

Treatment of zinc silicates by the Waelz Process

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SYNOPSIS

A review is given of the Waelz process. The chemistry of the process and the mechanism of crust formation (accretions) are briefly dealt with. The plant of Kiln Products Limited and its operation are described. The problems encountered and methods for their elimination are presented.

SAMEVATTING

'n Oorsig van die Waelz proses word gegee. Die chemie van die proses en die meganisme van die korsformasie word saaklik behandel. Die aanleg te Kiln Products Limited en die operasie daarvan word beskryf. Die probleme wat teengekom is asook die oplossing daarvan word gestel.

INTRODUCTION

Kiln Products Limited, which is adjacent to the Berg Aukas Mine, is situated approximately 21 kilometres north-east of Grootfontein in South West Africa. The mine, which is operated by the South West Africa Company Limited, produces lead-zinc vanadate, lead and zinc sulphides, and zinc silicate concentrates by froth flotation.

The production of zinc silicate (willemite) concentrate, which contains about 45 per cent zinc, amounts to approximately 3000 tonnes per month. An appreciable amount of zinc silicate in the form of a fine slime, which is not recoverable by froth flotation, is also produced. The slime, which contains about 18 per cent zinc, is collected in settling ponds for later treatment in the Waelz Kiln.

In March 1969, an associated company, Kiln Products Limited, commissioned a Waelz Kiln at Berg Aukas to recover the zinc from the willemite concentrate, current slime tailings, and tailings from a dump previously accumulated. The zinc oxide produced is transported by road and rail over a distance of 2800 kilometres to Zinc Corporation of South Africa Limited, near Springs, where ingot zinc is produced by an electrolytic process.

The original pilot-plant investigations were carried out in West Germany by Messrs Frederick Krupp Forschungsinstitut. Additional testwork was subsequently done by Messrs Lurgi Gesellschaft für Chemie und Hüttenwesen M.B.H., and the latter company was the successful bidder for the commercial plant. The following conclusions were drawn from the testwork.

- It is possible to produce a zinc oxide averaging 63,3 per cent zinc and 10,2 per cent lead, with a magnesium content ranging from 0,4 per cent to 1,4 per cent.
- The burden starts softening at about 1100°C.
- To avoid excessive formation of accretions, the operating temperature should not exceed 1100°C.
- At least 90 per cent of the zinc present can be volatilized without exceeding 1100°C.
- As a source of additional heat, gas is preferable to either oil or pulverized coal owing to its softer flame.
- Although accretions are to be expected, it should be possible to treat the raw materials tested if the operating conditions are controlled.
- To overcome dust losses during transport and to

minimize health hazards, the final product should be pelletized.

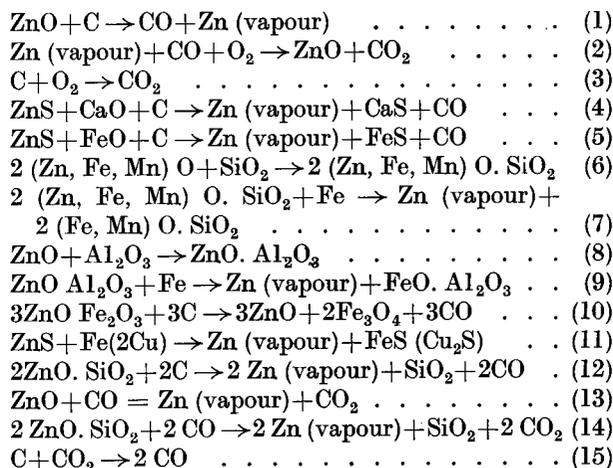
Further testwork indicated that, although the magnesium and fluorine might prove troublesome, high recoveries of zinc could be expected.

THE WAE LZ PROCESS

The use of a revolving tubular furnace for the volatilization of zinc was proposed for the first time in 1881 by George Druyee¹. However, it was not until 1923 that Krupp Grusonwerk, in collaboration with Metallgesellschaft A.G., started developing the process.

The process can treat ores, tailings, middlings, slimes, ashes, slags, and residues of any kind. The material containing zinc in the form of zinc oxide, zinc ferrite, zinc silicate, or zinc sulphide is mixed with any carbon-containing fuel. When heated in a horizontal rotary kiln at temperatures ranging from 1000 to 1500°C, the zinc is reduced, volatilized, and oxidized to zinc oxide. The zinc oxide is then separated from the exhaust gases by bag filters or electrostatic precipitators.

It is commonly accepted²⁻⁶ that the following reactions occur.



Bodenstein⁴ showed that no reactions took place directly between solids as shown in equations (1), (4), or (5). Simultaneous reactions actually occur in the gaseous phase as shown in equations (13) and (15) and, by analogy, (14) and (15). A study by Truesdale and Waring⁶ on rates of reactions revealed that, in the temperature range 900 to 1200°C, reaction (13) proceeded rather more rapidly than reaction (15), and reaction (14), the

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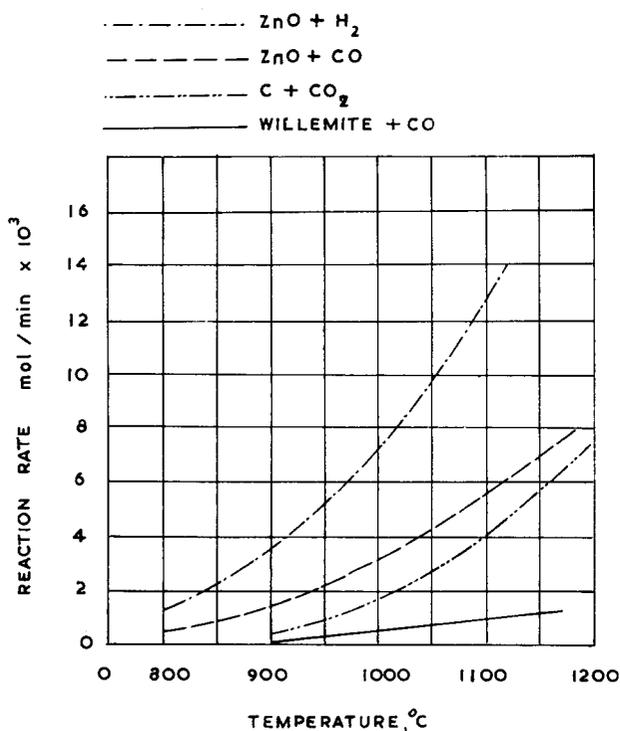


Fig. 1—Curves showing rates of reaction

reduction of willemite by carbon monoxide, was by far the slowest. This is illustrated in Fig. 1.

CRUST FORMATION

Crusts, in the form of outgrowths of adhering material, first of all cover the refractory lining in the reduction zone, and then move towards the charging end of the furnace. Microscopic and mineralogical analysis⁷ showed that the crusts are made up essentially of metallic iron, which accounts for 40 to 85 per cent of the volume. The iron forms a porous conglomerate with inclusions of pyroxenes, wustite, and coke fines. Wustite is most frequently found at the iron-slag boundary.

In an examination of the kinetics of iron oxide formation, it was established that the reduction process occurs autocatalytically and that the catalyst is metallic iron (the reaction product). Carbon is present in the iron-bearing part of the crust in the form of iron carbide-cementite in an amorphous form. During Waelz processing, the reduction is aided by the calcium oxide present in the feed material.

Studies by Lakernik on synthetic slags of the system FeO-SiO₂-CaO showed that, the greater the CaO:SiO₂ ratio, the higher the activity coefficient, i.e., the more iron will be reduced from the slags.

The mechanism of crust formation during the Waelz treatment of oxidized zinc ore can be represented as follows. As the material approaches the higher temperature zone and, consequently, the zone in which the basic technological reaction of zinc reduction begins, the low-carbon iron turns liquid when it comes into contact with the heated lining. Next, the refractory compounds of calcium and magnesium oxide adhere to the furnace lining and form annular crusts. The adhering crusts are

cooled as a result of the heat conductivity of the lining and the shell of the kiln, and they acquire a high mechanical strength.

To minimize crust formation, a (CaO+MgO):SiO₂ ratio of 1 is required. With this ratio, stable silicates of CaSiO₂ (pseudowollastonite), 2 CaOSiO₂ (orthosilicate), 2 MgOSiO₂ (forsterite), 2 FeOSiO₂ (fayalite), and mainly CaOMgO2 SiO₂ (pyroxene) are formed. Thus, reduction of iron oxide by CaO and MgO to a metallic form is minimized.

DESCRIPTION OF PLANT AND OPERATION

The flowsheet of the plant is shown in Fig. 2.

Handling of Feed

Anthracite and coke are stored in bulk in the open. Daily requirements of the reductants are charged onto an inclined conveyor belt and elevated to the stock silo, which is equipped with a Schenk weigh feeder that controls the feed rate.

Willemite concentrate is handled and stored in a similar fashion. The willemite silo is fitted with a table feeder capable of delivering up to 10 tonnes per hour.

Current slimes, together with reclaimed slimes tailings, are mixed with reclaimed reductant, and the requirements for the day are stored in a covered bunker. The addition of reclaimed reductant to the slimes is to assist in breaking up the lumps of very fine slime, which are extremely plastic, and also to make the product more transportable.

All the feed products are collected on a slow-moving conveyor belt in the following order: the mixture of slimes and reclaimed reductant, pre-oxide from the dust-settling chambers and cooling tower, willemite concentrate, reductants. The collecting conveyor belt is equipped with a weightometer that records the rate of feed and integrates the total tonnage. The combined feed is delivered into a pug-mill for mixing and then falls into a pelletizing disc for further mixing and granulation. The pelletizer discharges onto an inclined conveyor belt for delivery to the feed chute of the kiln.

Chemical analyses of the feed products are given in Table I, and Table II gives details of the feed to the kiln.

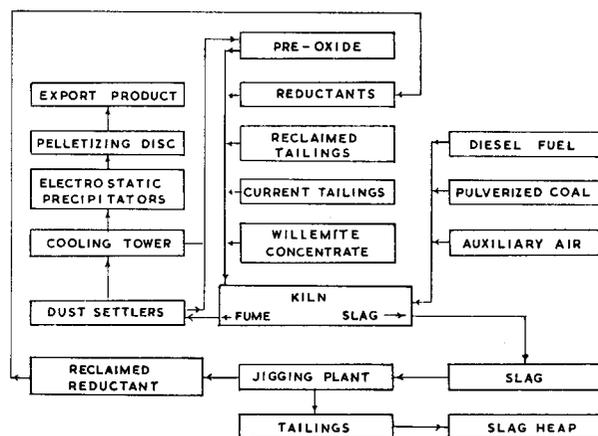


Fig. 2—Flow sheet at Kiln Products Limited

TABLE I
CHEMICAL ANALYSIS OF ZINC-BEARING FEED MATERIAL

Constituent	Willemite %	Reclaimed slime %	Current slime tailings %
Zn	48,1	18,7	20,7
Pb	2,1	4,3	6,1
Fe ₂ O ₃	2,6	4,4	4,4
FeO	0,4	0,5	0,5
MnO	0,06	0,13	0,13
V ₂ O ₅	0,20	0,87	1,20
As	0,08	0,03	0,03
P ₂ O ₅	0,36	0,14	0,14
S	0,09	0,14	0,14
SiO ₂	23,6	13,20	13,20
Al ₂ O ₃ + TiO ₂	0,25	0,54	0,54
CaO	0,8	14,7	14,7
MgO	1,3	8,9	8,9
Na ₂ O	0,4	0,14	0,14
K ₂ O	0,4	0,08	0,08
CO ₂	4,5	24,6	24,6
F	0,03	—	—

TABLE II
DATA ON FEED TO KILN

Material	Approximate tonnes per day
Reclaimed slime	135
Current slime	110
Willemite concentrate	55
Total revenue feed	300
Approximate zinc content, %	22,4
Anthracite duff	30
Coke breeze	65
Reclaimed reductant	40
Total mixed charge	435

The Kiln

The kiln is 4 m in diameter by 75 m long, and is fabricated of welded mild steel with four running tyres supported by eight rollers. The inlet and outlet sections of the kiln are tapered to 1,9 m and 2,87 m respectively. The inclination of the kiln is 2½ per cent to the horizontal. The kiln speed is variable from 0,25 to 1,25 r/min.

Feed to the kiln is by gravity via an inclined steel tube 5 m long and 500 mm in diameter. Air is blown down the feed chute to prevent the escape of hot gases.

The kiln is lined with a high silica-alumina wedge-shaped brick.

The temperature of material in the kiln is shown in Fig. 3.

Disposal of Slag

The hot slag discharged from the kiln drops down a transverse inclined chute lined with cast-iron blocks into a quench pond. The cooled slag is removed from the quench pond by a standard mining type of scraper winch.

Firing

Diesolene fuel is used to pre-heat the kiln to operating temperature, after which pulverized coal is used to maintain the temperature at the required level.

Slag discharge temperatures are normally kept at 1000°C, and exit gas temperatures at 500 to 600°C.

1 0,2 r/min 4 0,8 r/min
2 0,4 r/min 5 1,0 r/min
3 0,6 r/min

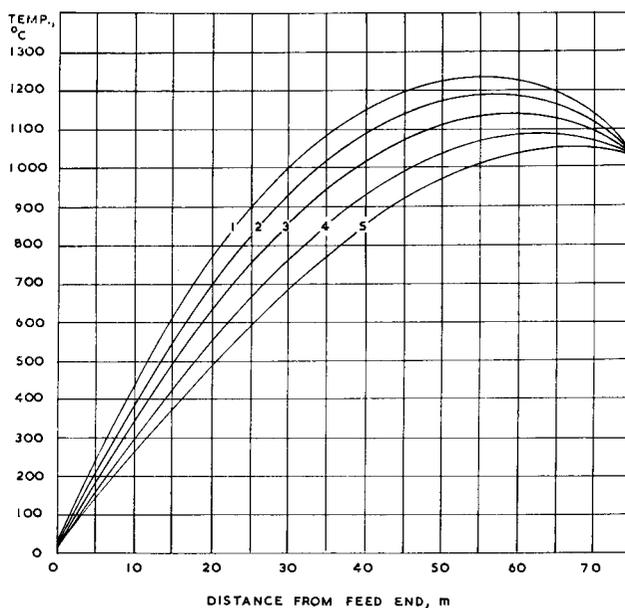


Fig. 3—Temperature gradient of material in the kiln

Recovery of Oxide from Exhaust Gases

The gases emerging from the feed end of the kiln pass through three settling chambers, and the pre-oxide collected in these chambers is discharged onto a redler conveyor and fed back to the feed circuit. After the settling chambers, the gases pass through a cooling tower, where the temperature is reduced from 450 to 200°C by water sprays. Pre-oxide that settles in the tower is discharged via a redler conveyor and returned to the feed circuit.

After cooling, the gases pass through two electrostatic precipitators in parallel. The precipitated oxide collects in the hopper-type bottoms, from where it is removed continuously by redler conveyors. These conveyors discharge via starfeeders into a pneumatic system that delivers the oxide through a cyclone and a bag house into storage silos.

The clean kiln gas, after emerging from the precipitators, passes through the exhaust fan to the stack.

Control Room

An air-conditioned control room is provided with a mimic flow diagram of the plant and the necessary indicating lights, recorders, switches, and alarms that enable the plant to be controlled from this point.

PROBLEMS ENCOUNTERED

Kiln Firing

The gas producer originally installed for firing the kiln was found to be too small to meet peak demands and also lacked flexibility. Because of the shortcomings of the gas producer, the necessary pumps and burners were installed to fire the kiln with diesolene fuel.

As a result of the oil crisis and the subsequent sharp increase in the cost of diesolene fuel, two attritors were installed and the kiln is now fired with pulverized bituminous coal.

Thermocouples

The kiln was initially provided with six platinum-rhodium thermocouples fitted through the shell and brick lining of the kiln. These thermocouples very rarely gave a reliable temperature signal for more than two or three days, after which they either became embedded in accretion or were physically damaged by large lumps of fallen accretion. The shell thermocouples have been removed, and the kiln temperatures are now controlled by the use of a radiation pyrometer, which measures the temperature of the slag discharge, and a thermocouple fitted in the dust-settling chambers, which measures the temperature of the gases leaving the kiln.

Shell Fans

It is highly desirable that air should be introduced into the kiln in stages proportional to the oxygen demand in the particular zone, and eight air fans were installed on the shell of the kiln for this purpose. The air inlet tubes on these fans started to fail shortly after commissioning owing to the development of circumferential cracks. The tubes were modified but still did not give satisfactory life. As a result of erroneously low temperature readings, the quantity of air introduced through the fan tubes was also faulty, which resulted in temperatures that were too high, followed by the formation of accretions in the areas of the shell fans.

It was decided to do away with this refinement of operation to achieve smoother operation of the kiln. Accordingly, the eight shell fans were removed and the openings were blocked off. A single fan with a capacity of 3500 Nm³ per hour was installed to supply additional combustion air along the kiln. This air is introduced at the discharge end of the kiln.

Slag Chute

The brick lining of the slag chute failed soon after the start-up. Refractory castings were tried but did not improve the situation. Cast-iron blocks are now used and have a long life.

Choking of Ducts

A series of baffles was built into the ducting to the cooling tower and electrostatic precipitators to ensure an even distribution of the gases. However, these baffles continually became choked with oxide and had to be removed.

After the baffles had been removed, the operation was smoother because the flow of gas was not being restricted.

Pneumatic Systems

The pneumatic system for transporting pre-oxide and Waelz oxide was a continuous source of trouble. The system frequently became choked, and the abrasive action on the pipelines was severe. Conversion from a vacuum to a pressure system, although an improvement, still resulted in continuous blockages.

The pneumatic system on the pre-oxide has now been replaced by redler conveyors, which work satisfactorily. Similar changes are to be made to the Waelz oxide circuit.

Brick Lining

Two qualities of bricks were used originally: Superlin for the first 30 m from the feed end, and Lusite for the remaining 45 m. From the start, trouble was experienced with the brick lining in the feed cone to the kiln. Initially, the bricks spalled rather severely and then started dropping out. Replacement of the bricks with a refractory casting solved the problem.

The first signs of failure in the Lusite bricks in the main body of the kiln were noticed after 196 days of operation. The top 5 to 10 cm of each brick was still extremely hard, as well as the 5 to 10 cm in contact with the steel shell. The middle portion, however, was completely friable and impregnated with slag, globules of metal, and carbon. Subsequently, a comparison test showed Superlin bricks to be superior to Lusite bricks.

From a critical examination of the type of brick failure, it appeared that the damage was caused by the penetration of carbon monoxide and zinc vapour, followed by the deposition of carbon and metallic zinc. This deposited carbon and zinc in the pores of the bricks set up stresses, which result in cracking. This phenomenon appeared to be catalysed by the presence of iron oxides.

The problem was solved by the use of Jumbo bricks, which have low porosity and permeability characteristics, as indicated in Table III.

TABLE III
TYPICAL ANALYSIS OF BRICKS

Constituent	Lusite	Superlin	Jumbo
SiO ₂ , %	44-46	53-55	53-55
Al ₂ O ₃ , %	51-53	42-44	42-44
Fe ₂ O ₃ , %	1,2-1,7	0,8-1,0	0,8-1,0
CaO, %	0,3-0,5	0,2-0,3	0,2-0,3
MgO, %	0,3-0,5	0,2-0,3	0,2-0,3
Alkalis	Trace	0,4-0,5	0,4-0,5
Porosity, %	14-18	10-15	6-11
Bulk density, g/cm ³	2,40	2,32	2,42
Permeability, c.g.s. units	0,10	0,05	0,03
Cold crushing strength, kg/cm ²	350-850	350-630	350-700

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