

Mathematical Model of Gold Lixiviation

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Abstract: Processing of different refractory gold ores by wet chlorination, followed by chloroauric complex (HAuCl₄) separation by adsorption on macroporous polymers (ion exchange resin) was studied and patented by INCDMRR – ICPMRR [1,2]. This work presents the theory and practice aspects of gold lixiviation by wet chlorination. The present work theoretically approaches the gold lixiviation from refractory gold ores. Thus, the gold lixiviation using nascent chlorine at the ambient temperature from hydrogravitationally refractory concentrate, was experimented. The gold lixiviation mechanism presumes the initial AuCl formation on the metallic gold surface followed by complexing with Cl⁻ to AuCl₂⁻. This complex is oxidized in solution with NaOCl to AuCl₄⁻ [3,4]. The success of gold lixiviation from hydrochlorous solutions using Cl⁻/NaOCl solutions depends on mineralogical composition of material. A mathematical model for lixiviation time computing was proposed, using as parameters the initial radius of gold particle (R_{in}) and molar fraction of chlorine in solution ($y_{Cl_{2\infty}}$).

$$\tau_s = \frac{\rho_{Au}}{M_{Au}} \frac{R_{in}^2}{D_{Cl_2} C_T \ln(1 - y_{Cl_{2\infty}})}$$

Keywords: gold, lixiviation, wet chlorination, mathematical model

1. Introduction

The technology of gold lixiviation from ores and concentrates, using hydrochloric acid and extraction from solution by adsorption using a net porous polymer, is applying for a special category of raw ores, namely the refractory gold ores.

In such ores, gold is disseminated into quartz, feldspar, chalcopyrite and arsenopyrite and the classical cyanidation procedure is inefficient due to the low extraction yields. The presence of carboniferous materials and clays in these refractory ores restrains the gold lixiviation, determining high cyanide consumption [1,2].

Additionally, the gold encapsulation into silica and its association with sulphurous minerals make that ore to become refractory, cyanidation-proof, even after a fine-grinding. In such situations, the gold ore has to be pretreated by calcination, high pressure oxidation, bio-oxidation or chemical oxidation, in order to decompose the carboniferous material or to oxidize the sulphides [3,4].

The cyanidation procedure applied for gold lixiviation in industry is extremely polluting; the free cyanide and the cyanide compounds resulting from process collect into sludge bed of the exploitation, where they could remain for a long time.

In order to remove these deficiencies but also considering the ecological aspects, the recently developed researches at national level [5] and international level allowed to develop some eco-technologies which operate

with high extraction yields and use environmental friendly reagents (non-polluting reagents).

Processing of different refractory gold ores by wet chlorination, followed by chloroauric complex (HAuCl₄) separation by adsorption on macroporous polymers (ion exchange resin) was studied and patented by R&D NIRM (INCDMRR – ICPMRR) [6-8].

This work presents the theory and practice aspects of gold lixiviation by wet chlorination.

2. Experimental

The raw ore that was used in experiments is a refractory gold ore with the chemical composition presented in table 1, grounded at 150 μm and concentrated using a Knelson gravitationally concentrator.

TABLE 1. Chemical composition of gold ore concentrate.

Compound	%	Compound	%
SiO ₂	2.26	S	8.58
Al ₂ O ₃	0.1	Cl	17.7
CaO	0.70	As	0.17
MgO	0.026	Ni	0.001
K ₂ O	1.46	Sb	0.1
MnO	0.015	Cd	0.03
CuO	0.97	Bi	0.25
PbO	42.90	Au	0.028
ZnO	0.618	Ag	0.164
Fe ₂ O ₃	5.01		

In order to develop the experiments, the following reagents were prepared: from hydrochloric acid (HCl) 32%, solutions of 3mol HCl /l and sodium hypochlorite (NaOCl) 6% were prepared. The gold leaching was performed in a glass reactor, see figure 1. This reactor is fitted with a teflon stirrer, thermometer, redox electrode, sodium hypochlorit inlet and chlorine excess outlet using an ascendent condenser connected to a NaOH 5% containing bubble flask.



Figure 1. Experimental installation for gold lixiviation

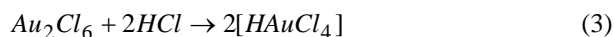
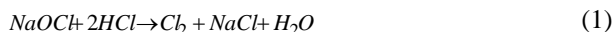
Thus, a sample of 0.05 kg solid and a HCl 3 M solution were introduced into reactor at S:L=1:1 ratio, setting the stirrer at 600 rpm. Working temperature is 20 °C. To a maximal lixiviation yield, the sodium hypochlorit amount required by active chlorine generation is 0.125 L NaOCl/kg of concentrate. The reaction is finished when the electrochemical potential of solution is exceeding 950 mV, this value being achieved after 6 hours.

When the reaction finished, the solution is filtered and analysed. Metals content of solution after lixiviation is: 0.2 g Au/L, 0.015 g Ag/L, 1.5 g Fe/L, 0.27 g Cu/L, 1 g Pb/L, 0.5 g Zn/L .

3. Results and discussion

3.1. Chemical processes related to solution used for gold lixiviation

Main chemical reactions that occur in gold lixiviation process, could be described by the following equations:

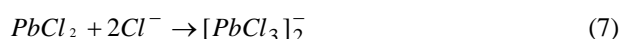
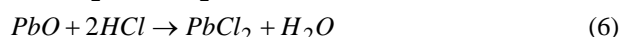


The gold lixiviation mechanism presume the initial AuCl formation on the metallic gold surface followed by complexing with Cl⁻ to AuCl₂⁻. This complex is oxidized in solution with NaOCl to AuCl₄⁻ [17,18]. The succes of gold lixiviation from hydrochlorous solutions using Cl⁻/NaOCl solutions depends on mineralogical composition of material.

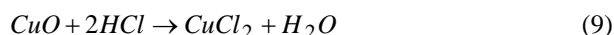
Concomitant with gold lixiviation, secondary reactions of accompanying metals are occurring. Silver is present in leaching residue as AgCl, which is obtaining as follows:



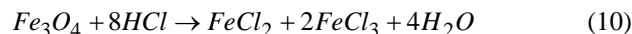
In concentrate solutions of HCl, silver chloride is more soluble then in water due to ions of [AgCl₂]⁻, [AgCl₃]²⁻, [AgCl₄]³⁻ that are obtaining. Hydrochloric acid has an weak effect to lead [19], because this is dissolving very slowly to the working temperature due to a film of PbCl₂ which deposits on Pb particles surface and inhibits the reaction. In dilluted solutions of HCl or in prezenze of Cl⁻, [PbCl₃]₂⁻ is slowly obtained:



Copper is stable in both chemical valences +1 and +2. The metallic copper is oxidized to +1 valence in the presence of different precipitating or oxidazing agents [20]. In the presence of Cl⁻ or other complexing groups from solution, the most stable state is the +1 valence one.



Fe₂O₃ from concentrate is coming from magnetite [20] and in hydrochloric acid medium a mixture of Fe(II) and Fe(III) is obtaining according to the following reaction:



3.2. Estimation of lixiviation time in batch contacting

As the figure 2 shows, for gold lixiviation using primary raw ore it need that a Cl₂ flow and its corresponding stoichiometric HCl flow to reach the gold particle surface.

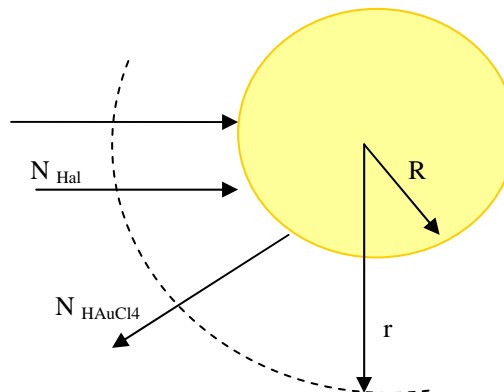
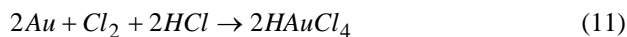


Figure 2. The basic sheet of gold particle lixiviation

In the figure mentioned above, a gold particle is considered to be a sphere with a R radius, which is located into the reaction Cl_2 and HCl containing medium. According to the overall reaction (11) of gold lixiviation, for chlorine N_{Cl_2} flow that is reaching the gold particle surface, it might be write the equation (12), where D_{Cl_2} is diffusion coefficient of chlorine in the reaction medium [21].



$$N_{\text{Cl}_2} = -D_{\text{Cl}_2} C_T \frac{dy_{\text{Cl}_2}}{dr} + y_{\text{Cl}_2} (N_{\text{Cl}_2} + N_{\text{HCl}} + N_{\text{HAuCl}_4}) \quad (12)$$

where: y_{Cl_2} is molar fraction of chlorine,

C_T is global molar concentration in the system

N_{HCl} and N_{HAuCl_4} are HCl flow, respective HAuCl_4 flow.

According to reaction stoichiometry described by equation (11), the flows of HCl and HAuCl_4 could be evaluated as a function of Cl_2 flow, as follows:

$$N_{\text{HCl}} = \frac{1}{2} N_{\text{Cl}_2} \quad (13)$$

$$N_{\text{HAuCl}_4} = -\frac{1}{2} N_{\text{Cl}_2} \quad (14)$$

Replacing the relations (13) and (14) in (12) relation, for chlorine flow is obtaining the following expression (15):

$$N_{\text{Cl}_2} = -D_{\text{Cl}_2} C_T \frac{1}{1 - y_{\text{Cl}_2}} \frac{dy_{\text{Cl}_2}}{dr} \quad (15)$$

For chlorine debit, that is actually constant relative to current radial position, the flow multiplication with surface of spherical film surrounding particle, leads to the relation (16).

$$n_{\text{Cl}_2} = -D_{\text{Cl}_2} C_T \frac{4\pi r^2}{1 - y_{\text{Cl}_2}} \frac{dy_{\text{Cl}_2}}{dr} \quad (16)$$

$$n_{\text{Cl}_2} \frac{dr}{r^2} = -D_{\text{Cl}_2} C_T 4\pi \frac{dy_{\text{Cl}_2}}{1 - y_{\text{Cl}_2}} \quad (17)$$

The separation of variables in the differential equation (16) and integration of it with the limit conditions (18, 19), leads to the integral form of chlorine debit that is consuming in a certain time by the gold particle in dissolution (relation 21).

$$r = \infty, \quad y_{\text{Cl}_2} = y_{\text{Cl}_2\infty} \quad (18)$$

$$r = R, \quad y_{\text{Cl}_2} = 0 \quad (19)$$

$$n_{\text{Cl}_2} \int_{R/2}^{\infty} \frac{dr}{r^2} = -D_{\text{Cl}_2} C_T 4\pi \int_0^{y_{\text{Cl}_2\infty}} \frac{dy_{\text{Cl}_2}}{1 - y_{\text{Cl}_2}} \quad (20)$$

$$n_{\text{Cl}_2} = -4\pi D_{\text{Cl}_2} C_T \ln(1 - y_{\text{Cl}_2\infty}) \quad (21)$$

We mention that, by limit condition (19), it was accepted from the beginning that chemical reaction from the surface is much faster relative to participants diffusion in the lixiviation process (reagents and reaction products).

As the relation (22) shows, the dissolved Au debit is obtaining according to reaction stoichiometry. The dissolved Au debit depends on bulk particle reducing, as the (23) relation shows.

$$n_{\text{Au}} = \frac{n_{\text{Cl}_2}}{2} \quad (22)$$

$$n_{\text{Au}} = \frac{\rho_{\text{Au}}}{M_{\text{Au}}} \frac{dV_p}{d\tau} \quad (23)$$

In relation (13) ρ_{Au} is gold density, M_{Au} is molecular mass of Au and τ refers to actual state of lixiviation. If the bulk particle is evaluated as a function of its momentary radius ($V_p = \frac{4}{3}\pi R^3$) this become the differential equation (24).

$$\frac{\rho_{\text{Au}}}{M_{\text{Au}}} 4\pi R^2 \frac{dR}{d\tau} = \frac{4\pi R D_{\text{Cl}_2} C_T \ln(1 - y_{\text{Cl}_2\infty})}{2} \quad (24)$$

The separation of variables in the differential equation (24) and integration of it with the limit conditions (26, 27), leads to the final expression of time period τ_s of lixiviation process (relation (30))

$$\frac{\rho_{\text{Au}}}{M_{\text{Au}}} R dR = \frac{D_{\text{Cl}_2} C_T}{2} \ln(1 - y_{\text{Cl}_2\infty}) d\tau \quad (25)$$

$$\tau = 0, \quad R = R_{\text{in}} \quad (26)$$

$$\tau = \tau_s, \quad R = 0 \quad (27)$$

$$\frac{\rho_{\text{Au}}}{M_{\text{Au}}} \int_{R_{\text{in}}}^0 R dR = \frac{D_{\text{Cl}_2} C_T}{2} \ln(1 - y_{\text{Cl}_2\infty}) \int_0^{\tau_s} d\tau \quad (28)$$

$$\frac{\rho_{\text{Au}}}{M_{\text{Au}}} \frac{R_{\text{in}}^2}{2} = \frac{D_{\text{Cl}_2} C_T}{2} \ln(1 - y_{\text{Cl}_2\infty}) \tau_s \quad (29)$$

$$\tau_s = \frac{\rho_{\text{Au}}}{M_{\text{Au}}} \frac{R_{\text{in}}^2}{D_{\text{Cl}_2} C_T \ln(1 - y_{\text{Cl}_2\infty})} \quad (30)$$

In the lixiviation experiment the solid:liquid ratio is 1:1, working temperature is 20°C , liquid phase containing NaOCl 6% and HCl 2M. In such conditions, the value of total molar concentration is evaluated to $C_T = 30 \text{ kmol/m}^3$ and the value of Cl diffusion coefficient is $D_{\text{Cl}_2} = 20.3 \times 10^{-10} \text{ m}^2/\text{s}$ [21]. Relative to value that the molar fraction of free chlorine could have in the attack solution, it has to be consider the data of its solubility in NaCl and HCl containing solutions.

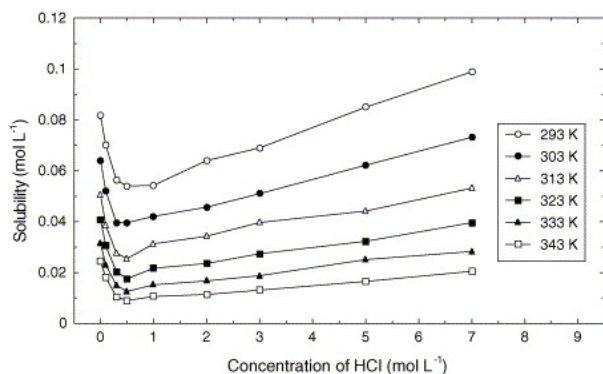


Figure 3. Chlorine solubility dependence on temperature and hydrochloric acid concentration in the attack solution

Thus, figure 3 (assumed from Mahir et al 2004), shows that the chlorine solubility depends on hydrochloric acid concentration and temperature of solution, this being modified from 0.01 mol/l to 0.08 mol/l, which is inducing the following molar fraction expression $0.0003 < y_{Cl_{2\infty}} < 0.0024$ kmol Cl_2 /Kmol mixture.

Figure 4 presents the estimation of lixiviation time starting from the following parameters: the initial radius of particle ($0.0002 < R_{in} < 0.002$ m) and molar fraction of chlorine from solution ($y_{Cl_{2\infty}}$).

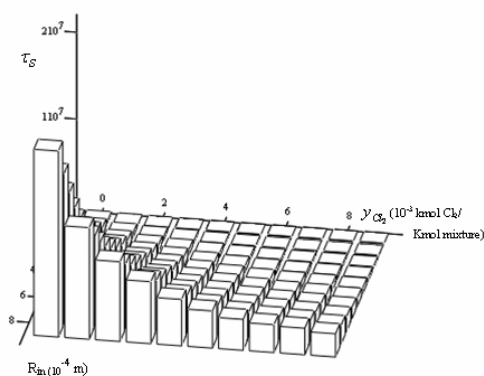


Figure 4. Variation of lixiviation times τ_s of gold particles as a function of particle radius (axa y) and molar fraction of active chlorine (axa x)

It is interesting to mention that the estimated lixiviation times using the proposed computing model are well corresponding to practice that contributed to the process scale-up.

It is to be expected that lixiviation times higher than those estimated to determine an increase of lead concentration in the attack solution without gold concentration significantly modify.

4. Conclusions

The new separation procedures are focusing on the most selective lixiviation of gold from the quartering solid, using reagents that not induces new pollutants in the environment. The present work theoretically approaches the gold lixiviation from refractory gold ores. Thus, the gold lixiviation using nascent chlorine at the ambient temperature from hydrogravitationally refractory concentrate, was experimented. A mathematical model for lixiviation time computing was proposed, using as parameters the initial radius of gold particle (R_{in}) and molar fraction of chlorine in solution ($y_{Cl_{2\infty}}$).

Although this computing model for lixiviation time has some vulnerable points (it considers that the gold particle is spheric, accepts that the surface reaction is fast relative to diffusion processes out of particle, considers that the concentration of chlorine resulted from sodium hypochlorite decomposing is practically constant in the reaction medium) it is still acceptable first of all due to its simplicity and second, that it intended to be only estimative.

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