

TEMPERATURE MODELLING IN A FURNACE

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Abstract

The smelting of Platinum group metals (PGM) can be conducted in a high temperature, continuously operating furnace, fuelled by coal and oxygen introduced by a lance inserted into the near-surface region. This is a violent process with large volumes of toxic and explosive gases being produced, and large temperature variations can occur in the slag and matte layers in the furnace. Such variations pose a major safety risk (there can be explosions) and cause control difficulties. We model various aspects of the operation of such a PMG furnace to determine possible causes for such variations. Our observations suggest that inappropriate tapping of the matte and slag layers is one likely cause of a major problem. It is also possible that two-phase flow instabilities may be initiated as operating parameters change.

1 Introduction

Platinum is a noble metal noted for its extreme resistance to tarnishing and corrosion, and it is also rare; about 30 times rarer than gold. It has a very high melting point ($1768^{\circ}C$), good electrical properties and, together with the other members of

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the platinum group of metals (PGM), is much valued for its catalytic properties. They are in great demand and short supply.

South Africa holds more than 80% of the world's platinum reserves, with more than 70% coming from the Bushveld Complex in the Transvaal in South Africa. The ore is mined, crushed and a flotation process is used to remove most of the gangue (useless minerals) to produce a concentrate which, after the addition of flux, is then smelted in a furnace. Smelting is a density separation process carried out at temperatures high enough to melt and chemically convert the in-feed. The metallic sulphides released during smelting separate out from the remaining gangue (oxides) because of their higher density (Specific gravity, $SG > 4.5$) compared with that of the in-feed ($SG < 3.5$).

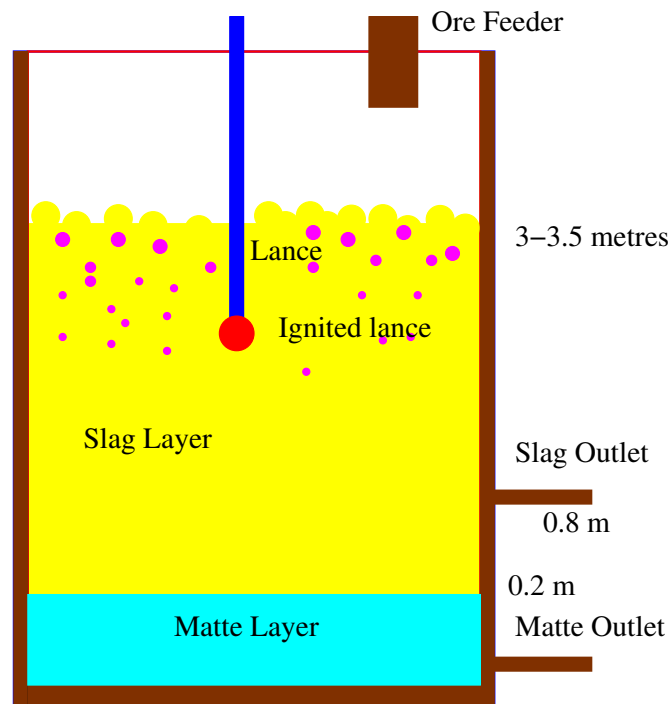


Figure 1: A combustion lance is inserted from the top of the furnace and into the concentrate. This raises the temperature above about 1600°C ; above the melting point of the in-feed and sufficient to cause smelting. There is significant turbulence and bubbling. Metallic sulphide droplets are formed in the in-feed and drip down into the matte layer formed under the slag. The furnace is run continuously with in-feed added and matte and slag extracted at appropriate time intervals.

In more modern furnaces, the heating is done using electrodes, but in the situation of interest here a combustion lance is inserted into the furnace and used to raise the temperature to the very high levels (1600°C) required for smelting, see Figure 1. The furnace is a cylindrical container of radius approximately 2 m and height about 20 m. The lance injects air, coal and oxygen, among other ingredients

and is “ignited” to input significant energy. A flux (normally limestone) is generally added to help separate out the gangue (removed as oxides) from the matte (primarily metal sulphides). The air jet assists in mixing the reacting components in the slag layer. The lance is thus the main initiator and controller of the process. Metal sulphide droplets are formed in the slag layer and gravitate down to the liquid matte below, leaving behind the gangue which float to the surface and are later discarded. The liquid matte layer largely contains liquid copper, iron and nickel sulphides, but small quantities of PMG are also present. Further chemical processing is needed to extract the PMGs. Typically the matte to slag volume ratio in the furnace is 1 to 8 with the matte depth small (typically 20 cm) compared with a slag depth of 1-3.5 m. The matte is strongly and stably stratified (and therefore motionless) because of the relatively large matte/slag density ratio. Vast quantities of dangerous gases (carbon and sulphur oxides) are produced and bubble up through the slag layer to burst through it’s surface. The gases are removed from the top of the furnace. This is a violent process with splashes appearing well up the very high (15m) furnace walls and explosions can occur that are a major safety concern.

The furnace operates continuously with in-feed added to the top of the furnace and with slag and matte tapped from different locations along the side of the furnace, see Figure 1. Ideally this in-feed and tapping process would be continuous and designed to ensure a steady state operation, but in practice the in-feed and tapping processes are intermittent and produce rapid changes in depth of the slag and matte layers, potentially causing a heating imbalance within the furnace. Other causes of potential mismatches between heat input and absorption are variable feed quality, misjudgement of the furnace state by the operator and errors in the lance height. Additionally superheating in the matte layer can cause difficulties. If such heat imbalances occur, the chemical reactions may experience thermal runaway, which occurs if the slag gets too hot, and could result in a sudden foaming and increase in volume of the slag layer.

The study group was asked to present some possible models to simulate the temperature distribution within the furnace and to identify processes likely to result in ‘instabilities’.

The depth of penetration of the lance into the slag will play a major role in determining the temperature distribution through the layer. In Section 2 we examine this effect using a simple fixed energy heat input/output model with variations only in the vertical direction. The strength of the heat sources and sinks will be temperature dependent so this simple ‘geometric’ model needs to be combined with a heat generation and loss model to determine the steady distribution through the furnace. This is a complicated task requiring sophisticated analysis and more information and data than supplied during the MISG. However, crude estimates can be made using global energy arguments (see Section 3). These estimates should suffice for a qualitative understanding of the effect of furnace operation on the temperature profile. As indicated earlier VERY large volumes of gases are produced in the furnace in the form of bubbles in the slag layer so any reasonably complete model will

certainly need to take into account the production of the gas and its effect on the energy and momentum balance within the furnace. Again as indicated earlier there are dramatic changes in flow behaviour with gas volume fraction and this could be critical. Not enough data or information was supplied during the study group to assess such effects, but some attempt was made to initiate this study in Section 4. Some tentative conclusions are drawn in Section 5.

1.1 Some background

The material in the slag layer consists mainly of oxides that were not removed in the pre-smelting flotation process. The carbon and oxygen mixture brought in by the lance combusts producing the heat required to smelt the concentrate. Also the carbon monoxide produced strips oxygen from the oxides and sulphates in the in-feed. Subsequent reductions occur leading eventually to the metal sulphides separating out from the gangue. Importantly these reduction reactions are exothermic with the reactive heat adding to the input coming directly from the lance. It is possible an instability could arise here due to change in quality of the in-feed.

In an attempt to moderate variability in the composition of the in-feed, it is composed of material from a range of sites. The usual practice is to do a mineralogical analysis of a typical sample. The composition of the sample at a temperature datum (typically 25°C) is determined and (external) heat is applied at a known rate with the temperature of the sample recorded. Initially the externally applied heat just causes a change in the sensible heat content of the sample but water evaporation may also occur. As the temperature rises, the sample melts, absorbing latent heat, and then at higher temperatures there will be a change in chemical composition with the associated heat release (the reactions are generally exothermic) adding to that supplied externally. Gases are released so that phase change and chemical change effects occur simultaneously. The primary concern is with the energy requirements of the process and, assuming the reactions are fast enough over the time scales of interest (hours), then thermodynamic equilibrium can be assumed [5, 7]. Under such circumstances the chemical composition at any prescribed temperature is simply the one that minimises the Gibbs free energy at that temperature [3], so that the enthalpy of the sample is just a function of temperature and the initial composition. The laboratory results thus provide guidance for the operation of the furnace for the particular in-feed, thus enabling one to estimate the energy requirements at any stage of the process.

In the past, detailed fluid dynamics simulations have been attempted [1], [4]. Based on reasonable assumptions these calculations suggest that the slag temperature is almost uniform due to bubble mixing and the matte is (stably) thermally stratified. They also indicate that there can be quite large temperature changes due to change in feed composition for the lance and ore make-up. These rapid changes may lead to a mismatch between combustion heat inflow and outflow and a consequent instability in the furnace. This may be exaggerated by misjudgement

of the conditions in the furnace, or delays in the response of the human operator. Two-phase flow transitions in the slag layer may reach the point where the volume gas fraction reaches about 0.3 (say), leading to a transition from bubbling flow to churn flow as major heat transfer occurs.

2 One-dimensional model

The presence of the lance as a major driver of the heating in the slag layer suggests it is worthwhile to do a one-dimensional, horizontally averaged model in the furnace. Although the actual depth of the layer is quite shallow compared to its width, the presence of significant heating at a particular height may lead to a vertical stratification in temperature in the layer.

Therefore, we assume the variation is mainly in the vertical direction and write a model equation for the temperature. It is clear that there is a lot of turbulence and this will lead to rapid diffusion of heat (defined here as α_{Turb} as a turbulent diffusion coefficient). We also assume that only the slag layer is important, since the matte layer is very stable and can be modelled as a boundary condition.

If Θ is the dimensional temperature in $^{\circ}C$, then we may choose to write a modified, non-dimensional temperature as $T = \frac{\Theta - \Theta_{mat}}{\Theta_{mat}}$ where Θ_{mat} is the (stable) temperature of the matte layer. Then assuming a reasonably steady operating scenario, we obtain an equation for temperature,

$$\alpha_{Turb} \frac{d^2 T}{dz^2} - \alpha_M T = \gamma(z), \quad (1)$$

where,

α_{Turb}	is turbulent diffusion (mixing),
α_M	is the rate of heat loss through the sides of the furnace,
$\gamma(z)$	is heat loss/gain internally due to the lance and chemical reactions.

With this scaling, and a length scale H_L , the depth of the slag layer, we can write the boundary conditions at the top and bottom of the slag layer as,

$$T = 0, \text{ on } z = 0, \quad (2)$$

$$\frac{dT}{dz} = -\alpha_{top}(T - T_{air}), \text{ on } z = 1. \quad (3)$$

where T_{air} is the temperature in the air above the layer, and α_{top} is the rate of loss through the surface due to bubbling and Newton cooling. Note that with this scaling T_{air} will be less than zero and will be close to $T_{air} \approx -1$. Radiation is assumed to be small and has been ignored in this model, but could be considered (although it would introduce a nonlinearity). The assumption that the temperature at the base

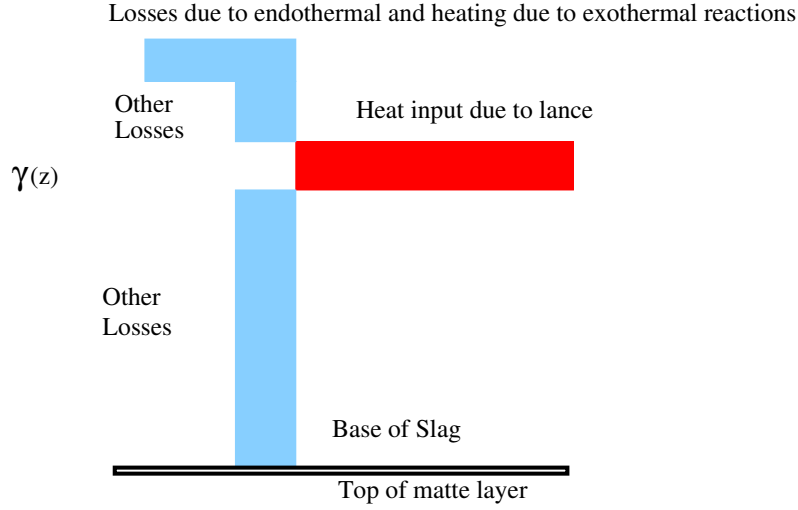


Figure 2: Indication of heating and cooling terms in the vertical one-dimensional model. Blue indicates regions in which there are chemical processes leading to heat losses (endothermic) and heat gains (exothermic).

of the layer is equal to the temperature of the matte layer is only approximate, but is unlikely to make a significant difference to the results.

As an example, we define a heat loss/gain function that corresponds to the near-surface melting, lance injection and general chemical background absorption or release of energy, as indicated in Figure 2, as

$$\begin{aligned}\gamma(z) &= \gamma_1 - (\gamma_1 + \gamma_2)\mathcal{U}(z - L_1) \\ &+ (\gamma_1 + \gamma_2)\mathcal{U}(z - L_2) \\ &- (-\gamma_1 + \gamma_3)\mathcal{U}(z - L_3)\end{aligned}$$

where \mathcal{U} is the Heaviside step function, L_1 is the height at the bottom of the lance (region of influence), L_2 is the height of the top of the lance (region of influence), and L_3 is the height at which the melting of the ore has been “completed”, γ_1 is average heat absorption due to chemical processes, γ_2 is heat input from the lance, γ_3 is losses due to melting of the ore, and these parameters correspond spatially to the regions given by L_1 , L_2 and L_3 . More information about the chemistry would allow this example calculation to be more accurate, but the principle would be unchanged.

2.1 Laplace transform solution

The presence of discontinuities in the forcing terms suggests that Laplace Transforms are a good method to solve this problem. Thus, transforming equation (1) leads to

$$\begin{aligned}&(s^2 - \lambda^2)\hat{T} - sT(0) - T'(0) \\ &= \frac{1}{s\alpha_{Turb}} \left(-\gamma_1 - (\gamma_1 + \gamma_2)e^{-L_1s} - (\gamma_1 + \gamma_2)e^{-L_2s} - (-\gamma_1 + \gamma_3)e^{-L_3s} \right)\end{aligned}$$

where \hat{T} is the Laplace transform of T , that is,

$$\hat{T}(s) = \mathcal{L}\{T(z)\} .$$

Inversion of the transform gives an equation for the temperature as a function of height,

$$\begin{aligned} T(z) = & - \left(\frac{\gamma_1}{\alpha_M} \right) (\cosh(\lambda z) - 1) \\ & + \left(\frac{\gamma_1 + \gamma_2}{\alpha_M} \right) \mathcal{U}(z - L_1) (\cosh(\lambda(z - L_1)) - 1) \\ & - \left(\frac{\gamma_1 + \gamma_2}{\alpha_M} \right) \mathcal{U}(z - L_2) (\cosh(\lambda(z - L_2)) - 1) \\ & - \left(\frac{-\gamma_1 + \gamma_3}{\alpha_M} \right) \mathcal{U}(z - L_3) (\cosh(\lambda(z - L_3)) - 1) \\ & + T(0) \cosh \lambda z + \frac{T'(0)}{\lambda} \sinh \lambda z , \end{aligned}$$

where $\lambda = \sqrt{\alpha_M/\alpha_{Turb}}$. The value of the two quantities, $T(0)$ and $T'(0)$, can be obtained by substituting this result into (2) and (3). If the temperature at the base of the layer is the matte temperature, then $T(0) = 0$, while the other condition has a rather complicated form, but can be satisfied by appropriate choice of $T'(0)$.

2.2 Results of the one-dimensional model

Some results of the vertical one-dimensional model are presented in Figure 3, which shows the case using assumed values ($\gamma_1 = 0.01$, $\gamma_2 = 1.2$, $\gamma_3 = 0.5$, $\alpha_{Turb} = 0.07$ and $\alpha_M = 0.005$) for all of the parameters when only the lance height, $H_L = 0.7$ (blue) and $H_L = 0.8$ (red), and the loss through the surface $\alpha_{top} = 0.01$ (dashed line) and $\alpha_{top} = 0.02$ (solid) are changed. These indicate that moving the lance deeper into the slag layer makes little difference to the temperature beneath the level of the lance, but results in lower temperatures near the surface. The hottest point always corresponds to the level of the lance and from there the heat diffuses up and down. The temperature is lower above the lance due to the endothermic reactions, energy absorbed by the melting feed, and losses through the slag-air interface. Higher losses through the surface make a difference to the temperature over the whole depth, but the effect is relatively small compared to the impact of the lance height. If the lance is closer to the surface there is a more even temperature distribution over the depth, and so it is desirable to keep the lance closer to the surface, albeit at a safe depth to prevent exposure to the air.

In practice it is possible that α_{Turb} is much larger than the values chosen here and so the temperature will be much more uniform over the full depth, but more details of the process and the parameters involved would be necessary to make this computation. The turbulence effect and the size of the losses through the surface can

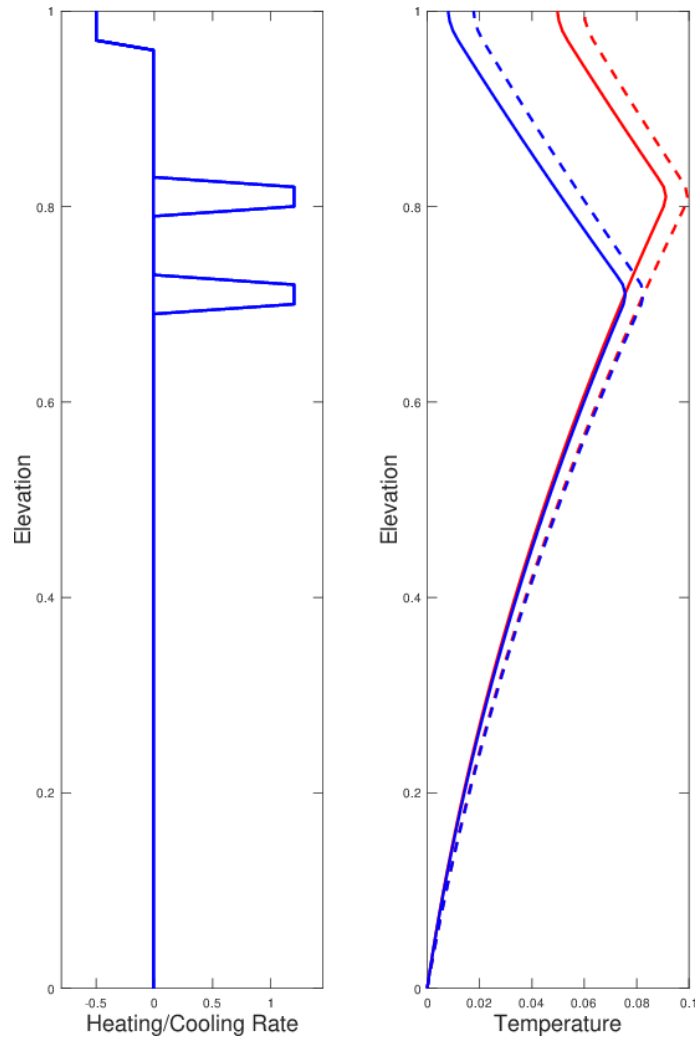


Figure 3: Temperature for two different values of lance height $H_L = 0.8$ (red) and $H_L = 0.7$ (blue), $\gamma_1 = 0.01$, $\gamma_2 = 1.2$, $\gamma_3 = 0.5$, $\alpha_{Turb} = 0.07$ and $\alpha_M = 0.005$. The dashed lines have a loss through the surface of $\alpha_{top} = 0.01$, the solid lines $\alpha_{top} = 0.02$.

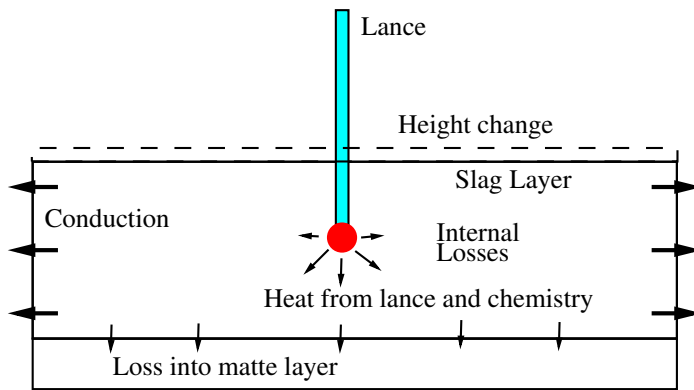


Figure 4: Terms in the balance of heat input and output in the furnace during operation.

be considered as a very rough model of the impact of the bubbling on the process, but here this is not explicitly considered. Since the bubbling may be a major factor in determining the outcome, this model needs to be interpreted with care. In Section 4 the basis of a gas production model is proposed, and this could be included with the current model.

3 Energy balance model and thermal runaway

The slag-to-matte volume ratios are very high (approximately 4:1 to 9:1) so that the slag temperature has a strong influence on matte temperature. This is a major concern due to the low matte melting temperature and its resultant high superheat. Maintaining a stable slag temperature is therefore a critical safety and operational issue (Andrew et. al. [1]).

Observations suggest that the material in the furnace exhibits a very violent mixing of the relatively shallow slag layer. This suggests a zero-dimensional “heat-balance” model might be useful. A balance of heat input and output may be achieved in equilibrium operation, a desirable steady state for the process. It is also desirable that this steady equilibrium be maintained as much as possible during variations in the conditions in the furnace, such as tapping of the slag layer and changes to feed rate. One approach is to balance each of the elements of heating and cooling within the slag layer, see Figure 4. These elements include the volumetric heat input due to the lance and exothermic and endothermic reactions within the slag, surface heat losses from the sides of the furnace, losses into the matte layer below, and through the slag surface due to gas and liquid exchanges associated with splashing and bubble bursting. There will also be radiative exchanges across the surface.

An obvious change that takes place frequently is the tapping of the slag layer, which takes place over a very short time. The removal of material while maintaining the heat input from the lance can result in a rapid increase in temperature, and lead

to the possibility of a sudden increase in gas formation or thermal runaway [2], potentially causing a rapid increase in level due to “foaming”. If there is a sudden increase in heat input per unit volume, then it may result in the onset of foaming (as in boiling milk) in which the bubbly region suddenly expands. An experimental study of the boiling of milk by Kumer et.al. [6], suggests that milk boils over if the gas creation at the walls of the container suffer a sudden increase in temperature. The same may happen in the furnace at the interfaces between the slag and gas, possibly near the tip of the lance. For Arrhenius reactions, in which the energy of the reaction is temperature dependent, such temperature jumps can be predicted by the mathematical theory of thermal runaway [2]. Thus, we might regard the slag/gas as a bubbly continuum in a quasi-steady state (equilibrium) and consider what happens if there is a sudden change in depth.

Balancing all of the inputs and outputs leads to an equilibrium equation in which all heat elements balance, so that

$$\begin{aligned} Q_L + Q_{EX}(h_T - h_M)\pi R^2 - Q_{EN}(h_T - h_M)\pi R^2 \\ - k(T - T_W)(h_T - h_M)2\pi R - k(T - T_A)\pi R^2 - k(T - T_M)\pi R^2 = 0, \end{aligned} \quad (4)$$

where Q_L is the heat input from the lance, Q_{EX} is the heat released during exothermic reactions per volume, Q_{EN} is the heat absorbed during endothermic reactions per volume, $T(t)$ is the temperature, T_M the matte temperature, T_W the wall temperature, T_A the air temperature, $h_T(t)$ the height at the top of the slag layer, $h_M(t)$ the height at the bottom of the slag layer (top of the matte layer), R is radius of the furnace and k is the exchange coefficient between the slag and its surroundings. A number of these terms would normally be represented as having non-linear temperature dependence, but crude estimates can be made by approximating these by linear terms, since all of the relevant temperatures will be close to the melting point of the slag.

Rearranging equation (4) gives an expression for the equilibrium temperature in the slag layer as

$$T_{eq} = \frac{Q_L/(\pi R^2) + C\xi + A\xi^2}{\xi(\xi + R)}, \quad (5)$$

where

$$A = (Q_{EX} - Q_{EN})\pi R^2 + 2\pi RT_W, \quad C = (T_A + T_M)\pi R^2$$

and $\xi = h_T - h_M$ is the height of the slag layer.

After tapping of the slag layer, the equilibrium will be disturbed and so we can write an approximate differential equation for the temperature as

$$\frac{dT}{dt} = \left[-\frac{Q_L}{\pi R^2} \left(\frac{2\xi + R}{\xi^2(\xi + R)^2} \right) + \frac{RA - C}{(\xi + R)^2} + A\xi \right] \frac{d\xi}{dt}. \quad (6)$$

This can be considered as a simple differential relationship near the equilibrium or more generally as a differential equation for the temperature in the slag. Clearly,

since we are interested in the case as ξ becomes smaller, the dominant term becomes

$$\frac{dT}{dt} \approx \frac{Q_L}{\pi R^2} \left(\frac{2\xi + R}{\xi^2(\xi + R)^2} \right) \frac{d\xi}{dt}. \quad (7)$$

This suggests that if the depth of the slag layer is reduced quickly, the change in temperature can be very large, even without considering the potentially strong impact of Arrhenius kinetics. For example if the slag layer is halved in depth, the differential becomes four times larger, signalling a dramatic temperature increase. A more detailed computation would require more information on the chemistry of the reactions in the material and the lance inputs, but this simple model indicates the potential for dramatic changes in operating conditions, and suggests that the operators should make such changes with care.

4 A simple global gas production model (slag layer)

Both of the models above neglect the presence of bubbles in the slag layer, yet it is clear that this is an important component of any analysis. The aim would be to determine changes in the gas content (bubbles) in the slag layer associated with changes in lance input and tapping of matte/slag. The thought is that if the volume fraction of gas exceeds a critical value then a bubble flow/churn flow transition will result. While we do not have sufficient information to put in details, we can conceptualise such a model. Assuming zero-dimensions, that is, a well-mixed model, and that the gas and liquid temperatures are the same and uniform in the slag region, we can estimate the volume fraction of gas (and temperature) as a result of combustion, chemical absorption and losses. We could then assume there is some volume fraction, for example, $V_g \approx 0.3$ (say) that results in flow regime change (bubble to churn).

4.1 The equations

Let α be the volume fraction of gas, so that $(1 - \alpha)$, is occupied by liquid/solid and that V_0 is the volume of the slag (assumed fixed for the steady state situation).

The equation for gas conservation would be

$$\frac{d}{dt}[V_0\rho_g\alpha] = L_g(t) + R_g(t) - S_g(t),$$

where $L_g(t)$ is gas input directly from the lance, $R_g(t)$ is the gas production rate and $S_g(t)$ is the loss through the surface. The densities of the gas and the liquid are ρ_g and ρ_l respectively.

Likewise, we can write an equation for the liquid/solid conservation as

$$\frac{d}{dt}[V_0\rho_l(1 - \alpha)] = L_l(t) - R_g(t) - S_l(t),$$

where L_t is the coal input, R_g the solid/liquid phase change component, and S_l is the loss from the surface due to splashing/wall sticking.

In addition, there will be an energy conservation equation,

$$\frac{d}{dt}[V_0(\rho_g\alpha c_g T + \rho_l(1 - \alpha)c_l T)] = H_{comb} - (H_{conv} + H_{lost})$$

where c_g and c_l are specific heats, H_{comb} is the combustion heat input, H_{conv} is the heat associated with feed conversion, and the various losses are included in H_{lost} . These equations would need to be informed by real data to enable them to be added to the earlier models. A scaling argument could be used to determine the relative importance of the individual terms, and then could be incorporated into a complete model such as proposed in Section 3. Unfortunately the group had insufficient information to detail this model.

5 Final comments

The work conducted in the study group was based on a number of assumptions about the behaviour and properties within the furnace. It is clear that in order to do a more detailed analysis much more information about the chemical reaction kinetics, feed rates, fluid levels and time series data is necessary.

However, it is possible to say that the best way to avoid the development of any dangerous instabilities is to keep the furnace as close as possible to a steady, stable equilibrium situation. To that end, minimising the rate at which any changes such as tapping or feed rate are made to enable the system and the operator to adjust to the changing dynamics.

More detailed work would consist of the influence of bubbling and churn of gases in the simple balance model and conditions for thermal runaway. The variation in feed rate and composition is clearly a potential problem and the use of more closely controlled electrical ‘‘lances’’ might reduce the danger of this issue, while providing a cleaner and more sustainable process.

The tapping and consequent reduction in the slag layer thickness is clearly a potential problem in terms of stability, and hence more frequent and smaller tapping might improve the stability of the system.

The study group identified several possible mechanisms for the development of instabilities that may be dangerous, but more detailed work will be required to identify which of these represent a major hazard to the safety and stability of the process.

References

- [1] N.J. Andrew, B. van Beek, A. Lexmond and J.H. Zietsman, “The effect of feed composition fluctuations on a platinum furnace energy balance and slag temperature”, *Southern African Inst. of Mining and Metallurgy: Pyrometallurgical Modelling*. pp117-124, 2014.
- [2] J.D. Buckmaster and G.S.S. Ludford, *Theory of Laminar Flames*, Cambridge University Press, 1982.
- [3] X. Wen, J. Wang and H. Wang, “Research on the mathematical model of local equilibrium in top-blown smelting process of electronic waste” *Metals*, 2021, 11(10), 1500. <https://doi.org/10.3390/met11101500>.
- [4] J.J. Bezuidenhout, J.J. Eksteen and S.M. Bradshaw. “CFD modelling of molten matte and slag flows in a circular three-phase smelting furnace”, *Progress in Computational Fluid Dynamics*, **9**, 316-324, 2009. <https://doi.org/10.1504/PCFD.2009.027362>.
- [5] T. Koshikawa, C.A. Gandin, M. Bellet, H. Yamamura and M. Bobadilla, “Computation of phase transformation paths in steels by a combination of the partial- and para-equilibrium thermodynamic approximations”. *ISIJ International*, **54** (6), 1274-1282, 2014. <https://doi.org/10.2355/isijinternational.54.1274>.
- [6] M. Kumar, O. Prakash, K.S. Kasana, “An experimental study on pool boiling of milk”, *Heat Transfer*, **40**, 159-170, 2011. <https://doi.org/10.1002/htj.20336>.
- [7] H.W. Zhang, Q. Liu, H. Shibata, Q. Wang, P. Jönsson, J.C. He and K. Nakajima, “Partial Equilibrium Prediction of Solidification and Carbide Precipitation in Ti-added High Cr Cast Irons”, *ISIJ International* **54**, 374-383, 2014. <https://doi.org/10.2355/isijinternational.54.374>.