Dr. Bruno Schwab (Germany, dr.schwab@gmx.net);

Bernd Böttcher (JL Goslar Anoden GmbH, Germany, b.boettcher@jlgoslar-anoden.de)

ZINC RECYCLING,

AN UPCOMING SOURCE FOR PRIMARY ZINC PRODUCTION

Keywords: Zinc – Recycling – Imperial Smelting Process – Electrowinning – Halogens

The use of zinc for galvanizing of steel provides galvanized scrap producing zinc containing dust when remelted in an electric arc furnace. After enrichment of the zinc content in for instance Waelz Kilns this material better known as Waelz Oxide is nowadays input material for more or less all zinc smelters replacing zinc concentrates. The use of higher amounts of zinc oxides up to 100% needs special technologies. Different technologies developed are in commercial use and will be discussed.

Introduction

About 14 Mio t/a of zinc are produced worldwide, of which about 50% are used for galvanizing of steel [1]. Although zinc protects steel against corrosion for a long period of time galvanized steel will at end of life end up as scrap. The remelting of scrap in an electric arc furnace creates the well known EAF-dust collecting the zinc content in the scrap. Estimates by the International Zinc Association (IZA) show that about 60% of the zinc available at end of life will be recycled [2]. This figure will increase over the next years because the IZA sees in comparison with the past an increase of zinc used for galvanizing and an decrease in other uses like brass, die casting etc. Together with residues from the brass industry, from galvanizing itself and other activities will this be the new source for zinc in future.

To make this recycling materials ready for primary zinc production usually an upgrading of the zinc content will be necessary. The most often used process to upgrade the zinc content is the so called Waelz Kiln Process . Under use of coke or coal a zinc rich dust will be formed with zinc contents up to 60%, called Waelzoxid or WOX [Table 1]. Beside the Waelz Kiln process other technologies are in use like for instance the Primus process or the Inmetco technology being less successful than the Waelz process.

in safe hands

Zinc Recycling - an upcoming source for primary zinc production

JL Goslar Anoden

	Crude Waelz Oxide - %
Zn	61,0
Pb	4,0
FeO	3,5
SiO_2	0,6
S	0,6
CaO	2,0
MgO	0,2
Mn	0,3
Cd	0,15
Cl	6,0
F	0,2

Table 1: Washed Waelz Oxide

Source: B. Schwab

On one hand the availability of zinc concentrates especially the easy ones consisting more or less of zinc and sulfur only becomes more and more difficult, so that the use of materials like WOX becomes more and more popular as a substitute for concentrates. On the other hand materials like WOX are free of sulfur. Therefor if a zinc smelter looks for an increased production WOX will be chosen because no additional acid plant is necessary. This reduces the capex needed on one hand and delivers no additional sulfuric acid into a very difficult market. But oxides like WOX or similar ones show another advantage: This materials are more or less free of iron which reduces the amount of residues associated with the production of zinc. Beside these advantages the halogen content in these type of materials is due to the enrichment processes quite high with for instance chlorine contents of about 7% [Table 1] Care must therefore be taken on chlorine and fluorine when using these oxides.

Pyrometallurgy

Zinc containing oxides like WOX can be used in pyrometallurgical zinc producing plants as well as in hydrometallurgical ones. The use in pyrometallurgical plants represented by the Imperial Smelting Process (ISP) has a long tradition. Already more than 40 years ago WOX was heated up in rotary furnaces and formed to so called hot briquettes being fed to the Imperial Smelting Furnace (ISF) together with sinter and coke [Figure 1]. Up to 30% of the input material was made with hot briquettes. Lead always associated in small amounts with the oxide was in the shaft furnace turned into the metal, too. The process was even capable to treat 100% briquettes. The halogen content reduces the melting point of possible accretions in the shaft furnace reducing the down time for cleaning operations.

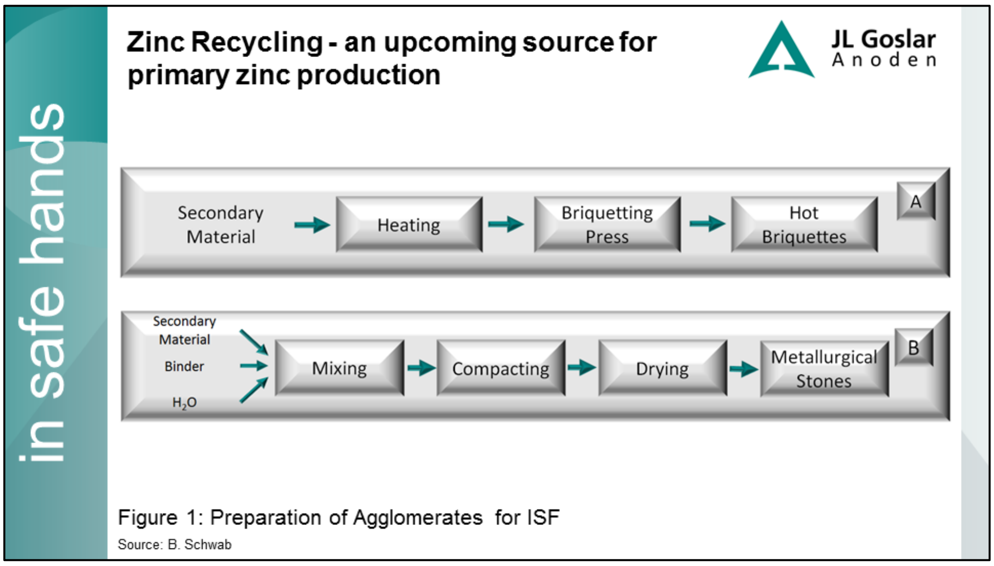

Figure 1: Preparation of Agglomerates for ISF
Source: B. Schwab

Beside this other possibilities for the use of WOX are given nowadays. WOX can be used in sinter plants substituting concentrates. To overcome the lack in energy coke fines must be added to run the process. It is possible to run the sinter process with WOX only, but usually a mixture of different secondary materials is used. These materials beside WOX can be for instance EAF-dust, residues from electro galvanizing or cupola furnace operations. Even residues from electrowinning plants like neutral leach residues or lead sulfate from WOX leaching can be used. Care must be taken on the lead content of the sinter. Too low figures will soften the sinter. In case of a feed mix without concentrate instead of the sulfuric acid production a new off gas cleaning system must be established. This can be for instance combined with the production of gypsum. The halogen content of the input material will distill off during the sinter process and end up in the sinter plant off gas cleaning system.

Another possibility to use these oxides is the so called direct injection technology [3]. The zinc containing material in mixture with coke fines is blown via the tuyeres into the furnace directly. No energy consuming pretreatment at the zinc smelters side is necessary. Even electric arc furnace dust with zinc content above 30% can be treated with this technology.

The last development in using zinc oxides for the ISF is the production of metallurgical stones. This technology already used in the steel industry to prepare residues for the blast furnace, starts with the production of porous stones made a with binder like cement. This stones are produced from oxides alone or in mixture with coke fines. After drying at room temperature this stones are hard enough to be charged to the ISF instead of sinter [Figure 1]. First successful test could be performed.

Hydrometallurgy

For the use of zinc oxides in hydrometallurgical plants two possibilities are given: As input material for the fluid bed roaster or after washing and dissolving as input material to the existing leaching plant. The amount of oxides fed to the roaster is limited because the material consumes energy. Another limitation will be the halogen content. Also here the halogens are distilled off in the roaster and end up in the acid producing part of the plant. Additionally chlorine and fluorine are leading to increased corrosion problems within the total plant. All this limits the input.

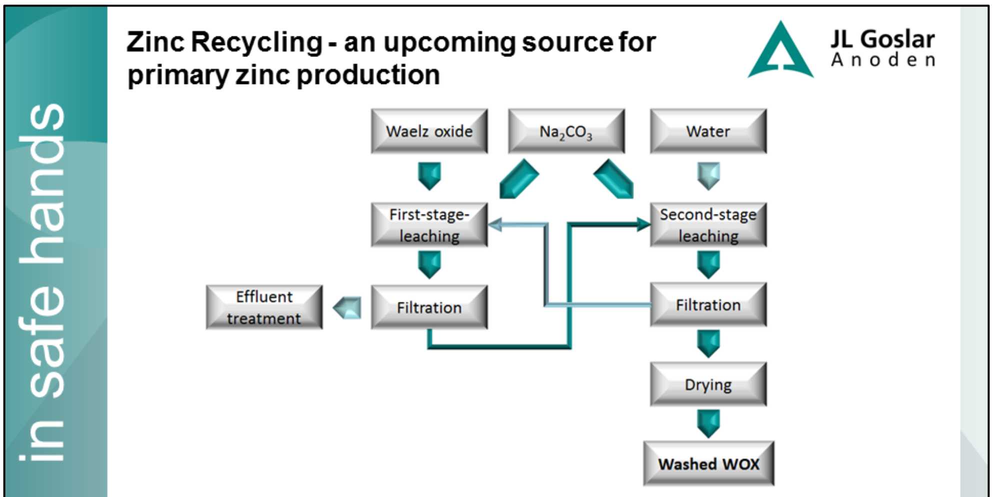

Figure 2: Flow Chart WOX Washing

Source: B. Schwab et al: Zinc, Ullmann´s Encyclopedia of Industrial Chemistry, Weinheim, 2015

The more direct use as input for the leaching unit makes the removing of the chlorine and especially the fluorine content necessary. This will be made by washing with water under addition of Soda at higher temperatures [Figure 2]. Two systems are in use to reduce the halogens: The washing under pressure at app. 2 bar or the washing at ambient pressure. Washing under pressure is leading to lower halogen contents but needs a more sophisticated technology [Table 2]. The washing will be done at the oxide producers site or at the zinc smelters site depending on the equipment and license available. After washing the oxide will dissolved by sulfuric acid. The leaching residue, a silver containing lead sulfate, can be used as input material for Imperial Smelting units or lead smelters. Even after thoroughly washing of the oxide the halogen content will not be at zero. The Fluoride and Chloride concentration in the electrolyte will increase over the time. Concentrations of Fluoride up to 60 or 80 mg/l can be managed when the cathode sheets are brushed following every stripping operation and stripping machines are used. The often assumed higher corrosion rate of lead/silver anodes at higher Chloride concentrations (i.e. 700 mg/l) was not observed in practice. A 4 to 5 year lifetime of the anodes could be achieved even under this conditions [4].

Zinc Recycling - an upcoming source for primary zinc production

	Atmospheric Washing	Pressure Washing
Cl	<0.1 - 0.2 %	<0.05 %
F	<0.1 - 0.2 %	<0.05 %

Table 2: Washed Waelz Oxide

Source: B. Schwab et al: Zinc, Ullmann´s Encyclopedia of Industrial Chemistry, Weinheim, 2015

Washing followed by leaching of zinc containing oxides looks nowadays a well established process. After leaching the liquor follows the existing steps of cleaning, removing elements like Cadmium, Lead, Copper, Nickel etc. An in principle different way is the use of solvent extraction technology [Figure 3]. The idea behind is to take zinc and no other element out of the liquor and separates it from all the impurities especially Chlorine and Fluorine. The first commercial large scale use for this technology was Skorpion Zinc in Namibia [5]. The ore body is free of sulfur but with very large amounts of SiO_2, which couldn´t be treated in the classical roasting-leaching-electrowinning route. This technology where the zinc extracting compound is dissolved in hydrocarbons is a new challenge in zinc winning. The handling of large amounts of hydrocarbons in combination with an increasing fire hazard, or the separation of hydrocarbons from the cell house are examples for these new challenges. Based on the know-how from Namibia new plants are in operation using solvent extraction technology. There a two plants using solvent extraction for the treatment of additional amounts of oxides in an existing smelter in Italy and Japan. And the Horsehead Corporation is in the ramp up phase of a brand new zinc electrowinning plant in the USA based on 100% Waelz oxide using solvent extraction technology.

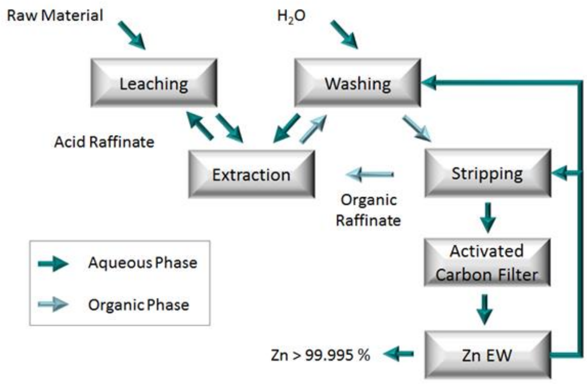

Figure 3: Flow Chart Solvent Extraction

Source: B. Schwab et al: Zinc, Ullmann´s Encyclopedia of Industrial Chemistry, Weinheim, 2015

Conclusion

Following the urban mining theory the amount of Zinc produced out of recycling materials will increase over the years. The relevant technologies to treat even 100% of secondary materials has been developed and is in commercial use.

References:

[1] B. Schwab et al: Zinc, Ullmann´s Encyclopedia of Industrial Chemistry, Weinheim, 2015.

[2] S. Grund: Resourcen- und Klimaschutz durch Zinkrecycling in der EU, Erzmetall 67(2014)No.4,pp 202-206.

[3] B. Schwab, W.-D. Schneider: Zinc Recycling via the Imperial Smelting Technology- Latest Developments and Possibilities, Proceedings of the 4th Industrial Symposium on Recycling of Metals and Engineered Materials, Pittsburgh 2000, pp 193 – 200.

[4] B. Böttcher, B. Schwab, E. Grab: Zinc Recycling, a Necessity for Mature Societies and a Challenge for Developing Societies, Proceedings of EMC 2013, pp 1093 -1110.

[5] J. Gnoinski: Skorpion Zinc: optimization and innovation, The Journal of the Southern African Institute of Mining and Metallurgy Vol. 107 (2007); pp 657 – 662.