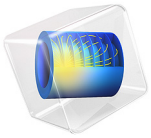

Model created in COMSOL Multiphysics 6.4

Gold Recycling Through Oxidative Dissolution

Introduction

Recovery of precious metals in recycling of electronics, or extraction from ore, is usually performed through leaching of the metal into an aqueous phase. Precious metals require the use of an oxidant and, often, a complexant. In the case of gold, the cyanide anion CN^- forms a soluble complex with gold(I) (that is, $Au(CN)^-_2$), that is so stable that molecular oxygen becomes a viable oxidant. The process is known as gold cyanidation, and it has — unsurprisingly — been studied extensively for the past century. Research into finding less toxic complexants is ongoing, but due to the availability of kinetic parameters, this model sticks to using cyanide.

The model studies the oxidative dissolution of this noble metal in an air saturated cyanide solution. The system encompasses three phases: a gaseous phase (air), an aqueous phase, and a solid gold phase. The system is assumed to be homogeneous on a macroscopic scale, for example fine particulate matter dispersed in water, which is continuously agitated by a stream of air bubbles.

Model Definition

Since this problem is not limited by mass transport in the bulk, it will be modeled in a 0D component. The rate limiting step is that of a surface reaction, and corresponds to a problem where diffusion is not a rate limiting step. Since the evolution of available surface area during dissolution depends on the geometry of the particles, the model includes two cases: flakes and spheres (see Figure 1), each in its separate 0D component.

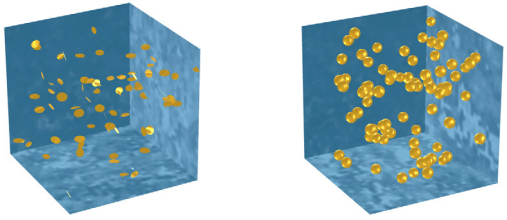

Figure 1: The two cases studied, flakes (to the left) and spheres (to the right).

LIQUID PHASE

In each component, two Reaction Engineering interfaces will be added, the first one will describe the liquid phase, in which the following reaction is added:

$$4Au + O_2 + 8CN^- + 2H_2O \rightarrow 4Au(CN)^-_2 + 4OH^-$$

The rate of reaction is, according to Ref. 1:

$$4r_1 = k_{\mathrm{Au}} \frac{c'}{1+c'} \frac{A}{V} \tag{1}$$

where A is total exposed surface area of gold, V is the volume of the liquid, k_{Au} is a parameterized rate constant, and c' is the product between the adsorption coefficient of cyanide on gold (K_{ads}), the concentration of aqueous dioxygen, and the concentration of cyanide to the power of three:

$$c' = K_{\mathrm{ads}}[\mathrm{O_2(aq)}][\mathrm{CN^-}]^3 \tag{2}$$

Assume that the starting material is monodisperse; that is, that all particles are of the same size. The total amount of gold per unit of volume (the so called loading) is set equal in the two components, and the thickness of the flakes is set such that initial surface areas of the two cases are equal. Since the system is assumed to be well mixed, the concentration of oxygen is set to be in equilibrium with the partial pressure in the gas phase.

GAS PHASE

The second Reaction Engineering interface will represent the gas phase (air). Add two species: O_2 and N_2, but only the former will participate in any reactions. A global constraint, requiring Henry's Law for O_2 to be fulfilled at all times, is added, and since the system is considered to be a batch reactor (where oxygen can be depleted), introduce an additional constraint, enforcing mass conservation of the total amount of oxygen.

DIFFERENCES BETWEEN THE COMPONENTS

In the first component, the dissolution of flakes is modeled. Here assume that the total surface area exposed remains constant throughout the reaction (the flakes are assumed to be utterly oblate) up to the point that the last bit of solid has been consumed, at which point the available surface area is assumed to drop to zero. In order not to introduce a discontinuity in the available surface area, assign a smoothed stepping function which rapidly falls around the point at which depletion occurs.

In the second component, describing dissolution of spheres, the surface area exposed does vary during the course of the dissolution process (the surface area is proportional to the mass loading of gold to the power of two thirds). Since the surface area naturally goes to zero as the amount of solid gold declines, it is possible to do away with the smoothed stepping function, but as the solver approaches the end of the reaction, care is taken to avoid evaluating the fractional power of a negative number.

Results and Discussion

The result of the time integration is shown in Figure 2.

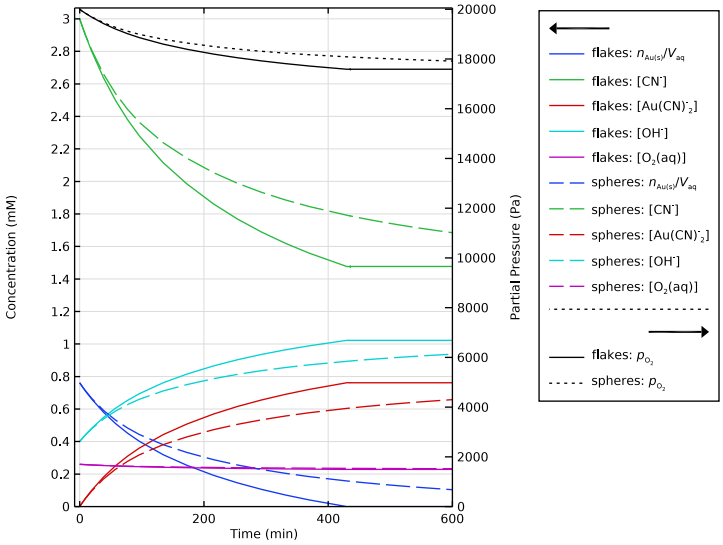

Figure 2: Time evolution of concentrations and partial pressure of oxygen for each of the two particle cases.

The initial conditions are the same for both studies, and also the initial rates of change are the same for the two components. But as the spheres dissolve, their total surface area decreases, leading to a slower leaching compared to the flakes. After some time the leaching process in the system with flakes stops runs out of solid gold and all reactions stop, whereas this quantity in the system with spherical particles is still asymptotically approaching zero.

Reference

1. G. Senanayake, "Kinetics and reaction mechanism of gold cyanidation: Surface reaction model via Au(I)–OH–CN complexes," *Hydrometallurgy*, vol. 80, pp. 1–12, 2005.

Application Library path: `Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/gold_recycling`

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **0D**.

2 In the **Select Physics** tree, select **Chemical Species Transport** > **Reaction Engineering (re)**.

3 Right-click and choose **Add Physics**.

4 Click **Study**.

5 In the **Select Study** tree, select **General Studies** > **Time Dependent**.

6 Click **Done**.

LIQUID PHASE

Add a **Reaction Engineering** interface, which will correspond to the liquid phase.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Reaction Engineering (re)**.

2 In the **Settings** window for **Reaction Engineering**, type `Liquid phase` in the **Label** text field.

3 Locate the **Reactor** section. Find the **Mass balance** subsection. In the V_r text field, type `V_liquid`.

4 Locate the **Energy Balance** section. In the T text field, type `T`.

5 Locate the **Mixture Properties** section. From the **Phase** list, choose **Liquid**.

GLOBAL DEFINITIONS

Parameters 1

Read in a set of parameters to be used in the model (`V_liquid` being one of them).

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `gold_recycling_parameters.txt`.

The first component describes a system with dispersed gold flakes dissolving in a liquid, while maintaining a constant interfacial area to the liquid phase. Read in variables describing this behavior into the variables section of **Component 1**.

DEFINITIONS

Variables 1

1. In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.
2. In the **Settings** window for **Variables**, locate the **Variables** section.
3. Click **Load from File**.
4. Browse to the model's Application Libraries folder and double-click the file `gold_recycling_variables_flakes.txt`.

LIQUID PHASE (RE)

Define a reaction describing the overall dissolution process, where gold is oxidized by molecular oxygen into a gold(I)dicyanide complex.

Reaction 1

1. In the **Reaction Engineering** toolbar, click **Reaction**.
2. In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.
3. In the **Formula** text field, type `Au(s) + CN- + O2(aq) + H2O => AuCNCN- + OH-`.

   Use the **Balance** feature to determine the coefficients for the reactants and products.
4. Click **Balance** in the upper-right corner of the **Reaction Formula** section.

   The effective rate expression does not follow the law of mass action, instead use the rate expression derived in the reference publication.
5. Locate the **Reaction Rate** section. From the list, choose **User defined**.
6. In the r_j text field, type `flakes_R_Au/4`.

   While not strictly needed, set the rate parameters to descriptive values.
7. Locate the **Reaction Orders** section. Find the **Volumetric overall reaction order** subsection. In the **Forward** text field, type `4`.
8. Locate the **Rate Constants** section. In the k^{f} text field, type `0`.

Initial Values 1

Enter initial values for a slightly alkaline (pH: 9.4) air saturated aqueous solution.

1. In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Volumetric Species Initial Values** section.

3 In the table, enter the following settings:

Species	Concentration (mol/m^3)
Au(s)	`liquid_c0_Au`
AuCNCN-	`0[mol/dm^3]`
CN-	`cyanide_c0`
H2O	`55[mol/dm^3]`
O2(aq)	`p0_O2g * H_O2`
OH-	`4e-4[mol/dm^3]`

DISSOLUTION OF GOLD FLAKES

Enter a descriptive label for the first component, which treats the case of thin foil or flakes of gold.

1 In the **Model Builder** window, click **Component 1 (comp1)**.

2 In the **Settings** window for **Component**, type `Dissolution of gold flakes` in the **Label** text field.

ADD PHYSICS

1 In the **Home** toolbar, click **Add Physics** to open the **Add Physics** window.

2 Go to the **Add Physics** window.

Add a second **Reaction Engineering** interface corresponding to the gas phase.

3 In the tree, select **Recently Used** > **Reaction Engineering (re)**.

4 Click the **Add to Dissolution of Gold Flakes** button in the window toolbar.

5 In the **Home** toolbar, click **Add Physics** to close the **Add Physics** window.

GAS PHASE

1 In the **Settings** window for **Reaction Engineering**, type `Gas Phase` in the **Label** text field.

The gas phase is compressible, hence its volume is not guaranteed to remain constant, change the reactor type to batch to reflect this fact.

2 Locate the **Reactor** section. From the **Reactor type** list, choose **Batch**.

The volume of the gas phase is defined as a variable depending on the total volume and the volume of the (assumed incompressible) liquid and solid phases.

3 Find the **Mass balance** subsection. In the V_r text field, type `V_gas`.

4 Locate the **Energy Balance** section. In the T text field, type `T`.

Oxygen will be present in both gas and liquid phase, next add it as a gas phase species.

Species 1

1 In the **Reaction Engineering** toolbar, click **Species**.

2 In the **Settings** window for **Species**, locate the **Name** section.

3 In the text field, type `O2(g)`.

For completeness, also add nitrogen, even though it will not participate in any chemical reactions.

4 In the **Reaction Engineering** toolbar, click **Species**.

1 In the **Settings** window for **Species**, locate the **Name** section.

2 In the text field, type `N2(g)`.

The concentration of oxygen in the gas phase and in the liquid phase, is assumed to equilibrate on a much shorter time scale than the chemical reaction consuming oxygen (for example, a well stirred system). Hence, at any given time, Henry's law is assumed to be fulfilled. We can impose this by introducing a **Global Constraint**

3 Click the **Show More Options** button in the **Model Builder** toolbar.

4 In the **Show More Options** dialog, in the tree, select the checkbox for the node **Physics** > **Equation Contributions**.

5 Click **OK**.

Henry's Law for Dioxygen

1 In the **Reaction Engineering** toolbar, click **Global Constraint**.

2 In the **Settings** window for **Global Constraint**, type `Henry's Law for Dioxygen` in the **Label** text field.

3 Locate the **Global Constraint** section. In the **Constraint expression** text field, type `re.c_O2_aq - H_O2*R_const*T*re2.c_O2_gas`.

Since Henry's law only dictates that the ratio of concentrations needs to remain constant, the solver would be free to, for example, increase both concentrations, but with different amounts. Clearly this would violate mass conservation. Therefore, add a second constraint on the total amount of oxygen atoms in our system.

Mass Conservation of Oxygen

1 In the **Reaction Engineering** toolbar, click **Global Constraint**.

2 In the **Settings** window for **Global Constraint**, type `Mass Conservation of Oxygen` in the **Label** text field.

3 Locate the **Global Constraint** section. In the **Constraint expression** text field, type `V0_gas*(2*re2.c_O2_gas - 2*re2.cO_O2_gas) + V_liquid*(2*re.c_O2_aq + re.c_H2O + re.c_OH_1m - 2*re.cO_O2_aq - re.cO_H2O - re.cO_OH_1m)`.

Initial Values 1

The model starts with air.

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Volumetric Species Initial Values** section.

3 In the table, enter the following settings:

Species	Concentration (mol/m^3)
N2(g)	`pO_N2g/R_const/T`
O2(g)	`gas_cO_O2g`

Currently the rate of reaction is assumed independent of the amount of gold in our system. This corresponds to a constant area of gold interface during the dissolution, which is a good assumption for flakes or foil. However, once the gold is consumed, the reaction will need to stop, or else we would obtain negative concentrations of gold. Therefore we will modulate our rate of reaction with a step function, essentially a smoothed version of Heaviside's step function.

GLOBAL DEFINITIONS

Step 1 (step1)

1 In the **Home** toolbar, click f(x) **Functions** and choose **Global** > **Step**.

2 In the **Settings** window for **Step**, click **Plot**.

3 Locate the **Parameters** section. In the **From** text field, type `-1`.

4 Click **Plot**.

This function, `step1` is already being referred to in the **Variables 1** section.

DISSOLUTION OF GOLD FLAKES (COMP1)

Copy the first component for modeling flakes of gold, and create a second component for a (spherical) particulate suspension.

1 In the **Model Builder** window, right-click **Dissolution of gold flakes (comp1)** and choose **Copy**.

DISSOLUTION OF GOLD FLAKES 1 (COMP2)

In the **Model Builder** window, right-click the root node and choose **Paste Multiple Items**.

DISSOLUTION OF SPHERICAL GOLD

1 In the **Messages from Paste** dialog, click **OK** to accept the new tags.

Give the component a descriptive label.

2 In the **Model Builder** window, click **Dissolution of gold flakes 1 (comp2)**.

3 In the **Settings** window for **Component**, type `Dissolution of spherical gold` in the **Label** text field.

DEFINITIONS (COMP2)

Variables 1

In the interest of minimizing the amount of manual input, load variable expressions from a file.

1 In the **Model Builder** window, under **Dissolution of spherical gold (comp2)** > **Definitions** click **Variables 1**.

2 In the **Settings** window for **Variables**, locate the **Variables** section.

3 Click  **Clear Table**.

4 Click  **Load from File**.

5 Browse to the model's Application Libraries folder and double-click the file `gold_recycling_variables_spheres.txt`.

Note how the rate of gold dissolution depends on remaining surface area, because of that, this formulation does not need a step function.

LIQUID PHASE (RE3)

1: 4 Au(s) + 8 CN- + O2(aq) + 2 H2O => 4 AuCNCN- + 4 OH-

Update the rate expression to refer to this spherical case.

1 In the **Model Builder** window, expand the **Dissolution of spherical gold (comp2)** > **Liquid phase (re3)** node, then click **1: 4 Au(s) + 8 CN- + O2(aq) + 2 H2O => 4 AuCNCN- + 4 OH-**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Rate** section.

3 In the r_j text field, type `spherical_R_Au/4`.

GAS PHASE (RE4)

Henry's Law for Dioxygen

Update the qualified names so that they refer to the interfaces in our new component.

1 In the **Model Builder** window, expand the **Dissolution of spherical gold (comp2)** > **Gas Phase (re4)** node, then click **Henry's Law for Dioxygen**.

2 In the **Settings** window for **Global Constraint**, locate the **Global Constraint** section.

3 In the **Constraint expression** text field, type `re3.c_O2_aq - H_O2*R_const*T* re4.c_O2_gas`.

Mass Conservation of Oxygen

1 In the **Model Builder** window, click **Mass Conservation of Oxygen**.

2 In the **Settings** window for **Global Constraint**, locate the **Global Constraint** section.

3 In the **Constraint expression** text field, type `V0_gas*(2*re4.c_O2_gas - 2* re4.c0_O2_gas) + V_liquid*(2*re3.c_O2_aq + re3.c_H2O + re3.c_OH_1m - 2*re3.c0_O2_aq - re3.c0_H2O - re3.c0_OH_1m)`.

At this point the model is ready for solving, solve for 15 h.

STUDY 1

1 In the **Model Builder** window, click **Study 1**.

2 In the **Settings** window for **Study**, locate the **Study Settings** section.

3 Clear the **Generate default plots** checkbox.

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 1** click **Step 1: Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 From the **Time unit** list, choose **min**.

4 In the **Output times** text field, type `range(0,1,600)`.

5 In the **Study** toolbar, click **Compute**.

RESULTS

Aqueous Gold Dissolution of Flakes and Spheres

1 In the **Results** toolbar, click **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Aqueous Gold Dissolution of Flakes and Spheres` in the **Label** text field.

Liquid (flakes)

1 Right-click **Aqueous Gold Dissolution of Flakes and Spheres** and choose **Global**.

   Load expressions for plotting from files.

2 In the **Settings** window for **Global**, type `Liquid (flakes)` in the **Label** text field.

3 Locate the **y-Axis Data** section. Click **Clear Table**.

4 Click **Load from File**.

5 Browse to the model's Application Libraries folder and double-click the file `gold_recycling_plot_global1.txt`.

6 Click to expand the **Legends** section. Find the **Include** subsection. Select the **Description** checkbox.

7 Clear the **Expression** checkbox.

Liquid (spheres)

1 In the **Model Builder** window, right-click **Aqueous Gold Dissolution of Flakes and Spheres** and choose **Global**.

2 In the **Settings** window for **Global**, type `Liquid (spheres)` in the **Label** text field.

3 Locate the **y-Axis Data** section. Click **Clear Table**.

4 Click **Load from File**.

5 Browse to the model's Application Libraries folder and double-click the file `gold_recycling_plot_global2.txt`.

6 Click to expand the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Dashed**.

7 From the **Color** list, choose **Cycle (reset)**.

8 Locate the **Legends** section. Find the **Include** subsection. Select the **Description** checkbox.

9 Clear the **Expression** checkbox.

Gas

1 Right-click **Aqueous Gold Dissolution of Flakes and Spheres** and choose **Global**.

2 In the **Settings** window for **Global**, type `Gas` in the **Label** text field.

3 Locate the **y-Axis Data** section. Click **Clear Table**.

4 Click **Load from File**.

5 Browse to the model's Application Libraries folder and double-click the file `gold_recycling_plot_global3.txt`.

6 Locate the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Cycle**.

7 From the **Color** list, choose **Black**.

8 Locate the **Legends** section. Find the **Include** subsection. Select the **Description** checkbox.

9 Clear the **Expression** checkbox.

Aqueous Gold Dissolution of Flakes and Spheres

1 In the **Model Builder** window, click **Aqueous Gold Dissolution of Flakes and Spheres**.

2 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

3 From the **Title type** list, choose **None**.

4 Locate the **Plot Settings** section. Select the **Two y-axes** checkbox.

5 In the table, select the **Plot on secondary y-axis** checkbox for **Gas**.

6 Select the **x-axis label** checkbox.

7 Select the **y-axis label** checkbox. In the associated text field, type `Concentration (mM)`.

8 Select the **Secondary y-axis label** checkbox. In the associated text field, type `Partial Pressure (Pa)`.

9 Locate the **Axis** section. Select the **Manual axis limits** checkbox.

10 In the **y minimum** text field, type `0`.

11 In the **Secondary y minimum** text field, type `0`.

12 In the **x maximum** text field, type `600`.

13 Locate the **Legend** section. From the **Layout** list, choose **Outside graph axis area**.

14 In the **Aqueous Gold Dissolution of Flakes and Spheres** toolbar, click **Plot**.

This is Figure 2.