

The Waelz Kiln

General

The pyro-metallurgical treatment of Zn bearing residues like filter-cakes from Zinc smelters or steel mill dust, especially EAF dust, is a well-known technology, which uses a rotary kiln as key-equipment. Its origin dates about 100 years ago where it was first applied for the enrichment of low grade Zinc ores in Germany.

Figure 1: History of the Waelz Technology

- 1881 Proposal for Zn volatilization by George Drue
- 1913 First patent applied on the process in Germany
- 1925 First Waelz plant set in operation for low grade ore enrichment (Lünen / Germany)
- 1940's Application on Zn/Fe residues of electrolytic Zn smelters
- 1970's First EAF dust co-treatment in Duisburg / Germany
- 1980's New Waelz kilns for EAF dust in USA, Europe and Japan
- 2009 About 80 % of EAF dust treated in Waelz kilns around the world

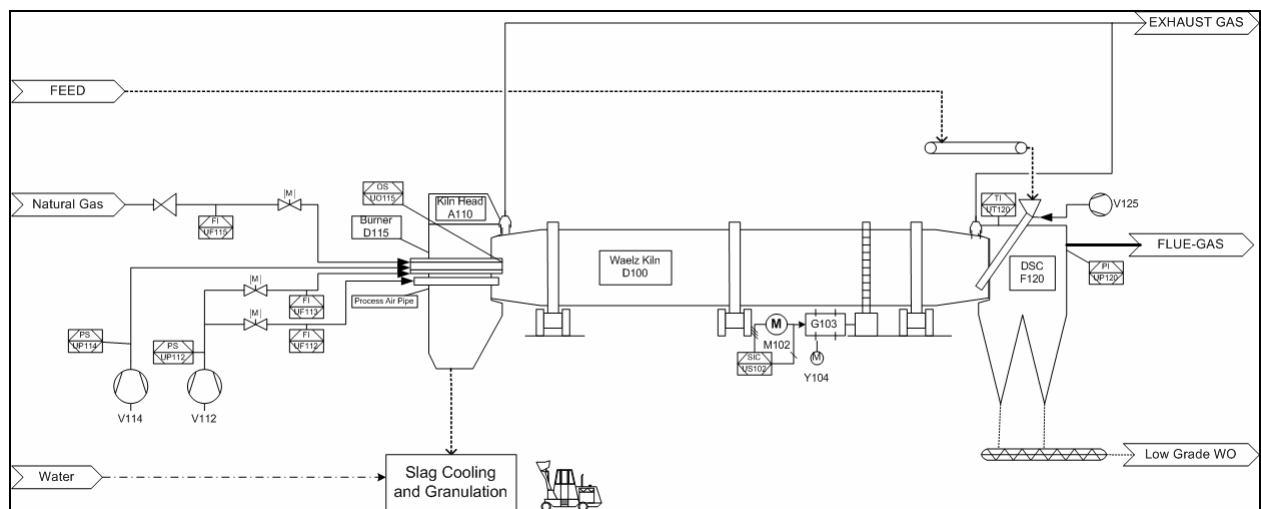
In the recent years this technology – also known as Waelz process – has been improved in terms of energy (coke) consumption and of gaseous emission control. The European Waelz plants fulfill the requirements of the Best Available Technology for environmental protection. The related Waelz process is notified in the BREF notes of the European Community.

The Waelz process is quite robust and can deal with a wide variety of feed materials. The standard application is dedicated to one major kind of Zn bearing material, in some plants a combined treatment is applied (e.g. Zn/Fe-concentrate with EAF dust). In any case the Waelz process is strongly depending on the raw material preparation which must be executed properly for a stable and homogeneous feed generation.

Aside of a stable and homogeneous kiln feed also the steady operation of the off-gas treatment department is indispensable for a good performance of the Waelz operation. Frequent interruptions of a sufficient suction (e.g. manual interventions, opening of holes in pipes for cleaning) might cause an imbalance of the kiln reactions which results in reduced throughput, poor Zinc recovery or even accretions in the kiln. Accretions are strong incrustations of slag which might achieve several centimeter of thickness and block the continuous flow of the charge through the kiln.

Process Description

Figure 2: Process Flow Diagram



Inside the Waelz kiln D100 the solid material (the charge) is transported from the feeding end to the discharge end by the rotation of the kiln (0.4 to 0.7 rpm) and its inclination (about 2 %). The residence time of the charge is about 8-10 hrs. The charge is first dried and heated up. Then the different reactions inside the charge takes place, while the material is further transported. Close to the discharge end nearly all zinc, other non-ferrous metals and salts are volatilized and most of the iron oxide is reduced; the charge has been transformed to slag. At this point air is blown into the kiln via the process air pipe and air fan V112 before the slag is discharged for cooling and granulation. The slag temperature at the kiln discharge end is normally in the range of 1050 to 1120 °C.

In addition to the process air, which is manually controlled by a valve (flow indication by UF112), secondary air is sucked into the kiln from the kiln head. The air oxidizes the volatilized metals and CO from the reduction reactions inside the charge. These oxidation reactions plus the re-oxidation of the iron in the slag produce enough energy for the endothermic processes in the charge. Additional energy (e.g. by burning fuels) is normally not required. The total amount of air, which is blown in or sucked into the kiln, is controlled by the kiln suction in order to achieve a total re-oxidation with low excess of air. The residence time of the gas in the kiln is only a few seconds.

Oxidation air and charge are in counter-flow: the air from the kiln head to the dust settling chamber A120 (DSC), the charge from the feeding end at DSC to the slag discharge in the kiln head A110. Due to the reactions the air is transformed to flue-gas, which consists mainly of N₂, CO₂ and H₂O and some O₂ and CO and which contains a

The Waelz Kiln

lot of dust. The dust consists mainly of ZnO, PbO and chloride salts and also of FeO, CaO, SiO₂ and C, which is due to the carry-over from the feed and the drying zone of the kiln. Normally, the flue-gas temperature entering the DSC is in the range of 750 to 850°C (UT120) and the negative pressure is in the range of -0.2 to -0.5 mbar (UP120).

At the kiln head A110 and at the connection to the DSC A120 an exhaust system is installed, which should reduce the diffuse emission of fumes. Due to the fact that a Waelz kiln is operated nearly at atmospheric conditions a small temporary release of reaction fumes at the kiln head can not be avoided. The exhaust system consists of the exhaust hoods and several pipes.

The natural gas (or sometimes fuel-oil) fired burner D115 is mainly used for the cold start-up of the kiln D100 after a maintenance standstill. During normal operation it is used for eventual heating up of the slag for achieving an easier outlet flow from the kiln. The combustion air is provided by the primary air fan V114 and by secondary air from fan V112 (flow indication by UF113). Pressure switches (UP112 and UP114) are installed for ensuring that there is always enough air blown-in. If the pressure is too low it interlocks the gas flow to the burner. As additional safety device the flame detector UO115 is installed. It interrupts also the gas flow in case of flame failure. For adjusting manually the gas flow to the burner a flow indicator UF115 is installed.

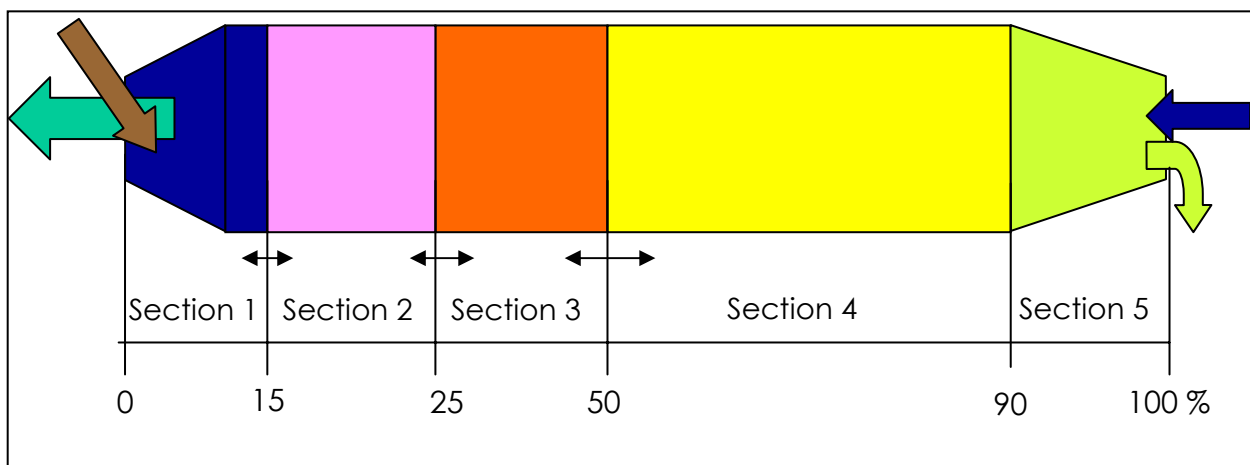
The turning of the kiln D100 is ensured by a drive system which consists of the girth gear ring with 1 pigeon, a gear box G103, the main motor M102 and the auxiliary motor Y104. The main electrical motor is normally equipped with a frequency inverter (US102) which allows to adjust the rotation speed continuously. The auxiliary motor might be a small combustion engine but can turn the kiln at low speed. If the hot, charged kiln is not turned (1 turn in a few minutes is sufficient) it will be deformed ("banana form"). This deformation will cause mechanical problems in the shell and overload of the support roller stations. In addition the kiln is slowly moved upward and downward for some millimeter in order to avoid mechanical stress in the tires and the support rolls. The lateral movement is controlled by an operator.

For avoiding the release of hot off-gas from the kiln by the feeding pipe, especially when the solid feed is stopped, sealing air is blown into the pipe. The sealing air is generated by a dedicated small fan (V125).

Detailed Description

Inside of the Waelz kiln a pyro-metallurgical process is executed which can be separated in 5 general sections along the length of the kiln. The length of a Waelz kiln is counted from the feeding side of the charge (the solid feed, starting with "0") to the slag outlet side (100 %, here equal to 55 m). The flue-gas flows through the Waelz kiln in counterflow to the charge: it starts as process air (and combustion air of the burner) at the slag outlet side and exits the kiln into the dust settling chamber (DSC) at the feeding side. The following figure defines the mentioned 5 sections.

Figure 3: Kiln Sections



Section 1: Drying Zone

Section 2: Preheating and Coke Combustion Zone

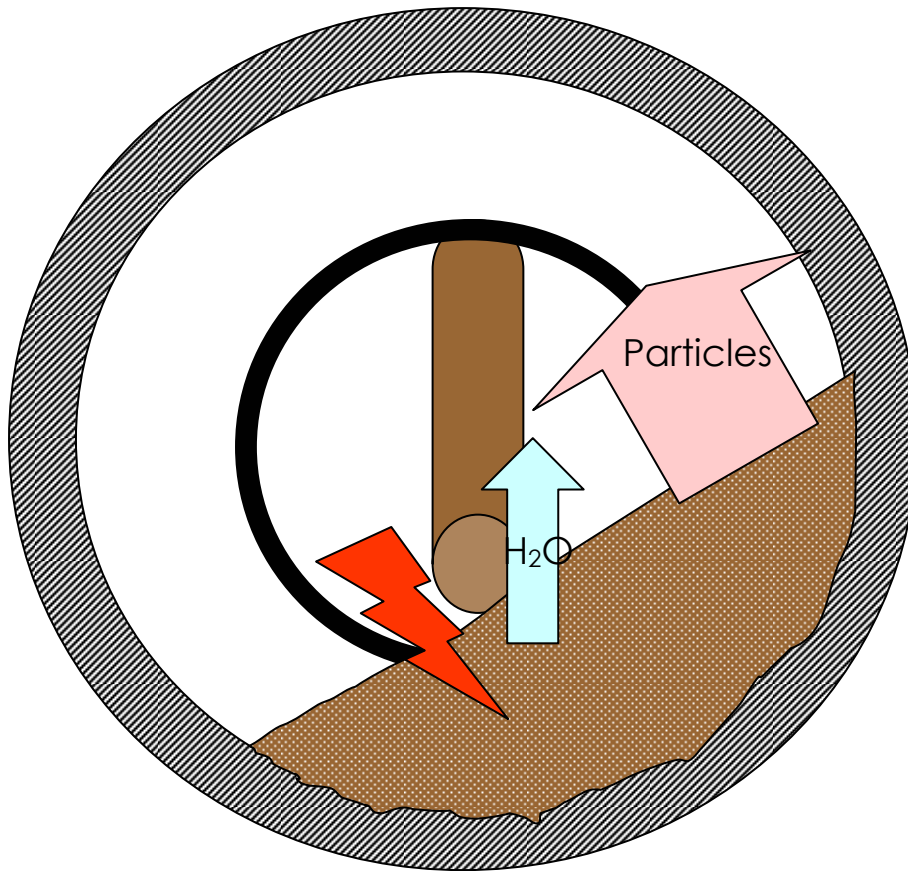
Section 3: Pre-reaction Zone

Section 4: Main Reaction Zone

Section 5: Slag Forming Zone

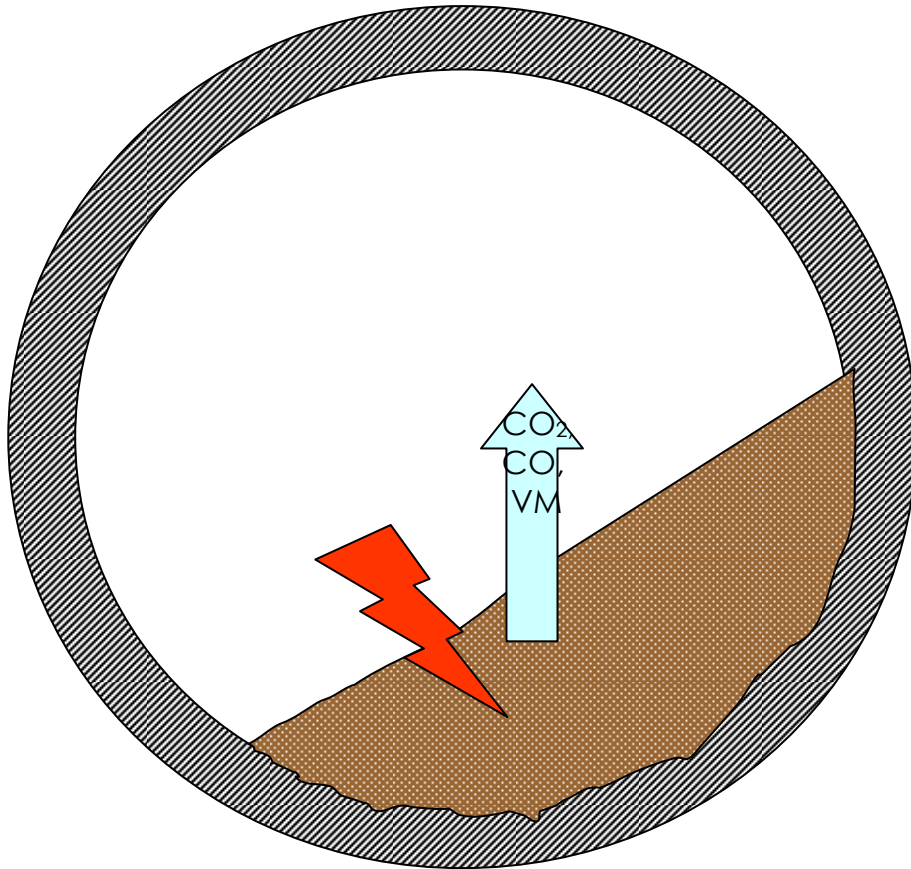
Following each section is described in detail by a sketch and an explanation of the reactions in the charge and in the freeboard. Charge and freeboard are independent reaction areas which exchange material and energy (heat) via the boundary layer in between these areas. Heat transfer is also executed from the freeboard to the refractory lining to the charge (and vice-versa).

Section 1, about 15 %



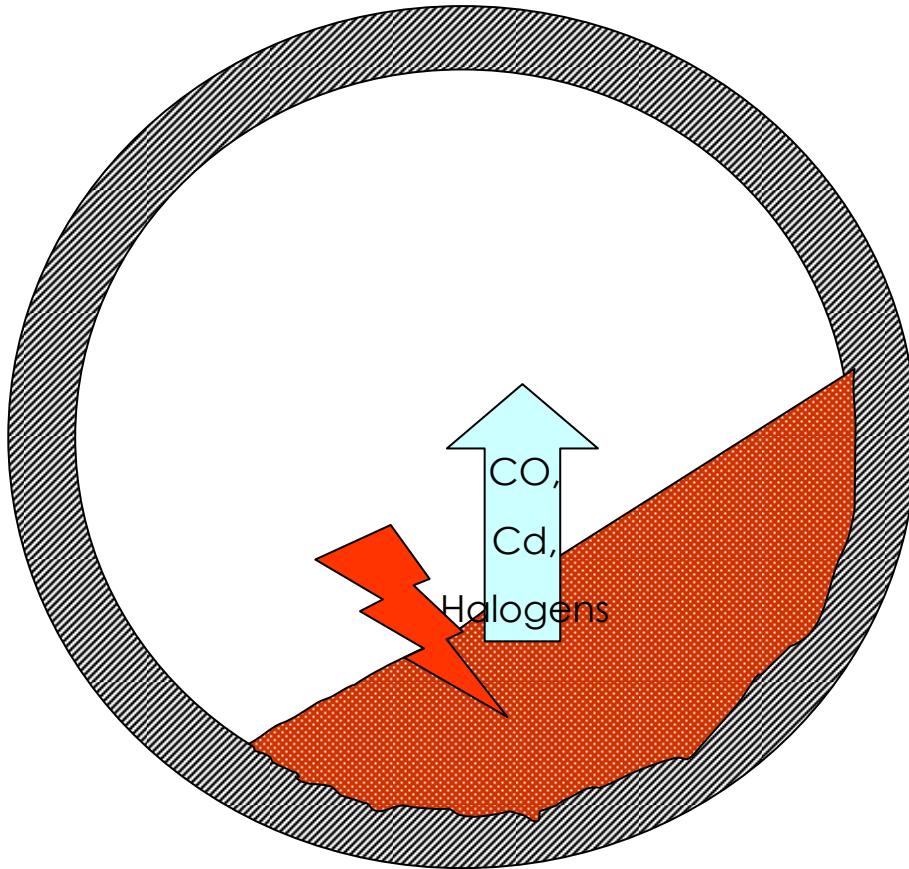
Freeboard	Charge
The gas is not reacting and cooled by convection and radiation.	The solid matter is heated and dried. Free and combined water is removed (evaporated).
T = 1000 – 720 °C	T = 25 – 150 °C

Section 2, about 10 %



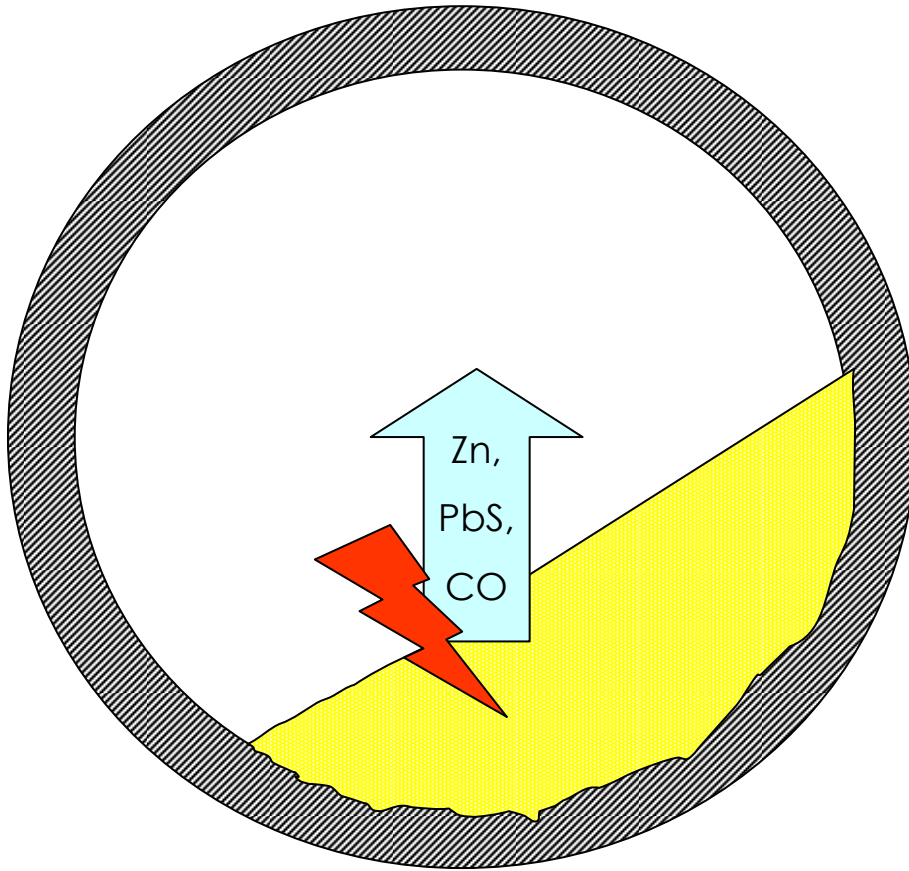
Freeboard	Charge
<p>Combustion occurs in the freeboard and at the contact surface of the charge with the gas. Heat transfer from gas to charge and to refractory is mainly by radiation.</p>	<p>The charge is further heated and the coke starts partly to burn (volatile matter and finest particles). Depending on the remaining oxygen the combustion might be incomplete (to CO).</p>
<p>T = 900 – 1100 °C</p>	<p>T = 150 – 500 °C</p>

Section 3, about 15 %



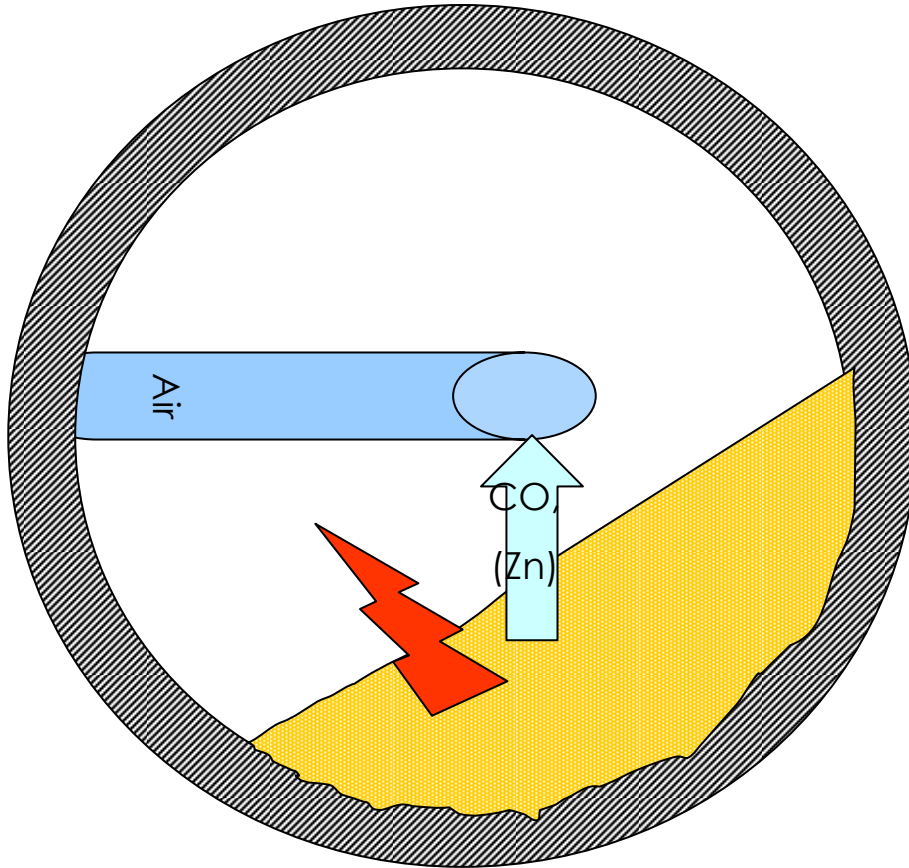
Freeboard	Charge
<p>The remaining oxygen reacts with the volatized CO partly to CO₂. Heat transfer from gas to charge and to refractory is mainly by radiation.</p>	<p>The charge is further heated and the first reduction of e.g. CdO and higher oxidized Fe starts. Sulfates and carbonates are decomposed. Halogen salts are volatized. The charge starts to form a slag.</p>
<p>T = 1100 -1300 °C</p>	<p>T = 500 – 900 °C</p>

Section 4, about 50 %



Freeboard	Charge
<p>The volatilized Zn vapor and CO are oxidized. The heat transfer is mainly by radiation.</p>	<p>The reduction of ZnO to Zn starts and becomes more and more important. Also the further reduction of FeO to Fe starts slowly and becomes more intensive to the outlet. As side reactions the decomposition of ZnS by metallic Cu and Fe and the sulfidization of Pb and its de-sublimation occur. At exceptional high temperatures (>1200 °C) large metallic iron lumps and metallic incrustation can be formed. The Boudouard-reaction is intensified. The formation of slag is ongoing with an eventual changing behavior.</p>
<p>T = 1100 -1400 °C</p>	<p>T = 900 – 1200 °C</p>
<p>Remark: For achieving a good recovery rate of Zn (Zn yield) this zone should be as long as possible. A use of 50 % of the kiln length is highly recommended.</p>	

Section 5, about 10 %



Freeboard	Charge
<p>The incoming air is heated up. Eventually the burner is used for additional heating. Only in the short outlet zone the gas is heated by the slag and the refractory, all over the other parts the gas heats the charge.</p>	<p>The reducing reactions are nearly finished. Thanks to the tuyère pipe the metallic Fe is partly re-oxidized while giving heat to form the slag and to heat the process air.</p>
<p>T = 20 – 1000 °C</p>	<p>T = 1000 -1150 °C</p>
<p>Remark: If a tuyère pipe is not installed in the Waelz kiln, the missing heat must be generated by the frequent use of the burner.</p>	

Summary of Chemical Reactions in the Waelz Kiln

Section 1 15 %	Charge: $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)}$ $\text{CaSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaSO}_4 + \text{H}_2\text{O (g)}$ $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O (g)}$ Freeboard: no reaction	Freeboard [°C] 720-1000	Charge [°C] 20-150
Section 2 10 %	Charge and Freeboard: $\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}$ $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$ $\text{C}_x\text{H}_y\text{O}_z + n\text{O}_2 \rightarrow a\text{CO} + b\text{CO}_2 + y/2\text{H}_2\text{O}$	900-1100	150-500
Section 3 15 %	Charge: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ $\text{CdO} + \text{CO} \rightarrow \text{Cd (g)} + \text{CO}_2$ $\text{CuO} + \text{CO} \rightarrow \text{Cu} + \text{CO}_2$ $\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2$ $\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2$ $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ Freeboard: $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	1100-1300	500-900
Section 4 50 %	Charge: $\text{ZnO} + \text{CO} \rightarrow \text{Zn (g)} + \text{CO}_2$ $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$ $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ $\text{ZnS} + \text{Cu} \rightarrow \text{Zn (g)} + \text{CuS}$ (Side-reaction) $\text{ZnS} + \text{Fe} \rightarrow \text{Zn (g)} + \text{FeS}$ $\text{FeS} + \text{Pb} \rightarrow \text{Fe} + \text{PbS (g)}$ $\text{Fe}_3\text{O}_4 \cdot \text{ZnO} + \text{CO} \rightarrow 3\text{FeO} + \text{ZnO} + \text{CO}_2$ $\text{ZnO} \cdot \text{SiO}_2 + \text{CO} \rightarrow \text{Zn (g)} + \text{SiO}_2 + \text{CO}_2$ Freeboard: $\text{Zn (g)} + \frac{1}{2} \text{O}_2 \rightarrow \text{ZnO}$ $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	1300 (1400)– 1000	900-1200 (1300)
Section 5 10 %	Charge: $\text{Fe} + \frac{1}{2} \text{O}_2 \rightarrow \text{FeO}$ Burner: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$	1000 – 20	1150 – 1000