Zinc accumulation during recycling of iron oxide wastes in the blast furnace

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Byproducts/wastes of iron- and steelmaking processes and steel scrap are the main sources of iron units recycled in the steel plants. Direct recycling of the iron oxide wastes (dusts and sludge) in the blast furnace (BF) is however hampered by its chemistry (>0.1%Zn in the charge). Vaporisation, condensation, oxidation and circulation of zinc may collectively lead to the accumulation in the furnace. Very fine particles are deposited on other particles that have high surface areas which diminish BF refractory life and impair the quality of high quality pig iron produced. For effective continuous recycling of iron units, it is necessary to identify their sources, determine their composition and evolve device and appropriate technology for the treatment of zinc bearing units. The present paper analyses the process of zinc accumulation in the BF and derives an algebraic model to determine the extent of the accumulation. On the basis of analysis of zinc base formation, its recirculation in the furnace and other related productive units, a homograph (alignment chart) of zinc accumulation is designed. The paper also outlines the feasible processes of zinc removal from the close-looped system (sinter plant–BF–sinter plant).

Keywords: Zinc, Blast furnace, Recycling system, Iron oxide wastes, Accumulation

Introduction

Zinc is present in the blast furnace (BF) as a constituent of the sinter charge in the form of oxides (ZnO), ferrite (ZnO.Fe2O3), silicates (2ZnO.SiO2) and sulphide (ZnS). Reduction, vaporisation, condensation, oxidation and circulation of zinc may occur in the BF:

ZnO(s) $\rightarrow$ 0.5C + CO(g) (1)

The volatilised Zn gas in contact with water vapour (steam) and carbon dioxide (equation (2)) oxidises and deposits its fine particles at the refractory of the non-cooled upper part of the furnace shaft profile forming dense and heavy crusts.

Zn(g) + H2O(CO2) = ZnO + H2(CO) (2)

These formations prevent the uniform distribution of gases and adversely affect the thermodynamic equilibrium of the BF process. This could lead to the collapse of the tuyeres and excess coke is consumed to reduce the Zn accumulated in the furnace. Zinc is highly gasified at the temperature zone of 1173–1373 K which results in the lowering of the temperature of the zone. Consequently, 11 kg of coke is consumed for every kilogram of zinc released.

The oxidised zinc (ZnO) penetrates into the regions with large surface areas such as pores, cracks, masonry and bricks enclosure (linings). Because the linear expansivity of zinc (39.7 × 10^-6 K^-1) is higher than that of the refractory – chamotte (11 × 10^-6 K^-1), the former expands at these areas causing severe damage. Some of the gasified Zn leaves the furnace through the off gas (flue). Such removal is enhanced by higher furnace top temperature 523–723 K and development of peripheral motion in gas stream.

Part of the reduced zinc in the lower part of the shaft, shoulder and hearth of the furnace dissolves in the iron and flows through the molten iron, creating what is known as phnom. When the crust of zinc oxide falls into the molten metal, zinc is absorbed into the pig iron. The remaining part of the gasified zinc is deposited on the iron oxides of the incoming charge in the form of ferrite.

Zn(g) + FeO(Fe3O4) + CO2$\rightarrow$ZnO + FeO(Fe5O4) + CO (3)

Through this process, greater amount of zinc moves back with the furnace burden to the zone of reduction, thus creating a recirculating (repetitive) system. The extension of the circulating zone is inversely proportional to the duration of the burden in the furnace, the value of fume/unit charge and the temperature at the upper part of the shaft.

The mechanism of zinc reduction, oxidation and circulation in the BF is illustrated in Fig. 1.
Zinc accumulation processes in BF

In the close-looped system of iron ores utilisation between sinter plant–BF–sinter plant, the inflow of zinc to the BF increases owing to the usage of iron bearing wastes especially BF and steelmaking fine dusts and sludge. Increased recycling of galvanised steel scrap in basic oxygen furnace (BOF) and electric arc furnace (EAF) processes increases the zinc content in steelmaking dusts and sludge. Consequently, application of these materials through sinter promotes the accumulation of zinc in the BF.

Analysis of the materials balance of most metallurgical plants has shown that 15–27% of overall zinc released from the BF is through the flue dust, 45–70% through sludge obtained from off gas cleaning, 5–10% with pig iron and 5% with slag, while 5–10% of zinc is deposited at the brickwork and linings. These values depend on many factors such as the temperature at the furnace top, moisture content of flue gas and mechanism of furnace charging. 4,5

The control level of zinc charged into the furnace is generally 0·15–0·5 kg t\(^{-1}\) of molten iron or 0·1% of the charge. The ultimate permissible intake of zinc in the BF in France is 0·15 kg t\(^{-1}\) of molten iron. In the UK the limit is 0·5 kg, while in the USA, the permissible zinc intake is 0·5–1·0 kg. 6

The schematic flow sheets and evaluation of zinc accumulation in the BF are shown in Figs. 2–5. The required level of zinc intake to the BF through dust and sludge should be considered individually for each plant from the result of zinc balance in the system. The saturation of the Zn intake to its accumulation can be evaluated or determined by studying the sources (in terms of mass and composition) of zinc movement within the ironmaking sector.

Determination of zinc accumulation

The initial constant of the coefficient of recirculation of zinc is assumed to be \(R\), the mass of zinc input to the BF \(\text{MZ}_{\text{total}}\) (tonne/year) and the combined value of zinc in pig iron, slag and those left in the furnace \(K\) (percentage of the total zinc inflow to the BF). Zinc accumulation may be derived using Figs. 2–5 for the various systems.

Closed loop system

The total mass of zinc inflow to the BF \(\text{MZ}_{\text{total}}\) (tonne/year) is given by

\[
\text{MZ}_{\text{total}} = \frac{\text{MZ}_{\text{ext}}}{(1 - R)}
\]

where \(R = 1 - K\) is the coefficient of recirculation of zinc for the closed loop system and \(\text{MZ}_{\text{ext}}\) is the mass of zinc from external sources (tonne/year).

\[
\text{MZ}_{\text{sludge}} = K\text{MZ}_{\text{total}} = 0·1\text{MZ}_{\text{total}}
\]

where \(K\) is the mass of zinc released annually through the molten iron and slag, and those left in the furnace, is given by

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where \(K\) is the mass of zinc released annually through the molten iron and slag, and those left in the furnace, is given by

Consequently, the mass of zinc inflow to BF through flue dust \(\text{MZ}_{\text{dust}}\) (tonne/year) is

\[
\text{MZ}_{\text{dust}} = 0·9\text{MZ}_{\text{total}}\text{M}_{\text{dust}}/(\text{M}_{\text{dust}} + n_1\text{M}_{\text{sludge}})
\]

where \(\text{M}_{\text{dust}}\) and \(\text{M}_{\text{sludge}}\) are the masses of flue dust and sludge (tonne/year) respectively and \(n_1\) is the mass ratio of zinc in BF sludge (Conc.Zn)\(_{\text{sludge}}\) to that in BF dust (Conc.Zn)\(_{\text{dust}}\).

\[
\text{M}_{\text{sludge}} = \text{MZ}_{\text{sludge}} - \text{MZ}_{\text{dust}} - \text{MZ}_{\text{ext}}
\]

Therefore, the percentage of zinc content in the flue dust (Conc.Zn)\(_{\text{dust}}\) is

\[
\text{Conc.Zn} = \frac{\text{MZ}_{\text{dust}}}{\text{M}_{\text{dust}} \times 10}
\]
Conc: Zn\(\text{sludge} = \text{Zn}\)sludge

\(\text{MZ}_{\text{sludge}} = \text{M}_{\text{sludge}} - \text{M}_{\text{dust}} - \text{M}_{\text{ref}}\)

\(\text{MZ}_{\text{total}} - \text{MZ}_{\text{dust}} - \text{MZ}_{\text{ref}}\)

\(\text{MZ}_{\text{sludge}}\) ~ \(\text{MZ}_{\text{sludge}}\)

\(\text{M}_{\text{sludge}}/\text{C}_{14}\text{M}_{\text{sludge}}/10\) \(\text{(13)}\)

The relative mass of zinc in hot metal \(q_c\) (kg/tonne) is given by

\(q_c = \text{MZ}_{\text{total}}/P\) \(\text{(14)}\)

where \(P\) is the mass of hot metal produced (tonne/year).

**Open circuit system**

In this system, \(\text{MZ}_{\text{total}}\) is given by

\(\text{MZ}_{\text{total}} = \text{MZ}_{\text{ext}}/(1 - R_2)\)

where the coefficient of circulation \(R_2\) of zinc for the open circuit system is given by

\(R_2 = (1 - K)\left[\text{M}_{\text{dust}}/\left(\text{M}_{\text{dust}} + n_1\text{M}_{\text{sludge}}\right)\right]\) \(\text{(15)}\)

\(\text{MZ}_{\text{msf}}, \text{MZ}_{\text{dust}}\) and \(\text{MZ}_{\text{sludge}}\) are calculated by the same method as in the closed loop system (see equations (9)–(11)).

**Partially closed loop system**

Here \(\text{MZ}_{\text{total}}\) is given by

\(\text{MZ}_{\text{total}} = \text{MZ}_{\text{ext}}/(1 - R_3)\)

where \(R_3\), the coefficient of recirculation of zinc for the

\(\text{MZ}_{\text{msf}}\), \(\text{MZ}_{\text{dust}}\) and \(\text{MZ}_{\text{sludge}}\) are calculated by the same method as in the closed loop system (see equations (9)–(11)).
4 Partially closed circuit flow sheet

5 Partially closed circuit zinc accumulation flow sheet with dezincification
Partially closed loop system is given by

\[ R_3 = (1 - K) \left( \frac{M_{\text{dust}} + n_1 M_{\text{rs}}}{M_{\text{dust}} + n_1 M_{\text{sludge}}} \right) \] (16)

where \( R_3 \) is the coefficient of recirculation of zinc for the partially closed loop system with dezincification and can be calculated as follows

\[ R_4 = (1 - K) \left\{ \frac{M_{\text{dust}} + 0.65 M_{\text{sludge}}}{0.65 n_1 + 0.35 n_2} \right\} \] (17)

where \( 0.35 \) represents the amount of sludge disposed off after dezincification (the value varies from 30 to 45%) and the efficiency of the hydrocloning system varies between 55 and 70% and \( n_2 \) is the ratio of zinc content in the zinc enriched product to zinc content in sludge after dezincification of the latter.

The mass of the sludge enriched with zinc \( M_{\text{ds}} \) is

\[ M_{\text{ds}} = 0.35 M_{\text{sludge}} \]

The mass of zinc disposed off with the zinc bearing product \( M_{\text{dispos}} \) (tonne/year) is

\[ M_{\text{dispos}} = M_{\text{ext}} - M_{\text{msf}} \]

The percentage of zinc content in zinc enriched product (Conc Zn) is given by

\[ \frac{(\text{Conc Zn})_{\text{dispos}}}{(\text{Conc Zn})_{\text{sludge}}} = \frac{M_{\text{dispos}}}{(0.35 M_{\text{sludge}} \times 10)} \]

Percentage of zinc content in recycled sludge after dezincification (Conc Zn)_{\text{recycled sludge}} is

\[ (\text{Conc Zn})_{\text{recycled sludge}} = M_{\text{recycled sludge}}/(0.65 M_{\text{rs}} \times 10) \]

**Disposable sludge**

The mass of sludge to be disposed of at the landfill so that the zinc inflow into the BF does not exceed the ultimate permissible limit (0.30 kg thm\(^{-1}\)), \( M_{\text{ds}} \) can be expressed as

\[ M_{\text{ds}} = M_{\text{sludge}} - M_{\text{rs}} \]

The reclaimable sludge after dezing \( M_{\text{rs}} \) is given by

\[ M_{\text{rs}} = \left( 1 - M_{\text{ext}}/0.3 P \right) \left( M_{\text{dust}} + n_1 M_{\text{sludge}} \right) / (1 - K) - M_{\text{dust}} \] (18)

The recycled sludge after dezing to the ultimate permissible limit level of zinc inflow into the BF is therefore given by

\[ z = \frac{n_2}{\left[ 1 - M_{\text{ext}}/0.3 P (M_{\text{dust}} + n_1 M_{\text{sludge}}) / (0.90 - M_{\text{dust}}) \right] - 1 + n_2} \] (19)

where 0.30 is the assumed ultimate permissible level of zinc intake into BF, kg/tonne hot metal, which ranges from 0.15 to 0.5 kg thm\(^{-1}\).

Evaluation of the data obtained from various metallurgical complexes showed that the rate of increase in zinc in sludge with respect to the total amount of zinc in the burden (charge) depends not only on its general content in the burden but also on the amount of generated wastes. The increase is more pronounced with recycling of galvanised steel.

**Algebraic model of zinc accumulation**

The mass of zinc, recirculating through the ‘furnace top dust’ (flue) stream \( \mu_4 \%) can be expressed as the ratio of zinc content in the flue dust (conc Zn) to that in the BF charge \( q_c \)

\[ \mu_4 = \frac{M_{\text{BF,sludge}} (\text{Conc Zn})_{\text{dust}}}{q_c} \] (20)

where \( M_{\text{BF,sludge}} \) is the mass of BF sludge (kg/tonne) in molten iron.

Similarly the mass of zinc, recirculating through the ‘BF sludge’ stream \( \mu_5 \%) can be expressed as

\[ \mu_5 = \frac{M_{\text{BF,sludge}} (\text{Conc Zn})_{\text{sludge}}}{q_c} \] (21)

where (Conc Zn)_{sludge} is the zinc content in the sludge in %. Utilisation of steelmaking \( M_{\text{(BOF)sludge}} \): The level of zinc in the BF charge significantly increases when BOF sludge is used to produce sinter, but the rate of recirculation of zinc through the ‘flue dust’ \( \mu_4 \) remains constant. Zinc content in the first moment of introduction increases by

\[ (\Delta \text{Conc Zn})_0 = 0.01 M_{\text{(BOF)sludge}} (\text{Conc Zn})_{\text{(BOF)}} \] (22)

where (\Delta Conc Zn)_0 is the increase in Zn content in iron at the initial stage (kg/tonne) in molten iron.

The Zn content increases geometrically within the range from 0 to \( M_{\text{(BOF)sludge}} \).
Therefore, the increases in Zn input at the first and second moments of sludge introduction into the charge, may be given as

\[(\Delta \text{Conc. Zn})_1 = (\Delta \text{Conc. Zn})_0 + \mu (\Delta \text{Conc. Zn})_0\]

\[= (\Delta \text{Conc. Zn})_0(1 + \mu)\text{ in the first cycle}\]

\[(\Delta \text{Conc. Zn})_2 = (\Delta \text{Conc. Zn})_0 + \mu (\Delta \text{Conc. Zn})_1\]

\[= (\Delta \text{Conc. Zn})_0(1 + \mu + \mu^2)\text{ in the second cycle}\]

\[(\Delta \text{Conc. Zn})_n = (\Delta \text{Conc. Zn})_0 + \mu (\Delta \text{Conc. Zn})_{n-1}\]

\[= (\Delta \text{Conc. Zn})_0(1 + \mu + \mu^2 + \cdots + \mu^n)\text{ in the } n^{th} \text{ cycle}\]

This can be simplified by the summation

\[\sum_{n} (\Delta \text{Conc. Zn})_n = (1 - \mu^n)/(1 - \mu)\] (23)

when \(\mu<1\) and \(n \to \infty\)

\[\sum_{n} (\Delta \text{Conc. Zn})_n = 1/(1 - \mu)\] (24)

This implies that zinc content increases by

\[(\Delta \text{Conc. Zn})_1 = (\Delta \text{Conc. Zn})_0/(1 - \mu)\]

\[(\Delta \text{Conc. Zn})_{\text{dust}} = (\Delta \text{Conc. Zn})_0/(1 - \mu_{\text{dust}})\]

Therefore, the total load of zinc into the BF\(\text{Conc Zn}_{\text{total,BF}}\) is

\[q_{Zn} + (\Delta \text{Conc. Zn})_{\text{dust}} = (\text{Conc. Zn})_{\text{total,BF}}\]

The use of BF sludge not only brings about a zinc increment but also create a new stream of zinc circulation with \(\mu_c\). Therefore, the change in zinc inflow \((\Delta \text{Conc. Zn})_{\text{sludge,BF}}\) is given by

\[(\text{Conc. Zn})_{\text{charge}}(1 - \mu_c) + 0.01 M_{\text{BF,sludge}}(\text{Conc. Zn})_{\text{sludge}}/\{1 - (\mu_d + \mu_s)\} = (\Delta \text{Conc. Zn})_{\text{sludge,BF}}\] (25)

where \((\text{Conc. Zn})_{\text{charge}}\) is the zinc content in the charge in %.

Use of BOF and BF sludge: the zinc load will increase by \((\Delta \text{Conc. Zn})_{\text{BOF,BF,sludge}}\), i.e.

\[(\text{Conc. Zn})_{\text{total,BF}}/(1 - \mu_c) + 0.01 M_{\text{BF,sludge}}(\text{Conc. Zn})_{\text{sludge}}/\{1 - (\mu_d + \mu_s)\} = (\Delta \text{Conc. Zn})_{\text{BF,sludge}} + \]

\[(\text{Conc. Zn})_{\text{total,BF}} - (\text{Conc. Zn})_{\text{charge}}]/(1 - \mu_c) = (\Delta \text{Conc. Zn})_{\text{BOF,BF,sludge}}\] (26)

During complete recycling of BOF sludge and partial reuse of BF sludge, zinc load is at 10% BF sludge

\[(\Delta \text{Conc. Zn})_{10} = (\text{Conc. Zn})_{\text{total,BF}}/(1 - \mu_c 0.1) + 0.01 M_{\text{BF,sludge}}(\text{Conc. Zn})_{\text{sludge}} \times 0.1/\{1 - (\mu_d + \mu_s 0.1)\}\]

at 20% BF sludge

\[(\Delta \text{Conc. Zn})_{20} = (\text{Conc. Zn})_{\text{total,BF}}/(1 - \mu_c 0.2) + 0.01 M_{\text{BF,sludge}}(\text{Conc. Zn})_{\text{sludge}} \times 0.2/\{1 - (\mu_d + \mu_s 0.2)\}\]

therefore at 10% BF sludge

\[(\Delta \text{Conc. Zn})_n = (\text{Conc. Zn})_{\text{total,BF}}/(1 - \mu_c 0.1n) + 0.01 M_{\text{BF,sludge}}(\text{Conc. Zn})_{\text{sludge}} \times 0.1n/\{1 - (\mu_d + \mu_s 0.1n)\}\]

### Homograph for zinc accumulation

In any recycling system, the circulated element increases geometrically (even from insignificant value) to a level of saturation. In a close looped system of recycling of BF sludge in the sinter plant, the relative intake of zinc to the BF occurs through two routes: the provisional constant inflow of zinc from the charge and the gradual progressive inflow of zinc from the BF sludge and flue dust. It should be noted that the zinc released from the BF top does not instantly return to the BF with the burden, but this occurs after a certain period of time. The duration of this lateness depends on dehydration (dewatering) and other treatment of sludge for recycling, the capacity of the stock houses during unification (blending) of iron ore materials in the sinter and BF workshops. The interval for returning zinc to BF after its removal from the latter through sinter produced from zinc bearing sludge and dust is assumed to be 10 days. This includes the period of sludge treatment, i.e. processing, storage and sintering before charge into the BF.

The mass of zinc that passes into the BF in every successive cycle can be expressed as

\[A_1 = A_o + RA_o\]

\[A_2 = A_o + RA_1 = A_o + R(A_o + RA_o) = A_o + RA_o(1 + R)\]

\[A_3 = A_o + RA_2 = A_o + R^2A_o(1 + R)\]

\[A_4 = A_o + RA_3 = A_o + R^3A_o(1 + R)\]

\[A_n = A_o + RA_{n-1} = A_o + R^{n-1}A_o(1 + R)\]

where \(A_o\) is the initial mass of zinc, per tonne of molten iron and \(R\) is the coefficient of recirculation, i.e. the mass of zinc transferred to the BF sludge and flue dust. In most steel plants, \(R\) ranges from 0.85 to 0.90 implying that 10–15% of the total zinc is released through the slag and pig iron and part of it remains in the furnace.

At \(n\) cycles

\[\sum_{n} A_n = \Delta A_o (1 - R^n)/(1 - R)\] (27)

The ultimate input of zinc at \(R<1\)

\[\lim_{n \to \infty} A_n = A_o/(1 - R)\]

when \(R=0.90, \lim_{n \to \infty} A_n = 10 \cdot 0.90 = 9\)

\[R=0.85, \lim_{n \to \infty} A_n = 6.67 \cdot 0.85 = 5.67\]

when \(R=0.85\) the number of cycles \(n\) at which \(A_o=0.30\) kg t\(^{-1}\) pig iron can be derived as follows

\[A_n = A_o(1 - R^n)/(1 - R)\]
The computations of equations (27) and (29) with the help of Mathlab5.3 are illustrated in Fig. 6. The influx of zinc increases sharply in the early stages of introduction of sludge and slowly at the later stages before it stabilises at a particular higher value. The graph shows that, at initial value of zinc inflow, \( A_0 = 0.05 \) kg thm\(^{-1}\), the influx of zinc increases by 0.03 kg thm\(^{-1}\) in the first three phases of sludge introduction into the BF. It increases by 0.023 kg at the next three phases and later stabilises at 0.500 kg thm\(^{-1}\) (see curve 5 in Fig. 6a). The inflow of zinc directly depends on the initial value of zinc intake in the BF.

Once the amounts and qualities of the zinc bearing inputs into the BF complex and the preceding sintering process are known, the dynamics of zinc accumulation in the BF can be fully determined (Fig. 6).

### Zinc removal in closed loop system

At the attainment of the ultimate level of zinc in the furnace, the zinc bearing materials can be withdrawn from the system within a phase or a cycle (10 days). The non-introduction of the BF sludge from the closed system at the appropriate time helps to retain the same amount of zinc as in the initial stage of its intake (see curves 5 in Fig. 6a and b). The period of attaining the maximum value reduces as the initial value of zinc increases. From Fig. 6, if the initial intake of Zn through the burden is 0.05 kg thm\(^{-1}\), the ultimate permissible level of zinc in the furnace will be attained after nine cycles of the recycling process. Withdrawal of the BF sludge from the system for a cycle (10 days) will bring the level of zinc to 0.05. The process could be repeated at every interval of attaining ultimate allowable level.

One of the most efficient methods of combating the accumulation of zinc in the BF is the separation of the finely dispersed sludge from scrubbers/precipitators enriched with zinc from the system for further treatment with zinc bearing products of steelmaking sludge while the denser dusts from the dust catchers are recycled to the sinter plant.

### Conclusions

The algebraic calculation of zinc accumulation, the corresponding alignment chart (monograph) portraying the concentration of zinc in the BF sludge and the dynamics of its inflow to the furnace have good implication for reclamation of steel iron oxide wastes.

Knowing the total allowable intake of zinc into BF, the interval of its attainment during recycling of wastes and the place where the zinc was deposited makes it easier to design removal processes and then to recycle the sludge solids.

Stopping introducing BF sludge from the system at an appropriate time (Fig. 6) helps retain the same amount of zinc as in the initial stage of its intake. The period of attaining the ultimate value reduces as the initial value of the zinc intake increases.

One of the low cost techniques to inhibit the accumulation of zinc in the BF is to separate finely dispersed sludge enriched with zinc from the system for further treatment from zinc bearing products of steelmaking sludge while the denser dusts are recycled to the sinter plant.

### References