




HIGH-TEMPERATURE PHASES AND PROCESSES FOR ENABLING CLEANER PRODUCTION OF METALS
AND ENERGY

The Thermodynamic Modelling of the Zn Slag Fuming with the Use of Coal and Ammonia

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Slag fuming process is used to extract zinc from the lead blast furnace slags and recently for the extraction of multiple elements from the complex primary and recycling feed streams, making the thermochemistry of the process challenging. To meet new challenges, computer models with predictive powers outside of the range of normal process conditions are necessary. These models cannot rely exclusively on sets of existing process data and must have a foundation in thermodynamics combined with reasonable kinetic factors. The accuracy of predictions largely depends on the quality of thermodynamic data, including phase equilibria, elemental distributions, and calorimetry measurements. Present study demonstrates the recent developments of the self-consistent thermodynamic model for the gas/slag/matte/metal/speiss/solid phases within the Cu-Pb-Zn-Fe-Ca-Si-O-S-Al-Mg-As-Sb system, applied to zinc fuming, with attention to the phase equilibria and partitioning of minor elements in the process. As a demonstration of calculations far outside of normal operations, the use of ammonia as an alternative to coal is investigated. It was shown that from the thermodynamic point of view the process can reach the same final concentration of zinc and the heat balance of the reactor in the same amount of time when coal is replaced in the process by ammonia.

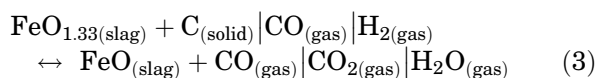
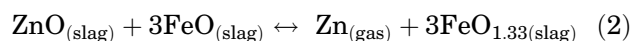
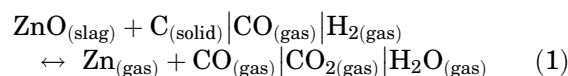
INTRODUCTION

Process Description

Slag fuming is a well-established process, soon celebrating its 100th anniversary since the launch of the first commercial furnace.¹ The process was initially developed to extract Zn from the slags of the lead-blast furnace and was used for Zn-rich slags; these days it is increasingly used for the extraction of a variety of metals from the complex feed allowing the content of valuable elements in the slag to be comparably low.^{2,3} The production of slags with a small concentration of impurities is also desirable for their potential use as construction materials.⁴ Adjustments of the operational

parameters to maximize the extraction of target metals and produce cleaner slags require a flexible model applicable to the wide range of operational conditions.

The slag fuming process is based on the high volatility of metallic Zn at high temperatures and reducing conditions.⁵ It can be effectively separated from other components of the slag by reduction and evaporation according to the following simplified reactions:^{1,6–10}



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After leaving the bath, Zn fumes are re-oxidised outside of the reactor by air. Zinc oxide precipitates from the gas stream as a solid phase (zincite), which is further refined using hydrometallurgy and electrowinning.

Typically, carbon and hydrogen are supplied to the reactor in the form of pulverised coal or oil, while other sources of carbon and/or hydrogen can be potentially used. They both act as reducing agents and fuel. Reaction (1) is highly endothermic. To achieve the energy balance, a portion of C and H is combusted by the oxygen from the blast, either directly or through reactions with the components of the liquid oxide (slag). Ferric iron (Fe^{3+}) in slag is also reduced during the process, first into ferrous iron (Fe^{2+}), and then potentially into metallic iron (Fe^0). The precipitation of the metallic iron is undesirable because of the formations of accretions and inefficient use of reductant and should be avoided or minimised during the process.¹ From the thermodynamic point of view, the conditions of formation of Fe^0 correspond to the lowest achievable concentration of zinc in the slag among other given conditions. Other elements, such as Pb, Sb and As, can be reduced from their oxidic form and potentially separated from the slag into metallic and sulphide phases⁶ or into gas. The presence of As and Sb may cause the formation Fe-rich speiss instead of solid metallic iron.

In practice, kinetic factors prevent achieving the thermodynamic limit in the zinc fuming process. On the macro level, the rate of gases that can safely be blown through the slag limits the speed of the process.¹¹ Heterogeneous gas-slag reactions and gas combustion reactions are relatively slow.¹² Coal particles entrained in the slag react with the slag components through the gas film; this reaction is limited by diffusion.^{10,13} The overall mass and heat balances of the reactor should comply with both thermodynamic and kinetic aspects of the process. Potential separation of liquid metal, matte or speiss phases would depend on the growth of droplets, coalescence and settling kinetics.

Process Models

The existing models of the Zn slag fuming can be divided into three groups: thermodynamic, kinetic and combined models. The models belonging to the first group assume the achievement of thermodynamic equilibrium at fixed time intervals in the reactor. Equilibrium calculations rely on the thermodynamic properties of the present chemical species and phases. They provide mass and heat balances. More advanced models give information on phase equilibria and behaviour of minor elements. The accuracy of these models depends on the quantity and quality of equilibrium experimental data of different types, used in the assessment of model parameters. Kinetic models consider a set of stoichiometric reactions. Their rates are established

using empirical coefficients. To increase the accuracy, a larger set of industrial data would have to be used. The models of this type can give accurate predictions of the dynamic behaviour for a given reactor, but they would have limited predictive power outside of the range of the typical conditions. The models of the third type combine the advantages of thermodynamic and kinetic approaches and can be complicated. Thermodynamic foundation of these models is independent from the process application, and kinetic factors are specific for the process. Kinetic factors must be calibrated using process data of the furnace in question. These advanced models can be difficult to use daily by furnace operators. The following sections provide examples of the earlier studies, without an intention to make a complete review, at the same time outlining the main features of the previously developed models, their advantages and disadvantages, and the existing discussion on the thermodynamic or kinetic nature of the process.

Bell et al.⁶ prepared the thermodynamic model based on the activity coefficient of zinc oxide derived from the industrial data. The obtained model was used for the sensitivity analysis of the process. Several parameters, such as fuel composition, oxygen enrichment and blast preheating, were tested. The list of different reductants and fuels for the calculations included hydrogen gas, natural gas, fuel oil, coals of different volatility and carbon. The main output of the model was the time of the process. It was predicted to increase in order of the reductants/fuels given above. Two sets of industrial data resulted in close activity coefficients of ZnO, but the third set gave lower values in the range of 2–8 wt.% of Zn in slag.

Quarm¹⁴ proposed the kinetic equation to describe the concentration of zinc in slag as a function of time. The simple equation contained a single adjustable parameter, velocity coefficient, that had to be calibrated for each time period. The heat balance was calculated using heats of reactions.

Kellogg⁷ developed a two-stage computer mathematical model of the process. The first stage included the direct reaction of the reductant and blast with the slag phase with the formation of the reduced Zn-containing vapour. The second stage included the oxidation of the produced vapour with tertiary air, forming zinc oxide. The 90-min fuming cycle was divided in 900 steps with 0.1-min integration steps; the thermodynamic calculations were made for every step. The presented model was the first to encounter for the fuming of Pb but, due to the lack of the knowledge on the process, contained simplifications of the chemistry and heat balance.⁷ The industrial data obtained during normal and extreme operational conditions (temporary absence of reductant supply¹²) were successfully reproduced by the authors. Additionally, the effects of the coal rate and preheated blast were investigated

Table I. Formulae of the phases used in the present study

Phase	Formula
Gas	(N ₂ , CO, CO ₂ , H ₂ , H ₂ O, S ₂ ...S ₈ , SO, SO ₂ , SO ₃ , Zn, ZnS, ZnO, As, AsS, AsO, Pb, PbS, PbO, Sb, SbS, SbO, Cu, CuS, CuO)
Slag (oxide liquid)	(Pb ²⁺ , Cu ⁺ , Fe ²⁺ , Fe ³⁺ , Si ⁴⁺ , Zn ²⁺ , Al ³⁺ , Ca ²⁺ , Mg ²⁺ , Sb ³⁺ , As ³⁺)[O ²⁻ , S ²⁻]
Spinel	(Cu ²⁺ , Fe ²⁺ , Fe ³⁺ , Al ³⁺ , Mg ²⁺ , Zn ²⁺) ^{tetr} [Cu ²⁺ , Fe ²⁺ , Fe ³⁺ , Al ³⁺ , Mg ²⁺ , Zn ²⁺ , Vacancy] ₂ ^{oct} O ₄ ²⁻
Wüstite	(FeO, FeO _{1.5} , CuO, AlO _{1.5} , CaO, MgO)
Melilite	(Ca,Pb) ₂ [Zn, Mg, Fe ²⁺ , Fe ³⁺ , Al](Fe ³⁺ , Al, Si) ₂ O ₇
Zincite	(ZnO, FeO, FeO _{1.5} , AlO _{1.5} , CaO, MgO)
Pseudowollastonite	(Ca, Pb)SiO ₃
Matte	(Pb ^{II} , Cu ^I , Fe ^{II} , Fe ^{III} , As ^{III} , Zn ^{II} , Sb ^{III} , O ^{II} , S ^{II})
Speiss	
Metal	

similarly to Bell et al.⁶ The model did not consider the solid phases present in equilibrium and possible precipitation of metallic Fe. The activity coefficients of the slag species were assumed to be independent of the starting slag composition.

Sundstrom¹¹ reported the mathematical model of the slag fuming process based on the numerous sets of plant data collected over the time. The model considered the ZnO content in the slag at different points in time, charge volume, slag composition and other not specified operating conditions. The presented model was based on the previously treated slag and was applicable only for the limited range of the slag compositions.

Blaskett¹⁵ developed a simplified thermodynamic model to study the effect of preheated blast on the operational parameters of the process. The chemistry of slag was described by the concentration of ZnO only, limiting the predicting power of the model.

Grant and Barnett¹⁶ prepared the computer model based on the one presented earlier by Kellogg.⁷ The previous model was extended by the incorporation of the recuperative heating of secondary air and waste heat boiler simulation “thereby closing the loop and enabling the model to calculate continuously varying secondary air preheat temperatures”.¹⁶ The predictions were shown by the authors to be in good agreement with the industrial data. In the following study, Grant¹⁷ showed that activity coefficients of slag species can be derived from the plant data using the discussed model to account for the difference in the slag complexity in a limited range of compositions. The developed model was compared with the industrial data in later studies by Richards et al.^{9,10,18,19} and was shown to underestimate the fuming rates (note that the thermodynamic predictions can only overestimate the fuming rates and not underestimate them²⁰).

Richards et al.^{9,10,18,19} proposed the mathematical model of the process based on the kinetic principles. Authors developed a system of 11 equations considering mass and heat balances of the reactor and rate

terms of selected reactions. The change in ZnO, FeO and Fe₂O₃ activity coefficients in the slag were accounted for by introducing the equations based on the available literature data and depended on the temperature and the lime-to-silica ratio of the slag. The potential fuming of other species, such as Pb, As or Sb, was not incorporated into the model. The model was shown to replicate most of the available industrial data reported. Cockroft et al.²¹ extended the discussed model by adding the oxidation/reduction and evaporation of Pb into the list of considered chemical reactions. In the later study Richards²² demonstrated the applicability of the model to the optimisation of the continuous slag fuming process.

Jak and Hayes²³ described the phase equilibria of the slag fuming using Factsage thermodynamic software.²⁴ The chemical behaviour of the slag, simplified by the authors to the PbO-ZnO-FeO-Fe₂O₃-CaO-SiO₂ system, was predicted for the wide range of ZnO concentrations and CaO/SiO₂ and Fe/SiO₂ ratios. The model was tested using the plant data presented earlier by Grant.¹⁷ The predictions were shown to be in good agreement with the plant results, and the difference in predicted and plant data was related by the authors to the kinetic limitations of the process taking place when the concentration of Zn in the slag decreases. The described model considered the interaction between liquid oxide and gas phases only and did not account for the heat balance of the process.

Verscheure et al.^{2,25-27} developed a mathematical model using Factsage thermodynamic software²⁴ to describe chemical, thermal and heat transfer outcomes of the submerged plasma and oxidative Isasmelt processes.^{25,26} The authors studied the effect of various process parameters on slag chemistry. Even though the formation of matte phase was considered, the thermodynamic database used could not describe the possible matte immiscibility, which can affect the predictions.

Lotfian^{28,29} studied the partial replacement of coal in the Zn fuming process by plastic materials of various types. After the industrial trial the author created the thermodynamic model of the process

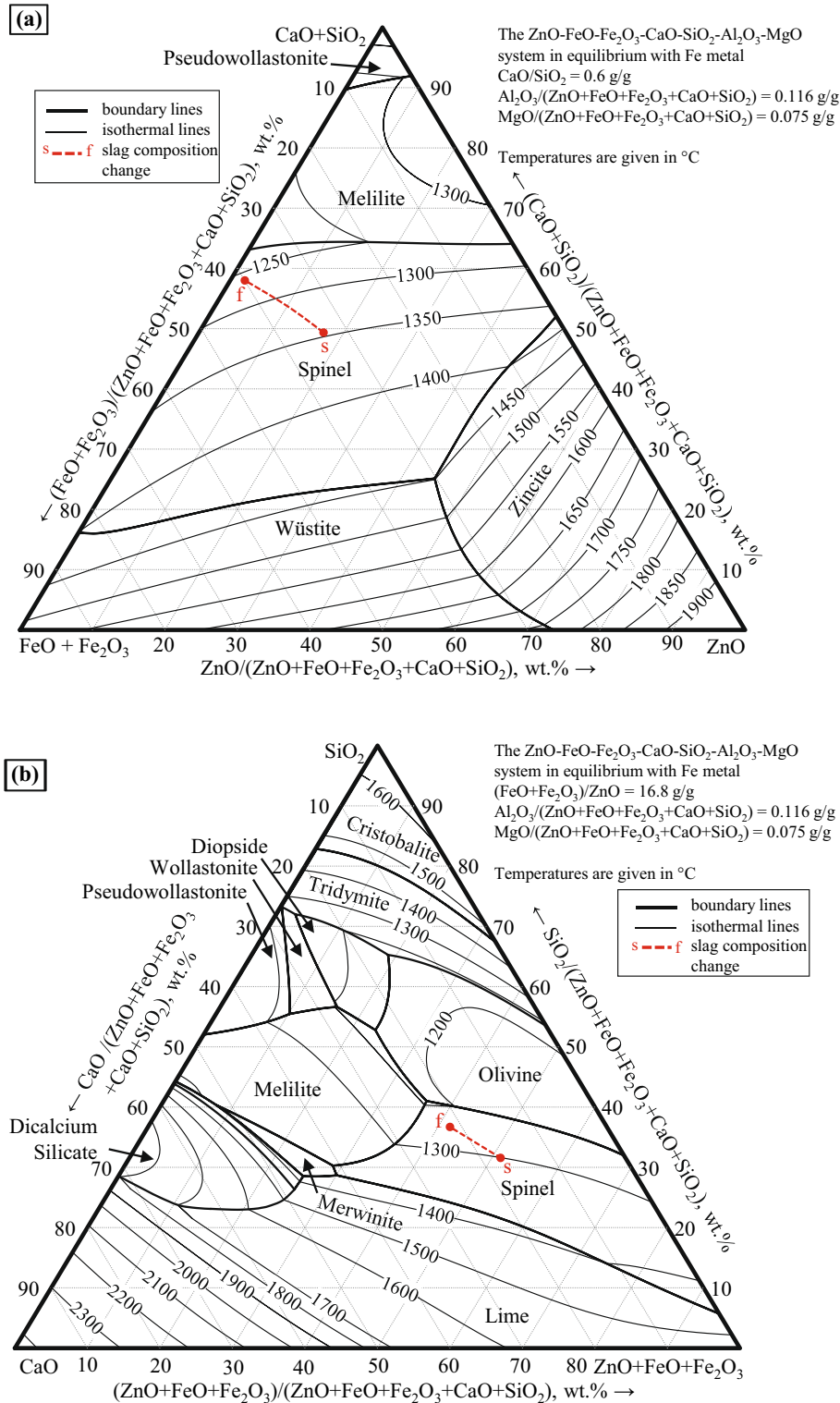


Fig. 1. Ternary liquidus projections of the ZnO-FeO-Fe₂O₃-CaO-SiO₂-Al₂O₃-MgO system in equilibrium with metallic Fe: (a) the ZnO – (FeO + Fe₂O₃) – (CaO + SiO₂) projection of the system; (b) (FeO + Fe₂O₃ – ZnO) – CaO – SiO₂ projection of the system.

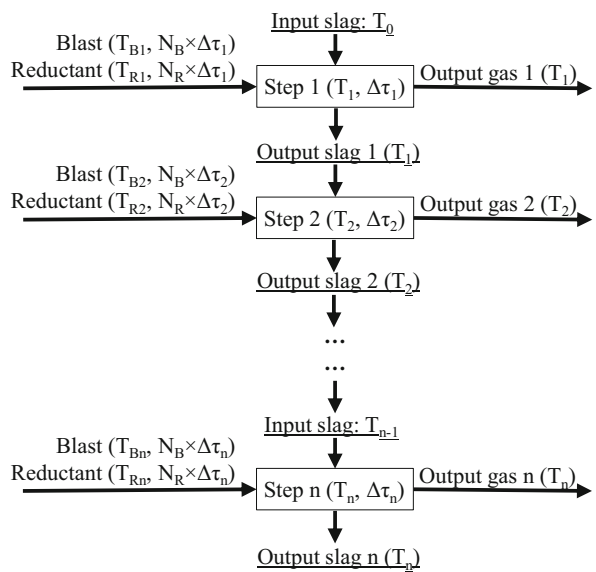
using public databases of Factsage thermodynamic software.³⁰ The calculations were made to reproduce the plant trial data. The duration of the process was divided into 10-min intervals with the

thermodynamic calculation corresponding to each of the intervals. The temperature of the process was kept constant at 1250°C. Only spinel, slag, monoxide and olivine were selected from all solid solutions

available. All possible pure solids and liquids formed in the PbO-ZnO-FeO-Fe₂O₃-CaO-SiO₂-Al₂O₃-MgO system were selected from FactPS and FT-Oxide databases. Cu and S were not included into the calculations, and the formation of matte and the heat of the bath were not considered.

Nagraj^{31,32} used private³³ and public thermodynamic data of Factsage thermodynamic software³⁰ to develop a combined thermodynamic-kinetic model of the submerged plasma fuming process. The kinetic correction factors were introduced by the author to “close the heat and mass balance” of the process. The slag chemistry was simplified to the Cu₂O-PbO-ZnO-FeO-Fe₂O₃-CaO-SiO₂-Al₂O₃ system. The predictions were stated by the author to be in a good agreement with the industrial data. The phases considered in the model were not specified by the author.

Cheng et al.³⁴ developed a kinetic model of Zn fuming based on the conducted laboratory study. The activity coefficients of the slag species were derived from the available thermodynamic data and used in a set of kinetic equations describing the volumetric mass transfer coefficients. In a later publication,³⁵ a combined thermodynamic and kinetic model using an effective equilibrium reaction zone approach has been presented. The resulting model was tested against the available experimental data. Rather complex functions for the reactive gas and slag fractions were necessary to describe the experimental data. The model focused on the Zn concentration profile without detailed review of phase equilibria, energy balance and



T_i – slag temperature, °C
 T_B and T_R – blast and reductant temperatures, °C
 $\Delta\tau_i$ – step duration, minutes
 N_B and N_R – blast and reductant rates, kg/min or Nm³/min

Fig. 2. Mass flow diagram of the present Zn fuming model.

Table II. Inputs for the slag fuming process based on the data by Grant¹⁷

Feed stream	T, °C	Mass, t/volume, Nm ³	Units	Zn	Pb	Fe	Si	Mg	Ca	Al	O	S	Cu	As	Sb	C	N	H
<i>Case 1: Coal as reductant and fuel</i>																		
Initial slag	1192.5	45.3 t	[wt.%]	12.1	0.097	21.8	12.3	3.2	11.2	4.2	33.9	0.62	0.46	0.04	0.04	0.00	0.00	0.00
Coal	28.3	4.7 t	[wt.%]	0.00	0.00	7.4	0.23	0.70	0.49	3.3	12.2	0.29	0.00	0.00	0.00	70.4	0.91	4.0
Primary air	28.3	402 Nm ³ /0.46 t	[vol.%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	21.3	0.00	0.00	0.00	0.00	0.00	77.3	1.4
Secondary air	493–522	21,101 Nm ³ /24.4 t	[vol.%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	21.3	0.00	0.00	0.00	0.00	0.00	77.3	1.4
Process duration: 81 min; primary air rate: 4.96 Nm ³ /min; secondary air rate: 260.51 Nm ³ /min; coal rate: 57.7 kg/min																		
<i>Case 2: Ammonia as reductant and fuel</i>																		
Initial slag	1192.5	45.3 t	[wt.%]	12.1	0.097	21.8	12.3	3.2	11.2	4.2	33.9	0.62	0.46	0.04	0.04	0.00	0.00	0.00
Ammonia	25	39,035 Nm ³ /6.7 t	[vol.%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.0	75.0
Primary air	28.3	393 Nm ³ /0.45 t	[vol.%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	21.3	0.00	0.00	0.00	0.00	0.00	77.3	1.4
Secondary air	493–522	20,655 Nm ³ /23.9 t	[vol.%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	21.3	0.00	0.00	0.00	0.00	0.00	77.3	1.4
Process duration: 81 min; primary air rate: 4.86 Nm ³ /min; secondary air rate: 255.0 Nm ³ /min; ammonia rate: 481.91 Nm ³ /min																		

The compositions of the slag and coal ash were given in the form of oxides but recalculated in the elemental basis to facilitate mass balance calculations.

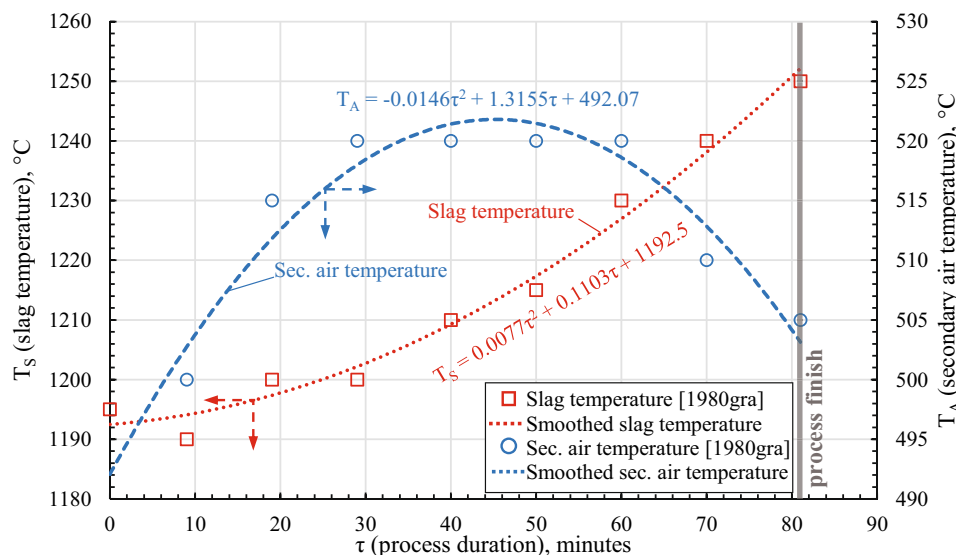


Fig. 3. Temperatures of the slag and secondary air. Symbols are those reported by Grant;¹⁷ lines are those used in model calculations of the present study for Cases 1 and 2.

distribution of minor elements. The temperature was kept constant.

In the previous publications,^{6–8,12,16,20,23,36,37} the authors discussed whether Zn fuming process reaches thermodynamic equilibrium at a given time step. General agreement is that purely kinetic or thermodynamic models cannot be used for the accurate description of the process if the wide range of input conditions is expected. Therefore, the combination of both should be applied, as done in the later publications.^{31,32,35} Rather complex models have been developed in these studies. In the present study, a relatively simple equilibrium thermodynamically based model is used to describe the plant data, and more attention is given to the predictions of phase equilibria and partitioning of minor elements. The thermodynamic data used in the presented model are those based on the recent outcomes of the integrated experimental and thermodynamic modelling study of the gas/slag/metal/matte/speiss/solid phase equilibria in the Cu-Pb-Zn-Fe-Ca-Si-O-S-Al-Mg-As-Sb system.^{38–46} The use of the self-consistent thermodynamic data allows a wide range of the slag compositions to be used in the presented model without limitations on the concentration of the major slag elements (Cu-Pb-Zn-Fe-Ca-Si-O-S-Al-Mg).

Phase Equilibria

Earlier review of the phase equilibria in the Zn slag fuming systems was done by Jak and Hayes.²³ The process is usually operated with fully liquid slag, but a small presence of solid phases is possible. According to Jak and Hayes,²³ the potential phases to be formed in the system are spinel, wüstite, melilite and pseudowollastonite. In the present study, zincite and matte/metal/speiss phases were also considered; Table I includes the formulae of the

main phases and species used in the present study and mentioned in the following text.

The thermodynamic model of the system was developed in the integrated experimental and thermodynamic modelling study of binary, ternary and higher order gas/slag/metal/matte/speiss/solid systems.^{38–46} The availability of accurate experimental data on the interactions between gas/slag/metal/matte/speiss/solid phases in the internal database is an advantage of the present model.

To ensure that the proportion of solid phases during slag fuming do not exceed the desirable level, fluxing diagrams similar to those given in Fig. 1 can be used. The common Zn fuming slag compositions can be described by the ZnO-FeO-Fe₂O₃-CaO-SiO₂-Al₂O₃-MgO system. Even though the concentrations of the Al₂O₃ and MgO in the slag are usually small compared to other elements, their presence stabilises the spinel over wüstite and therefore should be accounted for. Different ternary sections of the system such as ZnO-(FeO + Fe₂O₃)-(CaO + SiO₂) (Fig. 1A) or (FeO + Fe₂O₃ + ZnO)-CaO-SiO₂ (Fig. 1B) with constant concentrations of Al₂O₃ and MgO in the slag and fixed (FeO + Fe₂O₃)/ZnO and CaO/SiO₂ ratios, respectively, can then be used in industrial practise to adjust the fluxing strategy for any given batch. In addition to the slag (liquid oxide and solid phases), metal, matte and speiss can be formed in the bath collecting a part of the Cu, S, Sb and As. This presents an opportunity to settle and separate a portion of these elements from the slag.

Decarbonisation of the Process

Ammonia is considered one of the replacements for fossil fuels in a wide variety of industries.⁴⁷ Replacing coal in metallurgy is challenging in processes such as iron and lead blast furnace

reduction but more possible in others such as slag fuming as described in the present study. One of the goals of the present study is to thermodynamically analyse the difference in the slag fuming process parameters caused by the complete replacement of coal with ammonia. The findings of this study can then provide information to the metallurgical engineers seeking decarbonisation opportunities.

However, the presented study does not consider the difference in the kinetics of the process related to the difference in the reducing agents used. The kinetic aspects of the interaction of ammonia with slag should be additionally studied before any conclusions on the feasibility of the ammonia as a reductant in the described process can be made. The use of ammonia also brings other challenges such as storage and introduction into the reactor, which should be considered.

METHODOLOGY

The modelling of the Zn fuming process was performed using the combination of Factsage 8.0³⁰ (using the internal thermodynamic data³⁸⁻⁴⁶) and Microsoft Excel software. The former was used to calculate the phase equilibria in the system and the latter for the needs of automatization of the modelling process and graphical representation of the results. Zn slag fuming is an open system batch process and was modelled by multiple calculation steps followed by the removal of the formed gaseous phase from the reactor. Figure 2 provides the schematic explanation of the modelling steps. The initial input slag is supplied to the first step of calculation together with reductant (coal or ammonia) and blast. The temperature of the reductants and blast can vary for different steps of calculation, but their feed rates (kg/min or Nm³/min) are kept constant. The temperatures of the output slag and output gas are equal to the temperature of the corresponding calculation step. Formed gas phases are then removed from the system and the slag (oxide liquid, matte, metal, speiss and other solid solutions and stoichiometric compounds) is supplied to the next stage of calculation where another portion of the reductant and blast are added. After the desired number of calculations steps the output slag of the last calculation becomes the resulting slag of the process.

The heat balance for every step of the modelling is calculated according to Eqs. 4-5.

$$\Delta_R H_1 = H_1^{\text{sys}} - (H_0^{\text{slag}} + H_1^{\text{blast}} + H_1^{\text{red}}) \quad (4)$$

$$\Delta_R H_n = H_n^{\text{sys}} - (H_{n-1}^{\text{slag}} + H_n^{\text{blast}} + H_n^{\text{red}}) \quad (5)$$

where change in enthalpy $\Delta_R H_n$ represents an energy balance of the step n, H_n^{sys} is the resulting enthalpy of the system after step n, H_n^{slag} is the enthalpy of the slag phase (oxide liquid, matte, metal, speiss and other solid solutions and

Table III. Comparison of the input and output process streams of the process; slags and solids are oxides but presented in the elemental form for the purpose of the mass balance

Reference	Process stream	Stream mass, t	Stream composition, wt.%													Mean heat loss, MW				
			Zn	Pb	Fe	Si	Mg	Ca	Al	O	S	Cu	As	Sb						
<i>Process start</i>																				
Grant ¹⁷	Initial slag	45.3	12.2	0.097	22.0	12.4	3.3	11.3	4.2	34.0	0.62	-	-	-	-	-	-	-	-	-
Present study	Initial slag	45.3	12.1	0.097	21.8	12.3	3.2	11.2	4.2	33.9	0.62	0.46	0.04	0.04	-	-	-	-	-	-
<i>Process finish</i>																				
Grant ¹⁷	Slag	-	2.0	0.013	25.1	14.6	3.8	13.2	4.2	36.3	0.69	-	-	-	-	-	-	-	-	-
Case 1: Present study, coal	Slag (oxide liquid + spinel)	39.6	1.5	0.00	25.8	14.1	3.8	12.9	5.1	35.9	0.61	0.3	0.004	0.005	-	-	-	-	-	-
	Matte	0.17	1.2	0.006	23.5	0.00	0.00	0.002	0.00	1.6	21.9	50.0	0.74	1.1	-	-	-	-	-	-
Case 2: Present study, ammonia	Slag (oxide liquid)	38.7	1.5	0.00	25.5	14.4	3.8	13.1	4.8	36.0	0.51	0.32	0.003	0.003	-	-	-	-	-	-
	Matte + speiss	0.15	1.0	0.006	18.1	0.00	0.00	0.002	0.00	1.03	22.3	57.0	0.29	0.35	-	-	-	-	-	-

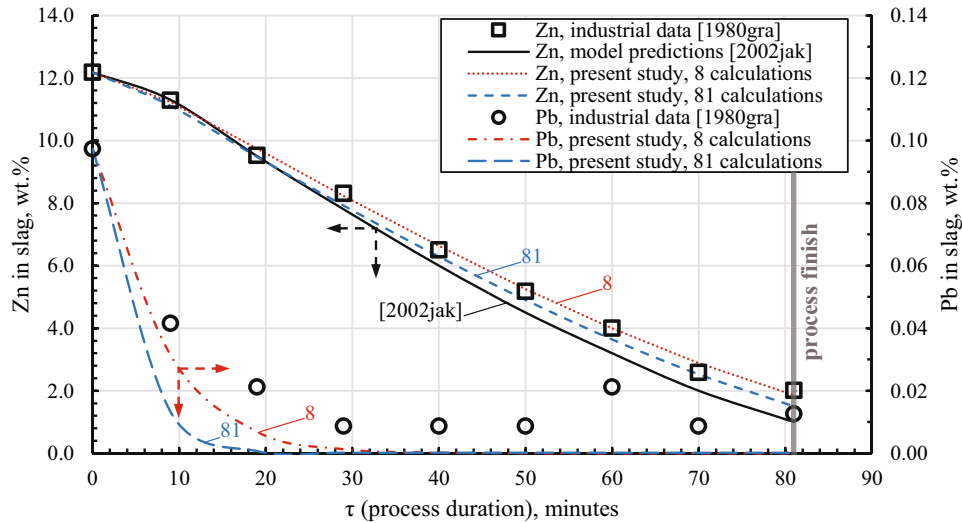


Fig. 4. Concentration of Zn and Pb in the slag as a function of time: symbols represent industrial data,¹⁷ lines show the modelling results of the present study and earlier modelling results by Jak and Hayes.²³

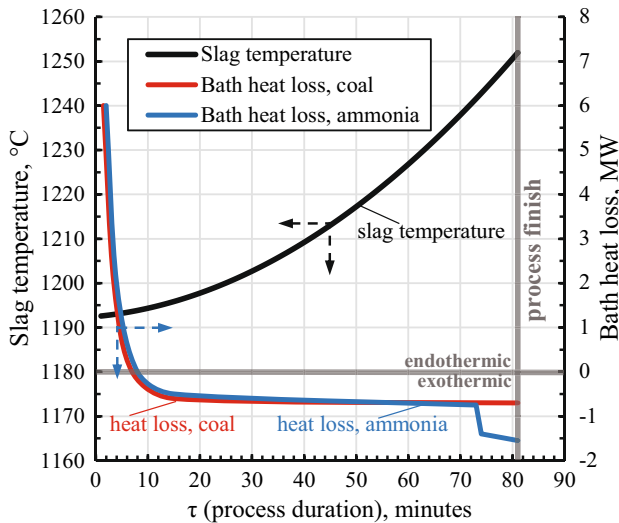


Fig. 5. Energy balance calculations for Zn slag fuming Case 1 and Case 2.

stoichiometric compounds) after step n (H_0^{slag} corresponds to the enthalpy of the initial slag of the process), H_n^{blast} is the enthalpy of the blast supplied to the step n , and H_n^{red} is the enthalpy of the reductant (coal or ammonia) supplied to step n . Negative values of $\Delta_R H_n$ mean that the reactor loses heat into the environment; positive values mean that the reactor needs an additional supply of energy to sustain the temperature.

The calculations were performed at 1 atm pressure. The chemistry of the described Zn fuming model was simplified to the Cu-Pb-Zn-Fe-Ca-Si-O-S-Al-Mg-As-Sb system. Numerous solution phases and compounds within the system were included in the calculation during every step of the modelling

of the process, and only those in Table I were stable in the process or appeared on the phase diagram in Fig. 1A.

Two modelling cases are presented:

Case 1 The input amounts, compositions of slag, coal and blast were used as reported by Grant¹⁷ and are listed in Table II. The starting composition of the slag was modified to include 0.5 wt.% Cu_2O , 0.05 wt.% As_2O_3 and 0.05 wt.% Sb_2O_3 to demonstrate the behaviour of these elements in the process. The addition of Cu leads to the formation of the matte while As and Sb promote the formation of speiss in the system; these phases can be potentially removed from the slag allowing the achievement of lower concentrations of the mentioned elements in the final product. The presence of As and Sb in the calculations allows to describe the behaviour of these elements throughout the process. Temperatures of the slag and secondary air as reported by Grant¹⁷ were used; they were smoothed for the multistep calculations as shown in Fig. 3. The process duration was divided in 81 or 8 equilibrium time steps. Predictions with higher number of steps (therefore smaller time intervals) are closer to the equilibrium conditions, so the number of steps may be used as one of the kinetic adjustment parameters.

Case 2 Same as Case 1, with ammonia used as a substitute for coal. The heat balance was calculated based on the gaseous NH_3 at 25°C and 1 atm pressure. The rates of primary and secondary air were then adjusted to reach the same bath heat loss and the concentration of Zn in the final slag as Case 1. The ratio of primary to secondary air was kept the same as in Case 1. In the real process, ammonia is likely to be stored in liquid form at low temperature under high pressure; energy required to bring ammonia into the reactor zone has to be considered, which presents the technical challenge of bringing it into the reaction zone without shifting the energy

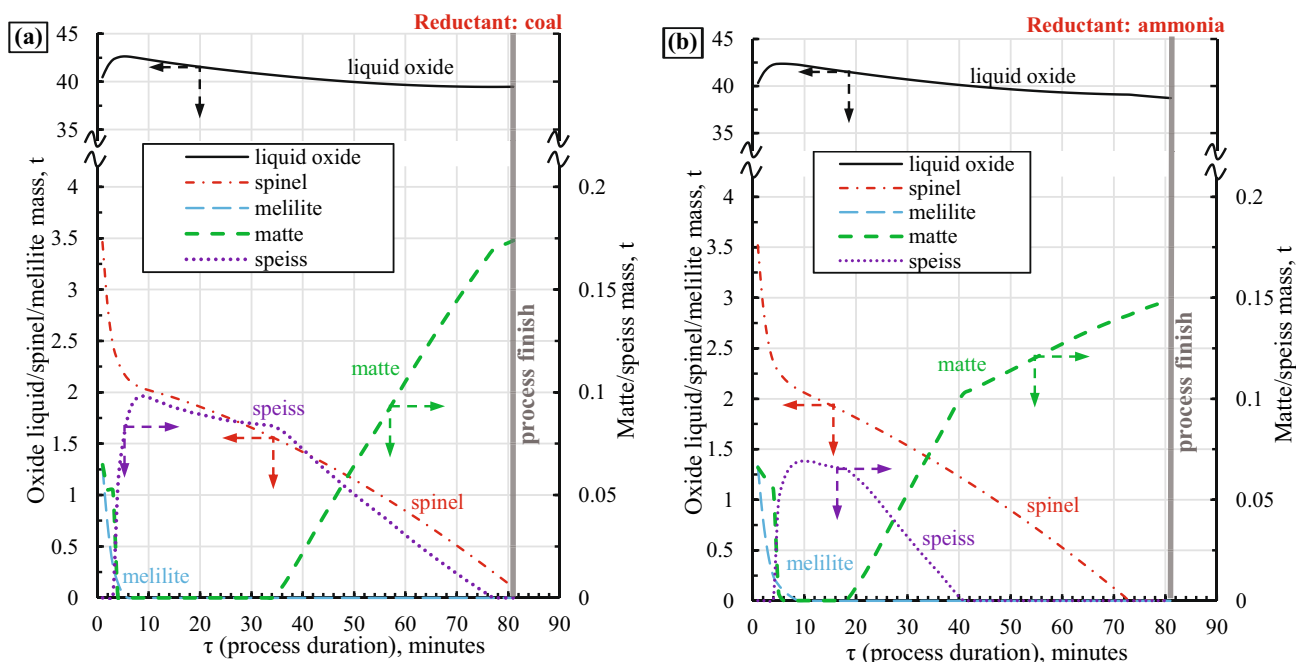


Fig. 6. Change of phase composition of the bath with time: (a) modelling of the process using coal as a reducing agent (Case 1) and (b) modelling of the process using ammonia as a reducing agent (Case 2).

balance. The difference in energy for the ammonia at 25°C and 11 atm and at 25°C and 1 atm can be estimated as 22.5 kW/kg of ammonia (energy input is required).

RESULTS AND DISCUSSION

Table III provides the comparison between the model predictions and industrial data¹⁷ for Cases 1 and 2. The concentrations of Zn and Pb in slag as functions of time are shown in Fig. 4. The calculations for Case 1 with 81 or 8 equilibrium time steps are compared to industrial data¹⁷ as well as an earlier modelling study by Jak and Hayes.²³ The concentrations of Zn and Pb in slag for Case 2 with 81 equilibrium time steps turned out to be practically the same as for Case 1 with 81 equilibrium time steps, so they are not shown in Fig. 4. A larger number of equilibrium time steps is demonstrated to have a small but noticeable effect on the results: a higher number of calculations resulted in higher removal of Zn and Pb at fixed total amount of air and coal. Overall, good agreement is observed for wt.% Zn in slag: industrial data¹⁷ points are in between those for Case 1 with 81 or 8 equilibrium time steps for all points, except for the last one. The difference between the model by Jak and Hayes²³ and the present study can be explained by the difference in thermodynamic models. The replacement of coal with ammonia in the role of reducing agent resulted in the same change in the concentration of Zn in Pb in the slag with time (Fig. 4). For Pb, the model predicted higher removal, which is an interesting topic for investigations. This can be a kinetic factor: the reactions with Pb at very low

concentrations do not reach equilibrium, even if reactions with Zn do; possible kinetic study of the evaporation of Pb from the slag can be beneficial for the future modelling studies of the process and will provide opportunities for reaching lower concentrations of Pb in the final slag. There also can be a sampling issue: concentration of elements < 0.05 wt.% are not measured with high accuracy with the x-ray fluorescence spectroscopy used by the author of the industrial data.¹⁷ At the same time these results demonstrate that discussion of thermodynamic and kinetic factors should be supported by the data for several elements, not just Zn.

The calculated furnace energy balance for Cases 1 and 2 is shown in Fig. 5. In the beginning of the process, between 0 min and 10 min, the energy balance is endothermic, which is likely caused by the lack of temperature measurements in this interval. The bath is heated over a period of time before the fuming, and some energy supplied was not reported. For the remaining duration of the process, the system was exothermic with the mean bath energy balance estimated to be -0.6 MW. This value can be treated as a calibration parameter to investigate changes in the process for the same bath. The sensitivity of the energy balance for the described process parameters was found to be approximately 0.2 MW/K. The balance includes some of the uncertainties, such as in enthalpy values of amorphous coal, the accuracy of the temperature measurements and others.

The modelled change in the phase assemblage of the bath content with time is shown in Fig. 6. The solid phases, represented by spinel and melilite,

dissolve in the oxide liquid with time because of the change of the bulk composition and increase of the system temperature. This can be correlated with the change in slag composition presented in Fig. 1 showing the decrease in the liquidus temperature with time. The use of ammonia resulted in the complete dissolution of the spinel before the end of the process and reduced stability of speiss and matte. These effects are explained by the absence of the constant introduction of Fe, Ca, Si, Al, Si oxides and S into the system (present in coal, but not ammonia). The dissolution of the spinel affected the bath heat balance closer to the end of the process making it more exothermic (Fig. 5). The mass of the oxide liquid also decreases with time, mostly because of the evaporation of the volatile elements and also the formation of matte phase stabilised by the presence of Cu in the system (added for the model demonstration purposes). The mass of matte increases closer to the end of the process, which is

related to the partitioning of larger amount of Fe in this phase. The Cu-As-Sb-S speiss was also formed in the bath but existed only in the limited range of the conditions and disappeared by the end of the process.

Figure 7 presents the calculated partitioning of Pb, Sb, As, Zn, Cu and S among gas, slag (oxide liquid + oxide solids) and matte + speiss with time. Strong evaporation of Pb in the form of PbS is observed, which requires further testing of the thermodynamic model. For Sb and As, a significant amount is removed to the gas and from the remaining amount approximately half accumulates in matte and speiss phase. These phases can potentially be settled from the slag. Zn does not partition into the matte and speiss in significant quantities and is therefore concentrated in the gas. Cu, opposite to Zn, does not partition into the gas in significant quantities and is distributed between the slag and matte and speiss. S is partially removed

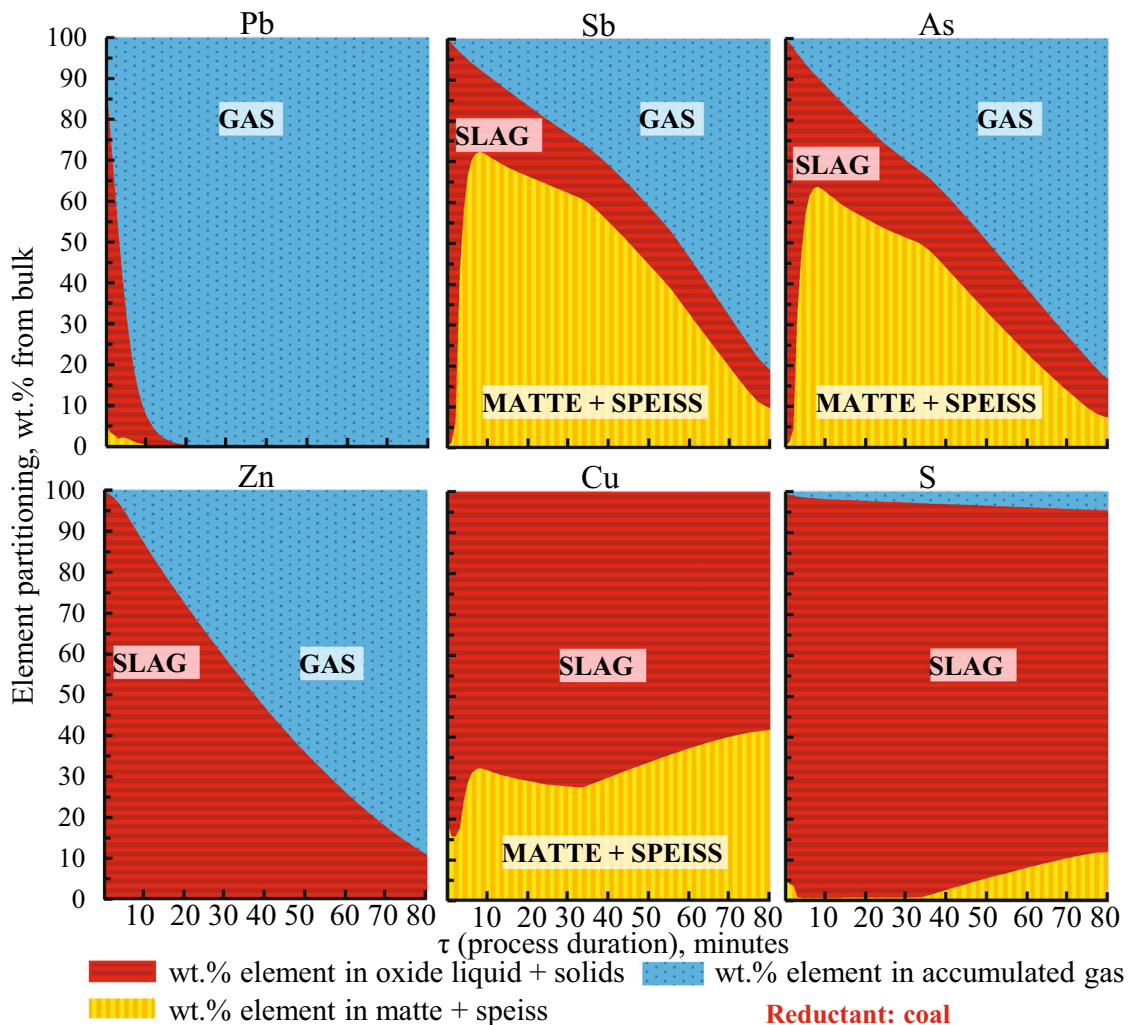


Fig. 7. Change in partitioning of Pb, Sb, As, Zn, Cu and S into slag (oxide liquid + solids), matte + speiss and gas with time for the modelling of the process using coal as a reducing agent (Case 1).

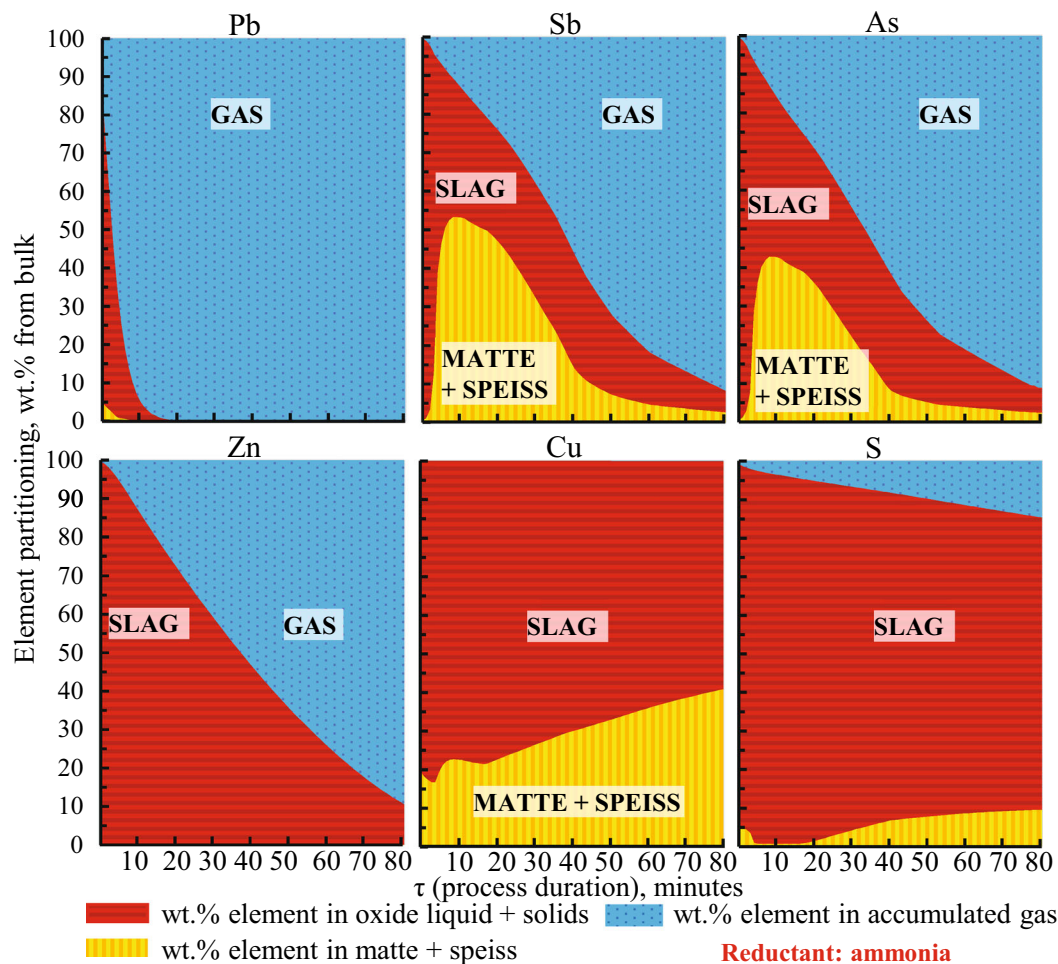


Fig. 8. Change in partitioning of Pb, Sb, As, Zn, Cu and S into slag (oxide liquid + solids), matte + speiss and gas with time for the modelling of the process using ammonia as a reducing agent (Case 2).

from the system with gas but most of it is concentrated in the slag. The calculation results for minor elements were not verified by the industrial data, but they highlight the importance of including such information when studying the kinetics and thermodynamics of zinc fuming. The absence of an additional feed source of sulphur has also affected the partitioning of Sb, As and S (Fig. 8) allowing a bigger part of these elements to be removed with the gas phase while reducing the partitioning to the matte and speiss.

SUMMARY

The Zn slag fuming process was modelled using the combination of the Factsage 8.0 and Microsoft Excel software. The latest thermodynamic data on the Cu-Pb-Fe-Zn-Ca-Si-O-S-Al-Mg-As-Sb system used in the presented model allowed increasing the accuracy of the phase equilibria predictions among the gas/slag/metal/matte/speiss/solid phases in the wide range of slag compositions. The

presented model has successfully reproduced the literature industrial data. The only kinetic factor in the model was the size of equilibrium time step interval.

The use of ammonia in Zn slag fuming as an alternative to coal was reviewed from the thermodynamic point of view. It was shown that the same final concentration of Zn in the slag can be obtained in the same period of time and with the same heat balance of the bath area of the reactor. For the given industrial dataset, the replacement of coal with ammonia led to the increase in the partitioning of Sb and As into the gas phase and to the reduced stability of spinel, matte and speiss. The use of primary and secondary air of the blast decreased when ammonia was used as the reductant. The presented model can be used for the assessment of the thermodynamic limitations of the process and can predict the changes in the mass and heat balance with changes in process parameters.

The replacement of coal with ammonia can be beneficial for the decarbonisation of the process and the removal of minor elements from the treated slag. However, the difference in the kinetics of the process cannot be predicted using the presented model and requires additional study prior to any implementation of the presented results.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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