

Recent developments in slag-fuming process

S. K. DAS and S. SARKAR

IN most lead-zinc run-of-mine ores, the main valuable minerals are galena and sphalerite. Two products, namely a lead concentrate and a zinc concentrate are obtained by the differential froth flotation process. The separation is never complete; the lead concentrates contain a certain percentage of zinc and the zinc concentrates contain some lead.

The indigenous source of lead-zinc ore is the Zawar Mines situated at a distance of about 50 km from Udaipur, Rajasthan. Zawar Mines are located in one of the oldest lead, zinc and silver zones of the world. The underground working is at present being carried out in the Mochia Mogra and Balaria Hills area of the mines. The lead concentrates and zinc concentrates are produced by the differential froth flotation process. The lead concentrate contains 72-75 per cent lead, 5.3 per cent zinc and 22 oz/ton of silver. The zinc concentrate contains about 55 per cent zinc, 1 per cent lead and 5 oz/ton of silver.

In the treatment of lead concentrates for the recovery of lead in smelting process, the zinc content of the concentrate becomes concentrated in the slag in the oxidised form. It has been the practice of lead smelters for many years to maintain the zinc content of the slag at the highest practical level with a view to its subsequent recovery.

The lead blast furnace slags obtained in lead smelters average about 2-3 per cent lead and 10-16 per cent zinc and can be considered as a valuable raw material for the recovery of lead and zinc as by-products. The only production of lead blast furnace slag from an indigenous source is from the lead smelter of Hindusthan Zinc Limited (previously Metal Corporation of India Limited), at Tundoo, Dhanbad, Bihar. For a 6000 tons rated yearly capacity of the lead smelter, about 6000 tons of slag are also expected to be produced.

In 1905, the lead metallurgists started investigations with a view to recovering zinc from lead blast furnace slag. In earlier attempts, the idea of reducing zinc oxide to metallic zinc and then to fume was abandoned after trying compressed air blast without fuel. In 1925, the Waelz process of treating oxidised zinc ores for the recovery of zinc oxide was started in Germany. This method could not be properly applied to lead

SYNOPSIS

The various aspects of the processes for the recovery of valuable materials i.e. lead and zinc as by-products from lead blast furnace slags are discussed. The technology and mechanism of the conventional slag fuming process and the recent developments of a cyclone process and a suspension smelting and volatilization process are reviewed. The installation of a slag fuming plant in the country for the recovery of by-products from indigenous sources is advocated; such a plant would help to ease the present acute shortage of the two major non-ferrous metals and diminish foreign exchange difficulties.

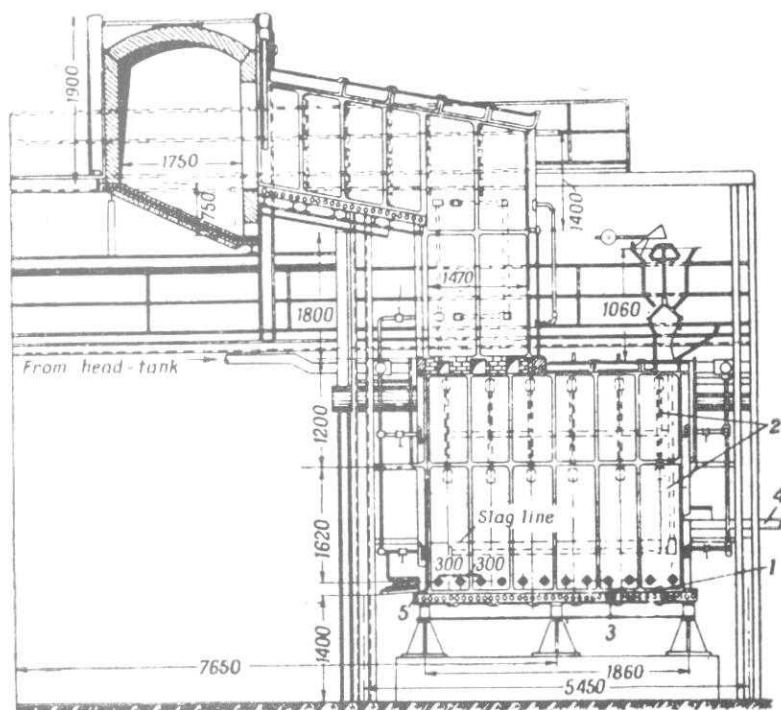
blast furnace slag on account of the difficulty experienced in handling the fusible charges in kilns. The first slag fuming plant was started in East Helena, Montana, U.S.A. in 1927. At present, several slag fuming plants are in operation all over the world. Developments in the slag fuming process techniques have been reported from Australia and Germany. These are (i) a cyclone furnace for slag fuming at Port Pirie, Australia, (ii) suspension smelting and volatilization at Sachsen, D.D.R.

Technology of the fuming process

Molten slag is subjected to a blowing treatment with a mixture of fuel and air the combustion of which heats the slag to a very high temperature. Molten zinc is volatilized from the slag and reoxidized to form zinc oxide (fume) which is recovered from the process gases. The operation is carried out in a rectangular, completely water-jacketted furnace with tuyeres on all sides except the roof. The roof is arched over with fire brick and an outlet leading to a flue having waste-heat boilers is provided.

The longitudinal section and transverse section of a conventional slag-fuming furnace are shown in Figs. 1 (a) and 1 (b).

There has been some difference of opinion among research workers as to whether elemental carbon or carbon monoxide is the active reducing agent in the slag-fuming process. Some workers have also noted that high volatile coals are more efficient than the low volatile coals suggesting that hydrogen could also be



1a Slag fuming furnace¹⁶; longitudinal section; dimensions in mm

an active reducing agent. However, according to experiments carried out by Bell, Turner and Peters¹, it was found that both hydrogen and carbon monoxide are effective reducing agents for the zinc oxide content of the slag.

The following reactions supply the thermal requirements :



The reducing reactions are :



The reactions 1, 2 and 3 evolve heat and 4 and 5 absorb heat. The other reactions taking place in the furnace are :



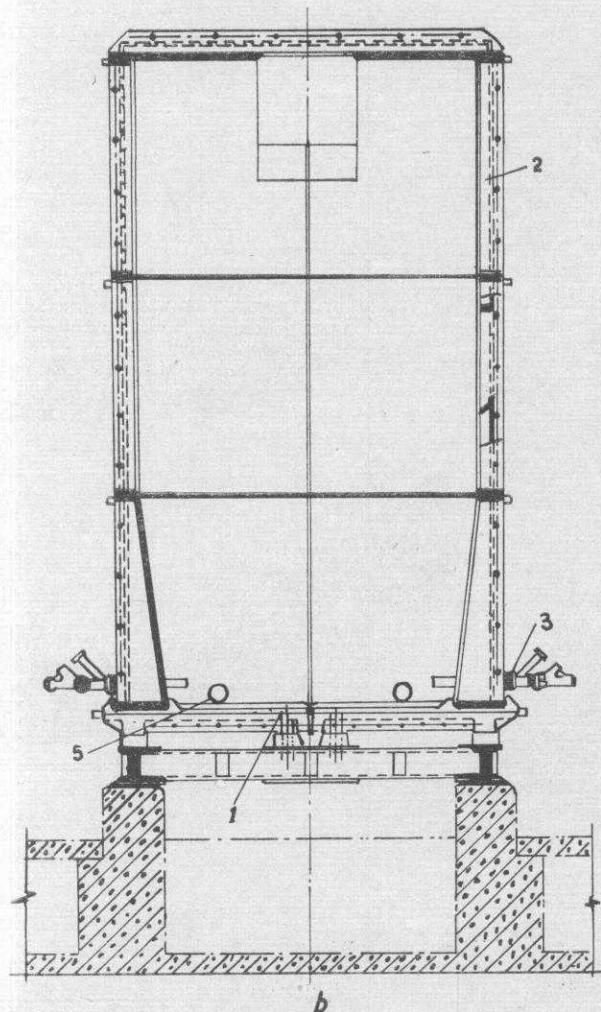
In addition to the main reactions mentioned above in connection with the reduction of the oxidized zinc content of Fe-Zn-Ca silicate slag to zinc by CO

and H_2 , other reactions also take place. Lead is assumed to be volatilized in the form of sulphide and a small amount of zinc is also volatilized in this form. Other minor metals are believed to be fumed also. The major components of the slag, i.e. lime, iron, silica, alumina and sulphur affect the rate at which zinc is volatilized.

One important fact in fuming lead blast furnace slag is that the fuel first supplies the heat and then works as a reducing agent. If the heat requirements of the process could be reduced by enriching the air blast with oxygen or preheating the air, more CO and H_2 would be available for reduction. The use of oxygen-enriched air in different slag-fuming plants has considerably increased the efficiency of the process.

Treatment of the slag is divided into charging, blowing and tapping periods. The whole cycle of treatment is completed in about two hours. In the beginning, the elimination of zinc is slow but on reaching $1000^\circ C$, the process accelerates and is carried on at a rapid rate till the zinc content of the slag is reduced to about 1 per cent. The metal elimination curve for lead and zinc during the period of blow at variable temperatures, reaching a maximum of about $1100^\circ C$, is given in Fig. 2.

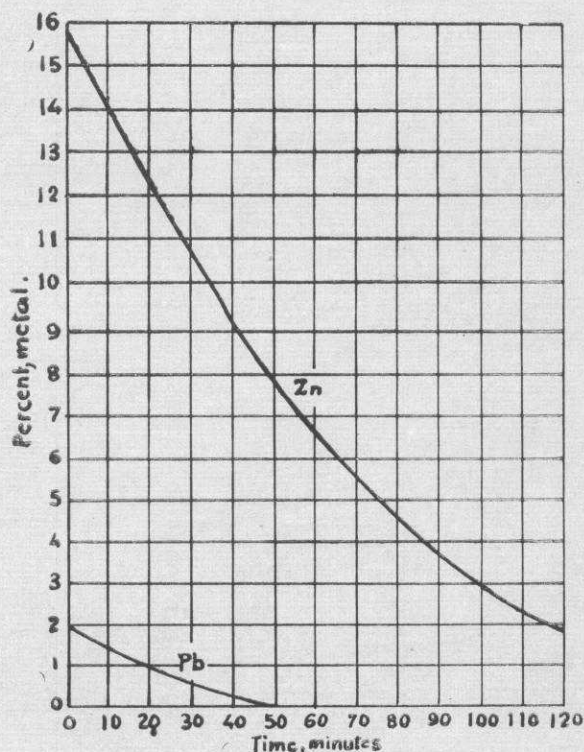
The mixture of the metal vapour and condensed oxide fume above the slag bath is carried by the flow of combustion gases into the combustion chamber of the waste-heat unit. Along this path of flow, via a horizontal flue prior to entering the boiler, oxidation of the metal vapour and the combustion of carbon monoxide takes place. The dust-laden air leaves the



1b Slag-fuming furnace—transverse section

furnace at about 1100°C and enters the waste heat boiler at 1000°C . In its passage through the unit, the temperature is reduced to $400\text{--}500^{\circ}\text{C}$. Further cooling is effected by a water-spray cooling chamber and towers and at 200°C the fume enters the bag house. The dusts collected in the waste-heat unit flue, cooling towers and the bag-house (known as "zinc bag-house" to differentiate from the other bag-house known as the "lead bag-house" and mentioned later) are mixed. The mixed fume assays about 63–70 per cent zinc and 5–10 per cent lead.

The mixed fume is treated in a kiln with about 1.5 per cent of coke breeze by weight to reduce the lead content of the fume and to recover the lead removed from the fume. The de-leaded fume is then discharged from the kiln. The product is cooled in water-cooled rotating coolers and shipped to the zinc smelter for the recovery of zinc metal. This fume assays between 70 and 72 per cent zinc and 0.5 and 1.5 per cent lead. The gases from the kiln containing PbO enter another bag-house, known as the lead bag-house, through cooling



2 Oyetal eliminative curve

chambers. The dust obtained from the lead bag-house assays about 50–52 per cent lead and 20–23 per cent zinc and is returned to the lead smelting system. Details of the operation and construction of different slag-fuming furnaces are given in Tables I and II. A generalised flow-sheet of the slag-fuming process is given in Fig. 3.

Mechanism of zinc fuming

The original theory was that solid fuel particles (coal) are necessary for the mechanism of fuming. A large area of contact between the reducing agent and slag is provided by the particulate form and this is necessary for a rapid fuming rate. To support this view, it was pointed out that attempts to use natural gas as a fuming fuel were unsuccessful. It was also claimed that the area of contact between gas and slag in the fuming operation is too small to permit higher rates of fuming but no proof in support of this belief was forthcoming.

Bell, Turner and Peters made a study of the fuel requirements in slag fuming based on the assumption that, in conventional slag fuming, the slag, air and reducing agent reach equilibrium in the furnace. They did not prove that conventional slag fuming operates close to equilibrium but they did report several facts which they believe pointed to equilibrium.

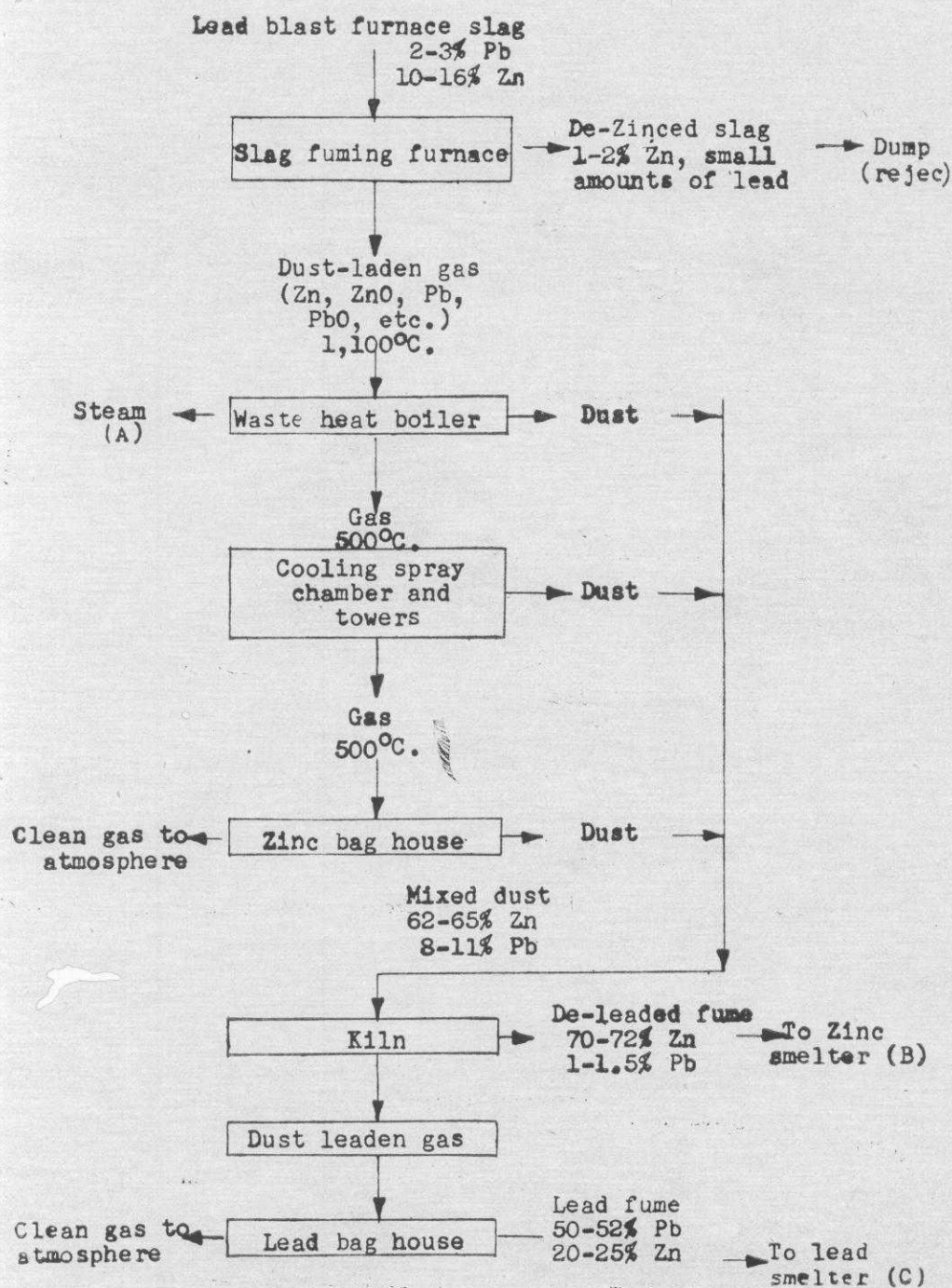
Quarm²⁴ did not agree with the assumption of equilibrium but proposed that the rate of reduction of zinc oxide indicated a pseudo first-order reaction involving

TABLE I Operating details of different slag-fuming furnaces

| Details | Kellogg | Trail | Elpaso | Chihuahua |
|--------------------------------------|--|-------------------|--------------------|--------------------|
| Slag charge per cycle | 37.5 tons | 55 tons | — | 45 tons |
| Cycle | a. charging 27 b. blowing 83 c. tapping 10 | | | |
| | | | | |
| | | | | |
| Treatment rate cycles per day | 12 | 9 | — | 12 |
| „ Tons/24 hours | 450 | 495 | 650 | 540 |
| Zn content of slag, tails, per cent | 16 | 16.8 | 16.2 | 12 |
| Zn content of slag, tails, per cent | 1.03 | 2.9 | 2.56 | 2 |
| Coal consumed during cycle | 12 450 lb. | 200 lb/min. | 122 tons/24 hours | — |
| Coal consumed per lb of zinc (lbs) | 1.19 | 1.1 | 1.0 | 1.2 |
| Steam generated per lb of coal (lbs) | 7.8 | 6.6 | 60 000 lb/ hours | — |
| Air volume | 9640 cu. ft/min. | 12000 cu. ft/min. | 16 000 cu. ft/min. | 12 000 cu. ft/min. |

TABLE II Details of plant and machinery

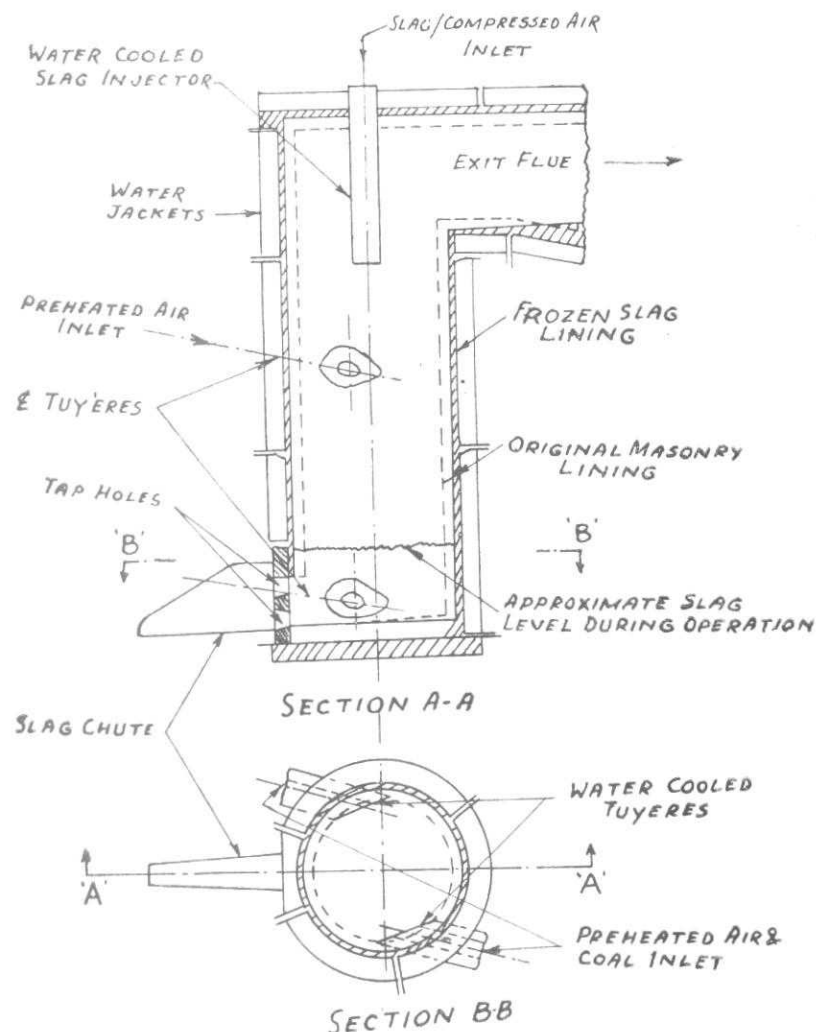
| Items | Kellogg | Trail | Elpaso | Chihuahua |
|--|-------------------------------|--------------------------------|--|---|
| Slag treatment furnace dimensions (feet) | 8×15×24 | 10×24×10 | 8×21×33 | 8×21×33 |
| Tuyers | 28 double inlet on each side | 35 double inlet on each side | 21 double inlet on each side | 21 double inlet on each side |
| Waste heat boiler | — | 17 350 sq. ft. heating surface | — | — |
| Flue | — | Brick partly water jacketted | — | 7 ft. dia. balloon flue 93 ft. long |
| Cooling towers | — | — | U tubes 30 in dia.× 58 ft. high | U tubes 80 nos. 3 ft. dia. 48 ft. high |
| Cooling chamber | — | — | — | Second spray chamber |
| Deleading kiln | 75 ft.×7 ft. | — | 75 ft.×5½ ft. | 75 ft. × 7 ft. |
| Zinc bag-house | — | Woollen bags | 8×160 no. of bags | 8-126 no. 18 in.×30 ft. standard bags |
| Cooling arrangement | — | — | — | U tubes 30 in. dia.×40 ft. high |
| Blowers, etc. | 12 000 cu. ft. min. at 10 lb. | 15 000 cu. ft. min. | Turbo-blower 18 000 cu. ft. min. at 10 lb. | 80 h.p. Ingersoll-Rand 14 000 cu. ft/min. at 12 lb. |



3 Flow sheet of slag-fuming plant

ferrous oxide in the slag. The reasoning put forward in this respect was based on 'the fact that the reaction proceeds is in itself prima facie evidence that equilibrium is not attained', a statement that is true only for a closed system. When zinc is removed continuously from the system as in slag-fuming, a close approach to equilibrium is attained.

Kellogg²¹ considered the processes at the gas-slag interface and concluded that the area of the interface within the slag-fuming bath was more than sufficient to account for the rate of removal of the zinc from the bath. He agreed that the equilibrium postulated by Bell, Turner and Peters contributed to the rate control. Reactions (4) and (5), mentioned earlier, are the



4 Cross-section of cyclone furnace

main reducing reactions in a slag-fuming process. Since in the combustion of coal, carbon is the predominating reactant, reaction (4) is the controlling reaction. The equilibria are affected to some extent by water-gas reactions arising from the combustion of hydrogen, but for a general discussion, their consideration is not necessary.

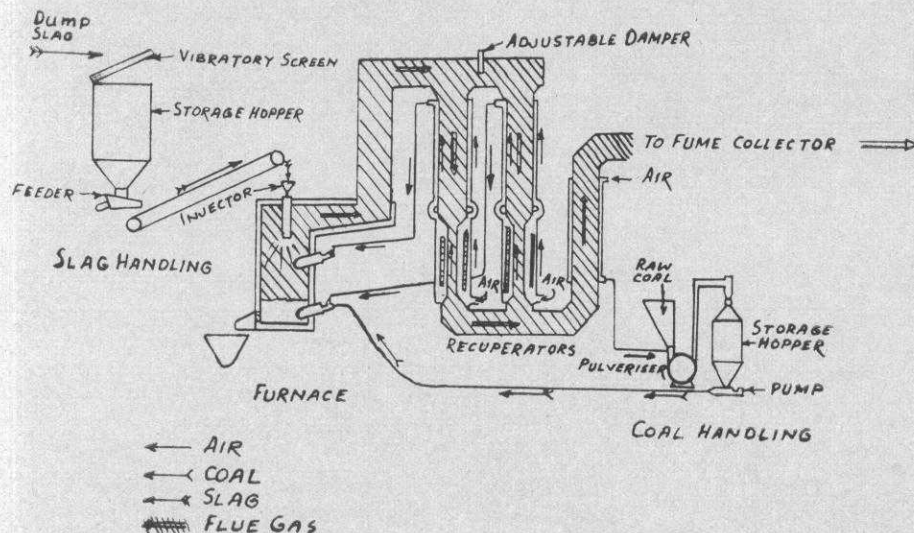
The slag-fuming process basically depends on the reduction of zinc oxide by carbon monoxide produced by the combustion of fine coal as per equation (4). This reducing reaction is highly endothermic. The heat necessary for the production of one gram-atom of zinc at about 1200°C is of the order of 43 Kcal. As the heat of formation of 1 gram-mole of carbon monoxide is only about 27 Kcal, a considerable excess of fuel must be burnt to provide the thermal requirements of the process and also the heat loss as is common in most pyrometallurgical processes. It would appear that it would be more economical to supply this heat by burning the excess fuel requirements to CO₂ (heat of

formation 95 Kg/per gram-mole of CO₂). Considering the reducing reaction, the equilibrium constant

$$K = \frac{p_{\text{CO}_2} \cdot p_{\text{Zn}}}{p_{\text{CO}} \cdot a_{\text{ZnO}}} = 0.4 \text{ atm. at } 1200^\circ\text{C.}$$

If the CO₂/CO ratio in the combustion gases becomes too high, the equilibrium partial pressure of zinc may be depressed to the point where the rate of reaction will be adversely affected. It is necessary to have a balance of the conflicting process requirements of a high proportion of CO to give: (i) reasonable reaction rates and (ii) a high proportion of CO₂ to provide economical heating.

The equilibrium constant K at 1000°C is only 0.01 atm. It is evident, therefore, that in order to recover zinc in the metallic form it is necessary to shock-chill the zinc vapour by inert gases or by using a lead splash condenser as in the Imperial Smelting Process.



5 Diagram of the cyclone furnace pilot plant

This is a practical impossibility. Sufficient quantity of air is blown above the bath in all slag-fuming furnaces to oxidise all metallic zinc vapour to ZnO and complete the combustion of the remaining carbon monoxide.

Development of the cyclone process

In all standard slag-fuming furnace operations, a proportion of cold slag from the dump is added in order to recover lead-zinc values from it. The melting of this granular material in the fuming furnace is somewhat inefficient and the economy of the process is affected. At Port Pirie, the Broken Hill Associated Smelters Pvt. Ltd. decided in 1965 to construct a plant in which two-thirds molten slag, as produced from the blast furnace, and one-third cold granular slag from the dump would be treated.

As discussed earlier, there are disadvantages in the conventional batch slag-fuming process in that—(i) the process requires a higher fuel consumption than is strictly necessary for the zinc oxide reduction and (ii) during the end period of the blow a high proportion of carbon monoxide is maintained in order to give reasonable reduction of zinc oxide in the slag. The full reducing power of the carbon monoxide is not utilised properly and it is lost to the waste gases.

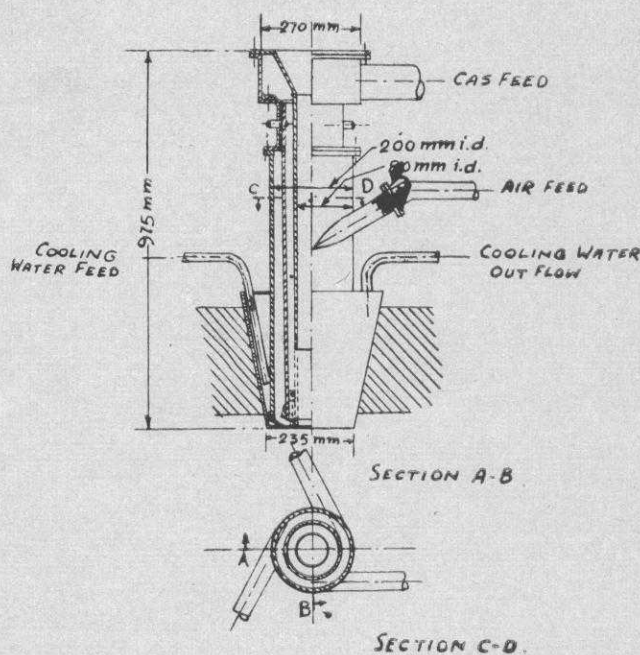
Blanks and Ward²³ mention the development of a cyclone furnace for the treatment of slag in order to minimise these disadvantages. The excess heat is utilised by flash-melting the cold granulated slag. The design of the furnace (Fig. 4) is such that the gases are given a swirling motion and through this cyclone action the molten slag is thrown to the walls of the furnace. The molten slag runs down into the slag bath counter-current to the rising reducing gases. The extended surface presented by the film of slag running down the furnace walls provides excellent conditions for reduction; efficient usage is thus made of the excess reduction capacity of the gases leaving the bath. The process can be made

continuous and the excessive use of fuel necessary towards the end of the cycle in the bath process can be avoided. A schematic diagram of the cyclone furnace plant is shown in Fig. 5.

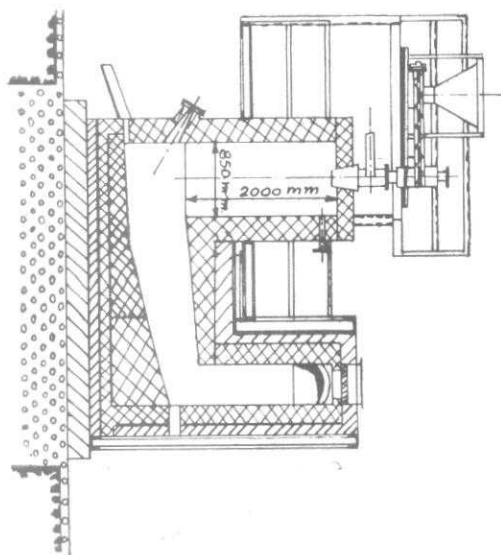
It is reported that the results of the pilot plant were very encouraging and a high degree of thermal efficiency and zinc elimination was achieved.

Suspension smelting and volatilization

The Lange-Barthel²⁴ suspension smelting process has



6 Section of the experimental furnace



7 Suspension smelting furnace burner

been applied to the fuming of blast furnace slag. This process has been found to compare favourably with the conventional slag treatment or fuming process in respect of (i) higher reaction kinetics, (ii) comparable fuel consumption and thermal requirements (iii) a high degree of metal elimination.

The process aims at having high space and time yields, i. e. the physical and chemical processes taking place in the treatment should occur rapidly and completely. The fundamentals of the process are outlined by the inventors as follows.

Volatilization at normal pressures, like most metallurgical processes, concerns heterogeneous reactions in which the gas phase participates. Both the extent and rate of volatilization should be determined by those parameters which influence the rate determining steps, inner and outer diffusion. These are (a) a sufficiently high temperature in the reaction space, (b) high partial pressures of the important gaseous constituents, (c) small particle size and high dispersion of solid or liquid reactants, (d) effective disturbance of the equilibrium between the vapour pressure of the volatile constituents at the surface and in the bulk gas phase, (e) avoidance of saturation by high relative velocities between solid and liquids on the one hand and solids and gases on the other and (f) turbulent flow.

It is possible for a non-volatile constituent of the solid charge to melt; the volatilization of the volatile constituents must have ceased before the aggregate can change, a volatile constituent can then dissolve in the resultant melt or form a compound with it, causing pronounced diminution of its activity which reduces the yield and more particularly the volatilization rates. The relatively long treatment times required by many fuming processes e. g. slag-fuming, are due to such an activity reduction accentuated by the decrease in the concentration of the volatile species,

which has an analogous effect. Increasing mass and heat transport and transfer, by satisfying the best aero-dynamic requirements in the reaction space and appropriate design are thus essential requisites for high space-time yields in metal recovery process by volatilization.

The construction of the pilot plant suspension furnace and burner are shown in Figs. 6 and 7.

Conclusion

The recent development of cyclone and suspension smelting for the recovery of zinc and lead and the conventional slag-fuming process have been discussed. Prior to the development of the process, much attention was given to obtaining a slag of low lead content to improve the economics of the lead blast-furnace smelting process. As the processes discussed recover almost all the lead content of the slag along with the zinc, there is no necessity for having such rigid control to have a very low lead slag.

Considerable research work has been carried out in the mechanism and physical chemistry of the process, increase in the capacity, in fuel efficiency by using oxygen or preheated air, and in the feeding arrangements for cold granulated slag.

It is reported that the lead smelter of Hindustan Zinc Limited at Tundoo, Dhanbad, has about 50 000 tons of cold slag in the slag dump. The slag contains on an average 2.56 per cent lead and 11.45 per cent of zinc. Over and above this reserve of cold slag a yearly production of 6 000 tons of slag is expected as mentioned earlier. It is hoped that serious consideration will be given to the installation of a slag-fuming plant in the country for the recovery of the two valuable metals—lead and zinc at this period of foreign exchange difficulty and acute shortage of non-ferrous metals.

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