

# A Kinetic Model for the Oxidation of Selenium and Tellurium in an Industrial Kaldofurnace

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A kinetic model for the oxidation of selenium and tellurium in the molten bath of an industrial Kaldofurnace during the refining step is presented in this article. During plant experiments, samples of the molten metal were collected hourly and chemically analyzed for selenium, tellurium, and silver. Selenium oxidized from the beginning of the refining step, whereas oxidation of tellurium only occurred until the Se/Te mass ratio decreased to a value of 0.55. Good agreement between the model predictions and the experimental data was obtained.

## INTRODUCTION

This study was conducted at the Mexicana de Cobre precious metals plant (PMP) in the La Caridad metallurgical complex, Nacozari, Mexico. The goal of the PMP is to produce high-purity, 99.99% gold and silver bars by processing decopperized anodic slime (DAS) from the copper refinery electrowinning plant. By-products of the PMP include commercial-grade, 99.5% selenium and 30% tellurium-rich slag. A typical composition of the DAS processed in the PMP is (wt.%) Ag-18 Au-0.07 Pb-25.5 Bi-2.2 As-2.3 Sb-8.4 Se-4.4 Te-0.55 Ba-1.0 SiO<sub>2</sub>-2.6 S-5.3 Cu-0.30 others (Ni, Sn, Al<sub>2</sub>O<sub>3</sub>, and Cl)-29.45.

The DAS is processed batchwise in a Kaldofurnace, shown schematically in Figure 1. The furnace can be rotated and tilted vertically and is enclosed in a metallic casing, thus avoiding fugitive emissions. A typical operation consists of the following steps:<sup>1</sup>

- Melting the DAS. The furnace temperature is held at 1,100°C with the aid of the primary lance; lead oxide, sodium carbonate, silica, and coke particles are

loaded into the reactor to produce molten metal and slag phases.

- Converting the molten metal. Silica particles are added to the molten metal to produce a slag phase at 1,150°C in which most of the lead is eliminated.
- Refining the molten metal. Air is injected through the secondary lance over the surface of the molten metal. The goal of refining is to eliminate the selenium as gaseous SeO<sub>2</sub>. The furnace temperature is held at 1,100–1,150°C.
- Tellurium slagging. Sodium carbonate is added to the molten metal to produce a slag phase in which the remaining tellurium concentrates. The slag phase is tapped off leaving behind the doré with approximately 98% silver.

This study focused on refining. Process engineers' experience suggested that selenium starts oxidizing and vaporizing as soon as the air gas stream is injected. As selenium is vaporized, its concentration decreases gradually. A

non-verified rule of thumb is that when the concentration of selenium in the molten bath decreases to approximately 3% by weight, tellurium starts oxidizing as gaseous TeO<sub>2</sub>, thus contaminating the selenium-rich gas stream.

The goal of this investigation was twofold: to clarify the kinetics of the oxidation of selenium and tellurium under typical operating conditions during refining, and to assess the feasibility for the selective separation of selenium and tellurium during the operation.

See the sidebar for experimental details. All equations and reactions are shown in Table I.

## RESULTS AND DISCUSSION

As a result of the strategy described in the experimental sidebar, the numerical values for the parameters  $k_i$  and  $p_i$  were determined. For all practical purposes, Reactions 1 and 2 showed apparent zero-order kinetics (i.e.,  $p_1 = p_2 \approx 0$ ). Similarly, the loss of silver that stuck to the gas hood showed a constant rate (i.e.,  $p_3 \approx 0$ ). Thus, Equation 4 reduced

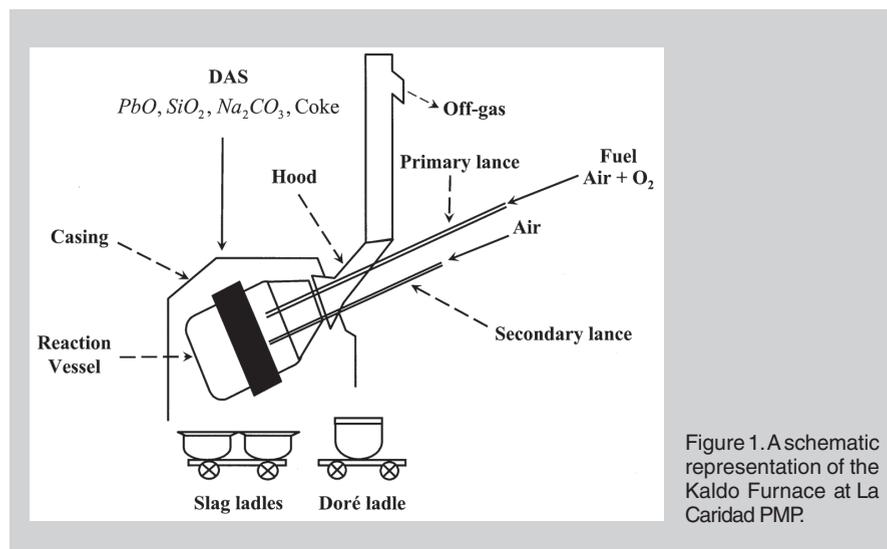
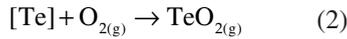
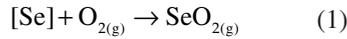


Figure 1. A schematic representation of the Kaldofurnace at La Caridad PMP.

Table I. Equations and Reactions



$$\frac{dm_i}{dt} = -k_i m_i^{p_i} \quad (3)$$

$$m_i = \left[ m_{i0}^{1-p_i} - (1-p_i)k_i t \right]^{\frac{1}{1-p_i}} \quad (4)$$

$$\omega_i = \frac{m_i}{\sum_{i=1}^c m_i} \quad (5)$$

$$F_{\text{OB}} = \sum_{j=1}^N \left[ \left( \omega_{\text{Se},e} - \omega_{\text{Se},c} \right)^2 + \left( \omega_{\text{Te},e} - \omega_{\text{Te},c} \right)^2 \right]_j \quad (6)$$

$$m_{\text{Se}} = m_{\text{Se},0} - k_1 t \quad (7)$$

$$m_{\text{Te}} = m_{\text{Te},0} - k_2 t [1 - U(\lambda)] \quad (8)$$

$$m_{\text{Ag}} = m_{\text{Ag},0} - k_3 t \quad (9)$$

$$U(\lambda) = \begin{cases} 1, & \text{if } \lambda > 0.55 \\ 0, & \text{otherwise} \end{cases} \quad (10)$$

to the forms shown in Equations 7–9, where  $\lambda = \omega_{\text{Se}} / \omega_{\text{Te}}$ , and  $U(\lambda)$  is the step function defined as Equation 10.

In a typical run,  $\lambda$  was greater than 0.55 at the beginning of the operation, and continuously decreased with time. Thus, according to Equation 8,  $m_{\text{Te}}$  is equal to  $m_{\text{Te},0}$  until  $\lambda$  reaches the characteristic value of 0.55.

The numerical values of the apparent reaction rate constants and the objective function are shown in Table II. The values of  $k_1$ ,  $k_2$ , and  $k_3$  varied in the ranges of 0.6–1.48, 0.67–2.57, and 0.14–1.89, respectively; the objective function varied between 3.8 and 59.1.

Under controlled conditions, it is expected that the apparent reaction rate constants do not vary from one experiment to the next. The variations observed in Table II were likely due to several factors:

- The fluctuations in the elemental composition of the molten metal processed; this determines the species composition present in the molten bath prior to the gas injection and, thus, the apparent

## EXPERIMENTAL WORK

Samples of the molten bath were collected every hour during the refining of doré under typical operating conditions. The samples (200 g–250 g) were chemically analyzed by atomic absorption spectroscopy (AAS) to determine the compositions of Ag, Se, Te, Cu, and Pb as functions of time. Seven experiments were carried out, with samples selected randomly from several batches during normal operation.

In all the experiments, the operating variables were set as follows: furnace inclination angle: 26° with respect to the horizontal; furnace rotation speed: 11 rpm; air flow rate through secondary lance: 720 m<sup>3</sup>/h at 25°C and 0.10 MPa total pressure; furnace temperature: 1,100°C–1,150°C; suction pressure in venting gas hood: –0.15 kPa to –0.2 kPa; and secondary lance nozzle inclination angle: 23°. The amount of decopperized anodic slime (DAS) processed per batch was allowed to vary according to the plant's normal fluctuations. At the beginning of the refining step, the amount of molten metal varied between 1,500 kg and 2,100 kg. The refining time varied from 240 min. to 360 min.

Based on the chemical analyses of the molten bath before and after refining, the composition of the tellurium-rich slag, and the amount of silver on the gas hood at the end of each operation, mass balance equations were written for all the major elements. As a result, the amounts of selenium, tellurium, and silver at the beginning of refining were computed. The amounts of minor elements such as copper and lead were determined similarly.

The goal of the kinetic model was to reasonably represent the compositions of selenium, tellurium, and silver as the oxidation proceeds. The model is based on the following assumptions: the oxidation of selenium and tellurium was represented by the overall chemical Reactions 1 and 2 (all reactions and equations are given in Table I), in which [Se] and [Te] represent the total selenium and total tellurium in the molten bath, respectively; Reaction 1 occurs from the beginning of the refining step; Reaction 2 occurs until the Se/Te mass ratio,  $\lambda = \omega_{\text{Se}} / \omega_{\text{Te}}$ , decreases down to a value of 0.55; and the molten bath is perfectly mixed. The first assumption was adopted because the reaction mechanisms have yet not been established.<sup>2,3</sup> The second and third assumptions resulted from the a-posteriori analysis of the experimental data. The last assumption was adopted here for simplicity.

Under these considerations, the overall kinetic model (Equation 3) was proposed, in which  $m_i$  is the amount of the  $i$ -th element ( $1=\text{Se}$ ,  $2=\text{Te}$ , and  $3=\text{Ag}$ ) in the molten bath in any form at time  $t$ , in kg.  $k_1$  and  $k_2$  are the apparent reaction rate constants for the oxidation of selenium and tellurium, respectively, whose apparent reaction orders are  $p_1$  and  $p_2$ . Because silver is assumed not to volatilize,  $k_3$  and  $p_3$  represent the loss of silver due to sticking to the hood, which is a common problem during operation. Note that Equation 3 does not take into consideration the reaction order with respect to oxygen concentration. This is because the oxygen supply for Reactions 1 and 2 was largely in excess. Therefore, the overall reaction rate was assumed to depend on the concentration of the limiting reactants only.

By integrating Equation 3, the mass of the  $i$ -th element at time  $t$  is obtained, as shown in Equation 4, where  $m_{i0}$  is the initial mass of the  $i$ -th element in the molten bath. Once  $m_i$  is known, the mass fraction of the  $i$ -th element is computed from Equation 5, where  $c$  is the number of elements in the molten bath. In this study,  $c = 4$  (selenium, tellurium, silver, and inerts). When the values of  $k_i$  and  $p_i$  were specified, the composition of the molten bath at time  $t$  was computed from Equations 4 and 5. To assess the validity of the kinetic model, the objective function was computed as shown in Equation 6, in which the subscripts  $e$  and  $c$  indicate experimental and computed values, respectively, and  $N$  is the number of experimental data. The values of the model parameters  $k_i$  and  $p_i$  were determined by minimizing Equation 6 using the Solver algorithm built in the commercial spreadsheet *Excel*.<sup>4</sup>

kinetic properties of the elements.

- The fluctuations in the batch size as shown in Table II. Because the furnace rotation speed was held constant in all the experiments, fluctuations in the amount of metal processed produced different hydrodynamic conditions in the furnace and, thus, variations in the efficiency of the molten bath-gas phase contact.
- The continuous wear of the reactor walls. It has been observed that the time needed to complete the refining step becomes longer as the wear of the reactor walls proceeds. As the internal reactor

volume increases, the separation between the molten bath surface and the gas jet (i.e., the oxygen diffusion path) also increases. The overall reaction rate is likely to be controlled by mass transfer of oxygen from the bulk gas to the molten bath surface, which explains this observation.

During this study, the described sources of variability were not controlled because the experiments were conducted along with the normal operation of the plant.

The following discussion emphasizes the results of experiment 3 only. Similar results were obtained for all the experiments in Table II, and thus are not shown.

Experiment 3 was selected because it closely approaches a typical case in the operation of the Kaldo furnace.

Figure 2 shows the predicted and experimental values of selenium concentration during the refining of the doré. It is noted that  $\omega_{\text{Se}}$  gradually decreased throughout the operation. This is in fairly good agreement with the model assumption that selenium starts oxidizing from the beginning of the refining step. Overall, the values predicted by the kinetic model reasonably agreed with the experimental data.

The predicted and experimental values of tellurium concentration in the molten bath are shown in Figure 3. The value

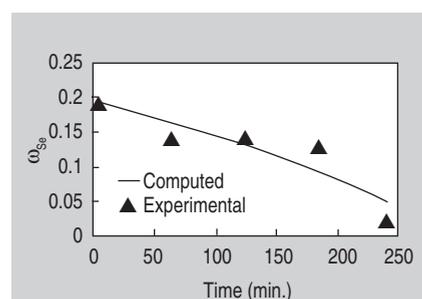


Figure 2. The computed and experimental values of selenium concentration for experiment 3.

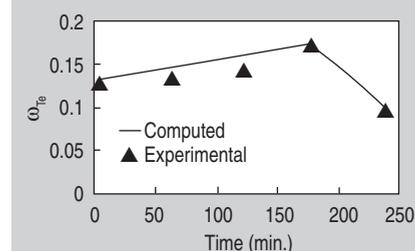


Figure 3. The computed and experimental values of tellurium concentration for experiment 3.

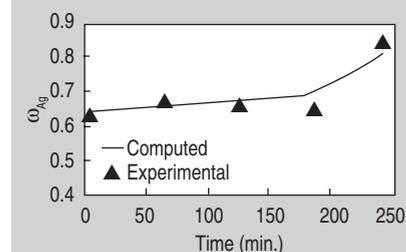


Figure 4. The computed and experimental values of silver concentration for experiment 3.

Experiment No.	Batch Size (kg)	Refining Time (min.)	$k_1$	$k_2$	$k_3$	$F_{\text{OB}}$
1	2,155	360	0.73	1.10	0.14	24.7
2	1,995	300	1.07	1.02	0.47	6.3
3	2,139	240	1.49	2.57	1.41	30.2
4	2,028	300	1.15	1.40	1.89	18.4
5	1,503	300	0.80	0.67	1.57	59.1
6	1,633	300	0.60	2.02	0.92	37.2
7	1,743	300	1.08	1.45	1.68	3.8

of  $\omega_{\text{Te}}$  increased gradually with time in the range of  $0 < t < 180$  min. It reached a maximum at  $t = 180$  min., and it later decreased for  $t > 180$  min. This behavior is consistent with the hypothesis that tellurium remains in the molten bath until the characteristic value of  $\lambda = 0.55$  is reached. When this condition was satisfied, tellurium started oxidation and vaporization, and its concentration decreased gradually with time. Once again, the model predictions show good agreement with the experimental data.

Finally, Figure 4 shows the concentration of silver, the major component in the molten bath. The substantial increase in  $\omega_{\text{Ag}}$  for  $t > 180$  min. corresponds to the conditions in which  $\lambda < 0.55$  and both selenium and tellurium oxidize simultaneously. Overall, good agreement between the predicted and the experimental values is observed.

Based on both the experimental observations and the computed results, it is clear that a selective separation of selenium and tellurium during the refining step is not feasible under the current operating conditions. For practical purposes, it is desirable that the characteristic value of  $\lambda$  be as small as possible so that selenium can be selectively vaporized according to Reaction 1 whereas tellurium remains in the molten bath. It is noted that the characteristic value of  $\lambda = 0.55$  remained fairly constant in all the experiments. This behavior was observed even though the composition of the molten bath initially charged to the furnace varied from one batch to another. This suggests that the characteristic value of  $\lambda$  is a thermodynamic property of the system and is insensitive to changes in the overall composition of the molten metal. Further studies on the phase equilibria of the multi-component system Se-Te-Ag-O are necessary to clarify this point.

## CONCLUSION

This study showed that a characteristic value of Se/Te mass ratio determines the point at which the oxidation of tellurium begins during the refining step. This parameter seems to be a thermodynamic restriction of the system and deserves further attention from a fundamental perspective. The fact that both selenium and tellurium showed apparent zero-order reaction kinetics suggests that the oxidation of these elements may be controlled by rate processes rather than by intrinsic kinetics. It is likely that hydrodynamics as well as oxygen potential may affect the overall reaction rates. To clarify this point, future experimentation is necessary so that the exact stoichiometry of the chemical reactions is established and a fundamental model for the reaction rates is developed.

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