

An Overview of the Zincor Process

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Abstract - Zincor has been producing zinc since 1969 via the roast-leach-electrowinning process. It is the only primary zinc producer in South Africa, and currently supplies the entire country with zinc. The plant was built by Goldfields of South Africa, on the site of an old gold and uranium mine. Since then, the ownership of the plant has changed a couple of times, and the plant and process have also been improved. Production output has increased from around 80 000 tons per year to more than 110 000 tons per year. This was done mainly through increasing the capacity of the roasters and acid plant. Zincor produces four main grades of zinc: SHG, Zn1, Zn2, and Zn4, in three shapes: a 25 kg ingot and 1 and 2 ton jumbos. In 2005, a pre-alloy furnace was built that enabled the production of jumbos pre-alloyed with aluminium. This has allowed Zincor's customers to improve the efficiency of their continuous galvanizing lines and to lower their production costs.

INTRODUCTION

Zinc and zinc-containing products contribute around US\$ 40 billion to the global economy each year. US\$ 18.5 billion is related to mining, smelting, and refining of zinc.¹ The rest is related to its many applications.

Galvanizing, the protection of steel against corrosion by metallurgically bonding zinc to steel, is the most important application of zinc. Other applications include die casting of precision components, alloys such as brass, as a component in pharmaceuticals and cosmetics, in batteries and as a micronutrient for humans, animals, and plants. The distribution of these products for the South African market is displayed in Figure 1.

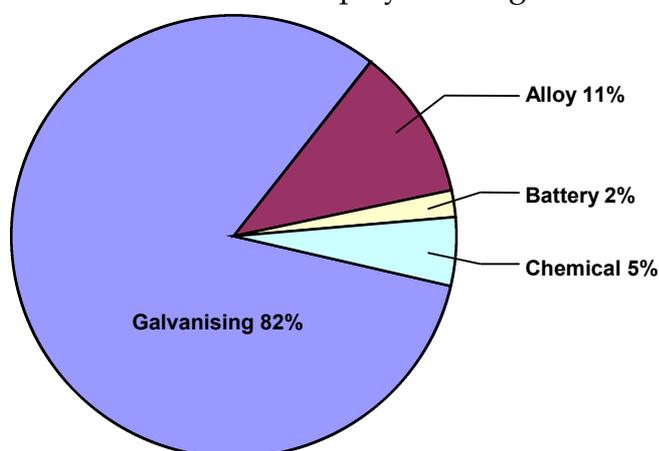


Figure 1: Zinc product distribution in the South African market

The distribution between the types of galvanizing done in South Africa is shown in Figure 2.

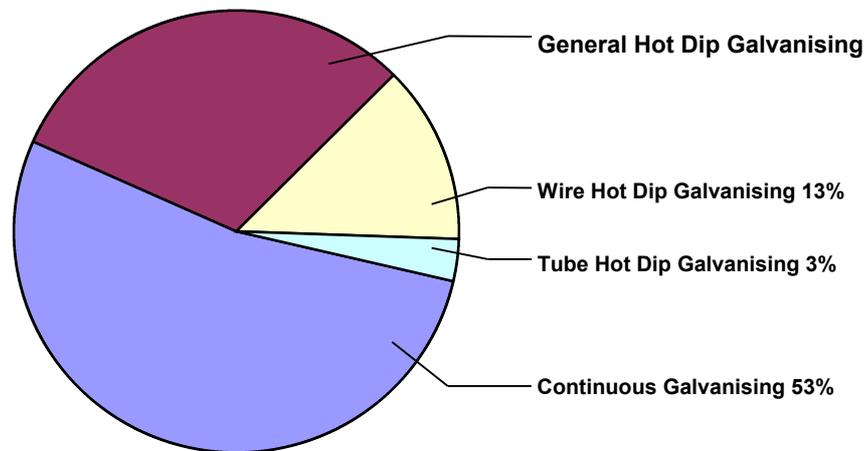


Figure 2: Distribution between the types of galvanizing in South Africa.

The distribution between the two main zinc alloys for the South African market is shown in Figure 3.

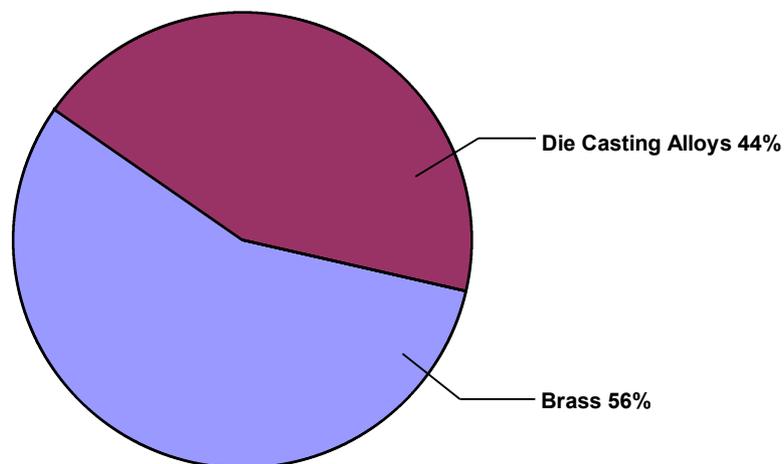


Figure 3: Distribution between zinc used for alloying purposes

HISTORY

Zincor operates an integrated roast-leach-electrowinning zinc production plant near Springs in the Republic of South Africa.^{2,3} Zincor is South Africa's only zinc refinery and is currently one of the operations of Kumba Base Metals, a division of Kumba Resources.

Zincor was originally managed by Gold Fields of South Africa and was built on the premises of the defunct Vogelstruisbult gold mine that dates back to 1933. The associated uranium plant was converted for the production of electrolytic zinc. Sulphuric acid was first produced in December 1968, and the first zinc slab approximately four months later. Previously, zinc metal was imported from the then 'Zaire' and Zambia.

The zinc processing plant at the time comprised neutral leach, purification, electrowinning, and melting /casting steps. A fair amount of Waelz oxide was initially treated in a parallel circuit. This material yielded high zinc recoveries. Zinc production increased over the years from an initial 37 000 t/a to the current 110 000 t/a zinc slab. By the end of 1970, production of zinc from Waelz oxides decreased to virtually nothing, with zinc sulphide concentrates being introduced to make up the difference.

With the increased treatment of zinc sulphide concentrates, zinc recoveries could not be maintained at an acceptable level. In 1976, a hot acid leach circuit, incorporating iron removal, was commissioned. The iron removal process was an internally developed process that was patented in 1976. An extra leach stage - a super hot acid leach stage - was added to the residue treatment circuit in 1984 to handle the increased residue loading associated with a continuous increase in plant capacity⁴.

Concentrate supply

Zincor was initially fed with concentrates imported from Australia (Broken Hill South, Broken Hill North, Cobar, and Mathilda) and Canada (Pine Point).² These concentrates were later replaced with local concentrates from South Africa and Namibia. The following mines supplied concentrate: Prieska, Rosh Pinah (Namibia), and Pering.

During the 1990s and early 2000s, Zincor's concentrate was procured from four local mines: Rosh Pinah, Black Mountain, Pering, and Maranda. Concentrate was also occasionally imported from various sources. In the early 2000s, the main source of imported concentrate was Lennard Shelf in Australia. The local concentrates were delivered via rail to Zincor's siding. The imported concentrate was offloaded in Durban, and subsequently also transported to Zincor via rail.

Where possible, the concentrates were stockpiled according to their iron content. Careful blending of the concentrates allowed for the production of high and low iron calcines. The former proceeded to leaching and the latter were used for iron precipitation. Typical concentrate compositions are given in Table I.

Table I: Typical concentrate compositions, mass %

	Zn	Fe	Cu	Pb	SiO₂	S
Maranda	54.5	9	1	0.05	1	32.5
Rosh Pinah	53	3.8	0.5	2	1.5	30
Black Mountain	49	10	1	5.5	3.5	28
Pering	57.5	2.5	0.2	3	0.8	30.5
Lennard Shelf	60.5	1.5	0.06	1.8	0.3	30

From 2002 onwards, the concentrate quality started to decrease. Pering closed down in 2003, and Maranda in 2004. Black Mountain moved over from their traditional ore bodies to the new Deeps ore-body and in the process supplied significant quantities of Gamsberg concentrate (high in manganese) to Zincor to maintain concentrate volumes. Rosh Pinah concentrate has traditionally been high in magnesium. The closure of Pering and Maranda resulted in an increase in the percentage of Rosh Pinah and Black Mountain concentrates in the blend, and this allowed unprecedented levels of magnesium and manganese to enter the hydrometallurgical circuit. There is no natural bleed for these two elements from the circuit. Solution densities increased and current efficiency and plating efficiency suffered as a consequence.

By 2005, the magnesium pre-leach plant at Zincor had been re-commissioned to remove magnesium. The levels of manganese also declined towards the end of 2005, as the volumes were increased from the Black Mountain Deeps ore-body. This led to an improvement in electrowinning conditions in the cell house.

Process flow

An overview of the Zincor process flow is presented in Figure 4. This flow diagram is discussed in detail below.

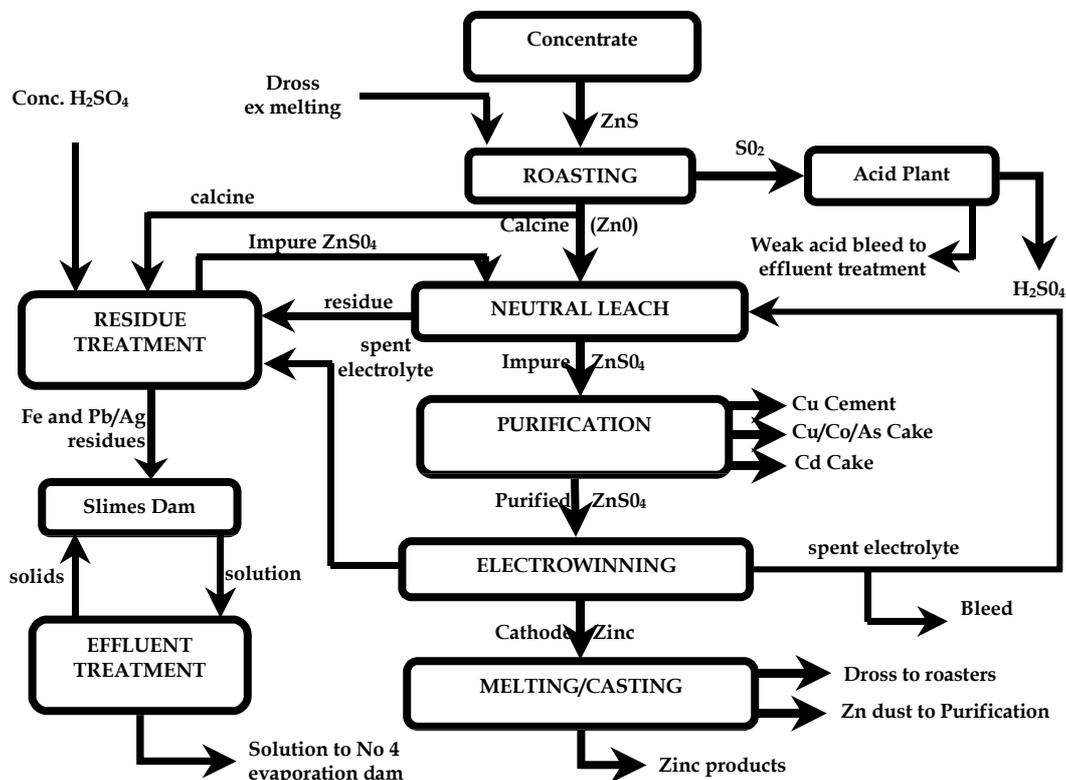
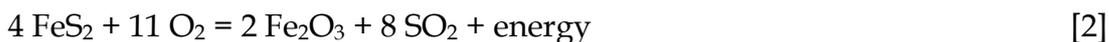


Figure 4: A flow diagram of the Zincor process.

Roasting

Zincor uses four Lurgi turbulent-layer roasters to roast zinc sulphide concentrates to zinc oxide.² The off-gases are fed to two Monsanto inter-pass absorption acid plants built by Simon Carves. The total roasting capacity is 720 tons of concentrate per day, and the two acid plants were designed for

540 tons of acid per day. Concentrates with a moisture content of 8 to 10% are fed into the roaster beds via slinger belts. The roasting temperatures are maintained at about 930°C with water addition. The following chemical reactions take place:



Reactions [1] and [2] proceed to more than 99% completion, whereas the extent of reaction [3] depends on the roasting temperature and on the association of the iron with the zinc. Iron that is part of the crystal, such as marmatite, reacts completely with the zinc to form ferrite, while iron contained in separate minerals, such as pyrite, will react only partly to form ferrite. Reaction [4] proceeds to approximately 6% completion.

Oxygen injection into the roasters was introduced in the mid 1990s at Zincor, to increase production.⁵ The fineness of the concentrate makes it difficult to increase production in the roasters by simply increasing the amount of air blown into the roasters, as this will lead to excessive solids carry-over. By injecting oxygen, this problem is overcome and production rates could be increased from around 630 tons per day to the current 820 tons per day.

In 2005, a pelletization plant was commissioned. The purpose of this plant is to pelletize part of the concentrate feed to the roasters. By increasing the particle size of the concentrate, oxygen injection can be reduced without negatively affecting production rates, as the risk of solids carry-over is reduced.

Acid production

The energy generated in the roaster is subsequently used to raise steam by passing the sulphur dioxide gas through a waste heat boiler.

The sulphur dioxide gas is then cleaned, dried and passed over a vanadium pentoxide catalyst at 450°C, where the SO₂ is converted to SO₃ gas. The SO₃ gas is absorbed in 99% sulphuric acid to 99.5% sulphuric acid and this is then diluted back to 99% sulphuric acid. This reaction takes place in ceramic packed towers.

Leaching

The calcine (zinc oxide) produced during roasting is milled in ball mills until it is a fine powder where after it is leached in four stages (as shown in Figures 5 and 6). The first stage is conducted continuously by adding dry calcine to an air-agitated pachuca, together with return acid from the electrolytic section (in the form of spent electrolyte). Slurry overflows from the first pachuca to three

other pachucas in series with the first one. After leaving the fourth tank, the slurry is diverted to three thickeners that are operated in parallel.

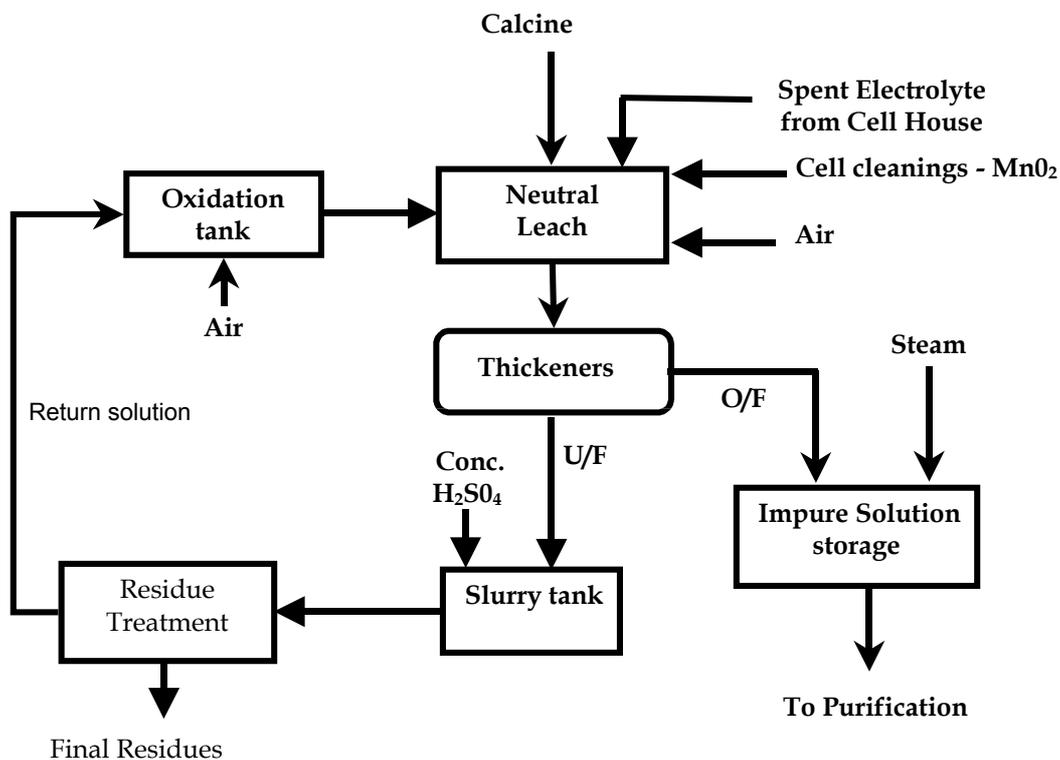


Figure 5: Flow diagram of the first-stage leach process

The thickener underflow is pumped to the second stage of leaching. The second leaching stage is conducted in a counter current configuration with the third and fourth leaching stages. Concentrated sulphuric acid is added in the final leach stage. After solid/liquid separation, via thickeners, the solution is pumped to the third leach stage, and, from there, after another solid/liquid separation step, to the second leach stage. The acid profile in these stages is typically 10 g/l H_2SO_4 , 50 g/l H_2SO_4 , and 100 g/l H_2SO_4 .

Two residues are produced during the leaching stage. The first is the insoluble residue after the fourth stage leach. This residue contains predominantly lead, silver, and silica.

The solution from the second leach stage proceeds to iron precipitation. Iron precipitation is conducted via neutralization with calcine. This yields the second, predominantly iron-containing, residue.

Spent electrolyte is constantly bled from the circuit to remove unwanted impurities (Mg and Mn), to control the sulphate balance and occasionally to control the solution inventory level. The solution is neutralized with lime and calcium carbonate to precipitate all the metals where after the zinc is re-dissolved with spent electrolyte.

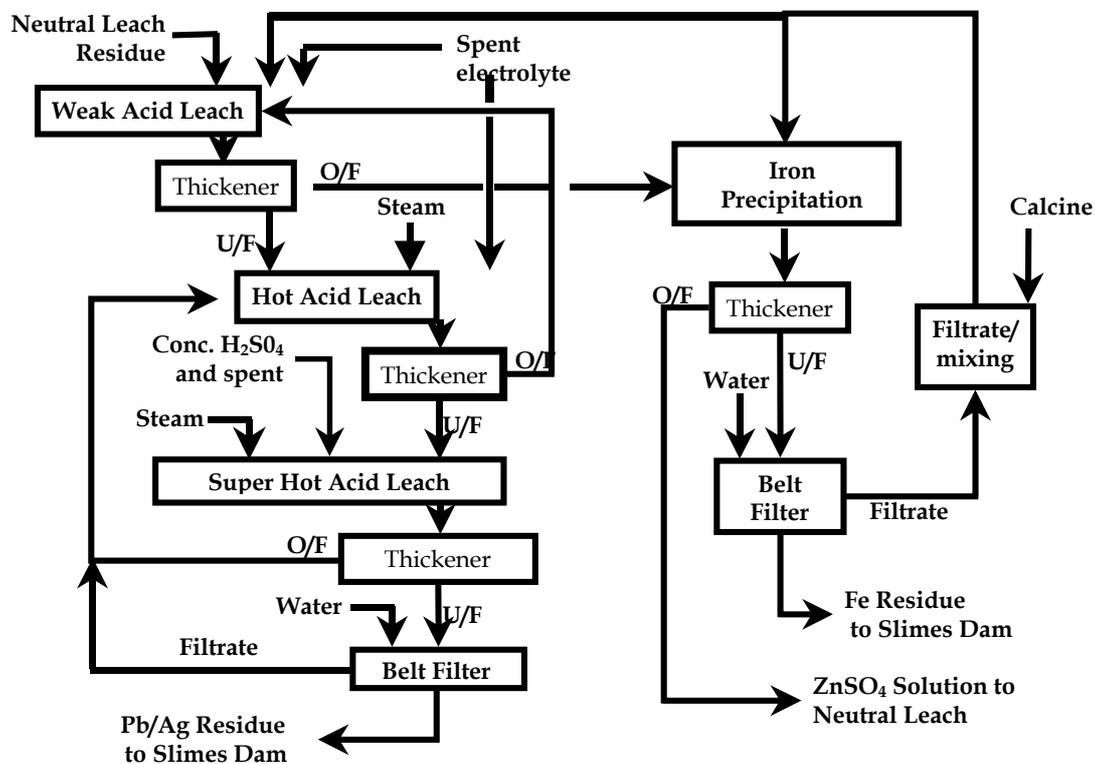


Figure 6: Flow diagram of the residue treatment plant that contains the second, third, and fourth stage leach processes

Effluent treatment plant

All solution spillages as well as the bleed cake from the solution bleed plant, rain water run-off collected on the plant, and the weak acid bleed solution from the acid plants, report to an effluent treatment plant for neutralization up to a pH of 9. Solid/liquid separation is conducted in a thickener where after the clear solution is pumped to an evaporation pond, and the underflow is pumped to a tailings dam for separate storage.

Tailings facilities

The two main residues, lead/silver and iron, as well as the thickener underflow from the effluent treatment plant, are disposed of to a tailings dam. The dam in use was constructed for the original gold mining operations. The dam is not lined and is coming to the end of its useful life. A new lined dam will be built within the next couple of years to cater for future residues. Solution run-off from the dam is collected and returned to the effluent treatment plant for neutralization.

Purification

The zinc sulphate solution obtained after leaching contains impurities that are detrimental to electrolysis. These are removed in a three-stage process. Copper is first precipitated in an agitated tank, with zinc powder as the precipitant. The copper cement is filtered off on plate-and-frame filter presses, and the solution proceeds to the next stage of purification where zinc dust is used to precipitate cobalt, copper, nickel, antimony, and germanium. The final traces of cobalt are removed through the addition of arsenic trioxide into the tanks. After precipitation, this cake is also removed with plate-and-frame filter

presses. The solution then proceeds to the final purification stage, where cadmium is cemented out with zinc dust. After final solid/liquid separation, the purified solution is pumped via two cooling towers to the cell house. Rapid cooling of the purified solution results in the crystallization of gypsum from solution. The gypsum is removed via a thickener. Before entering the cell house, the purified solution, containing around 135 g/l zinc, is mixed with spent electrolyte, containing around 40 g/l zinc, to control the inlet zinc concentration to around 60 g/l zinc.

Electrowinning

Electrolysis is used to plate the zinc from solution onto aluminium cathodes. The plated zinc is stripped manually on a 24-hour cycle. Oxygen is liberated at the anodes, which are manufactured from lead containing 0.5% Ag and 0.05% Ca. The current density is ~600 A/m², and the cathode/anode potential is ~3.6 V. The power consumption is ~3 400 kWh/ton cathode zinc.

Zincor uses three transformer rectifier units. The incoming feed of 42 kV is stepped down and rectified to direct current which is fed to the electrolytic cells, each of which contains 40 cathodes and 41 anodes connected electrically in parallel. 12 cells are connected in series to form a bank, and 14 to 16 banks are further connected in series to form a circuit. Each cell is fed individually with electrolyte, and the overflows from the individual cells are collected in a main return launder. Half of the spent electrolyte is pumped to the leach circuit, and the other half is added to the purified solution. The reactions taking place during electrolysis are:



During the electrolysis process, energy is generated in the cells. This energy is removed from the solution by circulating it through nine spent-electrolyte cooling towers.

Some of the manganese sulphate in solution is oxidised to manganese dioxide at the anodes, forming a sludge. This sludge is periodically removed during cell cleaning operations.

Melting and Casting

After the stripping cycle, the stripped cathode is melted at 550°C and cast into one of the following shapes: 25 kg slab, 1-ton jumbo, or 2-ton jumbo. The 25 kg slabs are strapped into 1-ton pallets. Demag induction heating furnaces are used to melt the zinc with a small amount of ammonium chloride as a fluxing agent. Four grades of zinc are produced according to SABS standards. These are shown in Table II.

Table II: Specifications for the grades of zinc produced by Zincor, mass %

SA code no	Zn (Min)	Pb (Max)	Cd (Max)	Fe (Max)	Sn (Max)	Cu (Max)	Al (Max)	Tl (Max)	In (Max)	Total (Max) Pb+Cd+Fe+Sn+Cu+Al+Tl+In
SHG	99.995	0.0030	0.0030	0.0020	0.0010	0.0010	0.0010	0.0010	0.0005	0.0050
Zn1	99.99	0.0030	0.0030	0.0030	0.0010	0.0020	0.0010	0.0010	0.0005	0.0100
Zn2	99.95	0.0080	0.0200	0.0100	0.0010	0.0020	0.0050	0.0010	0.0005	0.05
Zn4	98.5	0.95 min 1.35 max	0.1500	0.04	0.02	-	0.005	-	-	1.5

Zincor intends to start production of pre-alloyed jumbos in 2006. Currently ZincAl 10, containing 10% Al, is produced in slab form for aluminium addition into galvanizing baths. This will be replaced by jumbos containing 0.6% Al for the continuous galvanizing lines. A master alloy containing 20% Al will first be produced by melting aluminium in a melter, and then adding it to molten zinc in a dedicated furnace. The master alloy will then be cast continuously on a dedicated casting belt. A pre-alloy furnace with a 12-ton casting capacity per cycle was recently installed next to the jumbo furnace. Zinc will be poured from the jumbo furnace into the pre-alloy furnace. Master alloy will then be added to raise the aluminium content to 0.6%. Once the required grade has been achieved, the zinc will be cast out into the existing jumbo moulds by tilting the pre-alloy furnace.

Zinc powder is produced in the melt house operations. Zinc scrap, produced during the casting process, and hot zinc slabs are melted in an electrically heated bath.⁶ The molten zinc flows into a tundish, before it is contacted with air to produce zinc powder. The powder is collected in a blowing bin, with the finest fraction being collected in the furthest compartment. The zinc powder product is screened and blended before usage, whilst the air is filtered in a bag-house before release to the atmosphere. The zinc powder is then recycled back to the purification circuit.

CONCLUSION

The Zincor process has remained essentially the same since the plant was started in 1969. A number of process improvements have, however, been implemented over the years to increase production, decrease production cost, and improve flexibility and product offerings. This has proved valuable in giving Zincor the ability to withstand fluctuations in concentrate quality and market conditions.

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