigating the influence of retention time at constant treatment temperature of 1100 °C:

Table 16-7: Test series – NaF, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
1.1.1	5	58.10	63.12	62.90	5.02	0.22	4.38	3.69
1.1.2		64.33	69.33	69.18	5.00	0.15	3.00	
1.2.1	10	66.00	71.03	70.75	5.03	0.28	5.57	4.96
1.2.2		62.16	67.22	67.00	5.06	0.22	4.35	
1.3.1	20	64.80	69.81	69.48	5.01	0.33	6.59	6.78
1.3.2		62.77	67.79	67.44	5.02	0.35	6.97	
1.4.1	30	58.84	63.86	63.47	5.02	0.39	7.77	8.25
1.4.2		68.03	72.95	72.52	4.92	0.43	8.74	
1.5.1	60	58.12	63.74	63.13	5.62	0.61	10.85	10.85

Table 16-8: Test series – PbF_2, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
2.1.1	5	62.12	67.18	67.02	5.06	0.16	3.16	3.59
2.1.2		58.18	63.17	62.97	4.99	0.20	4.01	
2.2.1	10	65.98	70.94	70.64	4.96	0.30	6.05	5.72
2.2.2		64.33	69.34	69.07	5.01	0.27	5.39	
2.3.1	20	64.75	69.75	69.35	5.00	0.40	8.00	7.31
2.3.2		62.69	67.67	67.34	4.98	0.33	6.63	
2.4.1	30	67.95	72.95	72.53	5.00	0.42	8.40	8.39
2.4.2		58.80	63.45	63.06	4.65	0.39	8.39	
2.5.1	60	65.17	70.21	69.67	5.04	0.54	10.71	10.71

Table 16-9: Test series – KF, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
3.1.1	5	64.25	69.26	69.08	5.01	0.18	3.59	3.79
3.1.2		58.10	63.12	62.92	5.02	0.20	3.98	
3.2.1	10	62.73	67.75	67.46	5.02	0.29	5.78	5.39
3.2.2		64.14	69.13	68.88	4.99	0.25	5.01	
3.3.1	20	67.92	73.95	73.54	6.03	0.41	6.80	6.61
3.3.2		62.07	67.06	66.74	4.99	0.32	6.41	
3.4.1	30	64.70	69.70	69.28	5.00	0.42	8.40	8.37
3.4.2		65.91	70.94	70.52	5.03	0.42	8.35	
3.5.1	60	66.04	71.1	70.41	5.06	0.69	13.64	13.64

Table 16-10: Test series – ZnF_2, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
4.1.1	5	62.72	67.73	67.50	5.01	0.23	4.59	4.19
4.1.2		64.72	69.74	69.55	5.02	0.19	3.78	
4.2.1	10	58.08	63.07	62.81	4.99	0.26	5.21	5.09
4.2.2		70.94	75.98	75.73	5.04	0.25	4.96	
4.3.1	20	65.87	70.90	70.52	5.03	0.38	7.55	7.27
4.3.2		64.14	69.15	68.80	5.01	0.35	6.99	
4.4.1	30	64.30	69.29	68.83	4.99	0.46	9.22	8.60
4.4.2		62.08	67.09	66.69	5.01	0.40	7.98	
4.5.1	60	64.81	69.81	69.17	5.00	0.64	12.80	12.80

Table 16-11: Test series – CaF_2, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
5.1.1	5	62.71	67.71	67.50	5.00	0.21	4.20	4.61
5.1.2		64.70	69.68	69.43	4.98	0.25	5.02	
5.2.1	10	70.93	75.93	75.66	5.00	0.27	5.40	4.68
5.2.2		58.09	63.15	62.95	5.06	0.20	3.95	
5.3.1	20	65.88	70.90	70.52	5.02	0.38	7.57	6.86
5.3.2		62.08	67.12	66.81	5.04	0.31	6.15	
5.4.1	30	64.18	69.20	68.78	5.02	0.42	8.37	7.79
5.4.2		64.30	69.29	68.93	4.99	0.36	7.21	
5.5.1	60	58.85	63.82	63.27	4.97	0.55	11.07	11.07

Table 16-12: Test series – FeF_2, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
6.1.1	5	62.76	67.76	67.54	5.00	0.22	4.40	4.03
6.1.2		67.92	73.93	73.71	6.01	0.22	3.66	
6.2.1	10	58.10	63.19	62.88	5.09	0.31	6.09	5.44
6.2.2		64.17	69.19	68.95	5.02	0.24	4.78	
6.3.1	20	62.11	67.13	66.77	5.02	0.36	7.17	6.57
6.3.2		64.28	69.30	69.00	5.02	0.30	5.98	
6.4.1	30	65.92	70.95	70.55	5.03	0.40	7.95	8.10
6.4.2		64.76	69.85	69.43	5.09	0.42	8.25	
6.5.1	60	67.85	72.91	72.37	5.06	0.54	10.67	10.67

Table 16-13: Test series – NaCl, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
7.1.1	5	58.03	63.01	62.84	4.98	0.17	3.41	2.95
7.1.2		62.06	68.08	67.93	6.02	0.15	2.49	
7.2.1	10	65.79	70.76	70.49	4.97	0.27	5.43	6.08
7.2.2		64.24	69.30	68.96	5.06	0.34	6.72	
7.3.1	20	64.10	69.04	68.47	4.94	0.57	11.54	11.35
7.3.2		62.62	67.64	67.08	5.02	0.56	11.16	
7.4.1	30	64.61	69.61	69.01	5.00	0.60	12.00	12.19
7.4.2		70.82	75.91	75.28	5.09	0.63	12.38	
70.5.1	60	60.105	61.603	61.369	1.50	0.23	15.62	16.07
70.5.2		61.619	63.249	62.969	1.63	0.28	17.18	
70.5.3		53.012	54.656	54.404	1.64	0.25	15.33	
70.5.4		53.258	54.799	54.561	1.54	0.24	15.44	
70.5.5		58.499	60.174	59.893	1.68	0.28	16.78	

Table 16-14: Test series – $PbCl_2$, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
8.1.1	5	64.17	69.19	68.68	5.02	0.51	10.16	10.34
8.1.2		62.71	67.75	67.22	5.04	0.53	10.52	
8.2.1	10	62.07	67.13	66.52	5.06	0.61	12.06	12.03
8.2.2		64.27	69.27	68.67	5.00	0.60	12.00	
8.3.1	20	64.68	69.69	69.02	5.01	0.67	13.37	13.37
8.3.2		70.89	75.90	75.23	5.01	0.67	13.37	
8.4.1	30	65.87	70.80	70.06	4.93	0.74	15.01	14.79
8.4.2		58.07	63.15	62.41	5.08	0.74	14.57	
71.5.1	60	63.990	65.510	65.299	1.52	0.21	13.88	14.52
71.5.2		64.615	66.093	65.883	1.48	0.21	14.21	
71.5.3		56.922	58.657	58.392	1.74	0.26	15.27	
71.5.4		56.044	57.814	57.560	1.77	0.25	14.35	
71.5.5		51.651	53.115	52.897	1.46	0.22	14.89	

Table 16-15: Test series – KCl, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
9.1.1	5	64.12	69.22	69.00	5.10	0.22	4.31	4.32
9.1.2		58.03	63.12	62.90	5.09	0.22	4.32	
9.2.1	10	62.04	67.19	66.68	5.15	0.51	9.90	9.61
9.2.2		64.26	69.30	68.83	5.04	0.47	9.33	
9.3.1	20	70.90	75.92	75.20	5.02	0.72	14.34	14.87
9.3.2		64.65	69.65	68.88	5.00	0.77	15.40	
9.4.1	30	62.70	67.75	66.90	5.05	0.85	16.83	16.52
9.4.2		65.83	70.89	70.07	5.06	0.82	16.21	
72.5.1	60	60.084	61.535	61.300	1.45	0.23	16.20	15.83
72.5.2		61.574	63.150	62.911	1.58	0.24	15.16	
72.5.3		52.963	54.637	54.371	1.67	0.27	15.89	
72.5.4		53.211	54.866	54.601	1.66	0.27	16.01	
72.5.5		58.444	60.060	59.803	1.62	0.26	15.90	

Table 16-16: Test series – $ZnCl_2$, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
10.1.1	5	58.08	63.09	62.26	5.01	0.83	16.57	17.11
10.1.2		62.72	67.76	66.87	5.04	0.89	17.66	
10.2.1	10	64.74	69.80	68.94	5.06	0.86	17.00	16.50
10.2.2		70.95	76.01	75.20	5.06	0.81	16.01	
10.3.1	20	65.88	70.89	70.08	5.01	0.81	16.17	16.22
10.3.2		64.28	69.26	68.45	4.98	0.81	16.27	
10.4.1	30	64.18	69.16	68.32	4.98	0.84	16.87	16.99
10.4.2		62.10	67.07	66.22	4.97	0.85	17.10	
73.5.1	60	60.116	61.473	61.286	1.36	0.19	13.78	14.08
73.5.2		61.646	63.206	62.999	1.56	0.21	13.27	
73.5.3		53.026	54.763	54.485	1.74	0.28	16.00	
73.5.4		53.287	55.057	54.821	1.77	0.24	13.33	
73.5.5		58.510	60.085	59.864	1.58	0.22	14.03	

Table 16-17: Test series – $CaCl_2$, constant temperature (1100 °C), variation of time [72]

Trial	time	ceramic boat	CB + sample		Δ sample	Δ vapour	volatization yield	average value
	[min]	empty [g]	Input [g]	Output [g]	[g]	[g]	[%]	[%]
11.1.1	5	64.26	69.28	68.84	5.02	0.44	8.76	8.76
11.1.2		62.07	67.10	66.66	5.03	0.44	8.75	
11.2.1	10	64.17	69.15	68.47	4.98	0.68	13.65	14.14
11.2.2		58.09	63.08	62.35	4.99	0.73	14.63	
11.3.1	20	62.70	67.77	66.93	5.07	0.84	16.57	16.97
11.3.2		65.86	70.81	69.95	4.95	0.86	17.37	
11.4.1	30	64.68	69.71	68.79	5.03	0.92	18.29	17.78
11.4.2		70.99	75.91	75.06	4.92	0.85	17.28	
74.5.1	60	64.019	65.463	65.246	1.44	0.22	15.03	15.30
74.5.2		64.638	66.310	66.055	1.67	0.25	15.25	
74.5.3		56.936	58.523	58.285	1.59	0.24	15.00	
74.5.4		56.092	57.735	57.472	1.64	0.26	16.01	
74.5.5		51.676	53.334	53.082	1.66	0.25	15.20	

Table 16-18: Test series – $FeCl_2$, constant temperature (1100 °C), variation of time [72]

Trial	time [min]	ceramic boat empty [g]	CB + sample		Δ sample [g]	H_2O [g]	Δ vapour [g]	Δ vap.-H_2O [g]	volatization yield [%]	average value [%]
			Input [g]	Output [g]						
12.1.1	5	64.64	69.67	68.73	5.03	0.200	0.94	0.74	15.32	15.60
12.1.2		70.89	75.88	74.92	4.99	0.199	0.96	0.76	15.89	
12.2.1	10	62.05	67.01	66.08	4.96	0.197	0.93	0.73	15.38	15.66
12.2.2		65.82	70.80	69.84	4.98	0.198	0.96	0.76	15.93	
12.3.1	20	64.15	69.27	68.24	5.12	0.204	1.03	0.83	16.81	16.48
12.3.2		64.25	69.28	68.30	5.03	0.200	0.98	0.78	16.15	
12.4.1	30	62.66	67.67	66.69	5.01	0.199	0.98	0.78	16.23	16.70
12.4.2		58.04	63.07	62.04	5.03	0.200	1.03	0.83	17.18	
75.5.1	60	64.019	65.581	65.322	1.56	0.062	0.26	0.20	13.12	13.51
75.5.2		64.647	66.308	66.029	1.66	0.066	0.28	0.21	13.35	
75.5.3		56.944	58.650	58.358	1.71	0.068	0.29	0.22	13.68	
75.5.4		56.093	57.812	57.521	1.72	0.068	0.29	0.22	13.49	
75.5.5		51.684	53.317	53.034	1.63	0.065	0.28	0.22	13.90	

16.3 Appendix – A3

Weights of samples used for selective vaporization trials and calculated overall vaporization for trials with constant retention time of 60 minutes and a variation of treatment temperature:

Table 16-19: Test series – chlorine trials, constant treatment time (60 min), temperature (900 °C)

trial	comp.	time [min]	empty boat [g]	boat + sample [g]	after trial [g]	Δ sample [g]	Δ volatilized [g]	volatilization [%]	average [%]
19	NaCl	60	63.911	65.081	64.947	1.170	0.134	11.453	10.774
		60	55.981	57.399	57.254	1.418	0.145	10.226	
		60	51.541	52.941	52.792	1.400	0.149	10.643	
21	KCl	60	68.468	69.696	69.562	1.228	0.134	10.912	10.912
		60	64.517	65.943	65.792	1.426	0.151	10.589	
		60	56.780	58.115	57.965	1.335	0.150	11.236	
20	$PbCl_2$	60	63.859	65.097	64.969	1.238	0.128	10.339	9.998
		60	59.845	61.172	61.041	1.327	0.131	9.872	
		60	55.939	57.360	57.221	1.421	0.139	9.782	
22	$ZnCl_2$	60	68.465	69.784	69.605	1.319	0.179	13.571	13.611
		60	64.506	65.775	65.600	1.269	0.175	13.790	
		60	56.775	58.230	58.034	1.455	0.196	13.471	
23	$CaCl_2$	60	63.892	65.187	64.961	1.295	0.226	17.452	17.570
		60	59.882	61.339	61.090	1.457	0.249	17.090	
		60	55.978	57.266	57.032	1.288	0.234	18.168	
24	$FeCl_2$	60	64.557	65.922	65.705	1.311	0.163	12.416	12.134
		60	59.875	61.206	61.000	1.278	0.153	11.979	
		60	56.813	58.277	58.050	1.406	0.169	12.008	

Table 16-20: Test series – fluorine trials, constant treatment time (60 min), temperature (900 °C)

trial	comp.	time [min]	empty boat [g]	boat + sample [g]	after trial [g]	Δ sample [g]	Δ volatilized [g]	volatilization [%]	average [%]
13	NaF	60	68.372	69.741	69.686	1.369	0.055	4.017	4.116
		60	64.421	65.731	65.678	1.310	0.053	4.046	
		60	56.690	57.997	57.941	1.307	0.056	4.285	
15	KF	60	65.908	67.168	67.114	1.260	0.054	4.286	4.197
		60	62.831	64.060	64.008	1.229	0.052	4.231	
		60	56.623	58.145	58.083	1.522	0.062	4.074	
14	PbF_2	60	63.788	65.011	64.966	1.223	0.045	3.679	3.771
		60	59.765	61.136	61.085	1.371	0.051	3.720	
		60	55.827	57.232	57.177	1.405	0.055	3.915	
16	ZnF_2	60	63.818	65.138	65.080	1.320	0.058	4.394	4.438
		60	59.798	61.102	61.048	1.304	0.054	4.141	
		60	55.874	57.234	57.169	1.360	0.065	4.779	
17	CaF_2	60	68.413	69.647	69.602	1.234	0.045	3.647	3.590
		60	64.462	65.812	65.765	1.350	0.047	3.481	
		60	56.714	58.114	58.063	1.400	0.051	3.643	
18	FeF_2	60	63.814	65.021	64.980	1.207	0.041	3.397	3.388
		60	59.795	61.177	61.131	1.382	0.046	3.329	
		60	55.865	57.261	57.213	1.396	0.048	3.438	

Table 16-21: Test series – chlorine trials, constant treatment time (60 min), temperature (1000 °C)

trial	comp.	time [min]	empty boat [g]	boat + sample [g]	after trial [g]	Δ sample [g]	Δ volatilized [g]	volatilization [%]	average [%]
31	$NaCl$	60	63.831	65.256	65.034	1.425	0.222	15.579	16.174
		60	59.817	61.054	60.850	1.237	0.204	16.492	
		60	55.893	57.218	57.000	1.325	0.218	16.453	
33	KCl	60	68.402	69.771	69.558	1.369	0.213	15.559	15.957
		60	64.456	65.950	65.714	1.494	0.236	15.797	
		60	56.715	57.829	57.645	1.114	0.184	16.517	
32	$PbCl_2$	60	68.383	69.624	69.428	1.241	0.196	15.794	15.141
		60	64.432	65.777	65.579	1.345	0.198	14.721	
		60	56.695	58.097	57.888	1.402	0.209	14.907	
34	$ZnCl_2$	60	68.417	69.656	69.472	1.239	0.184	14.851	14.360
		60	64.477	66.041	65.819	1.564	0.222	14.194	
		60	56.712	57.909	57.741	1.197	0.168	14.035	
35	$CaCl_2$	60	63.832	65.050	64.868	1.218	0.182	14.943	15.380
		60	59.821	61.190	60.979	1.369	0.211	15.413	
		60	55.897	57.335	57.108	1.438	0.227	15.786	
36	$FeCl_2$	60	64.561	65.950	65.717	1.334	0.178	13.327	13.135
		60	59.881	61.333	61.095	1.394	0.180	12.928	
		60	56.824	58.143	57.924	1.267	0.167	13.149	

Table 16-22: Test series – fluorine trials, constant treatment time (60 min), temperature (1000 °C)

trial	comp.	time [min]	empty boat [g]	boat + sample [g]	after trial [g]	Δ sample [g]	Δ volatilized [g]	volatilization [%]	average [%]
25	NaF	60	63.866	64.972	64.831	1.106	0.141	12.749	12.006
		60	59.846	61.080	60.945	1.234	0.135	10.940	
		60	55.930	57.171	57.018	1.241	0.153	12.329	
27	KF	61	68.369	69.642	69.498	1.273	0.144	11.312	11.001
		61	64.415	65.681	65.546	1.266	0.135	10.664	
		61	56.684	58.135	57.975	1.451	0.160	11.027	
26	PbF_2	60	68.377	69.648	69.510	1.271	0.138	10.858	10.784
		60	64.428	65.761	65.621	1.333	0.140	10.503	
		60	56.692	58.075	57.923	1.383	0.152	10.991	
28	ZnF_2	60	63.826	65.208	65.070	1.382	0.138	9.986	10.291
		60	59.822	61.107	60.978	1.285	0.129	10.039	
		60	55.894	57.212	57.069	1.318	0.143	10.850	
29	CaF_2	60	68.387	69.573	69.470	1.186	0.103	8.685	7.767
		60	64.437	65.722	65.628	1.285	0.094	7.315	
		60	56.705	58.225	58.114	1.520	0.111	7.303	
30	FeF_2	60	63.817	65.105	64.998	1.288	0.107	8.307	8.402
		60	59.797	61.140	61.029	1.343	0.111	8.265	
		60	55.861	57.216	57.099	1.355	0.117	8.635	

Table 16-23: Test series – chlorine trials, constant treatment time (60 min), temperature (1200 °C)

trial	comp.	time [min]	empty boat [g]	boat + sample [g]	after trial [g]	Δ sample [g]	Δ volatilized [g]	volatilization [%]	average [%]
43	NaCl	60	63.923	65.201	64.969	1.278	0.232	18.153	18.381
		60	56.011	57.276	57.028	1.265	0.248	19.605	
		60	51.565	53.003	52.753	1.438	0.250	17.385	
45	KCl	60	64.561	65.712	65.526	1.151	0.186	16.160	16.317
		60	59.876	61.196	60.976	1.320	0.220	16.667	
		60	56.842	58.349	58.106	1.507	0.243	16.125	
44	$PbCl_2$	60	63.913	65.257	65.048	1.344	0.209	15.551	15.653
		60	55.983	57.405	57.184	1.422	0.221	15.541	
		60	51.573	52.783	52.591	1.210	0.192	15.868	
46	$ZnCl_2$	60	64.573	65.806	65.630	1.233	0.176	14.274	14.605
		60	59.893	61.310	61.101	1.417	0.209	14.749	
		60	56.847	58.233	58.028	1.386	0.205	14.791	
47	$CaCl_2$	60	63.926	64.921	64.758	0.995	0.163	16.382	16.452
		60	55.982	57.508	57.260	1.526	0.248	16.252	
		60	51.574	53.105	52.849	1.531	0.256	16.721	
48	$FeCl_2$	60	64.564	65.949	65.716	1.330	0.178	13.379	13.344
		60	59.886	61.372	61.121	1.427	0.192	13.450	
		60	56.832	58.099	57.888	1.217	0.161	13.203	

Table 16-24: Test series – fluorine trials, constant treatment time (60 min), temperature (1200 °C)

trial	comp.	time [min]	empty boat [g]	boat + sample [g]	after trial [g]	Δ sample [g]	Δ volatilized [g]	volatilization [%]	average [%]
37	NaF	60	65.968	67.218	67.024	1.250	0.194	15.520	15.284
		60	62.885	64.218	64.016	1.333	0.202	15.154	
		60	56.679	58.089	57.875	1.410	0.214	15.177	
39	KF	60	65.929	67.215	67.064	1.286	0.151	11.742	12.296
		60	62.852	64.182	64.024	1.330	0.158	11.880	
		60	56.663	58.050	57.866	1.387	0.184	13.266	
38	PbF_2	60	63.827	65.093	64.892	1.266	0.201	15.877	15.874
		60	59.807	61.146	60.938	1.339	0.208	15.534	
		60	55.874	57.262	57.037	1.388	0.225	16.210	
40	ZnF_2	60	65.944	67.024	66.881	1.080	0.143	13.241	11.795
		60	62.866	64.334	64.183	1.468	0.151	10.286	
		60	56.680	58.122	57.951	1.442	0.171	11.859	
41	CaF_2	60	63.807	65.060	64.909	1.253	0.151	12.051	11.847
		60	59.787	61.151	60.985	1.364	0.166	12.170	
		60	55.855	57.233	57.077	1.378	0.156	11.321	
42	FeF_2	60	63.810	64.804	64.681	0.994	0.123	12.374	11.894
		60	59.797	61.258	61.089	1.461	0.169	11.567	
		60	55.858	57.391	57.211	1.533	0.180	11.742	

Table 16-25: Test series – chlorine trials, constant treatment time (60 min), temperature (1300 °C)

trial	comp.	time [min]	empty boat [g]	boat + sample [g]	after trial [g]	Δ sample [g]	Δ volatilized [g]	volatilization [%]	average [%]
64	NaCl	60	63.955	65.262	65.039	1.307	0.223	17.062	17.147
		60	56.014	57.292	57.070	1.278	0.222	17.371	
		60	51.613	53.030	52.789	1.417	0.241	17.008	
66	KCl	60	64.582	65.718	65.520	1.136	0.198	17.430	16.760
		60	56.878	58.291	58.054	1.413	0.237	16.773	
		60	60.048	61.491	61.259	1.443	0.232	16.078	
65	$PbCl_2$	60	64.569	65.724	65.544	1.155	0.180	15.584	16.170
		60	56.849	58.343	58.101	1.494	0.242	16.198	
		60	60.030	61.375	61.150	1.345	0.225	16.729	
67	$ZnCl_2$	60	63.930	65.207	65.009	1.277	0.198	15.505	15.520
		60	55.994	57.364	57.149	1.370	0.215	15.693	
		60	51.589	52.982	52.768	1.393	0.214	15.363	
68	$CaCl_2$	60	64.526	65.922	65.694	1.396	0.228	16.332	16.270
		60	59.840	61.193	60.976	1.353	0.217	16.038	
		60	56.787	58.034	57.829	1.247	0.205	16.439	
69	$FeCl_2$	60	64.582	65.869	65.640	1.236	0.178	14.390	13.780
		60	56.878	58.422	58.162	1.483	0.199	13.396	
		60	60.063	61.399	61.172	1.283	0.174	13.554	

Table 16-26: Test series – fluorine trials, constant treatment time (60 min), temperature (1300 °C)

trial	comp.	time [min]	empty boat [g]	boat + sample [g]	after trial [g]	Δ sample [g]	Δ volatilized [g]	volatilization [%]	average [%]
58	NaF	73	59.860	61.345	61.162	1.485	0.183	12.323	12.327
		73	56.786	58.112	57.945	1.326	0.167	12.594	
		73	59.958	61.135	60.993	1.177	0.142	12.065	
60	KF	60	63.908	65.155	65.009	1.247	0.146	11.708	12.323
		60	55.991	57.477	57.292	1.486	0.185	12.450	
		60	51.526	52.806	52.642	1.280	0.164	12.812	
59	PbF_2	60	63.923	65.059	64.921	1.136	0.138	12.148	12.121
		60	64.519	65.861	65.701	1.342	0.160	11.923	
		60	51.498	53.011	52.825	1.513	0.186	12.293	
61	ZnF_2	60	63.970	65.214	65.076	1.244	0.138	11.093	11.028
		60	56.022	57.414	57.259	1.392	0.155	11.135	
		60	51.630	52.975	52.829	1.345	0.146	10.855	
62	CaF_2	60	63.943	65.214	65.074	1.271	0.140	11.015	10.713
		60	56.006	57.306	57.169	1.300	0.137	10.538	
		60	51.607	53.024	52.874	1.417	0.150	10.586	
63	FeF_2	60	64.601	65.750	65.625	1.149	0.125	10.879	11.180
		60	56.909	58.394	58.228	1.485	0.166	11.178	
		60	60.079	61.429	61.274	1.350	0.155	11.481	

16.4 Appendix – A4

Chemical analysis of clinkered material and calculated vaporization yields for lead oxide and halide:

Table 16-27: Results (chemical analysis) of trials
at constant treatment time (60 min) and a temperature of 900 °C

		Chem. analysis [%]						Volatilization [%]	
Trial	Comp.	Cl	F	Pb	Element	Halid-compound	PbO	Comp.	PbO
13	NaF		0.1810	4.8600	0.2640	0.400	5.235	62.560	49.901
14	PbF_2		0.0030	4.0700		0.019	4.367	98.181	58.045
15	KF		0.0060	3.4600	0.0265	0.018	3.727	98.283	64.254
16	ZnF_2		0.0190	3.8600		0.052	4.158	95.176	60.425
17	CaF_2		0.2590	9.0500	0.4510	0.532	9.749	48.677	5.988
18	FeF_2		0.0160	7.5900	0.3700	0.040	8.176	96.179	21.343
19	NaCl	<0.100		3.2500	0.0700	<0.165	3.501	>97.904	61.027
20	$PbCl_2$	0.0180		3.7000		0.071	3.929	99.093	55.829
21	KCl	0.0230		3.8400	<0.0010	0.048	4.137	99.386	53.921
22	$ZnCl_2$	0.0070		1.0400		0.013	1.120	99.834	87.874
23	$CaCl_2$	0.0180		0.0490	2.8100	0.028	0.053	99.670	99.457
24	$FeCl_2$	<0.100		0.5600	3.3000	<0.179	0.603	>97.753	93.407

Table 16-28: Results (chemical analysis) of trials
at constant treatment time (60 min) and a temperature of 1000 °C

		Chem. analysis [%]						Volatilization [%]	
Trial	Comp.	Cl	F	Pb	Element	Halid-compound	PbO	Comp.	PbO
25	NaF		0.0010	4.8600	0.0262	0.002	5.235	99.810	54.216
26	PbF_2		<0.001	1.4700		<0.006	1.578	>99.437	85.936
27	KF		0.0020	1.1000	0.0043	0.006	1.185	99.469	89.449
28	ZnF_2		0.0010	1.3500		0.003	1.454	99.762	87.006
29	CaF_2		0.1280	1.4400	0.4860	0.263	1.551	75.710	85.674
30	FeF_2		0.0020	2.9900	0.3810	0.005	3.221	99.547	70.696
31	NaCl	0.0010		0.6660	0.0052	0.002	0.717	99.980	92.522
32	$PbCl_2$	0.0010		0.5510		0.004	0.590	99.953	93.770
33	KCl	0.0010		1.1050	<0.001	0.002	1.190	99.975	87.628
34	$ZnCl_2$	0.0160		0.2520		0.031	0.271	99.631	97.105
35	$CaCl_2$	0.1060		0.0396	2.6300	0.166	0.043	98.018	99.555
36	$FeCl_2$	<0.100		0.2000	3.5000	<0.179	0.215	>97.780	97.667

Table 16-29: Results (chemical analysis) of chlorine trials at different treatment times at a temperature of 1100 °C

		Chem. analysis [%]					Volatilization [%]	
Trial/Comp.	Time [min]	Cl	Pb	Element	Cl-compound	PbO	Comp.	PbO
7.1 NaCl	5	3.08	6.45		5.077	6.948	29.644	15.755
7.2 NaCl	10	2.06	6.61		3.396	7.120	54.482	16.487
7.3 NaCl	20	0.10	4.93		0.165	5.311	97.914	41.203
7.4 NaCl	30	0.10	3.04	0.01	0.165	3.275	97.934	64.090
70.5 NaCl	60	<0.10	0.18	<0.01	<0.165	0.194	>98.027	97.969
8.1 $PbCl_2$	5	0.39	7.73		1.530	7.099	80.425	20.509
8.2 $PbCl_2$	10	0.10	7.10		0.392	7.333	95.075	19.434
8.3 $PbCl_2$	20	0.10	4.39		0.392	4.414	95.151	52.247
8.4 $PbCl_2$	30	0.10	3.63		0.392	3.596	95.230	61.737
71.5 $PbCl_2$	60	<0.10	0.29		<0.392	0.000	>95.217	100.000
9.1 KCl	5	2.45	6.17	0.01	5.152	6.646	29.646	20.582
9.2 KCl	10	0.87	6.59		1.829	7.099	76.401	19.874
9.3 KCl	20	0.10	4.25		0.210	4.578	97.445	51.329
9.4 KCl	30	0.10	2.42		0.210	2.607	97.495	72.822
72.5 KCl	60	<0.10	0.18	<0.01	<0.210	0.194	>97.478	97.961
10.1 $ZnCl_2$	5	0.10	0.29		0.192	0.312	97.726	96.766
10.2 $ZnCl_2$	10	0.10	0.07		0.192	0.075	97.709	99.214
10.3 $ZnCl_2$	20	0.10	0.05		0.192	0.054	97.702	99.436
10.4 $ZnCl_2$	30	0.10	0.04	81.20	0.192	0.043	97.723	99.553
73.5 $ZnCl_2$	60	<0.10	0.10		<0.192	0.108	>97.644	98.845
11.1 $CaCl_2$	5	3.03	4.77		4.743	5.138	38.238	41.450
11.2 $CaCl_2$	10	1.48	1.14		2.317	1.228	71.613	86.833
11.3 $CaCl_2$	20	0.62	0.07		0.970	0.075	88.499	99.218
11.4 $CaCl_2$	30	0.54	0.02	2.60	0.845	0.022	90.083	99.779
74.5 $CaCl_2$	60	<0.10	0.024	2.66	<0.157	0.026	>98.112	99.727
12.1 $FeCl_2$	5	0.10	0.54		0.179	0.582	97.845	93.870
12.2 $FeCl_2$	10	0.10	0.18		0.179	0.194	97.846	97.958
12.3 $FeCl_2$	20	0.10	0.07		0.179	0.075	97.867	99.214
12.4 $FeCl_2$	30	0.10	0.04	3.36	0.179	0.043	97.873	99.552
75.5 $FeCl_2$	60	<0.10	0.07	4.00	<0.179	0.075	>97.791	99.185

Table 16-30: Results (chemical analysis) of fluorine trials
at different treatment times at a temperature of 1100 °C

		Chem. analysis [%]					Volatilization [%]	
Trial/Comp.	Time [min]	Cl	Pb	Element	Cl-compound	PbO	Comp.	PbO
1.1 NaF	5	0.35	8.9		0.774	9.587	26.146	7.375
1.2 NaF	10	0.14	8.43		0.309	9.081	70.846	13.417
1.3 NaF	20	0.01	6.6		0.022	7.110	97.958	33.513
1.4 NaF	30	0.004	5.24		0.009	5.645	99.196	48.046
1.5 NaF	60	0.004	1.46	0.02	0.009	1.573	99.219	85.935
2.1 PbF_2	5	0.05	9.41		0.323	9.843	69.153	4.965
2.2 PbF_2	10	0.007	7.49		0.045	8.027	95.777	24.212
2.3 PbF_2	20	0.004	6.11		0.026	6.558	97.628	39.130
2.4 PbF_2	30	0.004	5.17		0.026	5.546	97.655	49.127
2.5 PbF_2	60	0.004	2.67		0.026	2.853	97.715	74.494
3.1 KF	5	0.09	8.42		0.275	9.070	73.734	12.752
3.2 KF	10	0.02	7.98		0.061	8.596	94.260	18.691
3.3 KF	20	0.004	5.76		0.012	6.205	98.867	42.074
3.4 KF	30	0.004	4.59		0.012	4.944	98.888	54.706
3.5 KF	60	0.004	1.08	0.01	0.012	1.163	98.952	89.954
4.1 ZnF_2	5	0.06	8.52		0.163	9.178	84.488	12.099
4.2 ZnF_2	10	0.009	7.1		0.024	7.648	97.695	27.435
4.3 ZnF_2	20	0.004	7.13		0.011	7.681	98.999	28.807
4.4 ZnF_2	30	0.004	3.81		0.011	4.104	99.014	62.502
4.5 ZnF_2	60	0.004	1.02	81.10	0.011	1.099	99.059	90.423
5.1 CaF_2	5	0.47	8.13		0.966	8.758	8.633	16.492
5.2 CaF_2	10	0.42	7.53		0.863	8.111	18.407	22.706
5.3 CaF_2	20	0.37	5.81		0.760	6.259	29.769	41.729
5.4 CaF_2	30	0.35	5.11		0.719	5.505	34.231	49.264
5.5 CaF_2	60	0.21	2.62	0.66	0.432	2.822	61.940	74.910
6.1 FeF_2	5	0.07	8.74		0.173	9.415	83.539	9.649
6.2 FeF_2	10	0.01	8.3		0.025	8.941	97.684	15.488
6.3 FeF_2	20	0.004	6.08		0.010	6.549	99.085	38.835
6.4 FeF_2	30	0.004	6.12		0.010	6.593	99.100	39.440
6.5 FeF_2	60	0.004	3.04	0.48	0.010	3.275	99.125	70.759

Table 16-31: Results (chemical analysis) of trials
at constant treatment time (60 min) and a temperature of 1200 °C

		Chem. Analysis [%]						Volatilization [%]	
Trial	Comp.	Cl	F	Pb	Element	Halid-compound	PbO	Comp.	PbO
37	NaF		0.0130	0.0090	<0.020	0.029	0.010	97.565	99.918
38	PbF_2		<0.010	0.0060		<0.065	0.006	>94.567	99.946
39	KF		0.0120	0.0150	<0.020	0.037	0.016	96.858	99.858
40	ZnF_2		0.0100	0.0220		0.027	0.024	97.653	99.791
41	CaF_2		0.0170	<0.005	0.4400	0.035	<0.005	96.992	>99.953
42	FeF_2		0.0120	<0.005	0.5700	0.030	<0.005	97.448	>99.953
43	NaCl	<0.100		0.0180	<0.020	<0.165	0.019	>98.081	99.803
44	$PbCl_2$	<0.100		0.0350		<0.392	0.038	>95.299	99.604
45	KCl	<0.100		0.0200	<0.020	<0.210	0.022	>97.494	99.775
46	$ZnCl_2$	<0.100		0.0250		<0.192	0.027	>97.660	99.712
47	$CaCl_2$	<0.100		0.0110	2.4000	<0.157	0.012	>98.130	99.877
48	$FeCl_2$	<0.100		0.0090	3.6000	<0.179	0.010	>97.785	99.896

Table 16-32: Results (chemical analysis) of trials
at constant treatment time (60 min) and a temperature of 1300 °C

		Chem. Analysis [%]						Volatilization [%]	
Trial	Comp.	Cl	F	Pb	Element	Halid-compound	PbO	Comp.	PbO
58	NaF		<0.010	<0.005	<0.0200	<0.022	<0.005	>98.153	>99.953
59	PbF_2		0.1300	<0.005		0.839	<0.005	26.228	>99.953
60	KF		0.0520	<0.005	<0.0200	0.159	<0.005	87.851	>99.953
61	ZnF_2		<0.010	0.0060		<0.027	0.006	>97.579	99.942
62	CaF_2		0.2200	<0.005	0.5200	0.452	<0.005	60.579	>99.952
63	FeF_2		0.0110	<0.005	0.6000	0.027	<0.005	97.644	>99.952
64	NaCl	<0.100			0.0800	<0.165	0.000	>99.839	100.000
65	$PbCl_2$	<0.100		0.0060		<0.392	0.006	>95.310	99.933
66	KCl	<0.100		<0.005	<0.0200	<0.210	<0.005	>97.497	>99.944
67	$ZnCl_2$	<0.100		<0.005		<0.192	<0.005	>97.685	>99.943
68	$CaCl_2$	<0.100		<0.005	2.4000	<0.157	<0.005	>98.126	>99.944
69	$FeCl_2$	<0.100		<0.005	3.8000	<0.179	<0.005	>97.795	>99.942

16.5 Appendix – B1

Results and data related to the trials investigating additives for an increased lead oxide yield. The matrix is formed by 92 % ZnO and 8 % PbO.

Table 16-33: Test series – with addition of one time the stoichiometric amount of additive

		Time	Weight of boat [g]			Delta [g]		Volatilization	Average
trial	comp.	[min]	Empty	+Sample	After trial	Sample	Vapour	[%]	[%]
5	matrix + $ZnCl_2$	5	64.647	72.999	72.258	8.352	0.741	8.872	9.059
			57.893	66.859	66.030	8.966	0.829	9.246	
6	matrix + $ZnCl_2$	15	54.914	63.805	62.845	8.891	0.960	10.797	10.869
			60.855	68.972	68.084	8.117	0.888	10.940	
7	matrix + $ZnCl_2$	30	61.710	69.851	68.964	8.141	0.887	10.895	10.929
			56.185	64.532	63.617	8.347	0.915	10.962	
8	matrix + $ZnCl_2$	60	54.945	63.524	62.570	8.579	0.954	11.120	11.175
			60.881	69.189	68.256	8.308	0.933	11.230	
9	matrix + $CaCl_2$	5	53.092	61.222	61.024	8.130	0.198	2.435	2.421
			61.709	69.897	69.700	8.188	0.197	2.406	
10	matrix + $CaCl_2$	15	57.031	64.129	63.626	7.098	0.503	7.087	6.885
			63.934	72.074	71.530	8.140	0.544	6.683	
11	matrix + $CaCl_2$	30	63.951	72.382	71.543	8.431	0.839	9.951	10.155
			59.221	67.851	66.957	8.630	0.894	10.359	
12	matrix + $CaCl_2$	60	64.048	72.140	71.232	8.092	0.908	11.221	11.392
			57.992	65.136	64.310	7.144	0.826	11.562	
13	matrix + NaCl	5	56.166	64.764	64.678	8.598	0.086	1.000	1.009
			60.931	69.779	69.689	8.848	0.090	1.017	
14	matrix + NaCl	15	61.704	70.177	69.973	8.473	0.204	2.408	2.416
			53.077	61.282	61.083	8.205	0.199	2.425	
15	matrix + NaCl	30	63.951	72.185	71.865	8.234	0.320	3.886	3.768
			59.182	67.318	67.021	8.136	0.297	3.650	
16	matrix + NaCl	60	57.949	66.287	65.692	8.338	0.595	7.136	7.029
			64.061	72.280	71.711	8.219	0.569	6.923	

Table 16-34: Test series – with addition no addition of additive (only matrix as reference state)

		Time	Weight of boat [g]			Delta [g]		Volatilization	Average
trial	comp.	[min]	Empty	+Sample	After trial	Sample	Vapour	[%]	[%]
1	matrix	5	56.932	64.993	64.923	8.061	0.070	0.868	0.856
			53.049	61.465	61.394	8.416	0.071	0.844	
2	matrix	15	61.669	69.979	69.871	8.310	0.108	1.300	1.288
			56.104	64.964	64.851	8.860	0.113	1.275	
3	matrix	30	56.947	65.635	65.484	8.688	0.151	1.738	1.661
			53.065	61.210	61.081	8.145	0.129	1.584	
4	matrix	60	59.158	67.970	67.731	8.812	0.239	2.712	2.846

Table 16-35: Test series – with addition of two times the stoichiometric amount of additive

		Time	Weight of boat [g]			Delta [g]		Volatilization	Average
trial	comp.	[min]	Empty	+Sample	After trial	Sample	Vapour	[%]	[%]
17	matrix + $ZnCl_2$	5	64.124	72.601	71.416	8.477	1.185	13.979	14.121
			57.994	66.505	65.291	8.511	1.214	14.264	
18	matrix + $ZnCl_2$	15	59.256	67.588	66.286	8.332	1.302	15.627	15.598
			64.026	72.825	71.455	8.799	1.370	15.570	
19	matrix + $ZnCl_2$	30	60.917	69.038	67.793	8.121	1.245	15.331	15.519
			53.133	61.575	60.249	8.442	1.326	15.707	
20	matrix + $ZnCl_2$	60	61.771	70.017	68.692	8.246	1.325	16.068	15.879
			56.177	64.456	63.157	8.279	1.299	15.690	
21	matrix + $CaCl_2$	5	64.103	72.746	72.519	8.643	0.227	2.626	2.712
			56.964	65.614	65.372	8.650	0.242	2.798	
22	matrix + $CaCl_2$	15	61.713	70.048	69.410	8.335	0.638	7.654	7.587
			60.933	69.378	68.743	8.445	0.635	7.519	
23	matrix + $CaCl_2$	30	53.086	61.814	60.879	8.728	0.935	10.713	10.422
			63.987	72.545	71.678	8.558	0.867	10.131	
24	matrix + $CaCl_2$	60	60.111	69.037	67.894	8.926	1.143	12.805	12.876
			56.146	64.689	63.583	8.543	1.106	12.946	
25	matrix + NaCl	5	56.965	65.296	65.270	8.331	0.026	0.312	0.303
			64.098	72.250	72.226	8.152	0.024	0.294	
26	matrix + NaCl	15	60.937	69.428	69.288	8.491	0.140	1.649	1.698
			61.716	70.242	70.093	8.526	0.149	1.748	
27	matrix + NaCl	30	57.991	66.708	66.404	8.717	0.304	3.487	3.900
			53.099	61.144	60.797	8.045	0.347	4.313	
28	matrix + NaCl	60	56.156	64.806	64.025	8.650	0.781	9.029	8.868
			60.127	68.798	68.043	8.671	0.755	8.707	

Table 16-36: Test series – with addition of two times the stoichiometric amount of additive

		Time	Weight of boat [g]			Delta [g]		Volatilization	Average
trial	comp.	[min]	Empty	+Sample	After trial	Sample	Vapour	[%]	[%]
29	matrix + $ZnCl_2$	5	60.964	69.274	67.712	8.310	1.562	18.797	18.906
			60.158	68.514	66.925	8.356	1.589	19.016	
30	matrix + $ZnCl_2$	15	56.967	65.518	63.784	8.551	1.734	20.278	20.154
			61.742	69.990	68.338	8.248	1.652	20.029	
31	matrix + $ZnCl_2$	30	51.710	60.205	58.477	8.495	1.728	20.341	20.463
			56.230	64.707	62.962	8.477	1.745	20.585	
32	matrix + $ZnCl_2$	60	64.096	73.008	71.175	8.912	1.833	20.568	20.802
			55.044	63.415	61.654	8.371	1.761	21.037	
33	matrix + $CaCl_2$	5	60.207	68.249	67.958	8.042	0.291	3.619	3.646
			56.259	64.887	64.570	8.628	0.317	3.674	
34	matrix + $CaCl_2$	15	56.996	65.772	65.008	8.776	0.764	8.706	8.754
			64.115	72.521	71.781	8.406	0.740	8.803	
35	matrix + $CaCl_2$	30	61.067	69.670	68.728	8.603	0.942	10.950	11.145
			51.702	60.318	59.341	8.616	0.977	11.339	
36	matrix + $CaCl_2$	60	61.837	70.319	69.089	8.482	1.230	14.501	14.354
			54.737	62.832	61.682	8.095	1.150	14.206	
37	matrix + NaCl	5	61.006	69.666	69.598	8.660	0.068	0.785	0.782
			60.199	68.672	68.606	8.473	0.066	0.779	
38	matrix + NaCl	15	61.776	69.804	69.609	8.028	0.195	2.429	2.457
			57.011	65.341	65.134	8.330	0.207	2.485	
39	matrix + NaCl	30	56.241	64.663	64.271	8.422	0.392	4.654	4.928
			51.740	60.007	59.577	8.267	0.430	5.201	
40	matrix + NaCl	60	64.154	72.404	71.663	8.250	0.741	8.982	8.666
			54.642	62.906	62.216	8.264	0.690	8.349	

16.6 Appendix – B2

Chemical analysis of clinkered material and calculated lead oxide and zinc oxide loss for trials with additives for increased lead oxide yield:

Table 16-37: Chemical analysis of synthetic mixture (without additive addition)

	Stoichiometry	Time [min]	Chemical analysis [%] Pb	Cl	element
matrix	-	5	7.15	-	-
matrix	-	15	6.3	-	-
matrix	-	30	5.9	-	-
matrix	-	60	4.95	-	-

Table 16-38: Chemical analysis of synthetic mixture with $ZnCl_2$ addition

	Stoichiometry	Time [min]	Chemical analysis [%] Pb	Cl	element
matrix + $ZnCl_2$	1	5	1.95	0.33	-
matrix + $ZnCl_2$	1	15	0.9	0.1	-
matrix + $ZnCl_2$	1	30	0.9	0.1	-
matrix + $ZnCl_2$	1	60	0.25	0.1	-
matrix + $ZnCl_2$	2	5	1	0.1	-
matrix + $ZnCl_2$	2	15	0.07	0.1	-
matrix + $ZnCl_2$	2	30	0.06	0.1	-
matrix + $ZnCl_2$	2	60	0.07	0.1	-
matrix + $ZnCl_2$	3	5	0.75	0.45	-
matrix + $ZnCl_2$	3	15	0.02	0.1	-
matrix + $ZnCl_2$	3	30	0.04	0.1	-
matrix + $ZnCl_2$	3	60	0.02	0.1	-

Table 16-39: Chemical analysis of synthetic mixture with $CaCl_2$ addition

	Stoichiometry	Time [min]	Chemical analysis [%] Pb	Cl	element
matrix + $CaCl_2$	1	5	7.3	2.25	1.45
matrix + $CaCl_2$	1	15	4.4	0.94	1.5
matrix + $CaCl_2$	1	30	1.7	0.1	1.5
matrix + $CaCl_2$	1	60	0.65	0.1	1.6
matrix + $CaCl_2$	2	5	6	5.15	3.05
matrix + $CaCl_2$	2	15	2.8	3	3
matrix + $CaCl_2$	2	30	1	2.6	3.05
matrix + $CaCl_2$	2	60	0.03	1.3	2.95
matrix + $CaCl_2$	3	5	6.1	5.3	3.3
matrix + $CaCl_2$	3	15	2.9	5.3	4.1
matrix + $CaCl_2$	3	30	1.5	5.55	4.65
matrix + $CaCl_2$	3	60	0.2	4.1	3.9

Table 16-40: Chemical analysis of synthetic mixture with NaCl addition

	Stoichiometry	Time [min]	Chemical analysis [%] Pb	Cl	element
matrix + NaCl	1	5	7.2	2.7	1.4
matrix + NaCl	1	15	7	2	1
matrix + NaCl	1	30	6.3	1.1	0.5
matrix + NaCl	1	60	4.85	0.1	0.015
matrix + NaCl	2	5	6.45	6	3
matrix + NaCl	2	15	5.8	4.9	2.3
matrix + NaCl	2	30	5.15	3.9	1.85
matrix + NaCl	2	60	4.2	1.4	0.6
matrix + NaCl	3	5	5.8	7.9	4.9
matrix + NaCl	3	15	5.1	6.5	4.1
matrix + NaCl	3	30	4.6	5.65	3.2
matrix + NaCl	3	60	3.6	4.15	2.1

Table 16-41: Calculated PbO yield and zinc loss based on chemical analysis of clinkered material for the trials with NaCl addition

time [min]	Stoichiometry	PbO yield [%]	ZnO loss [%]
5	1	0.0	1.0
15		4.2	1.0
30		14.9	0.1
60		36.7	0.3
5	2	6.2	0.9
15		16.8	-0.6
30		27.8	-0.7
60		44.1	-0.5
5	3	12.8	1.6
15		24.6	-0.2
30		33.7	-0.5
60		50.2	-0.7

Table 16-42: Calculated PbO yield and zinc loss based on chemical analysis of clinkered material for the trials with $CaCl_2$ addition

time [min]	Stoichiometry	PbO yield [%]	ZnO loss [%]
5	1	0.3	2.5
15		42.6	2.7
30		78.6	2.5
60		91.9	2.9
5	2	15.1	2.6
15		62.4	1.9
30		87.0	2.6
60		99.6	3.0
5	3	11.4	0.7
15		60.1	3.4
30		79.9	5.3
60		97.4	5.0

Table 16-43: Calculated PbO yield and zinc loss based on chemical analysis of clinkered material for the trials with $ZnCl_2$ addition

time [min]	Stoichiometry	PbO yield [%]	ZnO loss [%]
5	1	75.0	-0.8
15		88.7	-0.4
30		88.7	-0.4
60		96.9	-0.8
5	2	87.3	-1.2
15		99.1	-0.4
30		99.3	-0.5
60		99.1	-0.1
5	3	90.6	0.6
15		99.8	0.7
30		99.5	1.1
60		99.8	1.5

16.7 Appendix – C1

Related data for market research:

Table 16-44: Summary of ZnO consumption in the different utilization areas [12, 65]

[%]	North America	Central & South America	Europe	CIS	Africa & Middle East	Japan	China, Korea, Taiwan	Other Asia & Oceania
rubber & tire	62	52	53	70	67	68	60	70
ceramics & glass	3	36	13	16	18	4	15	14
chemical	21	3	14	5	3	4	5	5
agriculture	8	3	7	5	5	4	-	6
paintings & coatings	4	3	4	3	3	4	-	2
others	3	2	9	2	3	16	20	2

Table 16-45: Summary of ZnO consumption in different utilization areas in thousand tons/year [12, 65]

[kilo tons/year]	North America	Central & South America	Europe	CIS	Africa & Middle East	Japan	China, Korea, Taiwan	Other Asia & Oceania
rubber & tire	124	47	129	45	40	54	250.2	123
ceramics & glass	6	32	31	10	11	3	62.55	25
chemical	41	3	35	3	2	3	20.85	9
agriculture	15	3	16	3	3	3	-	10
paintings & coatings	8	3	10	2	2	3	-	4
others	5	2	21	1	2	13	83.4	4