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E. KOLCZYK*,#, Z. MICZKOWSKI*, J. CZERNECKI*

INFLUENCE OF SELECTED PARAMETERS ON REDUCTION OF CONVERTER SLAG - STUDIES WITH CFD METHOD

In this study influence of selected parameters on the process of reduction of converter slag from refining of Cu-Pb-Fe alloy was numerically examined. The process of the slag reduction is carried out in Q 80 converters of Hoboken type for copper removal. Converter slags show high concentration of lead therefore they can be seen as an important component for further processing in rotary-rocking furnaces together with other lead-bearing materials. Three-dimensional simulation was performed using the IPSA (Inter Phase Slip Algorithm) module of two-phase flow from PHOENICS package. Numerical simulations have forecasted influence of changes in the slag chemical composition and the process time on the process course.

Keywords: numerical modelling, reduction process, converter slag, Cu-Pb-Fe alloy

1. Introduction

Converter slag contains 25-45 wt. % of Pb and 15-25 wt. % of Cu. Converter slags of high concentration of Pb represent an important component of the charge to rotary-rocking furnaces in the process of smelting of lead from lead-bearing materials in copper metallurgy.

The reduction process is carried out to remove copper from the slag by application of coke breeze and natural gas. The coke breeze is introduced onto the surface of the slag. Natural gas is supplied through nozzles which are located under the charge. The natural gas plays less important role in the reduction than the coke breeze due to the low depth of immersion of nozzles and its activity is limited mainly to mixing of the bath and providing a source of additional energy [1]. In the result of the process, slag with 25-55 wt. % of Pb and less than 5 wt. % of Cu and dust (approx. 50 wt.% of Pb) is produced. The material is used in production of lead, while the simultaneously produced CuPb alloy (approx. 5 wt.% of Pb) is subjected to the converting process.

In the literature, there are many studies focused on numerical modeling of processes which take place mainly in Peirce - Smith or Teniente converters. The authors considered in the first place the flow dynamics to analyze movement of the slag layer, movements in the bath, influence of bath height or depth of nozzle immersion on the process parameters [2-6].

In the presented study process of reduction of converter slag from Cu-Pb-Fe alloy refining was modeled. Converter slag reduction is carried out in Q 80 converters of Hoboken type. The study was focused on examination of the influence of selected parameters of reduction process on its course.

2. Thermodynamic analysis

Differences in chemical affinity to copper and lead oxides form the basis for carrying out the selective reduction of metal oxides from the converter slag. Considering reduction reactions of Cu_2O and PbO:

$$Cu_2O + CO = 2Cu + CO_2 \tag{1}$$

$$PbO + CO = Pb + CO_2 \tag{2}$$

$$K_{p(1)} = \frac{a_{Cu}^2}{a_{Cu_2O}} \cdot \frac{P_{CO_2}}{P_{CO}} \tag{3}$$

$$K_{p(2)} = \frac{a_{Pb}}{a_{PbO}} \cdot \frac{P_{CO_2}}{P_{CO}} \tag{4}$$

a relation between concentrations of Cu_2O and PbO in the slag in various phases of copper removal process can be determined, in a form:

$$X_{(PbO)} = \frac{K_{p(1)}}{K_{p(2)}} \cdot \frac{\gamma_{(Cu_2O)}}{X_{[Cu]}^2 \cdot \gamma^2{}_{[Cu]}} \cdot \frac{X_{[Pb]} \cdot \gamma_{[Pb]}}{\gamma_{(PbO)}} \cdot X_{(Cu_2O)} \tag{5}$$

where:
K_{p1}, K_{p2} - thermodynamic equilibrium constants of reactions (3) and (4)
X – mole fraction of a component in the solution,
γ - activity coefficient of a component in the solution,
( ) [ ] – refers to the component which is contained in slag and in alloy, respectively.

For the slag containing 20 wt. % of Cu and 36 wt. % of Pb at a temperature of 1573 K were carried out calculations of the equilibrium concentrations of Cu_2O and PbO. In the calculations thermodynamic data for pure substances were

* INSTITUTE OF NON FERROUS METALS, 5 SOWIŃSKIEGO STR., 44-100 GLIWICE, POLAND
# Corresponding author: ewa.kolczyk@imn.gliwice.pl

used placed in Outokumpu HSC program. It was assumed that the activity coefficients of individual components have the following values:

$\gamma_{[Cu]} = 1$

$\gamma_{(Cu2O)} = 4$ [7, 8]

$\gamma_{[Pb]} = 3$ [9]

$\gamma_{(PbO)} = 0.7$ [8]

In Fig. 1 is shown the relationship between the content of Cu_2O and PbO (converted into Cu and Pb as expressed in wt.%) in the slag during the reduction. When the concentration of Cu_2O is over 5 wt. % only Cu_2O is reduced, and below 5 wt. % also PbO is reduced. The whole process should be carried out to obtain the resulting product of the highest lead content (30-55 wt.% of Pb), and as low as possible copper content.

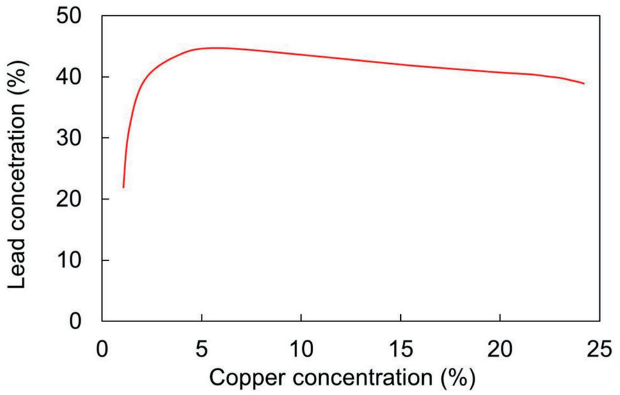

Fig. 1. Relationship between the concentration of lead and copper in slag at equilibrium state

Results of thermodynamic analysis provide the basis for determination of process conditions for reduction of slag from refining of CuPbFe alloy in the converter.

3. CFD model features

Based on the results of technological tests, it was assumed in the modeling that 100 Mg of converter slag is subjected to the reduction process, of phase composition as shown in TABLE 1 (slag before and after reduction). The duration of the reduction process was two hours, and the initial temperature of the slag was 1373 K.

TABLE 1

Phase composition of converter slag before and after reduction

Phase composition	Before reduction (wt. %)	After reduction (wt. %)
PbO	45	58
Cu_2O	28	5
As_2O_5	7	7
FeO	5.4	8.5
SiO_2	10	15
CaO	4.5	6.5

The numerical model was developed using the Phoenics software [10]. The developed geometrical model of converter slag reduction process consisted of the following components:

- liquid slag,
- one nozzle – inlet of natural gas,
- gas outlet – top surface of slag,
- slag coke breeze interface.

The geometrical model of the furnace equipped with a system of three nozzles was limited to 1/3 of the inner length of the furnace with one nozzle located in a central position. The analyzed domain had the following dimensions 2.54 × 3.19 × 1.17 m. The structural grid as generated in Phoenics consisted of 20 000 differential elements. In the directions of the X, Y, Z axes the number of elements amounted to 19, 50, 21 respectively.

In the calculations, the following conditions of the individual model phases were assumed:

- liquid slag of following properties:
  - temperature 1373 K
  - density 6500 kg/m^3
  - thermal conductivity 0.15 W/m K
  - kinetic viscosity 1.54 m^2/s
  - specific heat capacity 565 J/kg K
- nitrogen-rich natural gas of following properties:
  - temperature 293 K
  - density 0.84 kg/m^3
  - thermal conductivity 0.02 W/m K
  - kinetic viscosity 3.75 x 10-5 m^2/s
  - specific heat capacity 1902 J/kg K
  - calorific value 29.6 MJ/Nm^3

and simplified chemical composition: 80 vol % CH_4, 20 vol %. N_2.

The analyzed reduction process progresses in time therefore the calculations were performed for the system which was transient in time.

3.1. Two-phase flow

In the two-phase flow there is a need to deal with the continuous phase and the dispersed phase. The dispersed phase is in a form of bubbles, drops or solid particles [11].

Modeling of converter slag reduction process was based on the phenomenon of two-phase flow. Since the distribution of each phase is usually heterogeneous therefore it is necessary to apply multiphase models in the numerical simulation [12].

The model analysis was based on solving of differential equations in the form of equations of continuity describing the principle of conservation of mass and momentum, and taking into account the boundary conditions, the nature of the adopted model and interfacial correlations.

There are several methods provided by the Pheonics software to analyse the two-phase flow. One of the applied models was IPSA (Inter-Phase-Slip Algorithm) module, in which the Navier-Stokes equations are solved for each phase separately. The equation of each phase continuity is described by the equation in the following general form:

$$d(R\rho)/dt + div(R\rho V_i - G_{ri} grad(R)) = \tilde{n}_{ij} \quad (6)$$

where:

R – phase volume fraction

ρ – phase density, kg/m^3
V_i – phase velocity vector, m/s
G_{ri} – phase diffusion coefficient, Ns/m^2
$\tilde{n}_{ij}$ – net rate of mass entering phase i from phase j, kg/(m^3 s)
when meeting the condition that phase volume fractions $R_1 + R_2 = 1$ [13].

On the basis of the criterion which verifies the flow character, i.e. the Reynolds number, it was assumed that the flow is laminar in Stokes law range.

3.2. Modelling approach

The modelling approach is based on modifying the inter phase slip algorithm (IPSA) by adding (user-defined) sub-model described by interaction the slag and coke breeze.

The average rate of Cu_2O loss from slag during reduction was determined. It was 12.15 [Mg Cu_2O/h]. Then was determined the average rate of oxygen loss from Cu_2O -1.36 [Mg O_2/h].

By the equation 7 was defined oxygen loss $\dot{m}_{O2}$ on the surface between the slag and coke breeze by assuming a linear dependence of $\dot{m}_{O2}$ on the content of Cu_2O:

$$\dot{m}_{O2} = 0{,}0939 \times g_{Cu2O} \qquad (7)$$

where $\dot{m}_{O2}$ is expressed in kg/m^{2}s.

From the relation (8) were determined the masses of the components of the liquid slag phase (Cu_2O, PbO and other oxides) contained in the differential elements:

$$m_{compl} = V_{ER} \times R_l \times \rho_l \times g_{comp\,l} \qquad (8)$$

where:
R_l - volume fraction of liquid phase in the differential element,
ρ_l - density of liquid phase,
$g_{comp\,l}$ - mass concentration of liquid phase components.

Oxygen loss in the top differential element was described by the relation 9:

$$\Delta m_{O2\,ER} = \dot{m}_{O2} \times \Delta\tau \times F_{ER} \qquad (9)$$

where:
Δτ- time step
F_{ER} - surface area of horizontal cross-section of differential element.

After a certain time step the concentrations of the components of the liquid slag are calculated by using the formula described in the general notation:

$$g_{comp\,l} = \frac{m'_{ccomp\,l}}{m'_{ER}} \qquad (10)$$

The model calculations took under consideration:

- heat which is emitted as a result of the reduction reaction occurring at the interface of slag - coke breeze (350 kW),
- heat generated by the combustion of the natural gas (24 Nm^3/h) which is deliver through a one nozzle (150 kW),
- heat transferred from the slag to the environment through the layers of the lining and jacket (178 kW),
- heat transferred from the charge by one of the bottoms (located at the beginning of the domain) (9 kW).

4. Results of simulation

Distributions of Cu_2O concentrations after 2 hours of reduction process are shown in Fig. 2. The concentration of slag components was analyzed every 30 minutes. In selected intermediate stages the distribution of concentration of slag components was similar. TABLE 2 shows the minimum and maximum concentrations of slag components registered every 30 minutes.

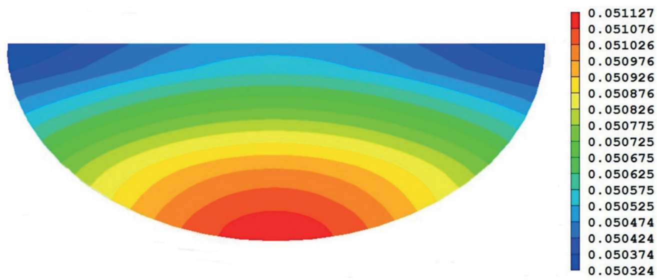

Fig. 2. Distribution of copper oxide concentration in the slag after 120 min of the reduction process

TABLE 2

Concentration of Cu_2O, PbO and other components in the slag

Reduction time	Cu_2O (%)		PbO (%)		Other (%)	
	min	max	min	max	min	max
0	-	28	-	45	-	27
30 min	19.07	19.33	49.88	50.02	30.75	30.86
60 min	12.57	12.75	53.6	53.7	33.63	33.7
90 min	9.12	9.26	56.19	56.26	35.63	35.69
120 min	5.03	5.11	57.91	57.96	36.96	36.99

Fig. 2 show uniform distribution of the converter slag components. The lowest concentration of Cu_2O is observed in the highest layer, i.e. at the interface of slag – coke breeze, where reduction process takes place. After the reduction process, deposition of the component in the result of sedimentation takes place, followed by its transfer to the alloy.

In the next step, calculations were made for the converter slag of the initial content of 23 wt. % and 33% wt. % of Cu_2O, respectively, and proportionally changed concentrations of the other components.

Fig. 3-4 show the change in concentration of Cu_2O and PbO for three different initial concentrations, depending on the process duration.

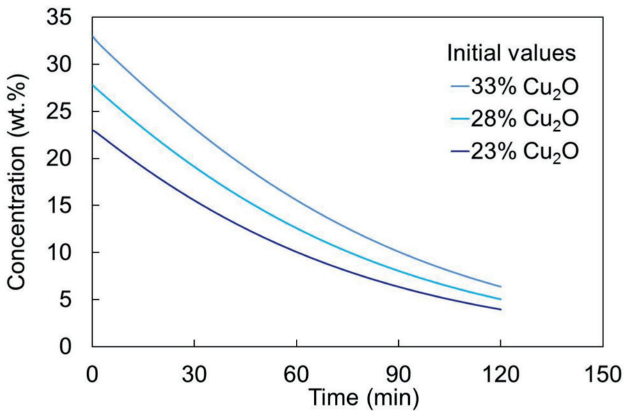

Fig. 3. Change of Cu_2O concentration in slag during reduction process

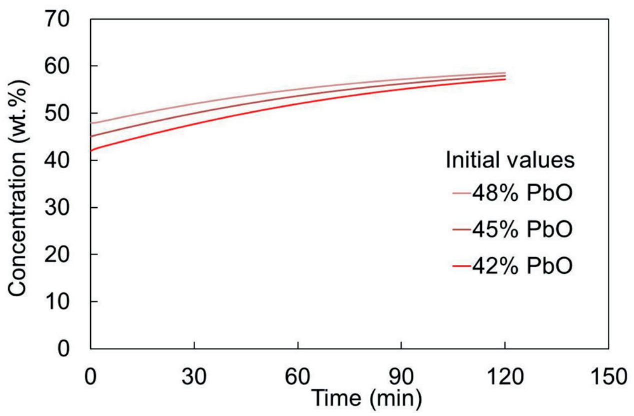

Fig. 4. Change of PbO concentration in slag during reduction process

TABLE 3 lists concentrations of Cu_2O, PbO and other components in the beginning and at the end of the reduction process for the three analyzed initial phase compositions of the slag.

TABLE 3

Concentrations of Cu_2O, PbO and other components in the slag in the beginning and at the end of the reduction process

Slag component	Concentration (wt. %) Process beginning	Concentration (wt. %) Process end
Cu_2O	33	6
	28	5
	23	4
PbO	48	59
	45	58
	42	57
Other	29	38
	27	37
	25	36

Comparison of the concentration of Cu_2O in converter slag for three different levels of the initial concentrations shows that in each of the analyzed variants the decrease of Cu_2O concentration during the process course is similar. In the first case for the concentration of 28 wt. % of Cu_2O in the slag, after 2 hours of the process, concentration of 5 wt. % is obtained. Increase of the initial concentration of Cu_2O by 5% brings its decrease from 33 to 6 wt. %. Reduction of Cu_2O concentration by 5 wt. % makes it possible to reach concentration of 4 wt. % after 2 hours. In order to obtain a final concentration of Cu_2O at 5 wt. % in the second case it would be necessary to lengthen the process up to 140 minutes, while in the third case to reduce it to about 105 minutes.

Analysis of changes in PbO concentration in the slag, as presented in Fig. 4 , in each case shows an upward tendency. For the initial concentration of 45 wt. % of PbO, after 2 hours of the process, concentration of 58 wt. % is reached. At lower initial concentrations of PbO of 42 wt. %, slightly lower concentration is reached, i.e. 57 wt. %. When running the process of reduction of the slag of initial PbO concentration of 48 wt. %, after 2 hours concentration of 59 wt. % is reached.

The highest concentration of PbO in the slag was reached after two hours of reduction of the slag with the following composition: 23 wt. % of Cu_2O, 48 wt. % of PbO and 29 wt. % of remaining components.

A similar upward tendency was observed for other components of the slag. The higher the concentration of a component at the beginning of the reduction process, the higher its concentration at the end of the process.

Process duration has a significant impact on the converter slag reduction. The temperature of the slag gradually increases with the reduction process progress. After two hours of the process slag of a starting temperature of 1373 K reaches a temperature of 1449-1495 K.

Extending the process time by further 30 minutes results in a further increase in slag temperature. The temperature distribution in the charge after 2.5 hours of reduction process is shown in Fig. 5.

Fig. 5. Temperature distribution in slag cross-section after 150 minutes reduction

Slag (Fig. 5) is heated by the fuel delivered by the nozzle and by interphase reaction which takes place at the border of slag – coke breeze. Conspicuous areas of heat dissipation from lining and steel jacket can be observed.

The determined average temperature of the slag for 2 hours process duration is at the level of 1485 K with the value of the standard deviation of 3.36. After 2.5 hours of the reduction the average temperature is higher, and amounts to 1508 K, with a value of standard deviation of 5.8 (Fig. 6).

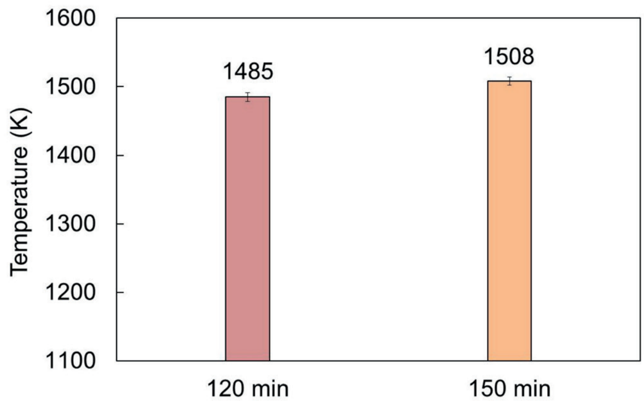

Fig. 6. Average slag temperature after 120 and 150 minutes of reduction

5. Conclusions

In this paper a numerical method was used to develop a model of converter slag reduction process which is carried out in Q 80 Hoboken type converters. The temperature distribution in the slag was determined and effects of changes in the chemical composition of the slag and the duration on the reduction process were studied.

The performed calculations and analyses led to the following conclusions:

1. Converter slag of Cu_2O concentration in the range 23-33 wt.%, PbO in the range 42-48 wt.%, after two-hour reduction process contains 4-6 wt. % of Cu_2O and 57-59 wt.% of PbO. Such slags can be further processed in a rotary-rocking furnaces for lead recovery.
2. Increase or decrease of Cu_2O concentration by 5% at the beginning of the process of slag reduction results in shortening or lengthening of the process time by about 15 minutes, respectively.
3. The average temperature of converter slag after two hours of reduction process is 1485K. Extension of the process time up to 2.5 hours results in 23 K higher final temperature of the slag and 1 wt. % lower copper oxide concentration.

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