# MODELING OF AN INDUSTRIAL COPPER LEACHING AND ELECTROWINNING PROCESS, WITH VALIDATION AGAINST EXPERIMENTAL DATA

Bernt Lie<sup>1</sup>, Tor Anders Hauge<sup>2</sup> <sup>1</sup>Telemark University College, P.O. Box 203, 3901 Porsgrunn, Norway <sup>2</sup>Xstrata Nikkelverk, Kristiansand, Norway *Bernt.Lie@hit.no, THauge@xstratanickel.no* 

## Abstract

The Cu process at Xstrata Nikkelverk, Kristiansand, Norway is considered. This process is an important part of the nickel refinery. With the current operation, the level of variation in measured quality variables is larger then desired, and it is of interest to reduce this variation through improved control. The process is characterized by time delays, multivariable behavior, and nonlinearities, and it is thus a candidate for model based control. A new dynamic model with 39 states is formulated based on steady state total mass balances and dynamic specie balances, and includes reaction kinetics in the leaching sections and use of an electrochemical description of the electrowinning section. Utilizing the simplifying assumptions and available measurements, steady states as well as the currency efficiency of the electrolvsis process are computed by solving linear equations for the electrowinning section. For the leaching sections, steady state balances with a second order reaction rate constitute overdetermined multivariable polynomial equations; solving a corresponding least squares problem yields the steady states and the reaction rate constant with a small error norm. Additional measurements from the process validate the steady states of the model. Using the steady states as initial values, steps in the 3 inputs indicate that the model is nonlinear and strongly coupled. The simulations confirm suggestions for signs of steady state gains as well as typical poles.

**Keywords:** Copper production, Leaching, Electrowinning, Dynamic model

# **1** Introduction

## 1.1 Background

In this paper, we consider a chlorine leaching and electrowinning process which is an important part of the nickel refinery of Xstrata Nikkelverk in Kristiansand, Norway.

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The raw material comes from a granulated matte produced by Xstrata's Sudbury smelter in Canada, BCL's smelter in Botswana, as well as custom feed from other sources. The granulated matte is crushed to a very fine powder (Calcine) and then transported to the chlorine leaching plant. The Calcine contains mostly CuO, but also impurities of Ni, Co, Fe and other metals; this Calcine is leached in a sulfuric acid mixture, the mixture is then pumped through filters where nondissolved metal oxides are removed, and then through scrap columns where other impurities (Ag, Te, and B) are cemented and removed. Next, the slurry, or electrolyte, is pumped to an electrowinning section where electrolysis is used to produce Cu metal at the cathode and  $H_2SO_4$  and  $O_2$ at the anode. The resulting anolyte from the electrowinning is then pumped back to the Cu leaching section.

Important quality measurements throughout the Cu process are the concentrationS of Cu and H<sub>2</sub>SO<sub>4</sub> (free and so-called *available*  $H_2SO_4$ ). The most important inputs to manipulate these quantities are the mass flow of Calcine to the leaching section, the volumetric flow of fresh H<sub>2</sub>SO<sub>4</sub> to the leaching section, and the volumetric flow of recirculated anolyte to the leaching section. The quality measurements represent a challenge to control due to time delays, strong couplings, and nonlinearities. In order to reduce the variation of the quality measurements, it is of interest to consider model based multivariable controllers such as Model predictive control (MPC). As the model is intended for control purposes, this will be reflected in the structure and choice of simplifying assumptions. A model intended for model based control, should be validated against process knowledge and measurements to assess its quality.

#### 1.2 Previous work

The process and its operation is described in [1] - [4]. Based on these, a M.Sc. project [5] was carried out with some initial work on dynamic models of the system. In [6], an attempt is made to develop a linear empirical

model of the system, and some useful ideas of expected signs in the transfer matrix are given. Still, no thorough dynamic mechanistic model of the system exists. General methods for formulating balance equations are given in e.g. [7] and [8], systematic methods to describe systems with chemical reactions is given in e.g. [8], basic reaction kinetics is discussed in e.g. [9], while e.g. [10] gives a thorough description of modeling of electrochemical systems.

#### **1.3** Structure of paper

In section 2, a description of the process is given, including a discussion of the flow sheet, how the process operates, and a discussion of inputs and outputs and their expected correlations. In section 3, a mechanistic model is developed. In section 4, the model is analyzed both from a steady state perspective and from a dynamic perspective. Finally, in section 5 a discussion is given and some conclusions are drawn, together with indications for future work.

## 2 **Process description**

#### 2.1 Flow sheet

The Xstrata copper production plant consists of 4 sections, fig. 1 (all figures and tables are given after the References section): (i) the *slurrification* section where the particulate raw material Calcine containing metal oxides such as CuO is slurrified by mixing it with recycled anolyte, (ii) the *leaching* section where sulfuric acid  $H_2SO_4$  is added to the slurry in order to leach the solid copper oxide into copper sulfate CuSO<sub>4</sub>; copper sulfate is a salt of the sulfuric acid, (iii) the *purification* section where various components are removed from the slurry: remaining copper oxide in the first filter, other metals are cemented in scrap columns and filtered out in the second filter, and (iv) the *electrowinning* section where copper sulfate is electrolyzed to release solid copper at the cathode and oxygen gas at the anode.

#### 2.2 **Process operation and assumptions**

#### 2.2.1 Slurrification and leaching sections

The raw material Calcine is transported into the *slurrification* tanks using several screw conveyors. The velocity of the first conveyor determines the mass flow rate  $\dot{m}_{\rm c}$ . The mass flow rate is calculated at a point close to the slurrification tanks using measured weight and conveyor velocity. Thus, there is a substantial time delay between the point where the mass flow rate is determined and the point where it is calculated. The mass fraction  $x_{\rm c,Cu}$  of copper in the form of copper oxide, is

analyzed three times per week and thus may represent a significant unknown disturbance between the samples.

In the process, all tanks are assumed to be perfectly mixed. The liquid content in all tanks is assumed to be constant, and the liquid density  $\rho$  is assumed to be the same everywhere. The scrap columns are assumed to perfectly cement unwanted metals, and filters are assumed to perfectly remove unwanted material in the purification section.

The Calcine needs to be slurrified in order to ease the transport and enable the leaching of copper. This is done by mixing the Calcine with recycled liquid from the electrowinning section, so-called *anolyte*: the anolyte is assumed to consist of copper sulfate CuSO<sub>4</sub> and sulfuric acid H<sub>2</sub>SO<sub>4</sub> dissolved in water. The Calcine is slurrified in two tanks, with volumes  $V_{\rm s}^{(1)}$  and  $V_{\rm s}^{(2)}$ , respectively, where  $j \in \{{\rm CuO}, {\rm CuSO}_4, {\rm H_2SO}_4\}$ . With perfect mixing, the mass concentrations of the species j are  $\rho_{{\rm s},j}^{(k)} = m_{{\rm s},j}^{(k)}/V_{\rm s}^{(k)}$ . Assuming constant density  $\rho$  in the liquid, the volumetric flow out of both of the volumes  $V_{\rm s}^{(k)}$  are  $\dot{V}_{{\rm s}2\ell} = \dot{V}_{{\rm e}2{\rm s}}$ .

The *leaching* section consists of 5 tanks in series, where the first tank with constant liquid volume  $V_{\ell}^{(1)}$  receives the slurrified mixture in flow  $\dot{V}_{s2\ell}$  and an acid feed  $\dot{V}_a$  with a mass concentration  $\rho_{a,H_2SO_4}$  of sulfuric acid. In the second tank in the leaching section, another acid feed containing hydrogen chloride (HCl) is added (not shown in fig. 1); the purpose is to enable the removal of additional metals in the slurry. Since we do not consider these other metals (perfectly removed in the purification section), and since this flow is negligible, we simply neglect this second acid feed in our description. In the fifth leaching tank,  $V_{\ell}^{(5)}$ , spilled water is added with a rate  $\dot{V}_{w2\ell}$ ; the purpose is to return water/liquid that is spilled throughout the process, and thus to enable keeping the liquid levels constant .

In the slurrification and leaching tanks, copper oxide undergoes the following irreversible stoichiometric reaction

$$CuO + H_2SO_4 \xrightarrow{k} CuSO_4 + H_2O;$$

since the temperature of the slurry is more or less constant, k is constant. With specie vector  $\sigma$  given by

$$\sigma^T = \left( \begin{array}{ccc} \text{CuO} & \text{H}_2\text{SO}_4 & \text{CuSO}_4 & \text{H}_2\text{O} \end{array} \right),$$

the stoichiometric matrix (vector) of the reaction is

 $\nu_{\sigma} = \begin{pmatrix} -1 & -1 & 1 & 1 \end{pmatrix}$ 

and the reaction can be written as

 $0 \rightarrow \nu_{\sigma} \sigma$ .

The reaction is assumed to be elementary, and the resulting molar reaction kinetics  $\mu$  is thus

$$\mu = k c_{\rm CuO} c_{\rm H_2SO_4}$$

Since the remaining of the description will be mass based, we use that

$$c_j = \frac{1}{M_j} \rho_j$$

where  $M_j$  is the molar mass and  $\rho_j$  is the mass concentration to arrive at

$$\mu = \frac{k}{M_{\rm CuO}M_{\rm H_2SO_4}}\rho_{\rm CuO}\rho_{\rm H_2SO_4}.$$
 (1)

The vector of reaction rates for the species,  $\tilde{r}_{\sigma}$  (mol based), is related to  $\mu$  by

$$\tilde{r}_{\sigma} = \nu_{\sigma}^T \mu.$$

We don't really care about the water content, so let us denote the first three elements of  $\sigma$  by  $\bar{\sigma}$ . Similarly, let  $\nu_{\bar{\sigma}}$  denote the first three elements of  $\nu$  and  $\tilde{r}_{\bar{\sigma}}$  denote the three first elements of  $\tilde{r}_{\sigma}$ . Then

$$\tilde{r}_{\bar{\sigma}} = v_{\bar{\sigma}}^T \mu.$$

To get rates in mass basis,  $\hat{r}_{\bar{\sigma}}$ , we need to multiply the rate of each specie by the molar mass  $M_j$ . Let

$$M_{\bar{\sigma}} = \operatorname{diag} \left( \begin{array}{cc} M_{\mathrm{CuO}} & M_{\mathrm{H}_2\mathrm{SO}_4} & M_{\mathrm{CuSO}_4} \end{array} \right).$$

Then

$$\hat{r}_{\bar{\sigma}} = M_{\bar{\sigma}} v_{\bar{\sigma}}^T \mu. \tag{2}$$

#### 2.2.2 Purification section

In the *purification* section, all remaining copper oxide is assumed to be removed in the first filter (filter presses). Thus, after these filter presses, there is no more copper oxide, and the leaching reaction is nonexistent for the remaining of the purification and electrowinning processes. Thus, the leaching reaction only takes place in the slurrification volumes  $V_{\rm s}^{(k)}$  and the leaching volumes  $V_{\ell}^{(k)}$ : these are the only volumes where the concentration of copper oxide is nonzero. The remaining purification section consists of 3 buffer tanks with volumes  $V_{\rm pb}^{(k)}$  before and after a group of scrap columns and filters which are used to remove the remaining undesired metals. The scrap columns are essentially filled with copper that helps in cementing these unwanted metals for removal in a subsequent filter bank (indicated by  $\dot{m}_{\rm MeO,o}$  in the flow sheet). Although the scrap columns have considerable volume, the void fractions  $\varepsilon_{\rm ps}^{(k)}$  are tiny so that these columns have fast dynamics.

#### 2.2.3 Electrowinning section

In the *electrowinning* section, the main unit is the electrolysis/electrowinning tank of volume  $V_{ew}$ ; in reality, this consists of a large number of small electrolysis tanks in parallel. The fluid at the exit of the electrolysis

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tanks is known as anolyte. The outlets from the electrolysis tanks are combined in a manifold, and is then sent to a *mixing* tank with volume  $V_{\rm em}$  before recycling the anolyte at rate  $\dot{V}_{\rm e2s}$  to the slurrification unit. There is also a certain bleed  $\dot{V}_{\rm em2bl}$  from the mixing tank to avoid the build-up of inerts/impurities. A flow  $\dot{V}_{\rm w2em}$  of make-up water is added to the mixing tank to replace spilled water. Because the fluid out of the purification section and into the electrowinning section has an unsuitably high concentration of copper sulfate, this fluid is *diluted* by a recycling  $\dot{V}_{\rm em2d}$  of anolyte from the postelectrolysis mixing tank of volume  $V_{\rm em}$  into the dilution tank of volume  $V_{\rm ed}$ .

The electrolysis can be described as follows: although the content of the liquid has been described as copper sulfate  $CuSO_4$  and sulfuric acid  $H_2SO_4$ , these molecules will in fact exist partially disassociated, i.e. in some equilibrium

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$
  
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}.$$

In addition, water is partially disassociated:

$$H_2O \rightleftharpoons H^+ + OH^-$$

This mixture is an electrical conductor, and by injecting an electric currency I through the mixture from the *anode* to the *cathode*, the following happens: (i) electrons  $e^-$  flow into the mixture at the cathode; electric currency is defined as positive in the opposite direction of the actual direction of electron flow, (ii) at the cathode, copper is neutralized:

$$\operatorname{Cu}^{2+} + 2e^{-} \to \operatorname{Cu}^{(s)},$$

(iii) at the anode, a similar amount of electrons are pulled out to uphold the currency *I*:

$$SO_4^{2-} + H_2O \rightarrow H_2SO_4 + \frac{1}{2}O_2^{(g)} + 2e^{-1}$$

Since the number of copper molecules produced in a time interval dt,  $\delta N_{\rm Cu}$ , is equal to half the number of electrons involved,  $\delta N_{\rm e^-}$ , we have  $\delta N_{\rm Cu} = \frac{1}{z_{\rm Cu}} \delta N_{\rm e^-}$  where  $z_{\rm Cu} = +2$  is the valency of copper. The production rate of copper (molecules produced per time unit) thus satisfies  $N_{\rm Cu,o} = \frac{1}{z_{\rm Cu}} \dot{N}_{\rm e^-}$ . The flow of electrons  $\dot{N}_{\rm e^-}$  can be converted to molar flow of electrons  $\dot{n}_{\rm e^-}$  by multiplying with Avogadro's number  $N_{\rm A}$ , and molar flow of electrons can be converted to charge flow  $\dot{Q}$  with units Coulomb/second by multiplying with Faraday's constant C,  $\dot{Q} = C \cdot \dot{n}_{\rm e^-}$ ; clearly  $\dot{Q} = I$ , i.e. the currency in Ampere. Finally, we find the mass based production rate of copper, i.e. the amount of copper pulled *out* of the electrowinning tank, by using the mo-

lar mass  $M_{\rm Cu}$  of copper:

$$\dot{m}_{\mathrm{Cu,o}} = M_{\mathrm{Cu}}\dot{n}_{\mathrm{Cu,o}} = M_{\mathrm{Cu}}N_{\mathrm{A}}\dot{N}_{\mathrm{Cu,o}}$$

$$= M_{\mathrm{Cu}}N_{\mathrm{A}}\frac{1}{z_{\mathrm{Cu}}}\dot{N}_{\mathrm{e}^{-}}$$

$$= M_{\mathrm{Cu}}\frac{1}{z_{\mathrm{Cu}}}\frac{1}{C}\underbrace{CN_{\mathrm{A}}\dot{N}_{\mathrm{e}^{-}}}_{\dot{Q}=I} = \frac{M_{\mathrm{Cu}}}{z_{\mathrm{Cu}}C}I.$$

Here it should be noted that if I is in units A = C/s, then  $\dot{m}_{Cu,o}$  is in units g/s. With the more convenient time unit of *hours*, then a unit conversion must be included.

In practice, the injected currency I will have some leakage/stray currency, i.e. not all of it will go through the mixture. It is thus in practice necessary to include a currency efficiency factor  $\eta$  to get the final expression

$$\dot{m}_{\rm Cu,o} = \eta \frac{M_{\rm Cu}}{z_{\rm Cu}C} I.$$

By comparing the anode reaction, we see that there is a simultaneous *production* of  $H_2SO_4$  in the electrowinning tank of

$$\dot{m}_{\rm H_2SO_4,g} = \frac{M_{\rm H_2SO_4}}{M_{\rm Cu}} \dot{m}_{\rm Cu,o}.$$

In reality, the electrolysis takes place in 8 groups of electrolysis units, where the units in each group are in series wrt. the currency (but in parallel wrt. electrolyte flow). Thus

$$\dot{m}_{\rm Cu,o} = \sum_{j=1}^{8} \eta_j \frac{M_{\rm Cu}}{z_{\rm Cu}C} I_j = \frac{M_{\rm Cu}}{z_{\rm Cu}C} \sum_{j=1}^{8} \sum_{k=1}^{n_j} \eta_j^k I_j^k.$$

In groups 1–3, the currency is the same,  $I_{\rm e}$ , in groups 4–6 the currency is the same,  $I_{\rm w}$ , while in group 7 the currency is  $I_{\rm w}+I_7$  and in group 8 the currency is  $I_{\rm e}+I_8$ . The number of tanks in each group is  $n_j$ . The efficiencies  $\eta_j$  are not known in detail, and it makes more sense to operate with an overall currency efficiency  $\bar{\eta}$ 

$$\sum_{j=1}^8 \sum_{k=1}^{n_j} \eta_j^k I_j^k = \bar{\eta} \bar{I}$$

which means that

$$\dot{m}_{\rm Cu,o} = \bar{\eta} \frac{M_{\rm Cu}}{z_{\rm Cu}C} \bar{I},\tag{3}$$

where

$$\bar{I} = (n_1 + n_2 + n_3 + n_8) I_e + (n_4 + n_5 + n_6 + n_7) I_w + n_7 I_7 + n_8 I_8.$$
(4)

The overall efficiency  $\bar{\eta}$  is less than unity, not only due to leakage currency, but also due to that at all times, some electrolysis tanks are out of production.

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2.3 System inputs and outputs

The purpose of the process is to produce copper. The most direct way to do this, is to control the currency I in the electrolysis process; this is what is done. However, electrolyzing copper in the tanks of volume  $V_{ew}$ will also remove copper sulfate; if no action is taken, the content of the system may end up in imbalance. The control problem thus is to ensure a suitable chemical composition in the system. Three measurements are used to measure the chemical composition of the system:  $y_1$  is the mass concentration  $\rho_{\mathrm{H}_2\mathrm{SO}_4}$  of sulfuric acid into the electrowinning section (so-called free sulfuric acid),  $y_2$  is the mass concentration  $ho_{\mathrm{Cu}|\mathrm{CuSO}_4}$  of copper in the form of copper sulfate at the outlet of the electrolysis tanks, while  $y_3$  is the mass concentration of so-called available sulfuric acid at the outlet of the electrolysis tanks; available sulfuric acid is the combined concentration of sulfates, assumed to be sulfuric acid, denoted  $\rho_{\mathrm{H}_2\mathrm{SO}_4}^{\equiv}$ .

For  $y_1$  we thus have

$$y_1 = \rho_{\rm pb, H_2SO_4}^{(3)}.$$
 (5)

 $y_2$  and  $y_3$  takes measurements from the analyte after the manifold at the outlet from the electrolysis tanks. The measurement technique used to measure  $y_2$  measures the copper part  $\rho_{\rm ew,Cu|CuSO_4}$  of the copper sulfate content  $\rho_{\rm ew,CuSO_4}$ , hence

$$y_2 = \rho_{\rm ew,Cu|CuSO_4} = \frac{M_{\rm Cu}}{M_{\rm CuSO_4}} \rho_{\rm ew,CuSO_4}.$$
 (6)

Finally,  $y_3$  measures the sulfate content and assumes that it is pure sulfuric acid,  $\rho_{\text{ew},\text{H}_2\text{SO}_4}^{\equiv}$ . Thus

$$y_3 = \rho_{\mathrm{ew},\mathrm{H}_2\mathrm{SO}_4}^{\equiv} = \rho_{\mathrm{ew},\mathrm{H}_2\mathrm{SO}_4} + \rho_{\mathrm{ew},\mathrm{H}_2\mathrm{SO}_4|\mathrm{CuSO}_4}$$

or

$$y_3 = \rho_{\text{ew},\text{H}_2\text{SO}_4}^{\equiv} = \rho_{\text{ew},\text{H}_2\text{SO}_4} + \frac{M_{\text{H}_2\text{SO}_4}}{M_{\text{CuSO}_4}}\rho_{\text{ew},\text{CuSO}_4}.$$
(7)

To control these 3 outputs, the following three control variables are used:  $u_1$  is the mass feed rate of Calcine,

$$u_1 = \dot{m}_c, \tag{8}$$

 $u_2$  is the volumetric recirculation of anolyte,

$$u_2 = \dot{V}_{e2s},\tag{9}$$

while  $u_3$  is the volumetric feed rate of acid,

$$u_3 = V_{\mathbf{a}}.\tag{10}$$

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#### 2.4 Operational experience

Typical values for manipulated inputs u, disturbances w, and measurements y are given in Tab. 1.

From operation of the system, some additional values known from experience are listen in Tab. 2.

Less systematic experience is available for the dynamics of the system, but Tab. 3 indicates the sign of the transfer matrix, as well as whether the system is assumed to have integrators using the notation  $s \mid T$ where s is the steady state sign and T is the T indicates the time constant.

## **3** Process model

The following dynamic models can now be formulated:

## 3.1 Overall mass balances

Using the total mass balances under the assumption of *constant liquid density* and *constant liquid level* in each volume, leads to the following relationships:

$$\begin{array}{rcl} \dot{V}_{e2s} &=& \dot{V}_{s2\ell} \\ \dot{V}_{s2\ell} + \dot{V}_{a} &=& \dot{V}_{\ell,o}^{(1)} \\ \dot{V}_{\ell,o}^{(1)} + \dot{V}_{w2\ell} &=& \dot{V}_{\ell 2p} \\ \dot{V}_{\ell 2p} &=& \dot{V}_{p2e} \\ \dot{V}_{p2e} + \dot{V}_{em2d} &=& \dot{V}_{ed2w} + \dot{V}_{ed2m} \\ \dot{V}_{ed2m} + \dot{V}_{ew2m} + \dot{V}_{w2em} &=& \dot{V}_{em2d} + \dot{V}_{em2bl} + \dot{V}_{e2s} \\ \dot{V}_{ed2w} &=& \dot{V}_{ew2m} + \dot{V}_{vap}. \end{array}$$

We thus have 14 variable volumetric flow rates and 7 steady state mass balances to relate them, which means that we must specify 7 of the variables. Clearly, two of these are the manipulatable volumetric flow rates  $u_2 = \dot{V}_{e2s}$  and  $u_3 = \dot{V}_a$ . In addition, we will specify the following 5 flow rates:  $\dot{V}_{w2\ell}$ ,  $\dot{V}_{ed2m}$ ,  $\dot{V}_{em2d}$ ,  $\dot{V}_{vap}$ , and  $\dot{V}_{em2bl}$ ; these can be considered as disturbances. The remaining 7 volumetric flows can then be computed from the steady state mass balances.

#### 3.2 Slurrification and leaching sections

These sections involve the leaching reaction. A typical specie balance has the form

$$\frac{d\rho_{i,j}}{dt} = \frac{1}{V_i} \left( \dot{m}_{i,j,\mathrm{i}} - \dot{V}_{i,\mathrm{o}}\rho_{i,j} + M_j \hat{r}_{i,j} V_i \right)$$

where  $\rho_{i,j}$  is the mass concentration of specie  $j \in \{\text{CuO}, \text{CuSO}_4, \text{H}_2\text{SO}_4\}$  in each of the 7 tanks of the slurrification and leaching sections.  $\dot{m}_{i,j,i}$  is the total input mass flow of specie j to tank i, while  $\dot{V}_{i,o}$  is the total volumetric flow out of tank i.  $M_j$  is the molar

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mass of specie j,  $V_i$  is the volume of tank i, and  $\hat{r}_{i,j}$  is the reaction rate in tank i of specie j.

The result is 21 ordinary differential equation, one for each of the 3 species in the 7 tanks.

## 3.3 Purification section

The specie balances for the 6 volumes in the purification section (3 buffer tanks and 3 scrap columns) are similar to the balances for the slurrification and leaching sections, except that in this section we have only two species,  $j \in {CuSO_4, H_2SO_4}$  and there is no reaction rate,  $\hat{r}_{i,j} \equiv 0$ .

This adds 12 ordinary differential equations to the total model, one for each of the 2 species in the 6 tanks.

#### 3.4 Electrowinning section

The specie balances for the dilution tank and the mixing tank of the electrowinning section is similar to the balances for the purification section. For the electrolysis/*electrowinning* tank, we have

$$\frac{d\rho_{\text{ew},\text{H}_2\text{SO}_4}}{dt} = \frac{1}{V_{\text{ew}}} \left( \rho_{\text{ed},\text{H}_2\text{SO}_4} \dot{V}_{\text{ed}2\text{w}} -\rho_{\text{ew},\text{H}_2\text{SO}_4} \dot{V}_{\text{ew}2\text{m}} + \dot{m}_{\text{ew},\text{H}_2\text{SO}_4,\text{g}} \right)$$

$$\frac{d\rho_{\text{ew},\text{CuSO}_4}}{dt} = \frac{1}{V_{\text{ew}}} \left( \rho_{\text{ed},\text{CuSO}_4} \dot{V}_{\text{ed}2\text{w}} -\rho_{\text{ew},\text{CuSO}_4} \dot{V}_{\text{ed}2\text{w}} -\rho_{\text{ew},\text{CuSO}_4} \dot{V}_{\text{ew}2\text{m}} - \dot{m}_{\text{ew},\text{CuSO}_4,\text{o}} \right)$$

This adds 6 ordinary differential equations to the total model, one for each of the 2 species in the 3 tanks.

## 4 Simulation and validation

#### 4.1 Steady state model

A steady state analysis will give useful information about the process when combined with known operating conditions. It turns out that steady state analysis will give sufficient information both to find the unknown electrolysis efficiency  $\eta$  and the leaching reaction constant k, as well as the steady states of the system. In addition to the operating conditions of Tab. 1, we need the parameters in Tab. 4.

By formulating the steady state specie balances for the electrowinning section as well as the steady state total mass balances, and combining these with the operating conditions and parameters, we get a number of linear equations which enables us to find the steady state mass concentrations for the electrowinning system, as well as the mass flow rate of copper produced. Combining the mass flow rate of copper with the known currency enables us to find the currency efficiency  $\bar{\eta} = 0.77779$ .

For the slurrification and leaching sections, the element balances (sulphur and copper) are reaction invariant. This can be used to compute the exit concentration of copper oxide,  $\rho_{\ell,\text{CuO}}^{(5)}$  and the feed concentration of sulfuric acid,  $\rho_{a,\text{S}|\text{H}_2\text{SO}_4}$ . Next, formulating the 21 steady state specie balances yields 21 equations in 19 unknowns, the least squares method is used to determine the remaining 19 unknowns uniquely, including the reaction rate constant which is found to be  $k = 2.9637 \frac{1^3}{\text{molg h}}$ .

The resulting steady states are given in Tab. 5. These steady state values should be compared to the experience values in Tab. 2, which indicates that the steady state model is relatively accurate.

## 4.2 Dynamic model

In addition to the steady states of Tab. 5 and parameters of Tab. 4, we need the parameters of Tab. 6 (the void fractions are "guesstimates"). Fig. 2 show the results of a 50% increase (solid line) and a 50% decrease (dashdot line) in  $u_1$  ( $\dot{m}_c$ ) after 5 h, as well as the results of a constant input  $u_1$  (dotted). Fig. 3 show similar results for  $u_2$  ( $\dot{V}_{e2s}$ ), while Fig. 4 show similar results for  $u_3$  ( $\dot{V}_a$ ).

# 5 Discussion and conclusions

A dynamic model of the Xstrata copper production process has been developed, based on specie balances and total mass balances. Emphasis has been put on making the model consistent so that there is no artificial accumulation of mass in the system, and so that only available measurements/knowledge is used. Available measurements are combined with the steady state model, and from this the unknown parameters (currency efficiency  $\bar{\eta}$  and reaction rate constant k) as well as the steady state values are computed in a least squares fashion; the computed steady state values are useful as initial values in simulations.

The additionally measured values of Tab. 2 when compared to the computed steady states of Tab. 5 indicate that the model is relatively good in steady state. That the steady states reported in Tab. 5 are the true steady states, is validated by the steadiness of the dotted lines in Figs. 2 - 4.

Also, the suggested signs in Tab. 3 are confirmed by the dynamic simulations. Furthermore, by comparing the responses of positive and negative input steps, the simulations show that the model is nonlinear. Finally, although the dynamic simulations does not show true integration of the measured concentrations, the plots suggests some extremely slow modes which are approaching integration.

In conclusion, the responses of the developed model are quite similar to what was expected, and the model is a valuable first step in developing a control relevant model for the copper production process. No similar model is known from the literature.

Planned future work with the modeling of the copper production plant includes further validation based on transient measurement, investigation of parameter sensitivity (e.g. the void fractions of the scrap columns are uncertain), and a study on the possibility to reduce the order of the model. Next, implementation of the model with a state estimator is of interest, perhaps with online parameter estimation. Finally, it is of interest to study how the model can be used in model based controllers.

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Variable	Value
$y_1 = \rho_{\rm pb, H_2 SO_4}^{(3)}$	$26\mathrm{g/l}$
$y_2 = \rho_{\mathrm{ew,Cu} \mathrm{CuSO}_4}$	60  g/l
$y_3 = \rho_{\mathrm{ew},\mathrm{H}_2\mathrm{SO}_4}^{\equiv}$	$183\mathrm{g/l}$
$u_1 = \dot{m}_c$	$733  imes 10^4  \mathrm{g/h}$
$u_2 = \dot{V}_{e2s}$	$82  imes 10^3  \mathrm{l/h}$
$u_3 = \dot{V}_a$	500  l/h
$w_1 = \dot{V}_{w2\ell}$	1700  l/h
$w_2 = \dot{V}_{ed2m}$	$20 \times 10^3  \mathrm{l/h}$
$w_3 = \dot{V}_{em2d}$	$330 \times 10^{3}$ l/ h
$w_4 = \dot{V}_{\rm vap}$	500  l/h
$w_5 = \dot{V}_{em2bl}$	5100  l/h
$w_6 = x_{c,Cu}$	$0.63\mathrm{gCu}/\mathrm{gmass}$
$w_7 = I_e$	$9.34 \times 10^3 \mathrm{A}$
$w_8 = I_w$	$8.82\times10^3{\rm A}$
$w_9 = I_7$	$7.74 \times 10^3 \mathrm{A}$
$w_{10} = I_8$	$3.38 \times 10^3 \mathrm{A}$

Table 1: Known operating conditions for measurements  $y_j$ , manipulated inputs  $u_j$ , and disturbances  $w_j$ .

Table 2: Additional values of process variables, known from experience.

Variable	Value
$\rho_{\mathrm{a,H_2SO_4}}$	$1834{ m g/l}$
$ ho_{ m pb,Cu CuSO_4}^{(3)}$	$100\mathrm{g/l}$
$ ho_{ m ed,Cu CuSO_4}$	$70\mathrm{g/l}$
$\rho_{\rm em,H_2SO_4}$	$90.4{ m g/l}$

Table 3: Dynamic characteristics of transfer matrix, given as "sign of steady state gain | dynamics". Dynamics indicated by "I" denotes whether the system is expected to have an "integrator" (or possibly: slow time constant). A question mark indicates uncertainty. A zero indicates zero gain.

	$u_1$	$u_2$	$u_3$
$y_1$	$  $ $I$	+  ?	$+ \mid I$
$y_2$	+  I	0	0
$y_3$	0	0	$+ \mid I$



Figure 1: Detailed principle flow sheet for the industrial copper leaching and electrowinning process.

Variable	Value
$n = (n_1, \ldots, n_8)$	(76, 76, 52, 84, 84, 30, 8, 10)
$M_{ m H}$	$1 \mathrm{g/mol}$
$M_{\rm O}$	$16 \mathrm{g/mol}$
$M_{\rm Cu}$	$63.5\mathrm{g/mol}$
$M_{\rm S}$	$32\mathrm{g/mol}$
$z_{ m Cu}$	2
C	$9.65 \times 10^4  \mathrm{C  mol}^{-1}$

Table 4: Constants and parameters for the model.

Table 5: Steady states computed from steady state models.

$ \begin{array}{ll} \rho_{\rm s,CuO}^{(1)} = 58.6158{\rm g}/1 & \rho_{\rm s,CuSO_4}^{(1)} = 174.4265{\rm g}/1 & \rho_{\rm s,H_2SO_4}^{(1)} = 74.3260{\rm g}/1 \\ \rho_{\rm s,CuO}^{(2)} = 53.2891{\rm g}/1 & \rho_{\rm s,CuSO_4}^{(2)} = 185.1135{\rm g}/1 & \rho_{\rm s,H_2SO_4}^{(2)} = 67.7597{\rm g}/1 \\ \rho_{\ell,CuO}^{(1)} = 34.0256{\rm g}/1 & \rho_{\ell,CuSO_4}^{(1)} = 221.9917{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(1)} = 55.2208{\rm g}/1 \\ \rho_{\ell,CuO}^{(2)} = 23.8008{\rm g}/1 & \rho_{\ell,CuSO_4}^{(2)} = 242.5056{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(2)} = 42.6167{\rm g}/1 \\ \rho_{\ell,CuO}^{(3)} = 17.5975{\rm g}/1 & \rho_{\ell,CuSO_4}^{(3)} = 254.9513{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(3)} = 34.9698{\rm g}/1 \\ \rho_{\ell,CuO}^{(5)} = 10.538{\rm g}/1 & \rho_{\ell,CuSO_4}^{(5)} = 263.1366{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(4)} = 26{\rm g}/1 \\ \rho_{\ell,CuO}^{(5)} = 0{\rm g}/1 & \rho_{\ell,CuSO_4}^{(5)} = 263.25{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(5)} = 26{\rm g}/1 \\ \vdots & \vdots & \vdots \\ \rho_{\rm pb,CuO}^{(3)} = 0{\rm g}/1 & \rho_{\rm pb,CuSO_4}^{(3)} = 263.25{\rm g}/1 & \rho_{\rm pb,H_2SO_4}^{(3)} = 26{\rm g}/1 \\ \rho_{\rm ed,CuO} = 0{\rm g}/1 & \rho_{\rm pb,CuSO_4}^{(3)} = 173.48{\rm g}/1 & \rho_{\rm ed,H_2SO_4}^{(3)} = 90.402{\rm g}/1 \\ \rho_{\rm em,CuO} = 0{\rm g}/1 & \rho_{\rm em,CuSO_4}^{(3)} = 150.57{\rm g}/1 & \rho_{\rm em,H_2SO_4}^{(3)} = 88.9827{\rm g}/1 \\ \end{array}$		5 1	5
$\begin{array}{ll} \rho_{\rm s,CuO}^{(2)} = 53.2891{\rm g}/1 & \rho_{\rm s,CuSO_4}^{(2)} = 185.1135{\rm g}/1 & \rho_{\rm s,H_2SO_4}^{(2)} = 67.7597{\rm g}/1 \\ \rho_{\ell,CuO}^{(1)} = 34.0256{\rm g}/1 & \rho_{\ell,CuSO_4}^{(1)} = 221.9917{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(1)} = 55.2208{\rm g}/1 \\ \rho_{\ell,CuO}^{(2)} = 23.8008{\rm g}/1 & \rho_{\ell,CuSO_4}^{(2)} = 242.5056{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(2)} = 42.6167{\rm g}/1 \\ \rho_{\ell,CuO}^{(3)} = 17.5975{\rm g}/1 & \rho_{\ell,CuSO_4}^{(3)} = 254.9513{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(4)} = 34.9698{\rm g}/1 \\ \rho_{\ell,CuO}^{(4)} = 13.5176{\rm g}/1 & \rho_{\ell,CuSO_4}^{(4)} = 263.1366{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(4)} = 29.9405{\rm g}/1 \\ \rho_{\ell,CuO}^{(5)} = 10.538{\rm g}/1 & \rho_{\ell,CuSO_4}^{(5)} = 263.25{\rm g}/1 & \rho_{\ell,H_2SO_4}^{(1)} = 26{\rm g}/1 \\ \rho_{\rm pb,CuO}^{(1)} = 0{\rm g}/1 & \rho_{\rm pb,CuSO_4}^{(1)} = 263.25{\rm g}/1 & \rho_{\rm pb,H_2SO_4}^{(3)} = 26{\rm g}/1 \\ \vdots & \vdots & \vdots & \vdots \\ \rho_{\rm pb,CuO}^{(3)} = 0{\rm g}/1 & \rho_{\rm pb,CuSO_4}^{(3)} = 263.25{\rm g}/1 & \rho_{\rm pb,H_2SO_4}^{(3)} = 26{\rm g}/1 \\ \rho_{\rm ed,CuO}^{(3)} = 0{\rm g}/1 & \rho_{\rm ed,CuSO_4}^{(3)} = 173.48{\rm g}/1 & \rho_{\rm ed,H_2SO_4}^{(3)} = 90.402{\rm g}/1 \\ \rho_{\rm ew,CuO}^{(3)} = 0{\rm g}/1 & \rho_{\rm ew,CuSO_4}^{(3)} = 150.71{\rm g}/1 & \rho_{\rm ew,H_2SO_4}^{(3)} = 88.9827{\rm g}/1 \\ \end{array}$	$\rho_{\rm s,CuO}^{(1)} = 58.6158 \mathrm{g/l}$	$ ho_{ m s,CuSO_4}^{(1)} = 174.4265{ m g/l}$	$\rho_{\rm s,H_2SO_4}^{(1)} = 74.3260{\rm g/l}$
$\begin{array}{ll} \rho_{\ell,\mathrm{CuO}}^{(1)} = 34.0256\mathrm{g}/1 & \rho_{\ell,\mathrm{CuSO}_4}^{(1)} = 221.9917\mathrm{g}/1 & \rho_{\ell,\mathrm{H_2SO}_4}^{(1)} = 55.2208\mathrm{g}/1 \\ \rho_{\ell,\mathrm{CuO}}^{(2)} = 23.8008\mathrm{g}/1 & \rho_{\ell,\mathrm{CuSO}_4}^{(2)} = 242.5056\mathrm{g}/1 & \rho_{\ell,\mathrm{H_2SO}_4}^{(2)} = 42.6167\mathrm{g}/1 \\ \rho_{\ell,\mathrm{CuO}}^{(3)} = 17.5975\mathrm{g}/1 & \rho_{\ell,\mathrm{CuSO}_4}^{(3)} = 254.9513\mathrm{g}/1 & \rho_{\ell,\mathrm{H_2SO}_4}^{(3)} = 34.9698\mathrm{g}/1 \\ \rho_{\ell,\mathrm{CuO}}^{(4)} = 13.5176\mathrm{g}/1 & \rho_{\ell,\mathrm{CuSO}_4}^{(4)} = 263.1366\mathrm{g}/1 & \rho_{\ell,\mathrm{H_2SO}_4}^{(4)} = 29.9405\mathrm{g}/1 \\ \rho_{\ell,\mathrm{CuO}}^{(5)} = 10.538\mathrm{g}/1 & \rho_{\ell,\mathrm{CuSO}_4}^{(5)} = 263.25\mathrm{g}/1 & \rho_{\ell,\mathrm{H_2SO}_4}^{(5)} = 26\mathrm{g}/1 \\ \rho_{\mathrm{pb},\mathrm{CuO}}^{(1)} = 0\mathrm{g}/1 & \rho_{\mathrm{pb},\mathrm{CuSO}_4}^{(1)} = 263.25\mathrm{g}/1 & \rho_{\mathrm{pb},\mathrm{H_2SO}_4}^{(1)} = 26\mathrm{g}/1 \\ \vdots & \vdots & \vdots & \vdots \\ \rho_{\mathrm{pb},\mathrm{CuO}}^{(3)} = 0\mathrm{g}/1 & \rho_{\mathrm{pb},\mathrm{CuSO}_4}^{(3)} = 263.25\mathrm{g}/1 & \rho_{\mathrm{pb},\mathrm{H_2SO}_4}^{(3)} = 26\mathrm{g}/1 \\ \rho_{\mathrm{ed},\mathrm{CuO}}^{(3)} = 0\mathrm{g}/1 & \rho_{\mathrm{pb},\mathrm{CuSO}_4}^{(3)} = 263.25\mathrm{g}/1 & \rho_{\mathrm{pb},\mathrm{H_2SO}_4}^{(3)} = 26\mathrm{g}/1 \\ \rho_{\mathrm{ed},\mathrm{CuO}}^{(3)} = 0\mathrm{g}/1 & \rho_{\mathrm{ed},\mathrm{CuSO}_4}^{(3)} = 173.48\mathrm{g}/1 & \rho_{\mathrm{ed},\mathrm{H_2SO}_4}^{(3)} = 90.402\mathrm{g}/1 \\ \rho_{\mathrm{em},\mathrm{CuO}}^{(3)} = 0\mathrm{g}/1 & \rho_{\mathrm{em},\mathrm{CuSO}_4}^{(3)} = 150.71\mathrm{g}/1 & \rho_{\mathrm{em},\mathrm{H_2SO}_4}^{(3)} = 90.402\mathrm{g}/1 \\ \rho_{\mathrm{em},\mathrm{CuO}}^{(3)} = 0\mathrm{g}/1 & \rho_{\mathrm{em},\mathrm{CuSO}_4}^{(3)} = 150.57\mathrm{g}/1 & \rho_{\mathrm{em},\mathrm{H_2SO}_4}^{(3)} = 88.9827\mathrm{g}/1 \end{array}$	$ ho_{ m s,CuO}^{(2)} = 53.2891{ m g/l}$	$ ho_{ m s,CuSO_4}^{(2)} = 185.1135{ m g/l}$	$ ho_{ m s,H_2SO_4}^{(2)} = 67.7597{ m g/l}$
$\begin{array}{ll} \rho^{(2)}_{\ell,{\rm CuO}} = 23.8008{\rm g}/1 & \rho^{(2)}_{\ell,{\rm CuSO}_4} = 242.5056{\rm g}/1 & \rho^{(2)}_{\ell,{\rm H}_2{\rm SO}_4} = 42.6167{\rm g}/1 \\ \rho^{(3)}_{\ell,{\rm CuO}} = 17.5975{\rm g}/1 & \rho^{(3)}_{\ell,{\rm CuSO}_4} = 254.9513{\rm g}/1 & \rho^{(3)}_{\ell,{\rm H}_2{\rm SO}_4} = 34.9698{\rm g}/1 \\ \rho^{(4)}_{\ell,{\rm CuO}} = 13.5176{\rm g}/1 & \rho^{(4)}_{\ell,{\rm CuSO}_4} = 263.1366{\rm g}/1 & \rho^{(4)}_{\ell,{\rm H}_2{\rm SO}_4} = 29.9405{\rm g}/1 \\ \rho^{(5)}_{\ell,{\rm CuO}} = 10.538{\rm g}/1 & \rho^{(5)}_{\ell,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(1)}_{\ell,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ \rho^{(1)}_{\rm pb,{\rm CuO}} = 0{\rm g}/1 & \rho^{(1)}_{\rm pb,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(1)}_{\rm pb,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ \vdots & \vdots & \vdots & \vdots \\ \rho^{(3)}_{\rm pb,{\rm CuO}} = 0{\rm g}/1 & \rho^{(3)}_{\rm pb,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(3)}_{\rm pb,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ \rho_{\rm ed,{\rm CuO}} = 0{\rm g}/1 & \rho_{\rm ed,{\rm CuSO}_4} = 173.48{\rm g}/1 & \rho_{\rm ed,{\rm H}_2{\rm SO}_4} = 90.402{\rm g}/1 \\ \rho_{\rm ew,{\rm CuO}} = 0{\rm g}/1 & \rho_{\rm ew,{\rm CuSO}_4} = 150.71{\rm g}/1 & \rho_{\rm ew,{\rm H}_2{\rm SO}_4} = 88.9827{\rm g}/1 \end{array}$	$ ho_{\ell,{ m CuO}}^{(1)} = 34.0256{ m g/l}$	$ ho_{\ell, \mathrm{CuSO}_4}^{(1)} = 221.9917\mathrm{g/l}$	$\rho_{\ell,\mathrm{H}_2\mathrm{SO}_4}^{(1)} = 55.2208\mathrm{g/l}$
$ \begin{array}{ll} \rho_{\ell,{\rm CuO}}^{(3)} = 17.5975{\rm g}/1 & \rho_{\ell,{\rm CuSO}_4}^{(3)} = 254.9513{\rm g}/1 & \rho_{\ell,{\rm H}_2{\rm SO}_4}^{(3)^-} = 34.9698{\rm g}/1 \\ \rho_{\ell,{\rm CuO}}^{(4)} = 13.5176{\rm g}/1 & \rho_{\ell,{\rm CuSO}_4}^{(4)} = 263.1366{\rm g}/1 & \rho_{\ell,{\rm H}_2{\rm SO}_4}^{(4)} = 29.9405{\rm g}/1 \\ \rho_{\ell,{\rm CuO}}^{(5)} = 10.538{\rm g}/1 & \rho_{\ell,{\rm CuSO}_4}^{(5)} = 263.25{\rm g}/1 & \rho_{\ell,{\rm H}_2{\rm SO}_4}^{(5)} = 26{\rm g}/1 \\ \rho_{\rm pb,{\rm CuO}}^{(1)} = 0{\rm g}/1 & \rho_{\rm pb,{\rm CuSO}_4}^{(1)} = 263.25{\rm g}/1 & \rho_{\rm pb,{\rm H}_2{\rm SO}_4}^{(5)} = 26{\rm g}/1 \\ & \vdots & \vdots & \vdots \\ \rho_{\rm pb,{\rm CuO}}^{(3)} = 0{\rm g}/1 & \rho_{\rm pb,{\rm CuSO}_4}^{(3)} = 263.25{\rm g}/1 & \rho_{\rm pb,{\rm H}_2{\rm SO}_4}^{(3)} = 26{\rm g}/1 \\ \rho_{\rm ed,{\rm CuO}}^{(3)} = 0{\rm g}/1 & \rho_{\rm pb,{\rm CuSO}_4}^{(3)} = 263.25{\rm g}/1 & \rho_{\rm pb,{\rm H}_2{\rm SO}_4}^{(3)} = 26{\rm g}/1 \\ \rho_{\rm ed,{\rm CuO}}^{(3)} = 0{\rm g}/1 & \rho_{\rm ed,{\rm CuSO}_4}^{(3)} = 173.48{\rm g}/1 & \rho_{\rm ed,{\rm H}_2{\rm SO}_4}^{(3)} = 90.402{\rm g}/1 \\ \rho_{\rm em,{\rm CuO}}^{(3)} = 0{\rm g}/1 & \rho_{\rm em,{\rm CuSO}_4}^{(3)} = 150.71{\rm g}/1 & \rho_{\rm em,{\rm H}_2{\rm SO}_4}^{(3)} = 88.9827{\rm g}/1 \\ \end{array}$	$ ho_{\ell,{ m CuO}}^{(2)} = 23.8008{ m g}/{ m l}$	$ ho_{\ell, \mathrm{CuSO}_4}^{(2)} = 242.5056 \mathrm{g/l}$	$\rho_{\ell,\mathrm{H}_2\mathrm{SO}_4}^{(2)^2} = 42.6167\mathrm{g/l}$
$ \begin{array}{ll} \rho^{(4)}_{\ell,{\rm CuO}} = 13.5176{\rm g}/1 & \rho^{(4)}_{\ell,{\rm CuSO}_4} = 263.1366{\rm g}/1 & \rho^{(4)}_{\ell,{\rm H}_2{\rm SO}_4} = 29.9405{\rm g}/1 \\ \rho^{(5)}_{\ell,{\rm CuO}} = 10.538{\rm g}/1 & \rho^{(5)}_{\ell,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(4)}_{\ell,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ \rho^{(1)}_{\rm pb,{\rm CuO}} = 0{\rm g}/1 & \rho^{(1)}_{\rm pb,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(1)}_{\rm pb,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ & \vdots & \vdots & \vdots & \vdots \\ \rho^{(3)}_{\rm pb,{\rm CuO}} = 0{\rm g}/1 & \rho^{(3)}_{\rm pb,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(3)}_{\rm pb,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ \rho_{\rm ed,{\rm CuO}} = 0{\rm g}/1 & \rho_{\rm ed,{\rm CuSO}_4} = 173.48{\rm g}/1 & \rho_{\rm ed,{\rm H}_2{\rm SO}_4} = 76.179{\rm g}/1 \\ \rho_{\rm ew,{\rm CuO}} = 0{\rm g}/1 & \rho_{\rm ew,{\rm CuSO}_4} = 150.71{\rm g}/1 & \rho_{\rm ew,{\rm H}_2{\rm SO}_4} = 90.402{\rm g}/1 \\ \rho_{\rm em,{\rm CuO}} = 0{\rm g}/1 & \rho_{\rm em,{\rm CuSO}_4} = 150.57{\rm g}/1 & \rho_{\rm em,{\rm H}_2{\rm SO}_4} = 88.9827{\rm g}/1 \\ \end{array} $	$ ho_{\ell,{ m CuO}}^{(3)} = 17.5975{ m g/l}$	$ ho_{\ell, \mathrm{CuSO}_4}^{(3)} = 254.9513\mathrm{g/l}$	$\rho_{\ell,\mathrm{H}_2\mathrm{SO}_4}^{(3)^2} = 34.9698\mathrm{g/l}$
$ \begin{array}{ll} \rho^{(5)}_{\ell,{\rm CuO}} = 10.538{\rm g}/1 & \rho^{(5)}_{\ell,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(5)}_{\ell,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ \rho^{(1)}_{\rm pb,{\rm CuO}} = 0{\rm g}/1 & \rho^{(1)}_{\rm pb,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(1)}_{\rm pb,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ & \vdots & \vdots & \vdots \\ \rho^{(3)}_{\rm pb,{\rm CuO}} = 0{\rm g}/1 & \rho^{(3)}_{\rm pb,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(3)}_{\rm pb,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ \rho_{\rm ed,{\rm CuO}} = 0{\rm g}/1 & \rho^{(3)}_{\rm ed,{\rm CuSO}_4} = 263.25{\rm g}/1 & \rho^{(3)}_{\rm pb,{\rm H}_2{\rm SO}_4} = 26{\rm g}/1 \\ \rho_{\rm ed,{\rm CuO}} = 0{\rm g}/1 & \rho_{\rm ed,{\rm CuSO}_4} = 173.48{\rm g}/1 & \rho_{\rm ed,{\rm H}_2{\rm SO}_4} = 76.179{\rm g}/1 \\ \rho_{\rm ew,{\rm CuO}} = 0{\rm g}/1 & \rho_{\rm ew,{\rm CuSO}_4} = 150.71{\rm g}/1 & \rho_{\rm ew,{\rm H}_2{\rm SO}_4} = 88.9827{\rm g}/1 \\ \end{array} $	$ ho_{\ell, CuO}^{(4)} = 13.5176  \mathrm{g/l}$	$ ho_{\ell, \mathrm{CuSO}_4}^{(4)} = 263.1366 \mathrm{g/l}$	$\rho_{\ell,\mathrm{H}_2\mathrm{SO}_4}^{(4)^2} = 29.9405\mathrm{g/l}$
$ \begin{array}{ll} \rho_{\rm pb,CuO}^{(1)} = 0{\rm g}/1 & \rho_{\rm pb,CuSO_4}^{(1)} = 263.25{\rm g}/1 & \rho_{\rm pb,H_2SO_4}^{(1)} = 26{\rm g}/1 \\ & \vdots & \vdots & \vdots \\ \rho_{\rm pb,CuO}^{(3)} = 0{\rm g}/1 & \rho_{\rm pb,CuSO_4}^{(3)} = 263.25{\rm g}/1 & \rho_{\rm pb,H_2SO_4}^{(3)} = 26{\rm g}/1 \\ \rho_{\rm ed,CuO} = 0{\rm g}/1 & \rho_{\rm ed,CuSO4} = 173.48{\rm g}/1 & \rho_{\rm ed,H_2SO_4} = 76.179{\rm g}/1 \\ \rho_{\rm ew,CuO} = 0{\rm g}/1 & \rho_{\rm ew,CuSO4} = 150.71{\rm g}/1 & \rho_{\rm ew,H_2SO_4} = 90.402{\rm g}/1 \\ \rho_{\rm em,CuO} = 0{\rm g}/1 & \rho_{\rm em,CuSO_4} = 150.57{\rm g}/1 & \rho_{\rm em,H_2SO_4} = 88.9827{\rm g}/1 \\ \end{array} $	$ ho_{\ell,{ m CuO}}^{(5)} = 10.538{ m g/l}$	$ ho_{\ell,{ m CuSO}_4}^{(5)} = 263.25{ m g}/{ m l}$	$\rho_{\ell,\mathrm{H}_2\mathrm{SO}_4}^{(5)^2} = 26\mathrm{g/l}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ ho_{ m pb,CuO}^{(1)} = 0{ m g}/1$	$ ho_{ m pb,CuSO_4}^{(1)} = 263.25{ m g}/{ m l}$	$\rho_{\rm pb,H_2SO_4}^{(1)} = 26{\rm g}/{\rm l}$
$ \begin{array}{ll} \rho^{(3)}_{\rm pb,CuO} = 0{\rm g}/1 & \rho^{(3)}_{\rm pb,CuSO_4} = 263.25{\rm g}/1 & \rho^{(3)}_{\rm pb,H_2SO_4} = 26{\rm g}/1 \\ \rho_{\rm ed,CuO} = 0{\rm g}/1 & \rho_{\rm ed,CuSO4} = 173.48{\rm g}/1 & \rho_{\rm ed,H_2SO_4} = 76.179{\rm g}/1 \\ \rho_{\rm ew,CuO} = 0{\rm g}/1 & \rho_{\rm ew,CuSO4} = 150.71{\rm g}/1 & \rho_{\rm ew,H_2SO_4} = 90.402{\rm g}/1 \\ \rho_{\rm em,CuO} = 0{\rm g}/1 & \rho_{\rm em,CuSO_4} = 150.57{\rm g}/1 & \rho_{\rm em,H_2SO_4} = 88.9827{\rm g}/1 \end{array} $	:	:	:
$ \begin{array}{ll} \rho_{\rm ed,CuO} = 0{\rm g}/1 & \rho_{\rm ed,CuSO4} = 173.48{\rm g}/1 & \rho_{\rm ed,H_2SO_4} = 76.179{\rm g}/1 \\ \rho_{\rm ew,CuO} = 0{\rm g}/1 & \rho_{\rm ew,CuSO4} = 150.71{\rm g}/1 & \rho_{\rm ew,H_2SO_4} = 90.402{\rm g}/1 \\ \rho_{\rm em,CuO} = 0{\rm g}/1 & \rho_{\rm em,CuSO_4} = 150.57{\rm g}/1 & \rho_{\rm em,H_2SO_4} = 88.9827{\rm g}/1 \\ \end{array} $	$ ho_{ m pb,CuO}^{(3)} = 0{ m g}/{ m l}$	$\rho^{(3)}_{\rm pb,CuSO_4} = 263.25{\rm g}/{\rm l}$	$\rho^{(3)}_{\rm pb, H_2SO_4} = 26{\rm g}/{\rm l}$
$ \begin{array}{ll} \rho_{\rm ew,CuO} = 0{\rm g}/l & \rho_{\rm ew,CuSO4} = 150.71{\rm g}/l & \rho_{\rm ew,H_2SO_4} = 90.402{\rm g}/l \\ \rho_{\rm em,CuO} = 0{\rm g}/l & \rho_{\rm em,CuSO_4} = 150.57{\rm g}/l & \rho_{\rm em,H_2SO_4} = 88.9827{\rm g}/l \\ \end{array} $	$ ho_{ m ed,CuO} = 0{ m g}/{ m l}$	$ ho_{ m ed,CuSO4}=173.48{ m g}/{ m l}$	$\rho_{\rm ed, H_2SO_4} = 76.179{\rm g/l}$
$\rho_{\rm em,CuO} = 0  {\rm g}/1 \qquad \rho_{\rm em,CuSO_4} = 150.57  {\rm g}/1 \qquad \rho_{\rm em,H_2SO_4} = 88.9827  {\rm g}/1$	$\rho_{\rm ew,CuO}=0{\rm g}/{\rm l}$	$\rho_{\rm ew,CuSO4}=150.71{\rm g/l}$	$\rho_{\rm ew, H_2SO_4} = 90.402{\rm g/l}$
	$\rho_{\rm em,CuO}=0{\rm g}/{\rm l}$	$\rho_{\rm em, CuSO_4} = 150.57{\rm g/l}$	$\rho_{\rm em, H_2SO_4} = 88.9827{\rm g/l}$

Variable	Value	Variable	Value
$V_{\rm s}^{(1)}$	$7.4\mathrm{m}^3$	$\varepsilon_{\rm ps}^{(1)}$	0.1
$V_{\rm s}^{(2)}$	$4\mathrm{m}^3$	$\varepsilon_{\rm ps}^{(2)}$	0.1
$V_{\ell}^{(k)}$	$27.5\mathrm{m}^3$	$\varepsilon_{\rm ps}^{(3)}$	0.1
$V_{\rm pb}^{(1)}$	$15\mathrm{m}^3$	$V_{\rm ed}$	$10\mathrm{m}^3$
$\dot{V_{\rm pb}^{(2)}}$	$15\mathrm{m}^3$	$V_{\rm ew}$	$430 \times 5 \mathrm{m}^3$
$V_{\rm pb}^{(3)}$	$45.3\mathrm{m}^3$	$V_{\rm em}$	$75\mathrm{m}^3$
$V_{\rm ps}^{(1)}$	$35\mathrm{m}^3$	k	$6.3267 \times 10^4 \frac{l^3}{mol  g  h}$
$V_{\rm ps}^{(2)}$	$40\mathrm{m}^3$	$ar\eta$	0.77779
$V_{\rm ps}^{(3)}$	$42\mathrm{m}^3$	$\rho_{\rm mix}$	1 kg/l

Table 6. More nodel na nati



Figure 2: Responses in outputs  $y_1 = \rho_{\text{pb},\text{H}_2\text{SO}_4}^{(3)}$ ,  $y_2 = \rho_{\text{ew},\text{Cu}|\text{CuSO}_4}$  and  $y_3 = \rho_{\text{ew},\text{H}_2\text{SO}_4}^{\equiv}$  upon a 50% step increase (solid line) and decrease (dash-dot line) in  $u_1 = \dot{m}_c$  after 5 h.



Figure 3: Responses in outputs  $y_1 = \rho_{\text{pb},\text{H}_2\text{SO}_4}^{(3)}$ ,  $y_2 = \rho_{\text{ew},\text{Cu}|\text{CuSO}_4}$  and  $y_3 = \rho_{\text{ew},\text{H}_2\text{SO}_4}^{\equiv}$  upon a 50% step increase (solid line) and decrease (dash-dot line) in  $u_2 = \dot{V}_{\text{e}_2\text{s}}$  after 5 h.



Figure 4: Responses in outputs  $y_1 = \rho_{\text{pb},\text{H}_2\text{SO}_4}^{(3)}$ ,  $y_2 = \rho_{\text{ew},\text{Cu}|\text{CuSO}_4}$  and  $y_3 = \rho_{\text{ew},\text{H}_2\text{SO}_4}^{\equiv}$  upon a 50% step increase (solid line) and decrease (dash-dot line) in  $u_3 = \dot{V}_a$  after 5 h.