metals

Article

Hydrometallurgical Treatment of Waste Printed Circuit Boards: Bromine Leaching

Hao Cui [1,*] and Corby Anderson [2]

[1] Nevada Gold Mines, LLC, 89801 Elko, NV, USA
[2] Department of Metallurgical & Materials Engineering, Colorado School of Mines, 80401 Golden, CO, USA; cganders@mines.edu
* Correspondence: hcui@nevadagoldmines.com; Tel.: +1-775-934-3627

Received: 15 March 2020; Accepted: 30 March 2020; Published: date

Abstract: This paper demonstrates the recovery of valuable metals from shredded Waste Printed Circuit Boards (WPCBs) by bromine leaching. Effects of sodium bromide concentration, bromine concentration, leaching time and inorganic acids were investigated. The most critical factors are sodium concentration and bromine concentration. It was found that more than 95% of copper, silver, lead, gold and nickel could be dissolved simultaneously under the optimal conditions: 50 g/L solid/liquid ratio, 1.17 M NaBr, 0.77 M Br_2, 2 M HCl, 400 RPM agitation speed and 23.5 °C for 10 hours. The study shows that the dissolution of gold from waste printed circuit boards in a Br_2-NaBr system is controlled by film diffusion and chemical reaction.

Keywords: shredded waste printed circuit boards; precious metals; bromine; leaching kinetics

1. Supplementary Materials A: Eh-pH Diagrams

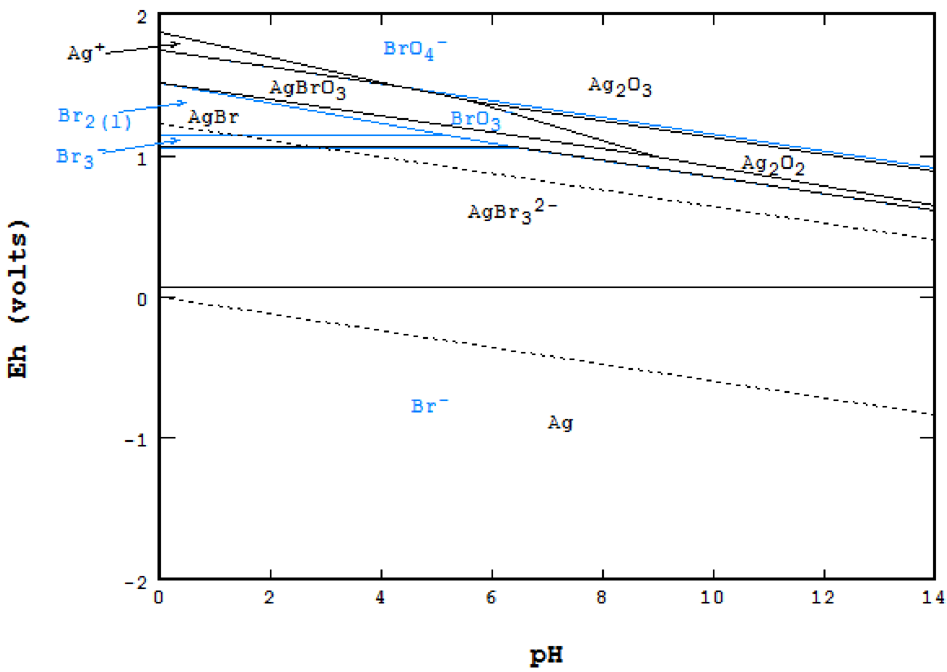

Figure S1. Eh-pH diagram of Br-Ag-H2O system at 25 °C ([Ag] = 10^{-4} M, [Br] = 0.775M) (Stabcal).

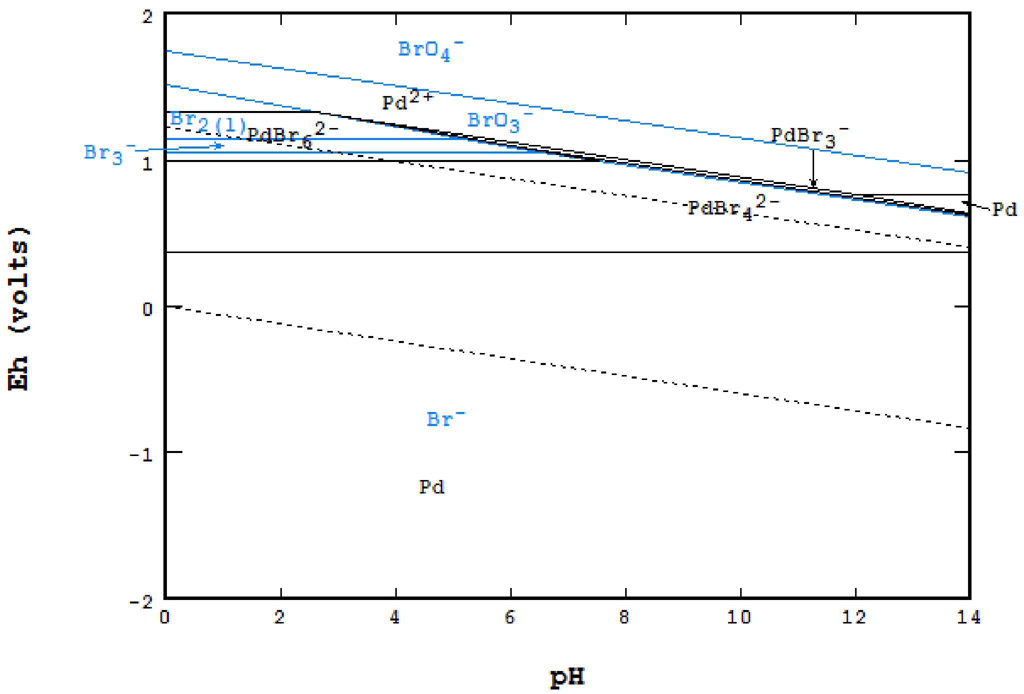

Figure S2. Eh-pH diagram of Br-Pd-H2O system at 25 °C ([Pd] = 10^{-5} M, [Br] = 0.775M) (Stabcal).

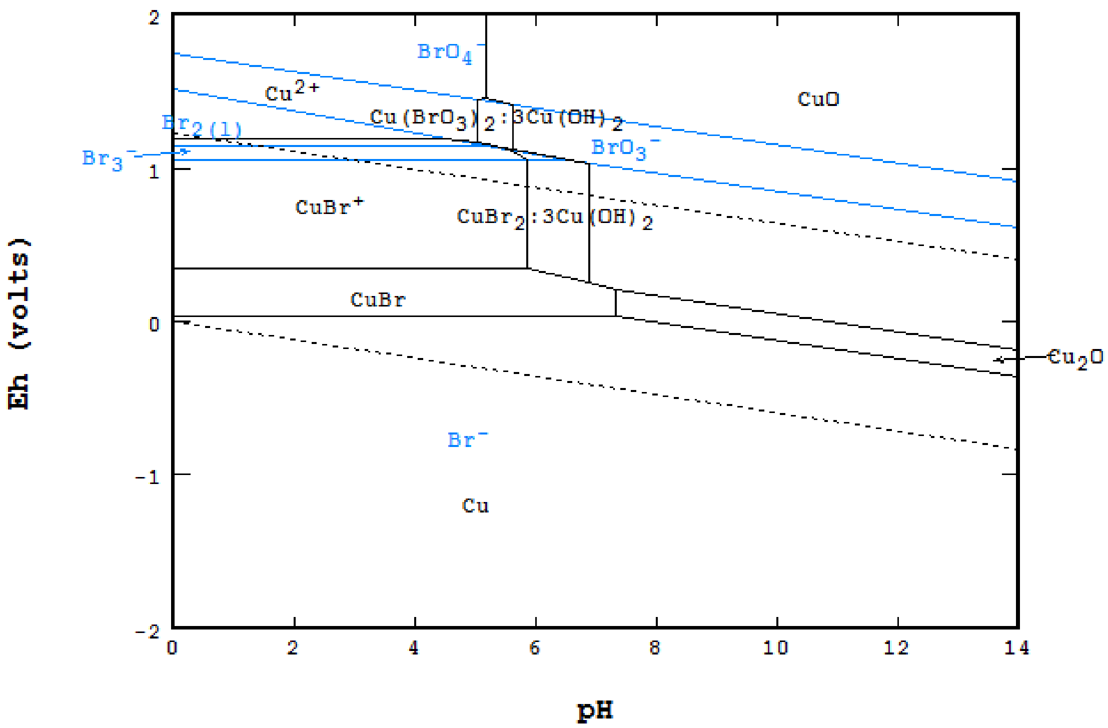

Figure S3. Eh-pH diagram of Br-Cu-H2O system at 25 °C ([Cu] = 10^{-3} M, [Br] = 0.775M) (Stabcal).

2. Supplementary Materials B: Kinetic Experimental Results

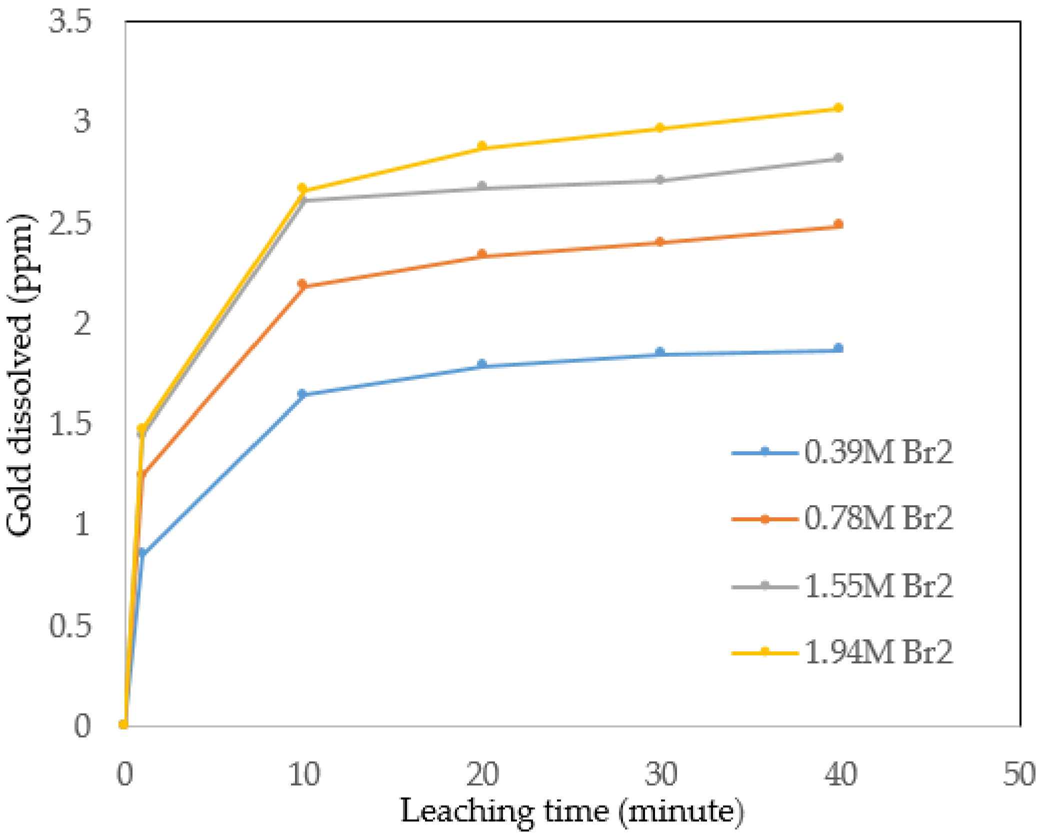

Figure S4. Effect of bromine concentration on gold dissolution at 23.5 °C and 400 RPM.

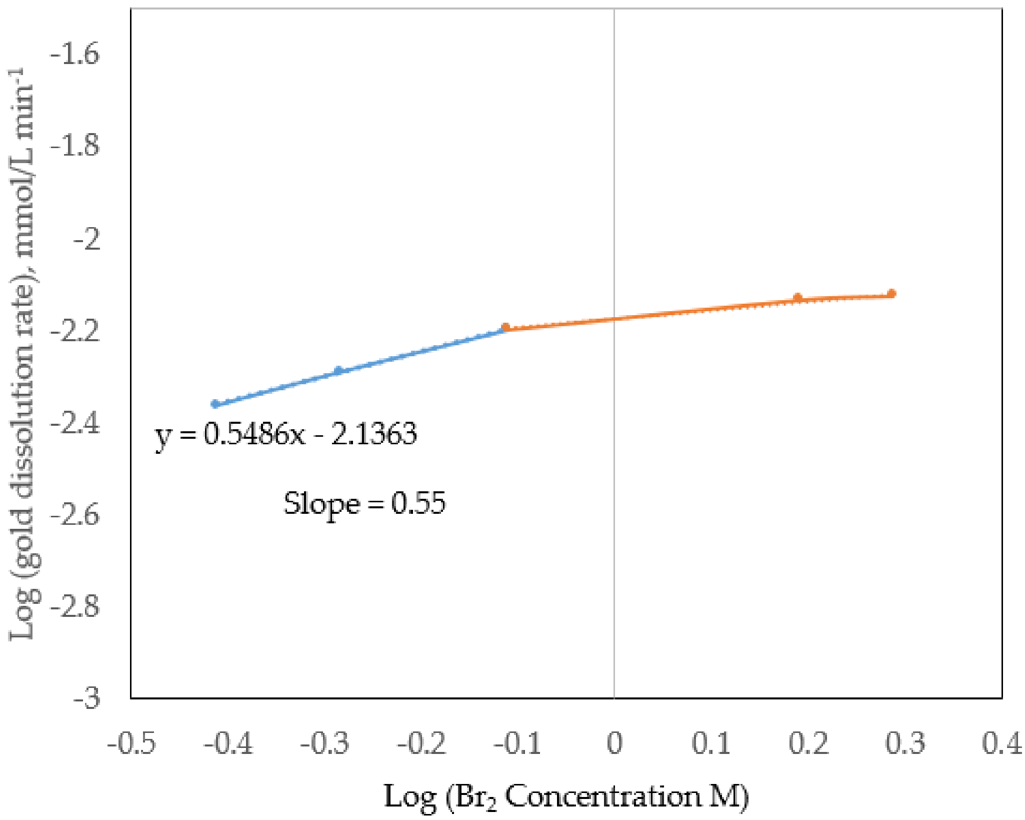

Figure S5. Reaction orders with bromine during gold dissolution.

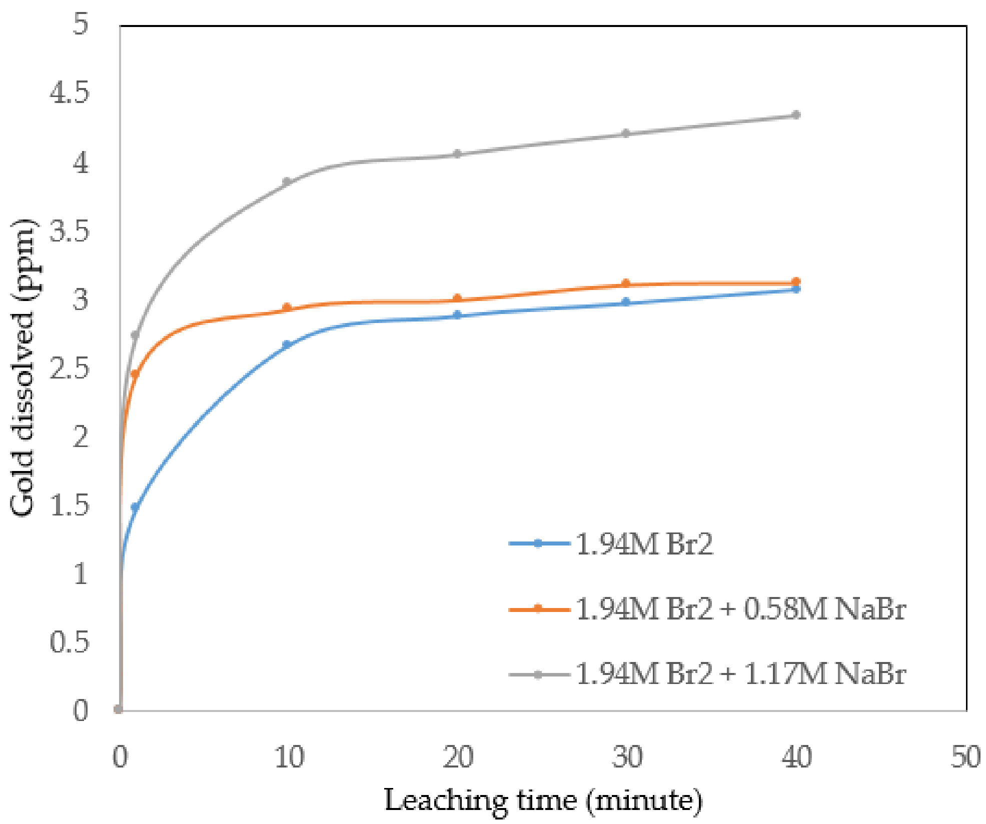

Figure S6. Effect of sodium bromide on gold dissolution at 23.5 °C and 400 RPM.

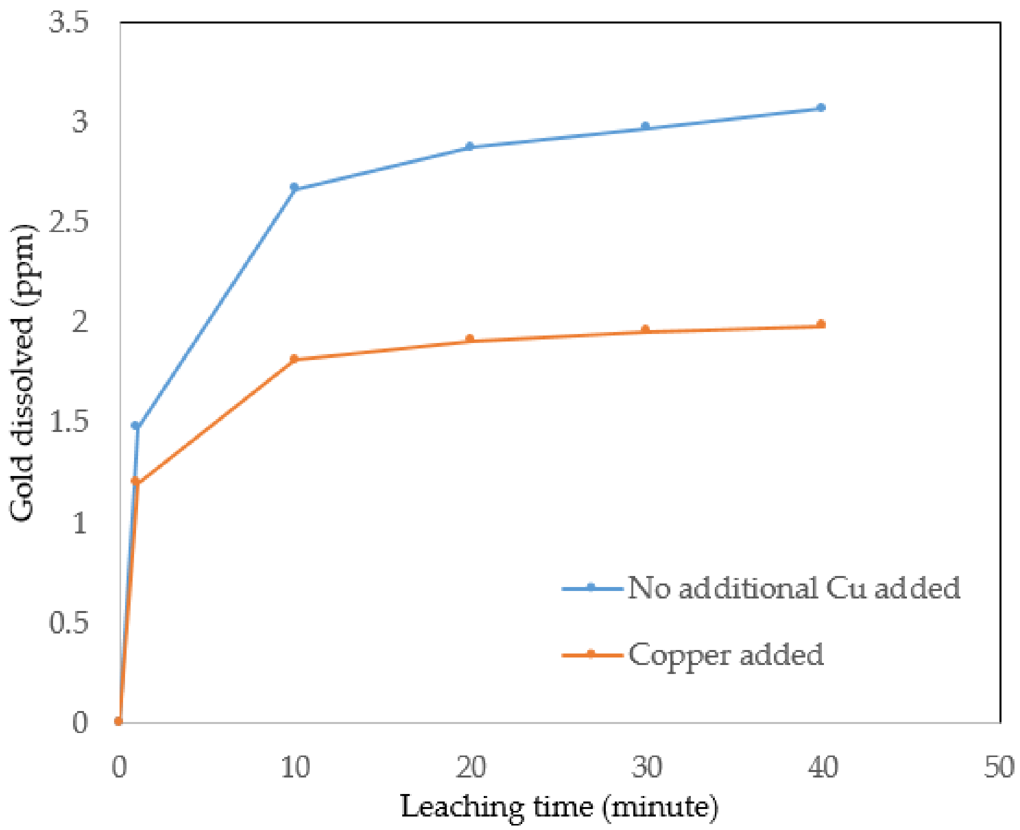

Figure S7. Effect of copper on gold dissolution at 23.5 °C and 400 RPM.

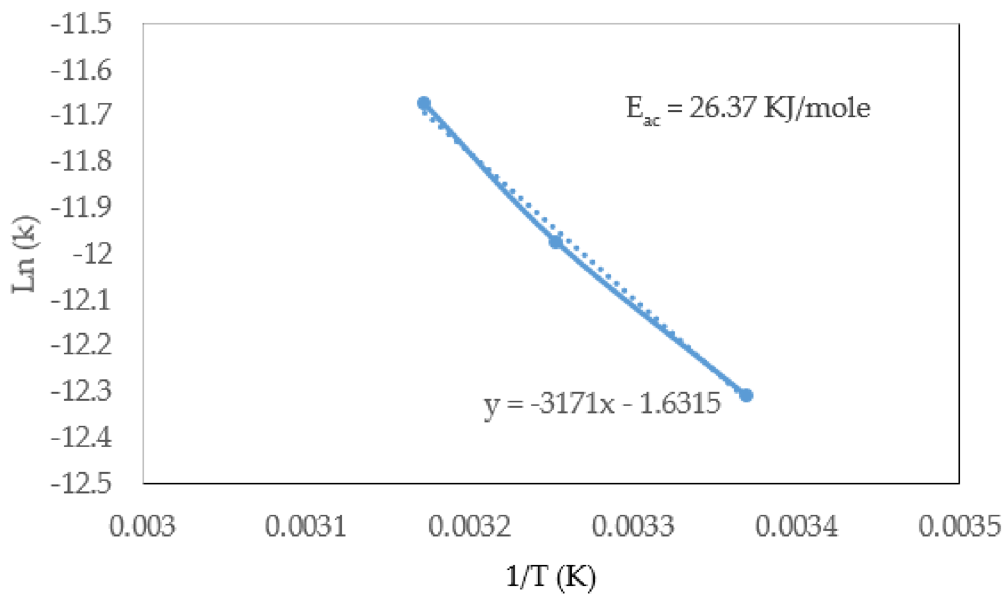

Figure S8. Arrhenius Plot for the gold-bromine leaching system.

3. Supplementary Materials C: Kinetic Model Derivations

3.1. Shrinking Model for Spherical Particles

In a quasi-steady state with a constant atmospheric pressure, with respect to the fluid film diffusion controlling, the reaction rate of Au can be described as follows:

$$-\frac{1}{S}\times\frac{dNAu}{dt}=\frac{1}{4\pi R^2}\times\frac{dNAu}{dt} \quad \text{(S1)}$$

where S is the surface area of the shredded waste print circuit board particle.

Since $dN_{Au} = \varrho_{Au} \cdot dV = 4\pi\varrho_{Au}R^2dR$

Thus, we have

$$-\frac{1}{S}*\frac{dNAu}{dt}=-\frac{1}{4\pi R^2}\times\frac{dNAu}{dt}=-\frac{1}{4\pi R^2}\times 4\pi\rho AuR^2\times\frac{dR}{dt}=-\rho Au\,\frac{dR}{dt}=h(C_{Gb}\text{-}C_{Gs}) \quad \text{(S2)}$$

where C_{Gb} represents the bulk concentration of the mixture of bromine and bromide ($Br_2 + 2Br^-$), and C_{Gs} is the concentration of the mixture of bromine and bromide at the gold surface ($Br_2 + 2Br^-$).

For a diffusion controlling process, $C_{Gs} = 0$.

In a Stroke's regime,

$$h = 2D/d = D/R \quad \text{(S3)}$$

Equation (S2) can be reduced to

$$R\rho_{Au}\frac{dR}{dt} = DC_{Gb} \quad \text{(S4)}$$

Two boundary conditions:

Condition 1: $R = R_0$, $t = 0$

Condition 2: $R = R$, $t = t$

By integrating Equation (C-4),

$$\rho\int_{Ro}^{R} -RdR = DC_{Gb}\times\int_0^t dt \quad \text{(S5)}$$

If t_c is defined as $t = tc$ when $R = 0$,

$$t_c = (\varrho_{Au}R_0^2)/(2C_{Gs}D) \quad \text{(S6)}$$

Therefore,

$$t/t_c = 1 - (1-X_{Au})^{2/3} \quad (S7)$$

where $X_{Au} = 1 - (Mass_{(unreacted)}/Mass_{(original)}) = 1 - (R/R_0)^3$

If the reaction is chemically controlling, we have

$$-\frac{1}{S} * \frac{dNAu}{dt} = -\frac{1}{4\pi R^2} \times 4\pi\rho Au R^2 \times \frac{dR}{dt} = -\rho Au\ \frac{dR}{dt}$$
$$= 0.196 \cdot EXP(-26365/RT) \times C_{Br2}^{0.55} \times C_{NaBr}^{0.16} \times C_{Cu}^{-0.41} \quad (S8)$$

Analogous to the two boundaries mentioned above and by integrating Equaion (S8),

$1 - R/R_0 = (0.196 \cdot EXP\ (-26365/RT) \times C_{Br2}^{0.55} \times C_{NaBr}^{0.16} \times C_{Cu}^{-0.41}/R_0\varrho_{Au})t$

If t_c is defined as t = tc when R = 0,

$$t_c = (\varrho_{Au}R_0)/(\ 0.196 \cdot EXP(-26365/RT) \cdot \times C_{Br2}^{0.55} \times C_{NaBr}^{0.16} \times C_{Cu}^{-0.41}) \quad (S9)$$

Therefore, at a constant temperature (23.5 °C)

$$t/t_c = 1 - (1 - X_{Au})^{1/3} \quad (S10)$$

3.2. Shrinking Model for flat plates

In a quasi-steady state with a constant atmospheric pressure, for the diffusion controlling, the reaction rate of Au can be described as follows:

$$-\frac{1}{S} \times \frac{dNAu}{dt} = \frac{1}{xy} \times \frac{dNAu}{dt} \quad (S11)$$

where S is the surface area of the shredded waste print circuit board particle, x and y are the two dimensions perceptional to the z axis which is the direction of the gold disappearance.

Since $dN_{Au} = \rho_{Au} \times dV = \rho_{Au} \times xydz$

Thus, we have

$$-\frac{1}{S} * \frac{dNAu}{dt} = -\frac{1}{xy} * \frac{dNAu}{dt} = -\frac{1}{xy} * \rho Auxy * \frac{dz}{dt} = -\rho Au\ \frac{dz}{dt} = h(C_{Gb}\text{-}C_{Gs}) \quad (S12)$$

where C_{Gb} represents the bulk concentration of the mixture of bromine and bromide ($Br_2 + 2Br^-$), and C_{Gs} is the concentration of the mixture of bromine and bromide at the gold surface ($Br_2 + 2Br^-$).

For a diffusion controlling process, $C_{Gs} = 0$.

Equation (S12) can be reduced to

$$\rho_{Au}\frac{dz}{dt} = hC_{Gb} \quad (S13)$$

Two boundary conditions:

Condition 1: $z = z_0$, $t = 0$

Condition 2: $z = z$, $t = t$

By integrating Equation (S13),

$$\rho \int_{zo}^{z} -dz = hC_{Gb} \int_0^t dt \quad (S14)$$

If t_c is defined as t = tc when z = 0,

$$t_c = (\rho_{Au}z_0)/(C_{Gs}h) \quad (S15)$$

Therefore,

$$t/t_c = X_{Au} \quad (S16)$$

where $X_{Au} = 1 - (Mass_{(unreacted)}/Mass_{(original)}) = 1 - (z/z_0)$

If the reaction is chemically controlling, we have

$$-\frac{1}{S} \times \frac{dNAu}{dt} = -\frac{1}{xy} \times xy\rho Au \times \frac{dz}{dt} = -\rho Au\ \frac{dz}{dt} \tag{S17}$$

$$= 0.196 \cdot EXP(-26365/RT) \times C_{Br2}^{0.55} \times C_{NaBr}^{0.16} \times C_{Cu}^{-0.41}$$

Analogous to the two boundaries mentioned above and by integrating Equation (S17),

$$1 - z/z_0 = (k\ C_{Br2}^{0.55} \times C_{NaBr}^{0.16} \times C_{Cu}^{-0.41}/z_0\rho_{Au})t \tag{S18}$$

If t_c is defined as t = tc when z = 0,

$$t_c = (\rho_{Au} z_0)/(\ k\ C_{Br2}^{0.55} \times C_{NaBr}^{0.16} \times C_{Cu}^{-0.41}) \tag{S19}$$

Therefore,

$$t/t_c = X_{Au} \tag{S20}$$