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**APPLICATION OF A REACTING CFD MODEL
TO DROP TUBE KINETICS AND FLASH SMELTER
COMBUSTION**

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Application of a reacting CFD model to drop tube kinetics and flash smelter combustion

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ABSTRACT

This paper discusses the use of a reacting CFD model to determine chalcopyrite kinetics in a drop tube furnace and to predict the reaction of a chalcopyrite concentrate in the reaction shaft of an industrial smelter. Reacting CFD codes can be applied to determine the consequences of the interaction of gas with particles and therefore improve the ability to derive kinetic parameters that take into account the temperature and oxidation histories that different particles will see. This paper describes the application of such a model to derive improved kinetic parameters for the pyrolysis and oxidation of chalcopyrite. The reaction shaft model includes the effects of turbulent fluid mechanics, entrained flow mixing, turbulent particle dispersion, heterogeneous particle reactions, radiative and convective heat transfer, and surface and bath deposition rates. Particle reaction and composition characteristics are predicted as a function of particle trajectory and deposition and are used to aid in evaluating shaft performance.

INTRODUCTION

This paper discusses the use of a reacting Computational Fluid Dynamics (CFD) model to determine chalcopyrite kinetics in a drop tube furnace and to predict the reaction of a chalcopyrite concentrate in the reaction shaft of an industrial smelter. Drop tube furnaces are commonly used to derive kinetic parameters for pyrolysis and oxidation of different grade concentrates, since they can provide well-defined temperatures, oxygen concentrations, and residence times. For injection of particles at very low concentrations, the gas composition and temperature are not appreciably affected by the injected particles. Only in-furnace optical observations via pyrometry or high-speed photography, or analysis of extracted particles by electron microscopy can be conducted at mass flow rates which are low enough to neglect perturbations of the gas temperature or concentration. At the higher concentrations needed for chemical or instrumental analysis, significant perturbations of the composition and temperature of the gas in the drop tubes can be expected. For such cases, reacting CFD codes can be applied to determine the consequences of the interaction of gas with particles and therefore improve the ability to derive kinetic parameters that take into account the different temperature and oxidation histories that different particles will see. The improved kinetic parameters derived from the drop tube studies can then be used to simulate chalcopyrite concentrate reactions in the reaction shaft of an industrial smelter.

REACTING COMPUTATIONAL FLUID DYNAMICS (CFD) CODE

General CFD Model

The computational reacting CFD tools used by Reaction Engineering International (REI) combine computational fluid dynamics, turbulent particle transport, radiative and convective heat transfer and heterogeneous (gas-liquid-solid-phase) chemical reactions to simulate complex reacting flows. Computations include full mass, momentum and energy coupling between the gas, liquid and particles as well as full coupling between turbulent fluid flow, chemical reactions and radiative and convective heat transfer. The extent of physics and chemistry modeled along with the full coupling between the different mechanisms allows the REI models to account for the controlling processes in a variety of combustion applications.

The REI codes are based on the finite volume concept and employ a combination of Eulerian and Lagrangian reference frames [1]. The governing equations for gas-phase fluid mechanics, chemical reactions and convective and radiative heat transfer are solved in an Eulerian framework. The governing equations for particle-phase mechanics are solved in a Lagrangian reference frame. The flow field is assumed to be a steady-state, turbulent, reacting continuum field that can be described locally by general conservation equations, i.e., mass, momentum and energy. Gas-phase reactions are assumed to be

limited by mixing rates for major species as opposed to chemical kinetic rates; gaseous reactions are calculated assuming local instantaneous equilibrium. The radiative intensity field is solved based on properties of the surfaces and participating medium, and the resulting local flux divergence appears as a source term in the gas phase energy equation.

Particle mechanics are solved by following the mean path for a discretized group of particles in a Lagrangian reference frame. The dispersion of the particle cloud is based on statistics gathered from the turbulent flow field. Particle mass, momentum and energy sources are converted from a Lagrangian to an Eulerian reference frame then coupled with gas phase fluid mechanics.

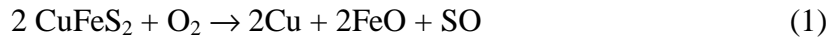
Chalcopyrite Reaction Model

REI's model of particle combustion was designed to be applicable for a variety of heterogeneous reactants (e.g., coal in air, evaporating droplets, mineral concentrates in oxygen/nitrogen). However, an accurate description of the chemistry and physics of copper concentrate smelting requires some modifications and additions. In order to formulate a manageable mathematical description of the processes occurring at the particle level, simplifying assumptions must be made and evaluated for conditions of interest. Several models of varying complexity have attempted to include the dominant physical phenomena necessary for use in simulating flash smelting of chalcopyrite [2,3,4,5]. However, the application of these models for the simulation of practical systems has been limited. The focus of this modeling effort is to include the necessary mechanistic information to accurately determine temperature, oxygen, and sulfur species fields in the gas phase as well as the temperature and composition of the particles. This information will allow evaluation of melt and shaft wall deposition as well as dust loading.

The particle reaction model used herein is formulated to handle multiple components with multiple reactions. For chalcopyrite, particle submodel consists of three components: sulfide, moisture, and ash. At this point the ash might be defined as that part of the particle that is inert in the combustion scheme. The reacting particle is assumed to be composed of specified amounts of sulfide and ash at any particular time. The sulfide is assumed to react heterogeneously after diffusion of the gaseous reactant (i.e., O₂) to the particle surface by one or more reactions.

The oxidation and gasification scheme combines the effects of film diffusion at high temperatures with chemical kinetics at low temperature. The kinetics are modeled from a global reaction rate (based on external surface area) with a selected oxidation mechanism. The effects of this mass transfer on diffusion (Stefan flow) are included by use of film theory.

Current efforts to describe the heterogeneous chemistry are limited to a one-step overall reaction mechanism described by (Equation 1):



Gas phase reactions completely oxidizing/reducing the sulfur are allowed in the gas phase. This mechanism is obviously a gross simplification of the particle combustion process. However, the importance of accurately capturing the details of the particle pyrolysis, solid oxidation, melt formation, and melt oxidation processes is still poorly understood in terms of practical results such as matte quality, shaft wall heat deposition, and dust loading. The model will continue to evolve as consideration of the dominant chemical and physical mechanisms improve and as the availability of detailed kinetic data continues to improve.

DROP TUBE STUDY

Drop Tube Approach

Drop tubes have been used extensively to study reactions of importance to shaft furnace. The advantages of drop tubes for kinetic studies are that the temperature and gas composition can be varied independently, that optical access is available for observations of physical transformations such as ignition and fragmentation, and closure of material balances is facilitated by complete collection of product streams. Drop tube furnaces, however, must be used judiciously for obtaining kinetic measurements. Each particle will see the furnace temperature and feed gas composition only when the drop-tube is operated in the 'single' particle mode where particles are separated by large enough distances so that they act independently. As particle concentrations increase to the point that boundary layers interact, the temperature and gas environments of the particles will be perturbed from the nominal values. For example, under oxidizing conditions there is a significant oxygen depletion along the axis which increases the time for reaction and decreases the peak temperature from the values observed for 'single' particle experiments. One mode of operation of the drop tube is under very dilute conditions where the particle boundary layers do not overlap. Under these conditions, the particle temperature can be obtained by means such as multiple-color optical pyrometry. If the overall stoichiometry and enthalpy change for the reaction is known, the chemical kinetics can then be obtained from an energy balance on the particle.

When the drop tube is operated at a high enough feed rate to obtain sufficient amounts of products for chemical analysis, compensation must be made for the effect of particle interaction on the temperature and gas compositions to which the particles are exposed. Computational simulations allow for oxygen depletion, the cooling of the gas as the feed is brought up to reaction temperature, and the heat release due to chemical reaction at a rate determined by the local gas composition and temperature. Jorgensen [6] has performed these types of experiments, which have been simulated as part of this effort for the conditions shown in Figure 1. The magnitude of the changes in gas temperature and oxygen concentration is shown in Figure 2.

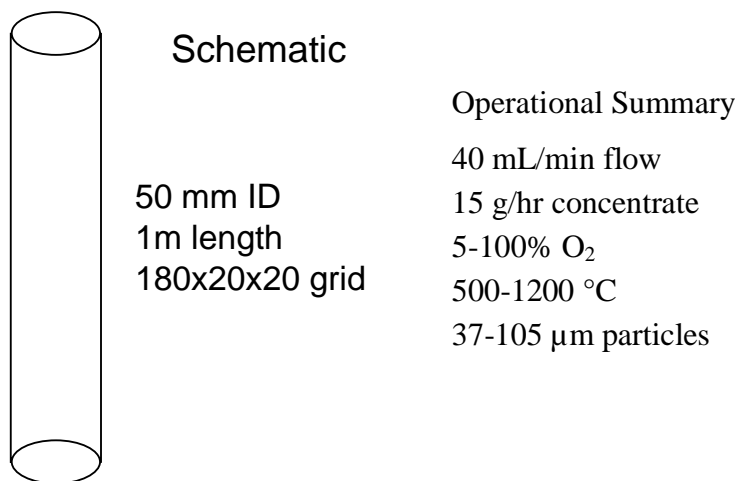


Figure 1 – Drop Tube Schematic and Operational Summary for Drop Tube Kinetics Simulations

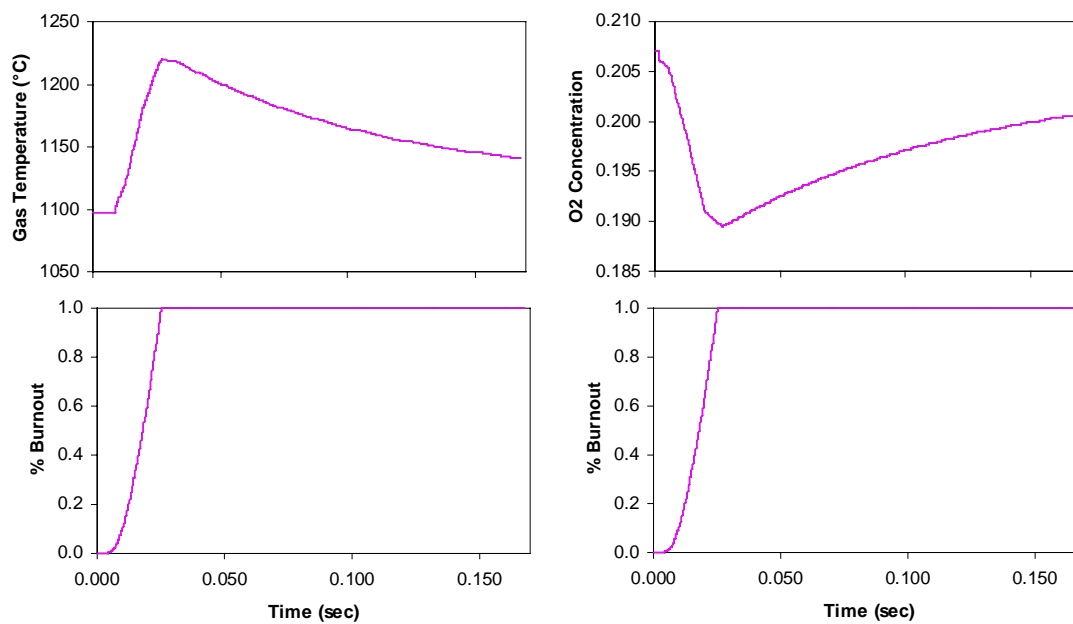


Figure 2 – Gas Temperature and Oxygen Concentration Variations along Particle Trajectories in a Drop Tube Furnace

Drop Tube Results

From the product recovered in the collection probe, the overall conversion and product composition can be determined. The overall reaction can then be determined from the feed and product compositions. With the overall reaction known, the kinetics can be obtained by trial and error using the code to match the calculated and measured conversions. Allowance is made in the program for the different temperature and oxidation histories of the individual particles. The use of this method to calculate the pre-exponential constant and activation energy for the chalcopyrite results of Jorgensen [6] are shown in Figure 3. Jorgensen reported both sulfur loss and temperature profiles obtained by two-color optical pyrometry. These figures summarize the concentrate reaction behavior based on a pre-exponential factor of $A = 3.5 \text{ m/sK}$ and an activation energy of $E = 7.0 \times 10^7 \text{ J/kmol}$. The results show reasonable agreement over the ranges considered. The kinetic parameters used in the figures were obtained by first fixing the activation energy and varying the pre-exponential factor (2 m/sK to 5 m/sK), then by fixing the pre-exponential factor and varying the activation energy ($2 \times 10^7 \text{ J/kmol}$ to $3 \times 10^7 \text{ J/kmol}$). By obtaining the best fit of the data, allowance is made for the oxygen depletion surrounding the particles both on the rate of reaction and the particle temperature.

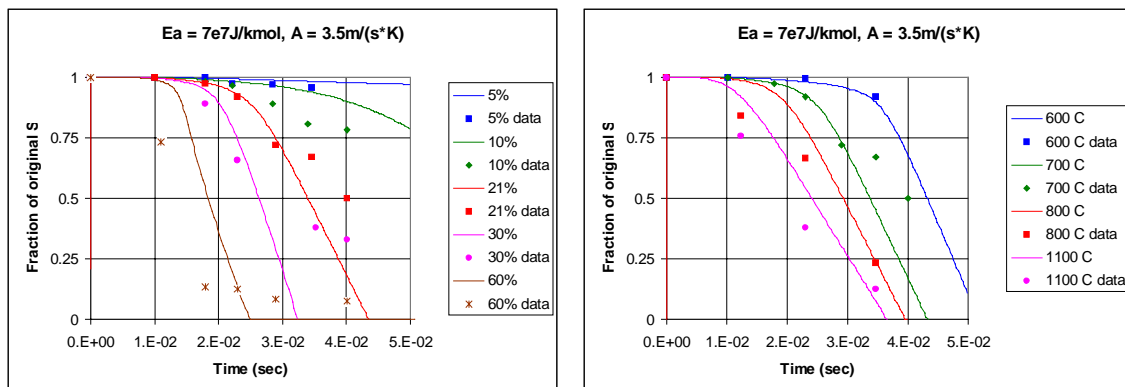


Figure 3 – Comparison of Drop Tube O₂ (left) and Temperature (right) Predictions and Measurements for Kinetic Rates Based on $E_a = 7.0 \times 10^7 \text{ J/kmol}$ and $A = 3.5 \text{ m/(sK)}$

REACTION SHAFT STUDY

Reaction Shaft Approach

Results of the drop tube kinetic study were used to model chalcopyrite concentrate reactions in the reaction shaft of an industrial copper flash smelting process. The three-dimensional model included flow down the reaction shaft (8 meters long by 6.5 meters diameter) and into the settler. More than 470,000 computational cells were

used in the model. The refinement of the computational cells was biased toward the burner region of the shaft as this is where the most complex flows occur and where the initial concentrate-gas mixing and the reactions occur. The furnace bath was modeled as a flat, smooth surface at a height approximating the bath height in the furnace.

Chalcopyrite concentrate particles (93.9% by weight) ranging in size from 11 to 75 μm were introduced into the shaft along with larger silica flux particles (6.1% by weight). The pre-exponential factor of $3.5 \text{ m}^3/(\text{sK})$ and activation energy of $7.0 \times 10^7 \text{ J/kmol}$ determined in the drop tube study were used along with local particle temperatures and local oxygen concentrations to determine global kinetic rates for the concentrate oxidation in the reaction shaft. Only sulfide oxidation and oxygen capture were considered in the particle reactions. The flux particles participated thermally but were treated as chemically inert. Gas flow in the shaft was provided by air enriched to 55% O_2 . Particle loading for the system was 2.24 (weight ratio of particles to gas flow).

Reaction shaft computations included turbulent gas flow, gas-phase chemical reactions, turbulent particle dispersion, heterogeneous sulfide oxidation and oxygen capture (Fe_xO_y reactions), particle deposition and convective and radiative heat transfer between gas, particles and shaft surfaces. Eight different size concentrate and flux particles were modeled as a series of particle clouds originating at 64 different locations in the shaft burner, resulting in 512 different disperse cloud trajectories being tracked throughout the shaft. Particle results presented here represent cloud mean properties for a given trajectory.

Reaction Shaft Results

Predicted reaction shaft results indicate several trends in shaft flow characteristics and concentrate reactions. The most significant of these include trends in shaft flow patterns, particle distribution, and concentrate sulfur evolution.

The flow field inside the shaft is characterized by a strong downward flow along the centerline of the shaft (i.e., below the burner) and recirculation zones with upward flow at the outer radius of the shaft around approximately three-quarters of the shaft circumference. The other one-quarter of the shaft on the uptake shaft side of the furnace does not exhibit a recirculation flow but rather a downward flow from the centerline towards the wall. The main jet of gas and particles flowing down the centerline does not spread sufficiently to directly impinge the shaft side walls. These flow patterns are illustrated schematically in Figure 4.

The flow patterns in the shaft are created by the central jet splashing on the bath surface and spreading radially outward. In regions open to the settler, the radial flow exits the shaft into the settler whereas in other regions, the flow recirculates back up along the shaft walls before being re-entrained into the core jet flow. There is also a small recirculation zone along the shaft centerline directly below the burner. This type of

recirculation zone is commonly observed for flow around bluff bodies with shapes similar to the base of the burner.

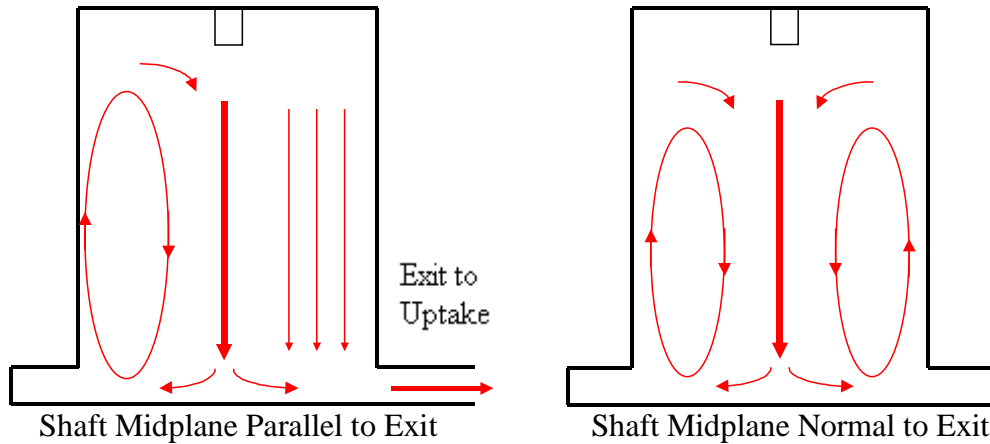


Figure 4 – Schematic of Reaction Shaft Flow Field

The flow patterns in the shaft have a significant effect on the trajectories of the concentrate particles. Concentrate particles that do not impact the bath at the bottom of the shaft follow different paths depending on where they enter the shaft. Concentrate particles exiting the burner on the uptake side of the shaft follow the gas flow down the shaft and out to the settler. Concentrate particles exiting the burner farthest from the uptake also tend to follow the local gas flow down the shaft and then recirculate back up the shaft side wall. These particles are eventually re-entrained into the core flow or pass around the core flow and move down to the uptake side of the shaft. Figure 5 illustrates two particle trajectories - one which exits the burner on the uptake side and flows directly out of the furnace and the other which exits the burner farthest from the uptake and recirculates up the shaft before exiting. Concentrate particles exiting the burner at 90 degree angles follow several different paths after entering the settler. Some move along the bath toward the uptake, some recirculate back up the shaft walls, and some are deposited on the settler walls and roof. The larger flux particles are less affected by the gas flow field due to their greater momentum. Essentially all flux particles impact the bath after flowing down the shaft; very few flux particles recirculate.

Analysis of predicted particle trajectories indicate a radial distribution based on particle size. Smaller particles tend to stay nearer the centerline whereas the larger particles tend to be farther from the centerline. Figure 6 shows the particle location in the center jet as function of particle size and radial distance from the shaft centerline. Plots are shown for particles at 1.4 m, 1.8 m, 3.0 m and 7.0 m from the shaft roof. The indicated radial distribution is attributed to a combination of the burner design and the jet aerodynamics. The burner causes all particles to be thrown outwards as they exit the burner. Below the burner recirculation zone, the jet flow moves back toward the shaft

centerline. Smaller particles are carried by the jet back toward centerline whereas the larger particles tend to be affected less by the air flow due to their greater inertia and remain farther from the centerline.

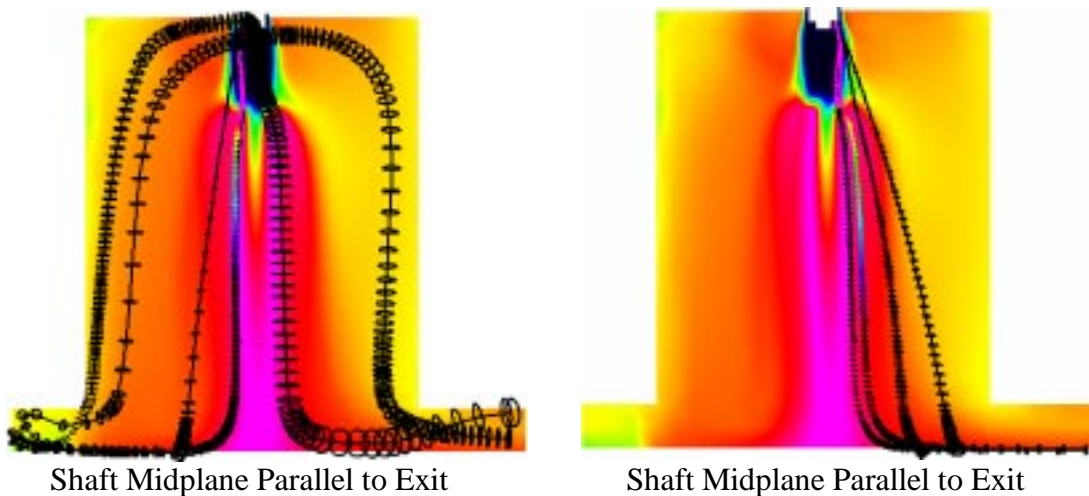


Figure 5 – Particle Trajectories for Three Particle Clouds Exiting Burner on the Side Farthest from the Uptake (left) and Four Particle Clouds Exiting on the Uptake Side (right)

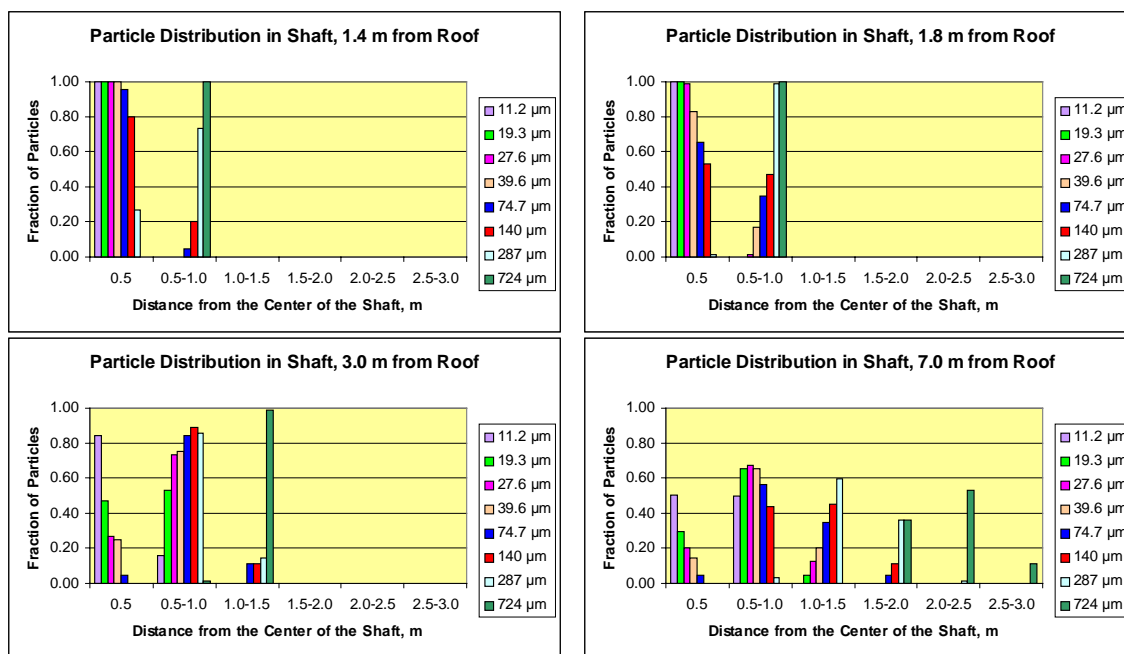


Figure 6 – Particle Distribution Characterized by Radial Distance from Shaft Centerline at Four Distances from the Shaft Roof

The differences in particle trajectories can impact the sulfur evolution of the concentrate because the different size particles experience different local stoichiometries, temperatures and oxygen levels. Sulfur evolution is also affected by the size of the concentrate particles. Figure 7 plots the sulfur remaining in the concentrate as a function of particle size and axial position in the shaft. The plots indicate that some larger particles react sooner, i.e., closer to the burner, than smaller particles. This is due to the larger particles following trajectories to oxygen rich and hot gas regions whereas smaller particles go to a cooler and lower oxygen environment directly under the burner. Overall however, smaller particles react to a greater extent than the larger particles. This is due primarily to the amount of initial sulfur in different size particles, but is also be affected by the different local environments experienced by the particles along different trajectories.

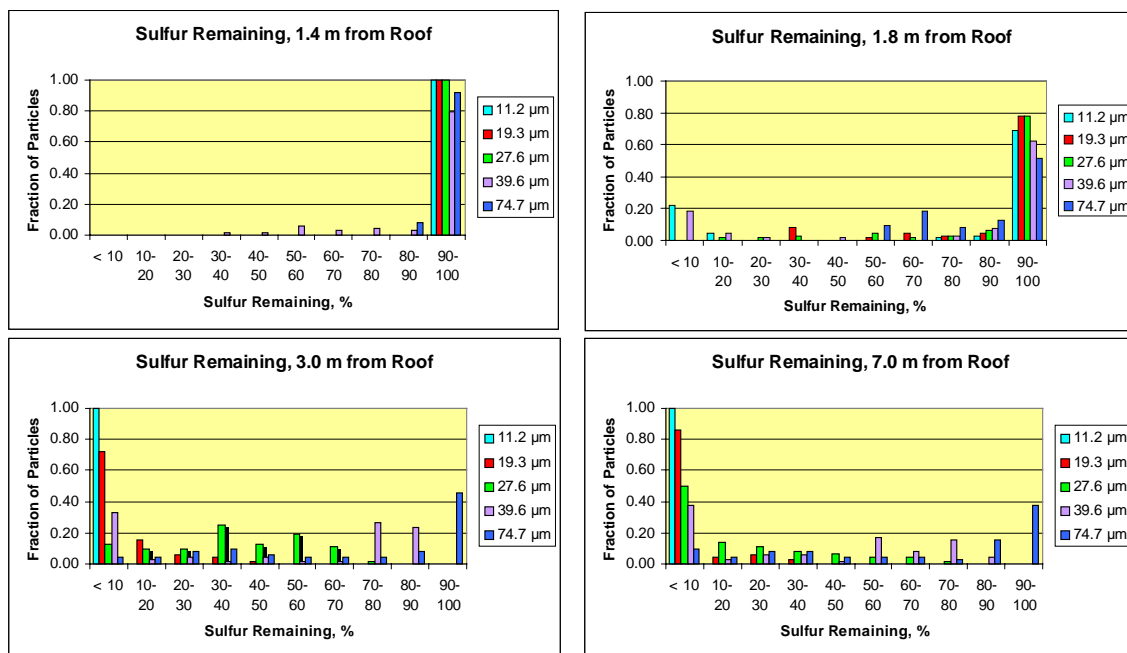


Figure 7 – Particle Sulfur Evolution Characterized by Remaining Sulfur at Four Distances from the Shaft Roof

Time history results of two concentrate cloud trajectories are plotted in Figure 8 and Figure 9. The plots include 28 μm and 40 μm diameter particles, respectively, and show the sulfur mass fraction, local gas-phase O₂ concentration, particle temperature and local gas temperature as a function of particle residence time. The residence time scale for each plot is focused in the region where the majority of each particle reaction occurs. Note that the residence times of the two plots should not be directly compared due to the different trajectories followed by the particle clouds. The two clouds originate from the same burner position but follow slightly different trajectories in the reaction shaft due to

the different particle momentum and mixing characteristics. Results of the concentrate reactions can be summarized as follows:

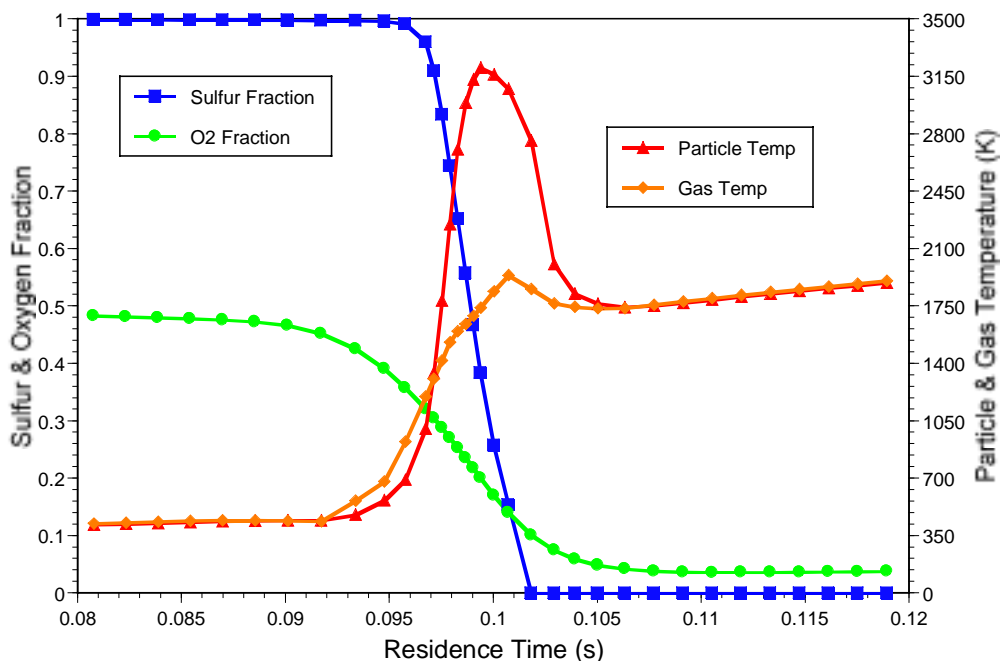


Figure 8 – Time - Temperature - Composition History for 28 μm Diameter Particle

- Peak concentrate temperatures are much higher than the local gas temperatures. This is due to the release of energy from chemical reactions occurring more rapidly than the transfer of energy from the particle via convective and radiative transfer. This behavior occurs during peak sulfide oxidation where there is both sufficient O_2 available for oxidation and sufficiently high particle temperatures to promote rapid oxidation rates. As shown in Figure 5, once the sulfur oxidation is completed the particle reaches a thermal equilibrium with the local gas flow and the particle temperature tracks the local gas temperature. Obviously the predicted peak temperatures are a function of the kinetic parameters used as well as the local gas temperature (heat transfer gradient), oxygen concentration, and radiant heat exchange with shaft walls and surrounding particles.
- The sulfur oxidation rate depends on both temperature and oxygen levels. Figure 9 illustrates particle behavior when the local O_2 concentration decreases before the sulfide oxidation is completed. In this case, after about 0.115 seconds, the local O_2 concentration has decreased so much that the sulfide oxidation rate is significantly reduced (as evidenced by the decreased slope of the sulfur mass fraction curve). The sulfide oxidation continues at a reduced rate because the particle temperature is still high and there is still some oxygen available. During this reduced oxidation period,

the particle temperature remains higher than the local gas temperature due to the continued liberation of reaction energy at a rate faster than the particle heat transfer rate. The effect of local heat transfer is illustrated by the particle temperature profile mimicking the gas temperature profile. As the oxidation rate nears zero, the heat transfer tends to dominate and the temperatures become increasingly close.

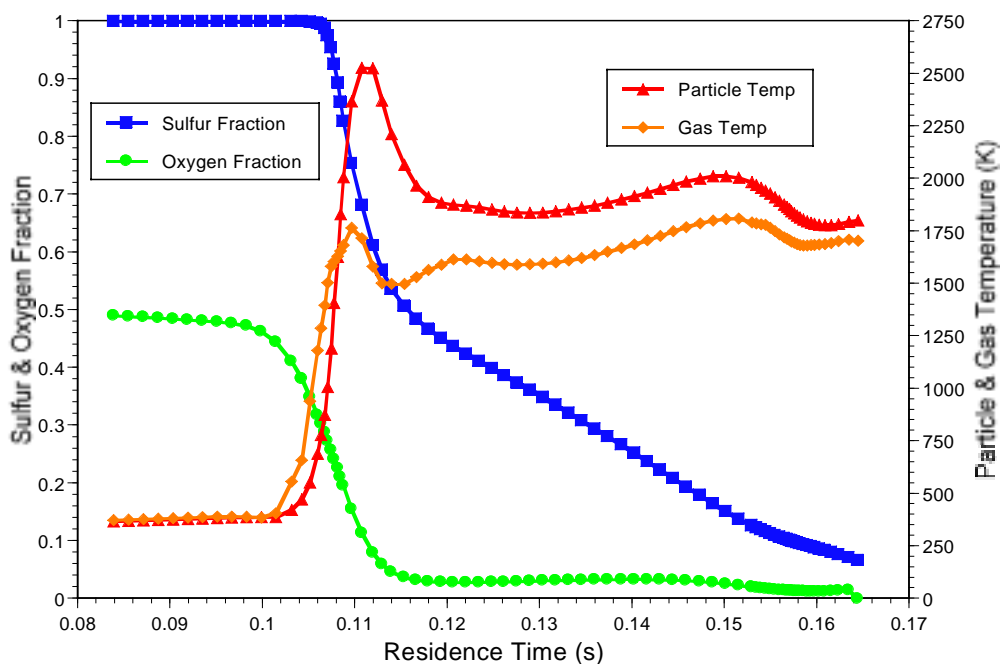


Figure 9 – Time - Temperature - Composition History for 40 μm Diameter Particle

- Insufficient heat transfer to the particle can limit oxidation rate. Both concentrate plots illustrate the lack of oxidation before the particles begin to heat up. Although there is sufficient O_2 in both cases, it is not until the local gas temperature increases that the particle temperature (lagging the gas) rises to a point where significant oxidation begins. Once oxidation begins, the particle temperature surpasses the gas temperature for reasons previously noted.
- The oxidation rates between different size particles are difficult to compare because the different trajectories followed by the particles provides different temperature/oxygen environments. The larger 40 μm particle does take longer to react and does not reach as high a peak temperature as the 28 μm particle, however this could be due to the difference in local gas temperature and O_2 concentration. For example, the gas temperature and O_2 concentration at 0.1 seconds is significantly different between the two trajectories, indicating that the two particles were in different locations in the shaft at that time in their respective trajectories.

Although not implemented in this model, the prediction of particle time-temperature-composition histories can provide a basis for characterizing particle fragmentation and agglomeration events, which affect dust loading, and can provide a basis for estimating the iron oxide states of deposits.

SUMMARY

A reacting CFD code was used to determine kinetic parameters for a chalcopyrite concentrate and to apply the parameters to simulation of the concentrate oxidation in the reaction shaft of a copper flash smelting furnace. The kinetic parameters were determined from simulations in a drop tube furnace and correlation with experimental drop tube data. From the drop tube simulations a self-consistent, single particle model, including a simple mechanism describing the chemistry of chalcopyrite, has been developed that accurately tracks the species, mass, momentum, and energy transfer between reaction shaft gas and chalcopyrite particles during combustion.

These results indicated that numerical simulations are a valuable tool for determining accurate kinetics from existing data regardless of sample size, as long as conditions are such that kinetic limitations to overall rate are significant. Application of the kinetic parameters to the simulation of concentrate reactions in a reaction shaft showed that concentrate temperature and sulfur loss could be predicted as a function of the local environment in the shaft. Concentrate temperatures were shown to exceed local gas temperatures during sulfide oxidation and to mimic the gas temperature at other times. Concentrate reactions (i.e., oxidation rates) were seen to depend on local heat transfer, oxygen availability and particle temperature.

Shaft gas flow patterns were shown to affect particle trajectories, which in turn could affect sulfur evolution. Recirculation zones in the shaft caused some smaller particles to recirculate back up into the shaft. A radial distribution of particles was predicted as a function of particle size with smaller particles nearer the shaft centerline and larger particles farther from the centerline. Sulfur evolution was also shown to be a function of particle size as nearly all smaller particles lost all their sulfur whereas many of the largest concentrate particles still retained 30-40% of the original sulfur.

Although limited in scope, the model developed under this program can provide several useful insights into shaft behavior. The ability to evaluate the sulfur evolution of the concentrate provides a basis for evaluating performance of different shaft designs and operating conditions. Additionally, the prediction of particle time-temperature-composition histories can provide a basis for characterizing particle fragmentation and agglomeration events, which affect dust loading, and can provide a basis for estimating the iron oxide states of deposits on shaft walls or in the bath.

REFERENCES

1. L.D. Smoot and P.J. Smith, Coal Combustion and Gasification, Plenum Press, NY, NY, USA, 1985.
2. Y.B. Hahn and H.Y. Sohn, "Radiative Heat Transfer in a Flash Smelting Furnace," Flash Reaction Processes, Center for Pyrometallurgy, Univ. Missouri-Rolla, Rolla, MO, USA, 1988, 287-317.
3. Y. Kim, "Studies of the Rate Phenomena in Particulate Flash Reaction Systems: Oxidation of Metal sulfides," Doctoral dissertation, Columbia University, 1986, 179.
4. A. Warczok, T.A. Utigard, W Mroz and J. Kowalczyk, "Oxidation of Copper Sulfide Minerals in Suspended State," EPD Congress, J.P. Hager, Ed., The Minerals, Metals, & Materials Society, Warrendale, PA, USA, 1992, 729-744.
5. T. Ahokainen, A. Jokilaakso, J. Vaarno and J. Järvi, "Modelling Chalcopyrite Combustion Together with Fluid Flow Simulation", Int. Conf. on CFD in Mineral & Metal Processing and Power Generation, CSIRO, Australia, 1997, 213-221.
6. F.R.A. Jorgensen, "Single-particle Combustion of Chalcopyrite," Proc. Australas. Inst. Min. Metall., No. 288, 1983, 37-46.