## Purpose

This precious metal electrowinning cell model was designed to simulate the process of electrowinning that would follow the leaching of crushed printed circuit boards using a thiosulfate solution. The inputs of this model primarily come from the leaching cell. The base metals from the crushed printed circuit boards were extracted using an iron and hydrochloride solution, and electrowon. This occurs in a separate model which then gets input into the precious metal leaching cell. Modelling the various parameters involved in this electrowinning cell will allow for the estimation of potential recovery of precious metals based on the design, and subsequent estimation of various economic, safety, and environmental aspects of the system.

## Inputs

The primary inputs into the system come from the leaching cell stream. This stream contains the aqueous components from the leaching cell system, which include:

Au(S2O3)23-

Ag(S2O3)23-

Pd(S2O3)46-

(S­2O3)2-

Fe3+

Fe2+

OH-

H+

The following components have not currently been modeled into the system to limit the complexity but would exist in the solution.

Ag(S2O3)25- : This is another complex thiosulfate forms with silver ions. It has a similar dissociation constant and characteristics to the modeled silver-thiosulfate complex.

Na+ : The thiosulfate in the system was generated from Na2S2O3, which also generates Na+. Additionally, to balance the pH to desired levels, NaOH is added into the solution, generating Na+ as well.

EDTA4-: This forms a stabilizing complex with the iron in solution and is added in equal amounts.

For all these components mentioned, their concentrations from the leaching cell would be used at inputs into the model. Currently, these concentrations are fixed at some amount, with H+ and OH- not modeled as it is assumed that the system is at a constant pH. Similarly, it is assumed that the whole system is operating at the same temperature.

## Parameters

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Meaning/units** | **Notes** |
| Fin | Total inlet flow from leaching unit, in L/s | If set to 0, unit will operate in a closed loop (concentration of metal complexes will continually decrease). |
| Fout | Total outlet flow from electrowinning cell, in L/s | This outlet is intended to go back to the leaching cell. In the model, this should currently be set to be the same as *Fin* as volume decreases are not currently modeled. |
| T | Temperature of cell, in K | The system is currently assumed to be an isothermal operation. Kinetics and energy release have not been accounted for in the model. Isothermal nature likely managed by a cooling jacket or similar configuration. |
| V | Volume of liquid in cell, in L | This will be a major parameter for optimization. Currently, it is just used for calculating the concentration of components in solution, not tied to any electrode area calculations, electrode distances, or reaction kinetics. |
| Cursivel | Characteristic distance between electrodes, in m | This parameter is not well known/estimated and should be investigated further. Will likely connect this parameter to a volume calculation. This value only currently affects the system resistance, and thus should likely be a more conservative estimate. |
| Acat | Cathode effective area | Area used for plating of the metals and hydrogen evolution. Different materials/configurations for the cathode (ex. Wire mesh, flat plate, etc.) will change this parameter and how it is set up in the cathode. Current assumption is that it is a flat plate. |
| Aan | Anode effective area | Area used for the oxygen evolution and iron oxidation. See cathode area notes above. |
| Vapp | Applied voltage | This is a key parameter for determining energy consumption, as well as modeling the reaction kinetics. |
| Rhardware | Resistance in system due to hardware | This is not currently very well known, and should be estimated as a value based on a best guess or some function based on system design. |
| tfinal | Duration of electrowinning, h | This is the total time for the system to be operating. The longer it is, the more the plating can proceed. |

### Process properties

These are parameters that could be tweaked but should be based on good estimations and data.

**Conductivity values:** These values are easily available for simple ions, but not readily apparent or available for complex ions in literature. That being said, having a lower conductivity only increases the system resistance, making the estimate more conservative (worst-case). It is also expected that complexes contribute to the system less due to greater charge neutrality compared to ions. Ideally, thiosulfate conductivity could be found or estimated, allowing for a conductivity estimation based on the ions outside of complexes. This solution conductivity is not currently updated in the model.

**Gamma values:** These values are for estimating the apparent activity of components in solution in conjunction with the concentration. Currently, they have all been set to 1, with the assumption that the modeled concentration is directly proportional to the activity of that component. These values will likely not be modified unless there is data suggesting they do not conform to this ideal activity assumption.

**Gas activity values:** For oxygen and hydrogen evolution, there needs to be activity values associated with them in order to estimate the Nernst potential of their reactions. The assumption used for oxygen currently is that the gas above the cell is atmospheric air. For hydrogen, a placeholder low partial pressure has been added in for the model to run, but it is currently unknown what the actual value should be.

**Transfer coefficient:** This is the transfer coefficient for the Butler-Vollmer equations used in the model. For most/many reactions, this value is close to 0.5. For all the reactions, this will be the base assumption unless transfer coefficient data is available.

**Exchange current density:** This is a key value for determining the reaction kinetics within the system for each reaction. For each reaction, this is based on data from literature, shown below (UPDATE WITH ACTUAL REFERENCED LINKS and quick writeup for each):

*Iron oxidation:* ChE331 course notes identify the iron oxidation reaction to have an exchange current density of 10-6.8 A/m2. (find an actual source at some point.

iAg0 = 7.3e-9; %A/m2, from https://link-springer-com.proxy.lib.uwaterloo.ca/article/10.1007/s10800-007-9434-x - verify this link applies

iAu0 = 2E-8; %A/m2, value of dissolution including Na2S in dissolution reaction from https://link-springer-com.proxy.lib.uwaterloo.ca/article/10.1134/S1023193506040021, converting A/cm2 to A/m2

iPd0 = 4e-9; %using a mix of a few from that reference

iH0 = 1E-10; %need to identify suitable electrode to help limit hydrogen evolution. From volcano plot in class, likely copper, gold or silver electrodes

iAn0 = 1E-12; %A/m2

For most of these reactions outside of hydrogen, it shall be assumed that the choice of electrode does not significantly affect or alter the exchange current densities found at these references. This assumption is because there is a limited amount of data on the system’s exchange current densities available. This assumption is generally reasonable for typical metal electrode reactions (GIVE PROOF HERE MAYBE?), and could eventually be validated by comparing the results of this model with results from studies of similar systems.

## Outputs

This is a transient model, outputting the system data at each time step. Other than sending the outlet flow concentrations to the leaching cell model, it also outputs the following information:

**Overpotentials for each reaction:** Helps demonstrate the kinetics of the reactions.

**Current through system:** Will enable identification of the power used by the system, as well as the deposition of metals on the cathode and production of gasses.

**Deposition of metals and production of gasses:** Key outputs for defining the system performance

**System conductivity and resistance**: Less notable but could help explain losses occurring in the system.

**Nernst potentials for each reaction:** Can help explain the reaction kinetics.

## Model function

The code used models an electrochemical cell using first principles and mass balance equations to quantify the system changes over time. More specifically, this reactor is assumed to be a CSTR with electrochemical reaction kinetics. This section will explain how the model and system functions by providing the equations used to model the system.

Based on the current system concentrations, various outputs are calculated at each time step:

System conductivity

System resistance

Nernst potentials of the reactions in the system:

For this system, the following reactions were identified as significant, identified below along with their Nernst potentials (WRITE OUT):

Anode reactions:

Oxygen evolution

Iron oxidation

Cathode reactions:

Gold deposition

Silver deposition

Palladium deposition

Hydrogen evolution

Once these parameters are calculated for the time step, the electrode potentials need to be calculated. This is specified by the current balance equation, and the applied voltage equation:

Current balance equation

Applied voltage equation

The current at each electrode is specified by the sum of the currents for each reaction at the electrode.

These currents are specified by the Butler Volmer equation, below:

General B-V equation

Each overpotential in the Butler Vollmer equation can be calculated from their respective electrode potential. This also means that if one overpotential at an electrode is known, the other overpotentials can be calculated from it as follows:

Electrode potential equation

This means that the current at an electrode can be calculated from one overpotential value. Using these relations, two overpotential values are needed in order to specify the whole system, using Butler-Volmer equations for each reaction and using the overpotential relations at each electrode in conjunction with the current balance equation and applied voltage equation as shown below:

Equations

In the model, fsolve is used with these equations to determine the overpotentials and individual currents associated with each reaction.

The 4th order Runge-Kutta method is used for mass balances on each component in the CSTR, where the inlet is specified by the leaching model (set as constant values), the outlet is specified by the bulk solution concentration, and the generation or consumption of the component is specified by the current according to Faradays law, below:

Faradays law equation

This value is used in each component’s differential equation as below:

Differential equation example

The Runge-Kutta method is used to estimate the concentrations at each time step of the model, allowing for a non-linear, transient model to be used. At each time step, the overpotentials and currents are calculated from the system conditions, which is then added into the differential equations used by the Runge-Kutta method.

### System characteristics (literature information here)

### Assumptions

**Constant volume:** the flow rate in and out is constant, all mixing is ideal and changes in solute concentrations have a negligible impact on the volume size.

**Isothermal operation:** it is assumed that a cooling jacket is used to maintain the cell at a constant temperature, with any temperature increases due to cell operation being eliminated by cooling.

**Well-mixed conditions:** It is assumed that some sort of mixer is used to ensure that the system is well-mixed, ensuring no diffusion or surface reaction limitations occur. This would complicate the kinetics and make it difficult to accurately model the system, and would also require too detailed a cell design for this stage in development.

**Constant pH:** It is assumed currently that the pH is maintained by the addition of powdered NaOH to the system. This is not currently modeled, except to maintain the concentration of H+ and OH- at the same concentrations as dictated by pH (and not modeling the addition of Na+ or any changes due to the reaction.

**Impact of reactions not currently modeled is negligible:** As specified in the previous section, literature identifies various additional reactions that have not been explicitly modeled. For the purposes of simplification, these intermediate steps or side reactions are not included in the model, with the assumption that they do not proceed to a significant amount to change any concentrations or add any significant new components that would change the system as modeled.

## Possible model improvements or next steps