# Modeling of the Reduction Stage During the Continuous Refining of Copper in a Packed Bed Reactor

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**Abstract:**

The refining of blister copper, is a traditional and essential operation during the pyrometallurgical production of anodic copper from sulphide concentrates, however, higher energy costs and environmental standards regarding fugitive combustion gas emissions are becoming increasingly stringent mainly because batch technologies have been widely used.

This study corresponds to the modeling of the reduction stage of a novel technology for continuous refining of blister copper at laboratory scale taking into account the mass and momentum transport as well as deoxidation reaction that occurs in graphite surface. The study considers four parameters: the initial oxygen concentration in copper, the packed bed height, the furnace outlet diameter and, the diameter of spheres. Results allow visualizing the copper flow and oxygen concentration inside the crucible and mainly verifying that is possible to achieve a product of anodic copper with oxygen values below 1500 [ppm].

**Keywords:** Pyrometallurgy, Blister copper, Anodic copper, Continuous Refining, Reduction stage, Packed bed reactor, CFD.

## 1. Introduction

Throughout history, the copper production by pyrometallurgical processes has been carried out mostly in discontinuous or batch systems. In recent decades new continuous technologies have been developed but focused only on smelting and converting operations leaving aside the last one before casting, the fire refining.

In 2002 the DIMin (Department of Mining Engineering of Chile University) and H.V. Lira smelter of ENAMI (National Mining Corporation of Chile) developed a novel process based on the continuous refining of molten blister copper in two cylindrical packed bed furnaces in cascade. The blister, which come from converting contains around 100 and 5000 [ppm] of dissolved sulfur and oxygen, respectively, the first furnace, containing a refractory packed bed has the function of removing the sulfur until about 25 [ppm] as $SO_2$ by blowing air in countercurrent, while the second furnace, containing a coal or coke packed bed that of reducing the oxygen from 10000 to around 1500 [ppm] as CO, $CO_2$ and $H_2O_{(g)}$.

Today, the process has been materialized in the technology of a pilot industrial plant and its projection presents both investment and operating costs lower than those of the traditional rotatory refining furnace one. Besides it is characterized by increasing the kinetics of refining and decreasing the amount of fugitive combustion gas emissions.

The purpose of the present work was to model the reduction stage of this technology at a laboratory scale in order to obtain design and operational optimum scaled parameters. Figure 1 represents a s chematic drawing of reduction packed bed reactor of the pilot industrial plant.

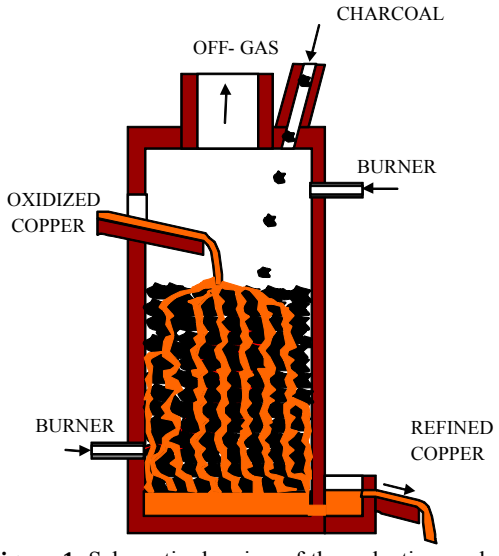



**Figure 1.** Schematic drawing of the reduction packed bed reactor of the pilot industrial plant.

The experimental array at laboratory scale is shown at Figure 2, it consists of a graphite crucible where 600 [gr] of oxidized copper is poured on different packed bed arrangements of graphite spheres to reduce its dissolved oxygen.

The modeling allowed investigating the profiles of oxygen concentration and copper flow during the reduction stage inside the reactor, this represents essential information to find optimal operational conditions for the actual pilot-industrial reactor and for the future industrial one.

## 2. Multiphysics Modeling

The mathematical complexity of the system with high temperature fluids, made it necessary to build a simplified laboratory prototype for modeling and after on scaled its results to the industrial process. Spherical packed beds were used because their geometry is feasible to build in computer using a wide variety of published algorithms and because porosity and reaction areas values are well known.

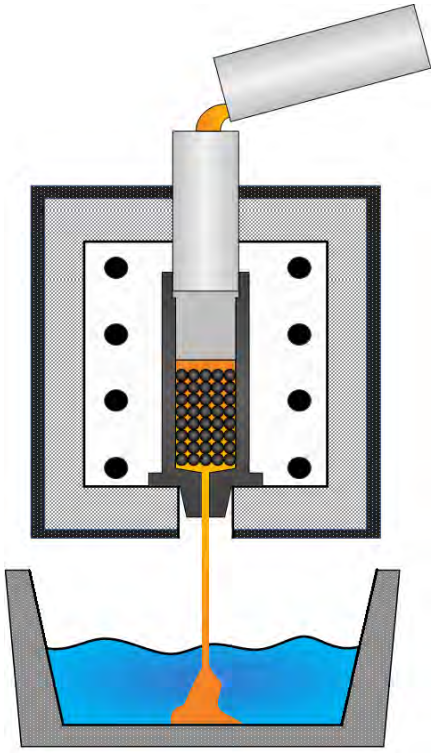
### 2.1 Geometry

The geometry considers a random mono-sized spherical graphite packed bed in a cylindrical container ($D_{in}$=4.5 [cm]) with a stationary gravitational flow of oxidized copper. The copper level inside the crucible is constant.

The 3D packed bed geometry was created with a soft spherical algorithm [1] in MATLAB using three different: sphere diameters ($d_p$= 1.608, 0.993 and 0.784 [cm]), bed heights ($h_{bed}$ =10, 7.5 and 5 [cm] approximately) and copper height ($h_{copper}$= 11.2, 8.4 and 5.7 [cm]). For convention $h_{bed}$ was the maximum sphere center z-coordinate in packed bed and $h_{copper}$ was an arbitrary value near to $h_{bed}$ (Table 3).

The bottom of the crucible was build following the laboratory prototype dimensions with diverse outlet diameters depending on simulation ($D_{out}$= 0.3, 0.2 and 0.12 [cm]).

The final geometry was exported to COMSOL Multiphysics using the Livelink for MATLAB. Figure 3 shows three created packings with different sphere diameters in COMSOL.



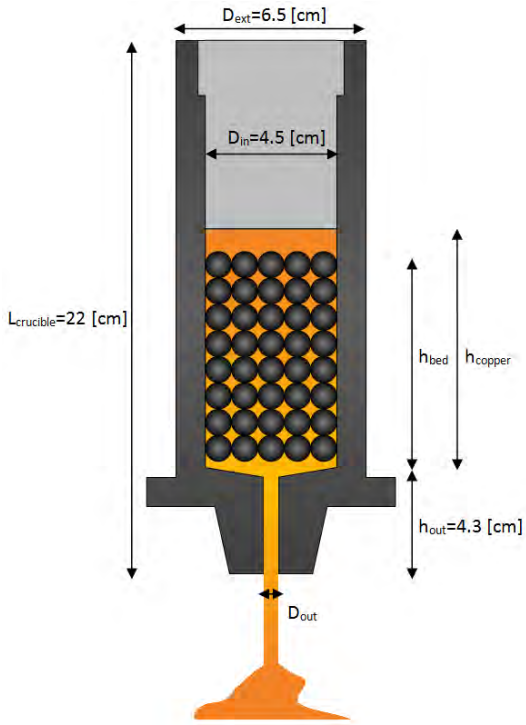


**Figure 2**. Schematic drawing of the experimental array at laboratory scale.

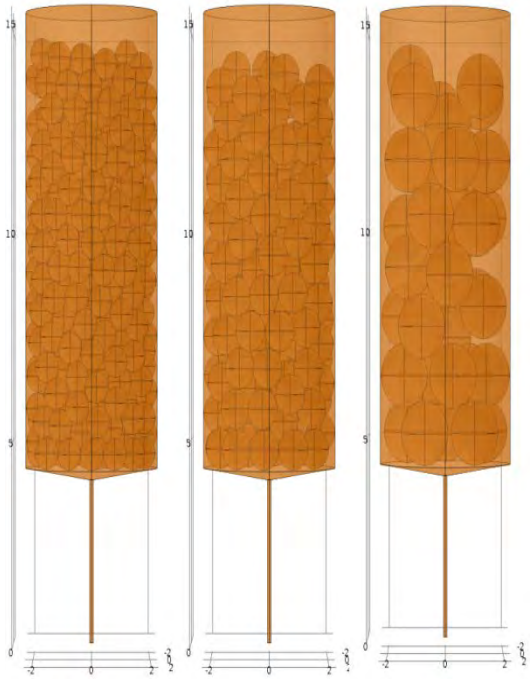


**Figure 3**. 3D packed bed geometry with the three different sphere diameters.

### 2.2 Governing Equations

Mass transport phenomena of oxygen in liquid copper were modeling with the stationary diffusion - convection equation:

$$\nabla \cdot (-D\nabla \mathrm{c}) + u\nabla \mathrm{c} = 0 \qquad (1)$$

According to the literature [2, 4, 7, 8], reduction of oxygen in liquid copper with graphite or carbon implies the following chemical reactions:

$$\mathrm{O_{(Cu)}} + \mathrm{C_{(s)}} \rightarrow \mathrm{CO_{(g)}} \qquad (2)$$
$$\mathrm{O_{(Cu)}} + \mathrm{CO_{(g)}} \rightarrow \mathrm{CO_{2(g)}} \qquad (3)$$
$$\mathrm{C_{(s)}} + \mathrm{CO_{2(g)}} \rightarrow 2\mathrm{CO_{(g)}} \qquad (4)$$

At operating temperature 1473 [K] between the studied concentration range, the kinetic follows a first order law regarding to oxygen concentration:

$$R = -k \cdot c \qquad (5)$$

In the model, this chemical reaction term was implemented using the Robin boundary condition [5] for all graphite surfaces, i.e. spheres and crucible:

$$-\hat{n} \cdot (-\mathrm{D}\nabla c + uc) = R \qquad (6)$$

The fluid dynamics was simulated by 3D stationary incompressible *Navier Stokes* equations neglecting the inertial term in free flow (Stokes flow), because are expected low velocities due to large viscosity of liquid copper and small length-scales of the flow in the packed bed:

$$0 = \nabla \cdot [-pI + \mu(\nabla u + (\nabla u)^T)] + \rho g \qquad (7)$$
$$\nabla \cdot u = 0 \qquad (8)$$

The value for velocity in the inlet boundary condition was estimated and measured using a closed circuit of stationary water flow in the laboratory prototype [6] for each different packed bed arrangement and outlet diameter.

To convert the value of the flow rate of water to copper, the Reynolds number was calculated and kept constant. The detail of the other boundaries and parameters used in simulations are shown in Tables 1 and 2.

**Table 1:** Parameters used in simulation

| Parameter | Value/Expression | Ref. |
|---|---|---|
| $\boldsymbol{T}$: Temperature | 1473 [K] | - |
| $\boldsymbol{\rho}$: Density of Liquid Cu | 7900 [kg/m$^3$] (at 1473 K) | |
| $\boldsymbol{\mu}$: Viscosity of Liquid Cu | $4.3 \cdot 10^{-3}$ [kg/(m·s)] (at 1473 K) | |
| $\boldsymbol{k}$: Kinetic constant | $3.3 \cdot 10^{-4}$ [m/s] (Rods at 1473 K) | [2] |
| $\boldsymbol{D}$: Diffusion Coefficient of Oxygen in liquid Cu | $6.9 \cdot 10^{-4} e^{(-12900/RT)}$ [m$^2$/s] (1000° to 1350°C) | [3] |
| $\boldsymbol{g}$: Acceleration of gravity | 9.8 [m/s$^2$] | - |

**Table 2:** Boundary settings

| Boundary | Expression |
|---|---|
| Inlet | • Normal inflow velocity $u = -u_0\hat{n}$ (Values of $u_0$ in table 3)<br>• Concentration: $c = c_0$ (10000, 6000 and 4000 [ppm]) |
| Surface of Spheres | • No Slip: $u = 0$<br>• Surface Oxygen Reaction: $-\hat{n} \cdot (-\mathrm{D}\nabla c + uc) = R = -kc$ |
| Crucible Surface | • No Slip: $u = 0$<br>• Surface Oxygen Reaction: $-\hat{n} \cdot (-\mathrm{D}\nabla c + uc) = R = -kc$ |
| Outlet | • Pressure: $p = p_0 = 0$ (atmospheric)<br>• No viscous Stress: $[\mu(\nabla u + (\nabla u)^T)] \cdot \hat{n} = 0$<br>• Outflow: $-\hat{n} \cdot D\nabla c = 0$ |

### 2.3 Solution

The finite element tool COMSOL Multiphysics 4.2 was used for setting up the model, generating an appropriate mesh to solve the model equations. The sphere diameters in each packed bed were reduced by about 2 % in order to avoid mesh failures in the vicinity of the sphere contact points [5]. The built in mesh generator of COMSOL with the "extra fine" setting for the mesh size was then used to create an unstructured tetrahedral mesh that consists of approximately between 2,000,000 and 6,000,000 mesh elements depending on simulation. The calculations were carried out on computer with a Core i7-3930K processor with six cores of 3.2 GHz and a total memory of 64 GByte.

## 3. Results and Discussion

Figure 4 shows that a spatially distributed in homogeneous flow profile is formed due to the irregular arrangement of the graphite spheres. Channeling through the cavities between particles can be observed and the flow profile is absolutely laminar for this and every simulation inside the packed bed with a maximum Reynolds number value of 175 for simulation with $D_{out}$= 0.3 [cm]. On the other hand, for crucible outlet due to drastically reduction of sectional area, Reynolds numbers reach its maximum values, depending on simulation between 773 and 2624.

As expected for a p acked bed, values for stationary copper mass flow ($F_{Cu}$) depend on sectional outlet area and pressure drop, this means that with smaller outlet diameter and smaller sphere sizes, the frictional loss is greater and thus the flow decreases. However, if packed bed height grows the hydrostatic column is higher and consequently the copper flow increases.

Relating to Oxygen concentration in final anodic copper, it can be said that is possible to achieve values below 1500 [ppm] ensuring copper quality with this technology. Figures 4, 5 and 6 show different concentration slices and we can see that outlet concentration decreases when: bed is higher (Figure 4), outlet diameter is smaller (Figure 5) and the same for sphere size (Figure 6). This can be explained due to oxygen reduction is proportional to the chemical reaction surface and because is inversely proportional to the retention or residence time.

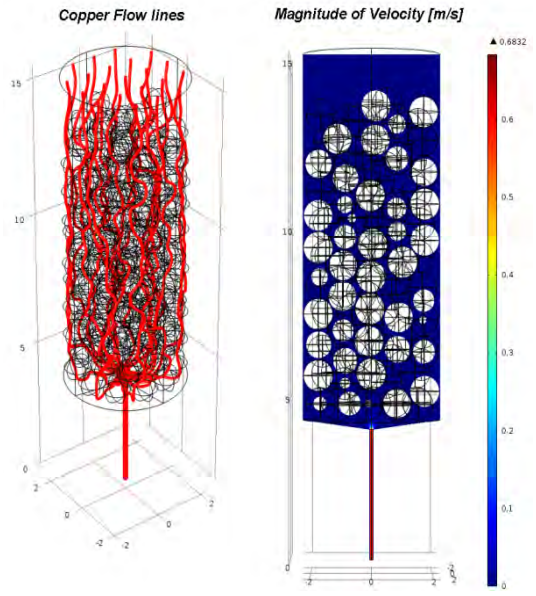



**Figure 4**. Copper flow lines and magnitude of velocity for a packed bed with: $d_p$=0.993 [cm], $D_{out}$= 0.12

[cm], $u_0$=3.49x10$^{-3}$ [m/s], $h_{bed}$= 10.35 [cm] and $h_{copper}$= 11.2 [cm].

**Table 3:** Initial values and results of each simulation

| Simulation | $u_0 \cdot 10^{-4}$ [m/s] | $d_p \cdot 10^{-3}$ [m] | $h_{bed}$ [m] | $h_{copper}$ [m] | $D_{out} \cdot 10^{-3}$ [m] | $Re_{out}$ | $F_{Cu}$ [kg/hr] | $c_0$ [ppm] | $c_f$ [ppm] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.03 | 16.08 | 0,1048 | 0,1120 | 1.2 | 1.249 | 17.7 | 10000 | 3912 |
| 2 | 3.49 | 9.93 | 0,1035 | 0,1120 | 1.2 | 1.082 | 15.4 | 10000 | 1646 |
| 3 | 3.20 | 7.84 | 0,1059 | 0,1120 | 1.2 | 992 | 14.2 | 10000 | 658 |
| 4 | 2.81 | 7.84 | 0,0776 | 0,0840 | 1.2 | 871 | 12.3 | 10000 | 1060 |
| 5 | 2.49 | 7.84 | 0,0532 | 0,0570 | 1.2 | 773 | 11.1 | 10000 | 1865 |
| 6 | 9.56 | 7.84 | 0,1059 | 0,1120 | 2 | 1.779 | 41.7 | 10000 | 2097 |
| 7 | 21.2 | 7.84 | 0,1059 | 0,1120 | 3 | 2.624 | 92.4 | 10000 | 3749 |
| 8 | 21.2 | 7.84 | 0,1059 | 0,1120 | 3 | 2.624 | 92.4 | 6000 | 2267 |
| 9 | 21.2 | 7.84 | 0,1059 | 0,1120 | 3 | 2.624 | 92.4 | 4000 | 1511 |

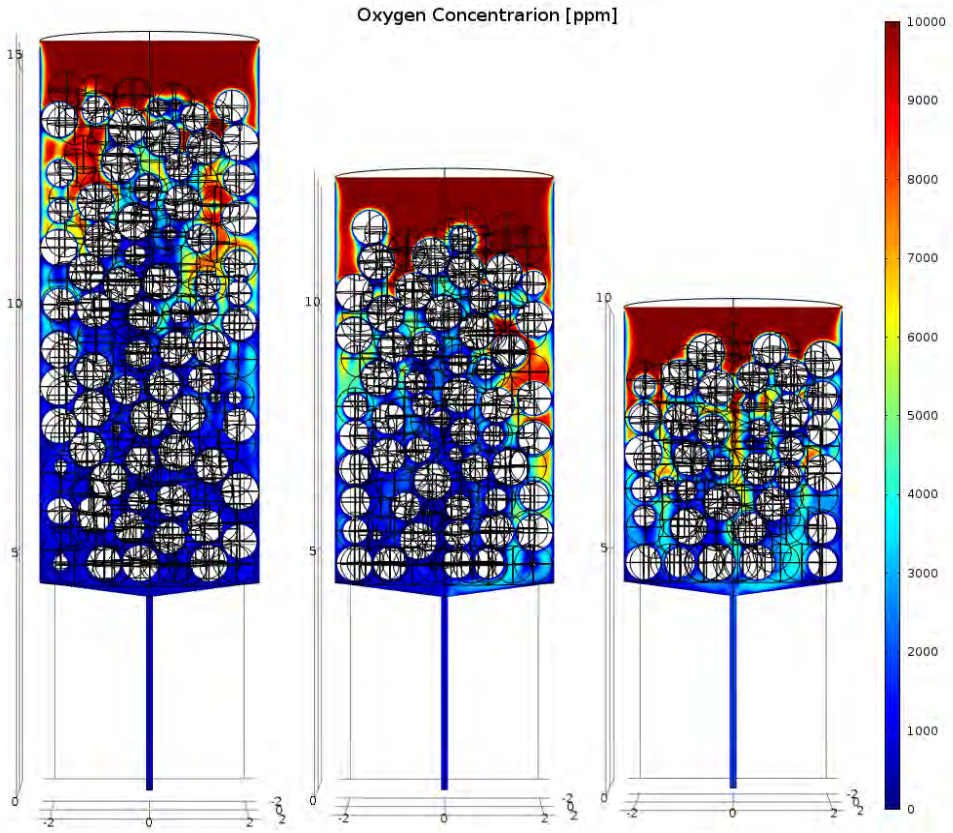



**Figure 5**
Oxygen concentration for three different packed bed heights with: $d_p$=0.784 [cm], $c_0$= 10000 [ppm] and $D_{out}$= 0.12

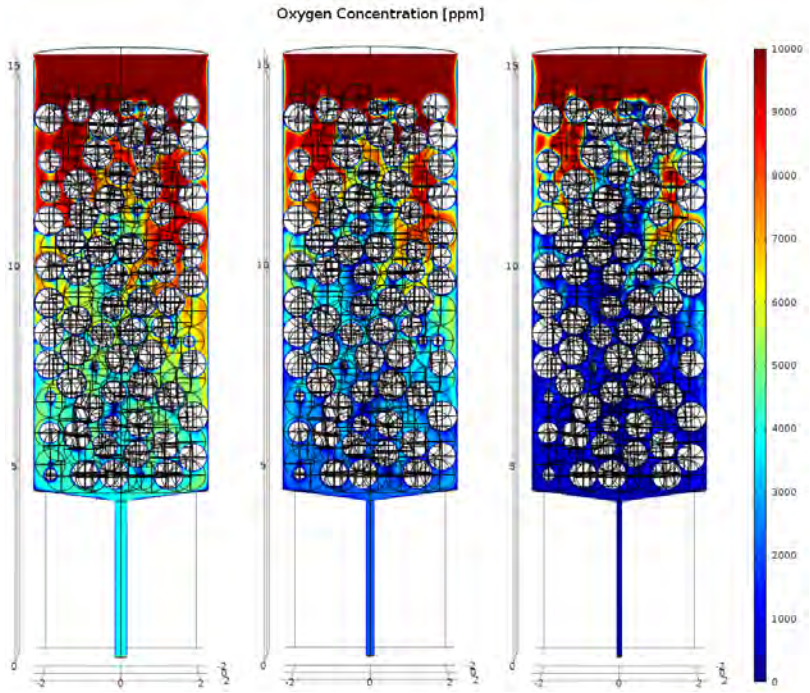



**Figure 6**. Oxygen concentration for three different outlet diameter with $d_p$=0.784 [cm], $h_{bed}$= 10.35 [cm], $c_0$=10000 [ppm] and $h_{copper}$= 11.2 [cm]. $D_{out}$= 0.3, 0.2 and 0.12 [cm] respectively.

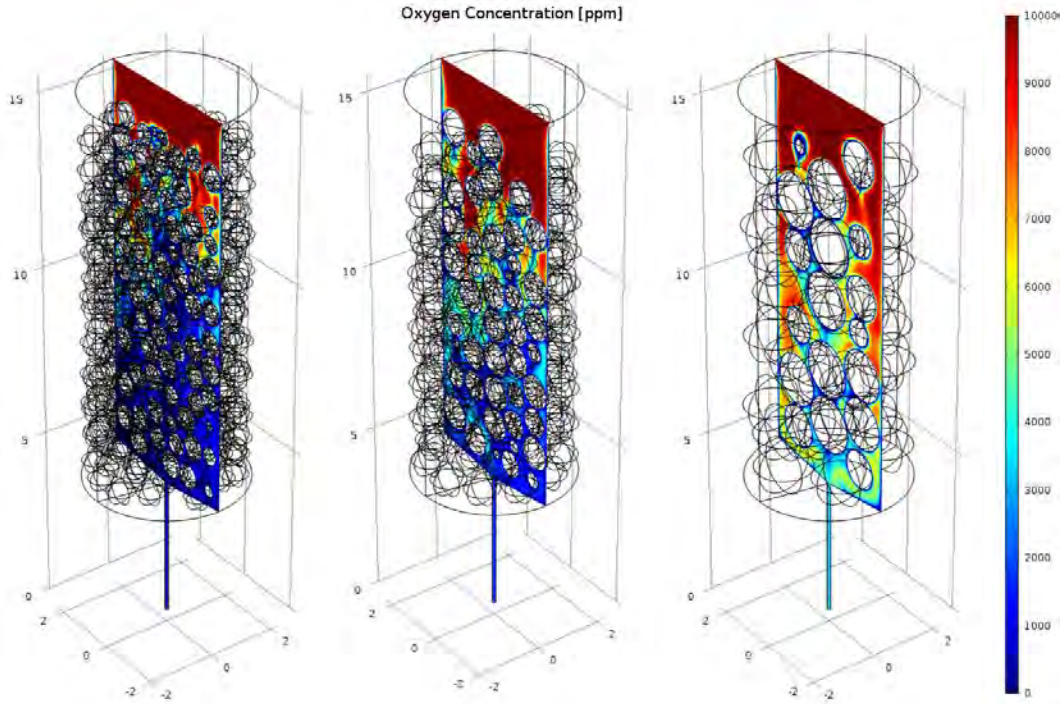



**Figure 7**. Oxygen concentration for three different sphere diameters with $h_{bed}$= 10.35 [cm], $c_0$=10000 [ppm], $h_{copper}$= 11.2 [cm] and $D_{out}$= 0.12 [cm]. $d_p$=0.784, 0.993, 1.608 [cm] respectively.

All the aforementioned was better visualized performing a multivariable linear regression with data in Table 3, where dimensionless and classical operational variables were used:

$$C_f = \beta_1.C_0 + \beta_2.\left(\frac{h_{bed}}{D_{in}}\right) + \beta_3.\left(\frac{D_{in}}{d_p}\right) + \beta_4.F_{Cu} \quad (9)$$

$$F_{Cu} = \frac{u_0.\pi.D_{out}^2.\rho}{4} \quad (10)$$

$C_f$ and $C_0$ are the final and initial concentrations respectively in [ppm], $F_{Cu}$ is the mass copper flow in [kg/hr] and $\beta_i$ is a r egression constant. The $\beta$ values can be seen in table below:

**Table 4:** Estimation constants

| | |
|---|---|
| $\beta_1$ | 0.5184 |
| $\beta_2$ | -337.1734 |
| $\beta_3$ | -688.8404 |
| $\beta_4$ | 41.0106 |

The determination coefficient ($R^2$) for this approximation was equal to 0.97, thus equation 9 could be a useful tool for planning future simulations in the range of studied variables.

It is important to note that all the simulations considered in this work are going to be validated with experimental tests in the laboratory prototype. In future studies irregular shape particles in packed beds and charcoal are considered to be used in order to bring our simulations closer to the industrial reality.

## 4. Conclusions

It was possible to build and simulate in COMSOL the laboratory packed bed reactor prototype for the reduction stage during the continuous refining.

The fluid dynamics of copper inside the reactor was completely laminar for all the simulations, whereas in outlet region with higher values of the opening diameter, the Reynolds number slightly reaches the turbulent regime.

In was possible to verify the dependence of each of the analyzed variables on the oxygen content into anodic copper by linear regression. The obtained values at the outlet were industrially accepted.

## 5. References


1. W.I. Salvat, N.J. Mariani, G.F. Barreto, O.M. Martinez, An algorithm to simulate packing structure in cylindrical containers, *Catalysis Today*, **Vol 107-108**, pp 513-519 (2005).

2. T. Marin, A. Warczok, G. Riveros, T. Utigard, G. Plascencia, Kinetics of liquid copper reduction with graphite, *Canadian Metallurgical Quarterly*, **Vol 46**, No 4 pp 379-384 (2007).

3. Karl E. Oberg, Lawrence M. Friedman, William M. Boorstein, Robert A. Rapp, The Diffusivity and Solubility of Oxygen in Liquid Copper and Liquid Silver From Electrochemical Measurements, *Metallurgical and Materials Transactions B*, **Vol 4**, No 1 pp 61-67 (1973).

4. E. B . Ten, I. B. Badmazhapova, B. M. Kimanov, Kinetics of the carbon reduction of liquid copper, *Steel in Translation*, **Vol 38**, No 7 pp 533-536 (2008).

5. S . Schnittert, R. Winz, E. von Lieres, Development of a 3 D model for packed bed liquid chromatography in micro-columns, *EMS Third UKSim European Symposium on Computer Modeling and Simulation*, pp 193-197 (2009).

6. P. Urzúa, *Modelo físico predictivo de la fluido dinámica de lecho empacado para conversión continua*, Chemical Engineer Thesis, Chile University (2008).

7. TMS, G. Riveros, A. Warczok, L. Voisin, T. Marin, Factors affecting the rate of copper reduction during copper refining, *Metallurgical and Materials Processing Principles and Technologies,* **Vol 2**, Chapter: Copper III (2003).

8. Haiyan Gao, Da Shu, Jun Wang, Baode Sun, Manufacturing OFC with recycled copper by charcoal-filtration, *Materials Latters,* **Vol 60**, Issue 4, pp 481-484 (2006).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