Recycling of Scrap Jewelry in Aqua regia :- A Case Study in Dissolution Kinetics

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Abstract:
This work covers dissolution of a scrap jewelry, plant sludge from gold refinery, jewelry unit shop floor dust in aqua-regia. The effects of temperature, stirring speed and particle size on the dissolution rate has been evaluated. Experimental results showed that scrap jewelry dissolution increases with increasing temperature, stirring speed and decreases with increase in particle size. Every kg gold content in scrap was dissolved in 4.5 kg aqua regia in 60-180 minutes depending upon scrap particle size at ambient temperature and a stirring speed of 200 rpm. The experimental leaching data was regressed to fit shrinking core model with diffusion process controlled as it seemed slowest step. The present study showed that leaching process followed order reaction 0.8, activation energy of 5.50 kJ/mole and Arrhenius Constant $1.67 \times 10^{-5}$ min$^{-1}$. In our another ongoing project on preliminary feasibility study of showed recycling scrap jewelry and or ewaste highly profitable business. Our understanding on application of shrinking unreacted core model on experimental data enabled us to reduce batch cycle time and thereby enhance plant capacity utilization significantly. This is a case of molecular diffusion rate step governing the overall process of recycling scrap jewelry using aqua regia solution.

Keywords: Scrap jewelry, recycling kinetics, diffusion, mass transfer, Shrinking core model.

Introduction:
Globally, the natural ore resources are on decline. Fresh ore mining is expensive and leads to evasion of ecology. There is stronger resistance by ecologists against mining than ever. Major portion of gold in India goes in ornaments. The ewaste from used printed circuit boards (PCBs), mobiles, CTVs, personal computers etc is another attractive economic source for precious metals recovery as it involves least cycle time, energy and investment contributing to community development in terms of employment and better quality of life and environment.

Hydrometallurgy emphasizes on extraction and purification of metals from ores; or recycling of scrap, slag anode slime waste processing etc. Hydrometallurgical processes although sluggish, the scale up is simple and economic as the material handling is by easy pumping. Scrap jewelry
dissolution for recovering gold is one of the finest example of simultaneous role play of all three processes viz. reaction kinetics, mass transfer and diffusion making overall system more complex and interesting situation.

Modeling of leaching process gives better insight on the mechanism for process parameters estimation and scale up. The metal leaching from mineral ores, process waste, ewaste, has to proceed through multiple process steps. A liquid comes in contact with solid, reacts non-catalytically with it forming product. This product layer formed blocks the reaction sites becoming barrier for transport of reactant species from liquid bulk. At the same time product/s released from reaction will have resistance from product layer, to flow towards bulk liquid. This can well be described by shrinking unreacted core model. In this case the model assumes reaction occurring first at outer layer of the particle and the reaction zone traverses deeper in to the solid. There exists an unreacted core of material that is shrinking during the course of reaction. Shrinking core model aptly describes complex leaching process as it considers simultaneously occurring chemical reaction kinetics, mass transport and diffusion steps.

Among amalgamation, cyanidation, cupellation, Miller chlorination and Modified Wohlwill process, aqua regia route options, the last one is environmentally benign and successfully practiced by medium and small scale refiners for recycling scrap jewelry to recover gold and silver. Various reactions involved include:

\[
\begin{align*}
\text{Au}^{(s)} & + 3 \text{NO}_3^{-} (aq) + 6 \text{H}^{+} (aq) = \text{Au}^{3+} (aq) + 3 \text{NO}_2 (g) + 3 \text{H}_2\text{O} (l) \\
\text{Au}^{+3} (aq) + 4 \text{Cl}^{-} (aq) & = \text{AuCl}_4^{-} (aq) \\
\text{Au} + 4 \text{HCl} + \text{HNO}_3 & = \text{HAuCl}_4 + \text{NO} + 2 \text{H}_2\text{O} \\
2 \text{AuCl}_4 + 2 \text{NaHSO}_3 & = 2 \text{Au} + 4 \text{HCl} + \text{Na}_2\text{SO}_4 + \text{SO}_2 \uparrow \\
\text{Au}^{(aq)} + 3 \text{HNO}_3(l) + 4 \text{HCl}_(l) & \rightarrow \text{HAuCl}_4^{(aq)} + 2 \text{H}_2\text{O}(l) + 3 \text{NO}_2(g) \\
2 \text{AuCl}_3^{(aq)} + 6 \text{NaHSO}_3(l) & \rightarrow 2 \text{Au}^{(s)} \downarrow + 3 \text{SO}_2(g) \uparrow + 3 \text{Na}_2\text{SO}_4(s) + 6 \text{HCl}_(aq)
\end{align*}
\]

Mechanism considered follows steps:

(a) Transport of solute from bulk mineral to solid-liquid interface,
(b) Diffusion of leaching solution through porous product layer at interface,
(c) Reaction between mineral and leaching agents (aqua regia) forming soluble HAuCl₄,
(d) Diffusion of Au from interface through product layer,
(e) Diffusion of Au from surface on adding NaHSO₃.

Consider initial radius of the sphere \( r_0 \) The fractional conversion \( X = 1 - \left( \frac{r}{r_0} \right)^3 \). Then we have,

For the chemical reaction controlled situation:

\[
1 - (1 - X)^{1/3} = \left( V_m C k_0 k'/r_0 \right) t = \left( b k_s C / \rho_B r_0 \right) t
\]

\[
1 - ( -X )^{1/3} = k_t t
\]

\[ (1) \]
For the diffusion through liquid film control the model takes form of

\[ 1 - (1 - X)^{1/3} = \left( \frac{\text{CVD}}{\delta \sigma r_0} \right) t \]
\[ 1 - (1 - X)^{2/3} = \left( \frac{2bCD}{\rho B r_0^2} \right) t \]
\[ \ln(1 - X) = -\left( \frac{KA}{V} \right) t \]

\[ 1 - 2X/3 - (1 - X)^{2/3} = k_{dt} \]

And for mass transport governed case, we have

\[ 1 - 2X/3 - (1 - X)^{2/3} + b [ 1 - (1 - X)^{1/3} ] = k_{mt} t \]  \( \text{(3)} \)

where \( X \) is the fraction of gold dissolved; \( t \) is contact time (minutes); \( k_r, k_d \) and \( k_m \) are the specific reaction rate constant, diffusion coefficient and mass transfer coefficient respectively.

Equation (1) is based on the chemically controlled reaction and its slope corresponds to the apparent rate constant \( k_r \). Equation (2) on diffusion controlled and its slope gives the apparent rate constant \( k_d \). Lastly, Equation (3) is based on a mixed controlled reaction and apparent rate constant \( k_m \). The Equation (2) fitted experimental data best and hence was chosen to describe model prediction for the gold dissolution.

This investigation aims to establish the conditions for leaching of scrap jewelry in aqua regia.

**Experimental:**

This study considers recycling scrap jewelry sample grains drawn from stock composition was \( \text{Au} = 80-85\%, \text{Ag} = 12-14\%, \text{Cu} = 4-8\% \). The scrap jewelry stock was micronized using locally fabricated compressed air with air jet atomization system. High concentration HCl and HNO\(_3\) and analar grade reagents from BDH, and LobaChemie; and RO water were used for analytical preparations. Samples drawn intermittently were analyzed for gold assay on XRF and ICP.

The process route uses environmentally benign aqua regia for the extracting and purification of precious metals from old ornaments. Dissolution of scrap jewelry is carried out in stirred glass reactor with propeller and baffles assembly. First aqua regia quantity is prepared as per gold content in the scrap jewelry batch charge and then the micronized scrap is added with strong agitation. Samples are withdrawn for analysis intermittently.

Kinetic specific reaction rate constant is determined essentially from continuous stirred tank reactor (CSTR) or from high precision initial rate data in the case of batch reactor. Mass transfer resistance have to be eliminated as far as possible to estimate specific reaction rate. 1 g. scrap micronized ornament sample was leached in 100 ml aqua regia. In every experiment, only one process parameter is varied at a time, keeping all other fixed.
Results and Discussion:

The model parameter estimation has been done by direct regression on reliable experimental data. A careful look at relative magnitudes of processes viz. specific reaction rate constant, mass transfer coefficient and diffusivity suggests that the diffusion rate being slowest governs the speed of overall process, although both specific reaction rate constant and mass transfer coefficients are comparable but nearly 10 times larger than molecular diffusion coefficient. Thus it is prudent to evaluate all these process parameters to understand the overall process soundly.

Effect of Temperature:

The effect of temperature was studied over 30–80°C and from the results presented in Figure 1.

![Figure 1: Gold dissolution in aqua regia at 30°C, 40°C, 60°C and 80°C agitation speed 200 rpm](image)

Clearly, at above 40°C, temperature effect on rate process appears to be mild because of prominence of both diffusion process and mass transfer. At the same time the NOx, HCl gases released during gold dissolution/silver precipitation step, escape from open system else build up of pressure in closed system. The flue gas is scrubbed and the liquid effluent is treated either with caustic or slaked lime.

Effect of Stirring Speed:

The percentage of gold dissolved versus stirring speed was investigated between 0–600 rpm is as indicated in Figure 2. The amount of gold dissolved increases with stirring speed between 0–200 rpm. Without putting agitator on, about 55% gold dissolved in around 3 hours where slight turbulence and surface renewal took place because of gases evolved inside during dissolution.
Effect of Particle Size:

The influence of particle size on the dissolution of gold from scrap in aqua regia is displayed in Figure 3. The 6-10 micron size scrap jewelry exhibited highest percentage gold dissolution. Obviously, this is due to very high reaction sites and surface area in which case diffusion boundary layer thickness is minimal and hence speeding up of dissolution process.
The model parameters values \( k_r \), \( k_d \) and \( k_m \) are estimated from regression on experimental data conversion vs time data using Eqns. (1), (2) and (3) respectively. From these estimates it is evident that the overall process of scrap dissolution in aqua regia is governed by molecular diffusion.

It should be noted that in the present complex system because of simultaneous role play of all three process steps of reaction, mass transfer and molecular diffusion, the first two rate constants show rather irregular variation with time. Therefore, the Arrhenius plot for only for \( k_d \) for its temperature dependence has been brought out in Figure 4. The Arrhenius constant (A) for the gold dissolution in aqua regia is \( 1.67 \times 10^{-5} \text{ min}^{-1} \).

A small positive value of 5.5 kJ/mole for activation energy suggests that the reaction is mildly endothermic. From the initial rate data plot of \(-\ln \left(1-X_A\right)\) versus \( t \) results a straight line with slope equal to specific reaction rate constant which is ample proof for near first order reaction. The values for all three steps are in close agreement with likewise solid-liquid physico-chemical-diffusion systems in literature.
Dimensionless numbers give quick understanding and physical significance of the chosen process and guide us to apply engineering principles more effectively. Some of the relevant dimensionless quantities have been computed and listed in the nomenclature section and they form the strong base for our firm conclusions.

Here, Peclet number is regarded as a measure of the role of convection against diffusion. It is product of Reynolds number and Schmidt number. \( N_{Pe} = \left( \frac{\text{convective diffusion}}{\text{molecular diffusion}} \right) \). In the present hydrometallurgical system, the Schmidt number is of the order of \( 1.11 \times 10^3 \); and Reynolds number is \( 1.131 \times 10^3 \). For Peclet number is \( > 1 \), implying convective diffusion is more dominating than molecular diffusion in such systems.

For systems with large Peclet numbers, it is assumed that there is a diffusion boundary layer at some distance from the solid surface. The units of \( k_m \) being same as those of \( \frac{D}{\delta} \), where \( \delta \) is the diffusion boundary layer thickness, \( k_m \), is often substituted by this ratio. The diffusion boundary layer thickness is often estimated by relationship \( k_m = \frac{D}{\delta} \), provided \( k_m \) is known. Our calculations show value of diffusion boundary layer thickness of about \( 5.77 \times 10^{-4} \) m which is about scrap jewel grain size.

The mass transfer coefficient for a flat plate where fluid flows past the plate at a velocity \( V_o \) has been well documented. Mass transfer coefficient for such a system can be estimated from first principles as follows:

\[
k_m = 0.664D^{2/3} V^{-1/6} L^{1/2} V_o^{1/2} \quad \text{For } Re < 10^6.
\]

Where, \( D = \) the diffusivity of the diffusing species; \( V = \) the kinematic viscosity of the fluid; \( L = \) the length of the plate. Both the calculated values of mass transfer coefficient and diffusion coefficient from empirical equations are in close agreement with those our earlier tabulated values. For the case of mass transfer coefficient for particulate systems is given by

\[
k_m = \left[ (2D/d) + 0.6V_{t}^{1/2}d^{-1/2}V^{-1/6}D^{2/3} \right].
\]

Since shrinking core model has all three features viz. kinetics, mass transfer and diffusion, it has greatest capability to represent experimental data almost closely. Such understanding enables right choice of reactor configuration which leads to significant reduction in cycle time, and plant productivity.

The author has witnessed in Titan Industries Ltd. Bangalore, India, earlier scrap jewelry was just introduced as such in the aqua regia solution prepared in the stirred reactor vessel in which case dissolution step alone took more than 5-6 hours. Whereas the finer grains of shredded jewelry using compressed air and water jet atomization up to 6-10 microns dissolve in about an hour time. Compared to earlier 4 kg batch size, currently 15 kg scrap jewelry is processed with greater ease in the same reactor/dissolution vessel. Incorporating up and down fluid motion by a novel agitator configuration with baffles assembly, two stage micro filter for effective separation of silver precipitate and in the later step washing gold grains with mineral acids and DM water, it is
possible now to produce 99.99% purity gold on regular basis. Thus the entire gold refining cycle time is completed in about 5 hours.

One can visualize direct financial impact of idle time of gold processing in terms of cash loss incurred. Therefore there is merit in recovering every trace of gold from scrap or in any waste/effluent containing it in compact cycle time. The material of construction is crucial to successfully withstand very aggressive environment of aqua regia and acid fumes to reduce plant downtime. Online sampling is done intermittently. Gold refinery effluent, jewelry shop floor dust, casting powder being richest wastes, it is worth recovering every microgram of gold.

Conclusions:

In this study, It was found that the rate of scrap gold dissolution increases with aqua regia concentration, stirring speed, (mildly with temperature) and decreasing particle size.

As per analysis of shrinking unreacted core model regressed on experimental data for dissolution of gold in aqua regia, it was found overall rate to be governed by slowest step molecular diffusion process.

Activation energy values of 5.5 kJmol$^{-1}$ and Arrhenius constant $1.67 \times 10^{-5}$ min$^{-1}$ were obtained for gold dissolution in aqua regia and the order of reaction was 0.8 (close to first order).

We strongly recommend scrap jewelry in micronized grains size to be used and robust agitator providing fluid both up and down motion; and in radial direction to effect renewal of surface area reaction sites.

From previous 20 years plant experience, we like to emphasize on appropriate material of construction for reaction vessel, storage tanks, pumps, piping etc would be glass, Polypropylene, PTFE, titanium. In the case of glass reactors, utmost care has to be exercised to avoid using caustic or hydrofluoric acid.

Understanding of reaction mechanism, modeling have benefited plant personnel reduce batch cycle time and enhance plant capacity utilization making business highly profitable and safe.

The finest contribution of this work is experiment data on commercial plant and most of the process parameters quantified shall be of great relevance to process/plant designers, practicing engineers, consultants and academicians.

Nomenclature and model parameters:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Total surface area of particle,</td>
<td>$4.0 \times 10^{-6}$ m$^2$</td>
</tr>
<tr>
<td>A</td>
<td>parameter = $5.0 \ [0.66 + 0.4 \log K]$</td>
<td>0.365</td>
</tr>
<tr>
<td>b</td>
<td>stoichiometric factor</td>
<td>$1 - 1.5$</td>
</tr>
<tr>
<td>C</td>
<td>concentration of Cl$^-$</td>
<td>$1.04 \times 10^4$ mol/m$^3$</td>
</tr>
<tr>
<td>$C_b$</td>
<td>concentration of species $i$ in the bulk solution</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$C_s$</td>
<td>concentration of species $i$ at the solid surface</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat capacity at constant pressure</td>
<td>0.031 kcal/kg K</td>
</tr>
</tbody>
</table>
D = diffusion coefficient 
1.50x10^9 m^2/s

D_{AB} = mass diffusivity 
6.4x10^{-5} m^2/s

D_p = particle diameter 
1x10^{-3} - 1x10^{-5} m

g = acceleration due to earth’s gravity 
9.81 m/s^2

h = convective heat transfer coefficient

K = parameter 
4gd^3p (\rho_S - \rho) / (3\mu^2) 
70.63

k = thermal conductivity

k_m = D/\delta for particulate system 
3.11x10^{-5} m/s

k_m = mass transfer coefficient (k_0k’) predicted 
2.6667x10^{-6} 1/s

k_m = by N_{Sh} D/L_{ch} = 2.004/ ( 1131x 0.00111) 
3 x 10^{-6} m/s

k_m = by ( 2 D/d ) + [ 0.6 V_t^{1/2} d^{-1/2} v^{1/6} D^{2/3} ] 
3.1x10^{-5} m/s

k_0 = number of reactive sites per unit area 
m^2

k’ = rate constant 
m^3/s

k_r = first order reaction rate constant (same as K) 
6.16 x10^{-5} m/s

L_{ch} = Characteristic length (value close to colloidal particle size) 
20x10^{-9} m

M = Molecular weight of Au + AuCl_3 
3.304x10^{-1} kg/mol

N_i = mass bulk of species i 
mol/m^2s

N_{Bi} = Biot number = h x l / kb < 0.1 means heat transfer resistance inside the body is very low

N_{Fo} = Fourier number = (\alpha t/R^2) = heat conduction/heat storage (for heat transfer)

N_{Fo} = Fourier number = Dt/L^2 = current time/time taken to reach steady state

N_{Gr} = Grashof number = g\beta (T_S-T_b) L^3 / \nu^2 = Buoyancy force/viscous force 
2.49x10^9

N_{Gz} = Graetz number = for heat transfer (D/L) N_{Re} N_{Pr} = for mass transfer (D/L) N_{Re} N_{Sc}

N_{Le} = Lewis number = K/(\rho C_p D_{AB}) = 70.63/(1200x0.031x1.5x10^{-9}) = 1.266x10^9

N_{Nu} = Nusselts number (HT) = L_{ch} x h/K = interface flux/molcular flux = 1.2x10^{-10}

N_{Nu} = Nusselts number (MT) = (f/2) x L_{ch} x V_{ch}/\mu = interface flux/molcular flux

= ch length x transfer coefficient/diffusivity = (f/2)xN_{Re} = (f/2) (1131) = 283
\[ N_{Pe} = \text{Peclet number (HT)} = \frac{L_{ch} x V_{ch}}{(K/\rho C_p)} \]
\[ = \text{ch length x ch. Velocity / diffusivity} \]
\[ N_{Pe} = \text{Peclet number (MT)} = \frac{L_{ch} x V_{ch}}{(D_{AB})} \]
\[ = \text{ch length x ch. Velocity / diffusivity} \]
\[ N_{Pr} = \text{Prandtl number} = \frac{C_p \mu}{k} = 0.031 x 2 \times 10^{-3}/70.63 \]
\[ = \text{momentum diffusivity/heat diffusivity} \]
\[ N_{Ra} = \text{Rayleigh number} = N_Gr x N_{Pr} = g \beta (T_s-T_b) L^3/\alpha \nu \]
\[ = \text{(Buoyancy force/viscous force)x(momentum diffusivity/heat diffusivity)} \]
\[ N_{Re} = \text{Reynold number} = \left[ 4g^2 (\rho_F - \rho_S)2D_i^3 / (225 \rho_S^2 \nu)^{0.33} \right] (Di/\nu) = 1131 \]
\[ = \text{Dup } \mu = \text{inertial forces / viscous forces} = 10^{-4} x 9.426 x 1200/(2x10^{-3}) \]
\[ N_{Sc} = \text{Schmidt number} = \nu/D = \mu C_p / p_c D_{AB} = 2 \times 10^{-3}/(1200x1.5x10^{-9}) \]
\[ = \text{momentum diffusivity/mass diffusivity} \]
\[ N_{Sh} = \text{Sherwood number} = \left( \frac{L_{ch} \times K}{D_{AB}} \right) = \text{interface flux/molecular flux} \]
\[ = \text{(ch. Length x transfer coefficient) /diffusivity} = 20 \times 10^{-3}/70.63/1.55 \times 10^{-9} \]
\[ N_{St} = \text{Stanton number (HT)} = \frac{2}{f} \left( \frac{h}{\rho C_p V_{ch}} \right) = 2.8 - 4.3 \]
\[ = \text{heat transfer coefficient / momentum transfer coefficient} \]
\[ N_{St} = \text{Stanton number (MT)} = \frac{2}{f} \left( \frac{K}{V_{ch}} \right) = \frac{N_{Sh}}{(N_{Re} N_{Sc})} = 1.60 \]
\[ = \text{mass transfer coefficient / momentum transfer coefficient} \]
\[ R = \text{diameter of solute} \]
\[ r_0 = \text{radius of solid sphere} \]
\[ T_b = \text{bulk temperature} \]
\[ T_s = \text{surface temperature} \]
\[ t = \text{characteristic time} \]
\[ u = \text{mean characteristic velocity of objective relative to fluid motion} \]
\[ V = \text{total volume of solution} \]
\[ V_{ch} = \text{characteristic velocity} \]
\[ V_m = \text{Molecular weight of Au} + \text{AuCl}_3 \left( \frac{M}{\rho} \right) \]
\[ V_0 = \text{velocity of fluid past flat plate} 4.6 \text{ cm/s} \]
\[ V_t = \text{terminal settling velocity} = \mu x 10^A / \nu = 2 \times 10^{-3} x 10^{0.365} / (10^{-4} x 1200) = 0.0386 \text{ m/s} \]

Greek letters
\[ \alpha = \text{thermal diffusivity} \]
\( \beta = \) volumetric thermal expansion coefficient \((= 1/T \text{ for ideal fluids, } T \text{ absolute temperature})\)

\( \delta = \) diffusion boundary layer thickness \(= D/(2 + 0.6 \, R_e^{0.5} \, S_e^{0.33}) = 5.77 \times 10^{-4} \, \text{m} \)

\( \delta = D/k_m = 1.5 \times 10^{-9}/2.6 \times 10^{-6} \) for particulate system \(= 0.6 \times 10^{-6} \, \text{m} \)

\( v = \) kinematic viscosity of the fluid \(= 1.3 \times 10^{-7} \, \text{m}^2/\text{s} \)

\( \rho = \) density of Au + AuCl\(_3\) \(= 1.5 \times 10^4 \, \text{kg/m}^3 \)

\( \rho_B = \) molar density of Au + AuCl\(_3\) in solid \(= (\rho / M) = 1.575 \times 10^{-2} \, \text{mol/m}^3 \)

\( \rho_F = \) Fluid density \(= 1.2 \times 10^3 \, \text{kg/m}^3 \)

\( \rho_p = \) particle density \(= \text{kg/m}^3 \)

\( \rho_s = \) solid density \(= 1.93 \times 10^4 \, \text{kg/m}^3 \)

\( \Delta \rho = [\rho_p - \rho_s] = 1.81 \times 10^4 \, \text{kg/m}^3 \)

\( \mu_C = \) dynamic viscosity of the solution \(= 2.0 \times 10^{-3} \, \text{kg/m/s} \)

References:


