

# Recovery of Gold from Alluvial Sand by Wet Chlorination

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*The more restrictive regulations for controlling the environmental pollution by cyanide bearing streams and materials have given an impetus to the researches aiming the discovery of some new, more ecological methods for gold leaching. This paper presents an alternative lixiviant system for the recovery of gold from secondary sources such as gravitational concentrates from alluvial sands. The gold leaching using nascent chlorine resulted from NaClO decomposition in hydrochloric acid medium was experimented. Also, the influence of the main parameters: solid: liquid ratio, temperature, chlorine and chloride ion concentration; redox potential is presented. A mathematical model for lixiviation time computing was proposed, using as parameters the initial radius of gold particle ( $R_m$ ) and molar fraction of chlorine in solution ( $y_{Cl_2}$ ):*

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

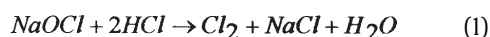
*Keywords: gold, alluvial sand, nascent chlorine*

The cyanidation method applied for gold lixiviation in industry is extremely polluting [1]; 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 international level [2-3] and national level [4-6] allowed to develop some eco-technologies which operate with high extraction yields and use environmental friendly reagents (non-polluting reagents).

Chlorine leaching has a few advantages due to the higher dissolution rate of gold, low price of leaching reagents and non-polluting character. Dissolution of metallic gold was studied [8] by generating chlorine « in situ » from the reaction between commercial sodium hypochlorite and hydrochloric acid.

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



The gold lixiviation mechanism presumes the initial AuCl formation on the metallic gold surface followed by complexing with Cl to AuCl<sub>2</sub>. This complex is oxidized in solution with NaOCl to AuCl<sub>4</sub> [7]. The success of gold lixiviation from hydrochloric solutions using Cl/NaOCl solutions depends on mineralogical composition of material.

The gold dissolved as [AuCl<sub>4</sub>]<sup>-</sup> can be extracted from chloride matrix by Amberlite XAD-7 resin containing weak ester groups (-R-COOR') and hence the high selectivity of gold [4-6].

The paper presents the theory and practice aspects of gold lixiviation by wet chlorination.

## Materials and experimental procedure

The materials used in the experiments are the gravity concentrates obtained from different alluvial sands. The gold contents in these materials range from 6.9 g/t to

1197.5 g/t and all amounts is free gold. Gangue minerals are silica, ilmenite, zircon, magnetite and other heavy minerals, especially lead. In order to develop the experiments were prepared the following reagents: solutions of 3 mol HCl /L from hydrochloric acid (HCl) 32%, and sodium hypochlorite (NaOCl) 6%.

Experimental tests were conducted using a laboratory installation, which is shown in figure 1. Facility consists of a reaction glass vessel (1) with an upper cover fitted with three connections, one for the thermometer (2), one for the redox potential electrode (3) and one for the supply of sodium hypochlorite (4) of storage vessel (5). Reaction vessel is equipped with a stirrer type anchor Teflon (6), driven by an electric motor (7) with adjustable speed. The reaction mass heating was achieved by placing the reaction vessel in a heating jacket thermostat (8). At the end of the leach, the slurry was filtered. Both filtered and residue were chemically analyzed. Filtrates were volumetrically analyzed for acid concentration. The filtrates obtained were used for the ion exchange study

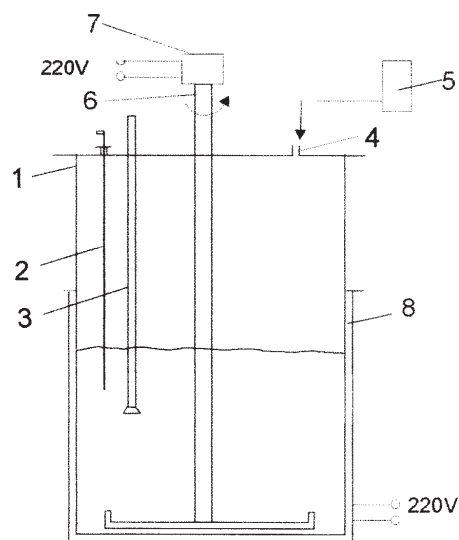


Fig. 1. Experimental installation: 1 - reaction vessel, 2- thermometer, 3- redox potential electrode, 4- feed inlet, 5- storage vessel ( NaOCl) , 6 - stirrer, 7- engine stirrer, 8- heating jacket

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## Results and discussion

### Process parameters studies

Taking into account the physico-chemical characteristics of the hydrogravitational gold concentrates, meaning the presence of gold particles lens-like and granular, with sizes from a few microns till several millimetres, dissipated into a mineral mass with a relative chemical inertia, there were studied the following dissolution factors: solid: liquid ratio; temperature; time; stirring speed; chlorine and chloride ion concentration; redox potential.

Because the gangue materials have a chemical inertia on leaching conditions and so the consumption of reagents is small, the optimum: liquid: solid ratio means the ratio proving a homogenous reaction mass allowing the intimate contact of dissolution agent with the grains of gold. Experimental results have shown an optimum liquid: solid 1.5:1.

The rate of dissolution is given by the correlated action of both temperature and time. The experimental results are shown in the figure 2.

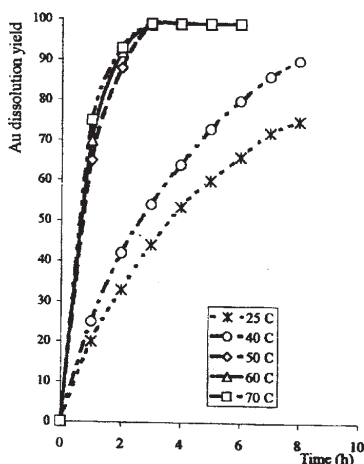


Fig. 2. Variation of dissolution yield in time at different temperatures, in the following experimental conditions: L:S ratio 1.5, conc. of HCl: 3N, conc. of NaClO :0,150 L/kg conc

After 3 h of reaction at 50-70°C, the dissolution yields of gold is > 98.5 %, and after 4 h, at 50°C temperature, the dissolution yield is > 99 %.

In the used reactor the concentrates become well suspended at minimum 800 min<sup>-1</sup> stirring speed, the specific rate is practically independent of the agitation intensity in conditions of full suspension.

The acid consumption is small because only a small part of the mass is reacting with the hydrochloric acid (the major part of the concentrate remaining inert). Up to a pH of 1,5 the rate of leaching was not affected by pH. Because the minimum free acidity required for the subsequent separation step of gold, from solutions, by ion exchange, is 2.2 – 2.8 M HCl, the free acidity needed in leaching process, to avoid a supplementary dilution of the leach is 3 M HCl.

The rate of the aqueous chlorination is determined by the concentration of the tri-chloride ion [19]. The correlation between the mixed potentials and the tri-chloride and chloride ion concentrations is presented in figure 3.

The potential required for a rapid leaching rate and for avoiding the reduction of gold is 900 mV (vs AgCl/Ag<sub>(KCl sat.)</sub>).

The sodium hypochlorite (commercial grade) optimum concentration for ensuring both the gold dissolution (fig. 4) and the maintenance of an oxidant redox potential for avoiding the reduction of the dissolute gold (fig. 5) were

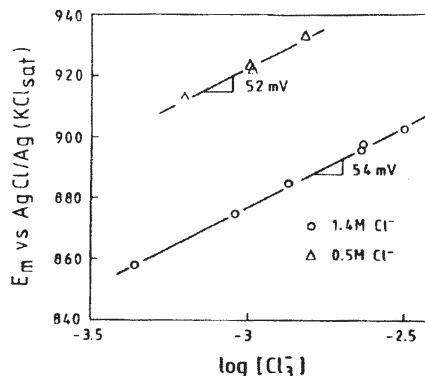


Fig. 3. The mixed potential as function of the tri-chloride and chloride ion concentration [9]

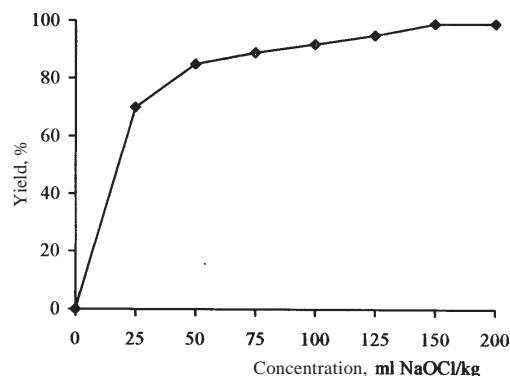


Fig. 4. Variation of dissolution yield depending on NaClO concentration, in the following experimental conditions: L:S ratio 1:1.5 conc. of HCl 3 N, temp. 50°, time 4 h

determined experimentally. The needed amount according to the both conditions is 0.150 l NaClO/kg conc.

The optimum conditions for the dissolution yield of gold are:

- liquid: solid ratio 1.5
- temperature 50° C
- lixiviation time 4 h
- stirring speed 800 min<sup>-1</sup>
- hydrochloric acid concentration 3M
- sodium hypochlorite concentration 0.150 L/kg conc.
- redox potential 900 mV(v.s.AgCl/Ag(KCl sat.))

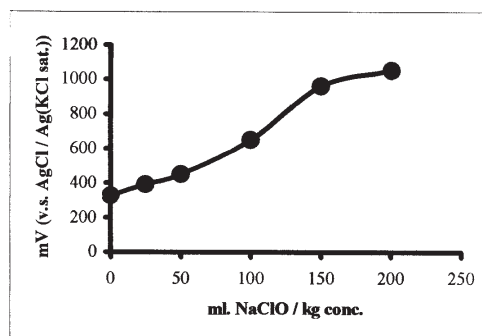


Fig. 5. Changes in redox potential depending on the consumption of NaClO in the following experimental conditions L:S ratio 1:1.5 conc. of HCl 3 N, temp. 50°, time 4 h

The experimental results are presented in table I. The average yield of gold is more than 99%.

### Estimation of lixiviation time in batch contacting

As the figure 6 shows, for gold lixiviation from raw material it needs that a Cl<sub>2</sub> flow and its corresponding stoichiometric HCl flow to reach the gold particle surface.

**Table 1**  
EXPERIMENTAL RESULTS OBTAINED IN THE DISSOLUTION STEP

Sample	Gold content			Yield, %
	Feed, g/t	Sterile, g/t	Leach, mg/L	
1	6.9	0.05	4.1	99.2
2	81.0	0.1	55.0	99.8
3	44.7	0.1	29.7	99.7
4	197.7	0.2	130.8	99.8
5	994.6	0.2	609.0	99.9
6	186.3	0.05	123.8	99.9
7	214.1	0.2	142.7	99.9
8	115.7	0.2	76.8	99.8
9	1197.5	0.1	790.3	99.9
10	153.0	0.2	105.1	99.8

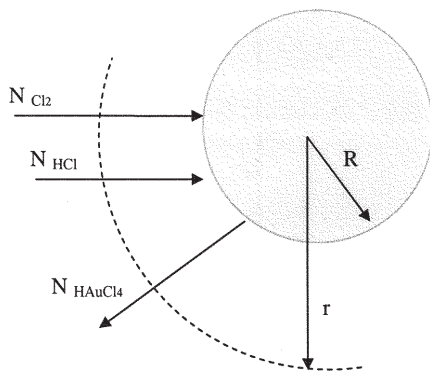


Fig. 6. Physical model of gold particle lixiviation

In figure 6 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 (4) of gold lixiviation, for chlorine  $N_{Cl_2}$  flow rate that is reaching the gold particle surface, it might be written the equation (5), where  $D_{Cl_2}$  is diffusion coefficient of chlorine in the reaction medium [8].



$$N_{Cl_2} = -D_{Cl_2} C_T \frac{dy_{Cl_2}}{dr} + y_{Cl_2} (N_{Cl_2} + N_{HCl} + N_{HAuCl_4}) \quad (5)$$

According to reaction stoichiometry described by equation (4), the flows rate of  $HCl$  and  $HAuCl_4$  could be evaluated as a function of  $Cl_2$  flow rate, as follows:

$$N_{HCl} = \frac{1}{2} N_{Cl_2} \quad (6)$$

$$N_{HAuCl_4} = -\frac{1}{2} N_{Cl_2} \quad (7)$$

Replacing the relations (6) and (7) in relation (5), for chlorine flow it is obtained the following expression (8):

$$N_{Cl_2} = -D_{Cl_2} C_T \frac{1}{1 - y_{Cl_2}} \frac{dy_{Cl_2}}{dr} \quad (8)$$

For chlorine mass flow, that is actually constant related to current radial position, the flow multiplication with surface of spherical film surrounding particle, leads to the relation (9).

$$n_{Cl_2} = -D_{Cl_2} C_T \frac{4\pi r^2}{1 - y_{Cl_2}} \frac{dy_{Cl_2}}{dr} \quad (9)$$

$$n_{Cl_2} \frac{dr}{r^2} = -D_{Cl_2} C_T 4\pi \frac{dy_{Cl_2}}{1 - y_{Cl_2}} \quad (10)$$

The separation of variables in the differential equation (9) and its integration with the limit conditions (11, 12), leads to the integral form of chlorine flow that is consuming in a certain time by the gold particle in dissolution (relation 14).

$$r = \infty, \quad y_{Cl_2} = y_{Cl_2\infty} \quad (11)$$

$$r = R, \quad y_{Cl_2} = 0 \quad (12)$$

$$n_{Cl_2} \int_R^\infty \frac{dr}{r^2} = -D_{Cl_2} C_T 4\pi \int_0^{y_{Cl_2\infty}} \frac{dy_{Cl_2}}{1 - y_{Cl_2}} \quad (13)$$

$$n_{Cl_2} = -4\pi D_{Cl_2} C_T \ln(1 - y_{Cl_2\infty}) \quad (14)$$

We mention that, by limit condition (12) it was accepted from the beginning that the chemical reaction from the surface is much faster related to participant diffusion in the lixiviation process (reagents and reaction products).

As the relation (15) shows, the mass flow of dissolved gold is obtained according to reaction stoichiometry. The mass flow of dissolved gold depends on the particle mass decreasing, as (16) relation shows.

$$n_{Au} = \frac{n_{Cl_2}}{2} \quad (15)$$

$$n_{Au} = \frac{\rho_{Au}}{M_{Au}} \frac{dV_p}{d\tau} \quad (16)$$

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 (14).

$$\frac{\rho_{Au}}{M_{Au}} 4\pi R^2 \frac{dR}{d\tau} = \frac{4\pi R D_{Cl_2} C_T \ln(1 - y_{Cl_2\infty})}{2} \quad (17)$$

The separation of variables in the differential equation (17), and its integration with the limit conditions (18, 19) leads to the final expression of time period  $\tau_s$  of lixiviation process (relation (23)).

$$\frac{\rho_{Au}}{M_{Au}} R dR = \frac{D_{Cl_2} C_T}{2} \ln(1 - y_{Cl_2\infty}) d\tau \quad (18)$$

$$\tau = 0, \quad R = R_{in} \quad (19)$$

$$\tau = \tau_s, \quad R = 0 \quad (20)$$

$$\frac{\rho_{Au}}{M_{Au}} \int_{R_{in}}^0 R dR = \frac{D_{Cl_2} C_T}{2} \ln(1 - y_{Cl_2\infty}) \int_0^{\tau_s} d\tau \quad (21)$$

$$\frac{\rho_{Au}}{M_{Au}} \frac{R_{in}^2}{2} = \frac{D_{Cl_2} C_T}{2} \ln(1 - y_{Cl_2}) \tau_s \quad (22)$$

$$\tau_s = \frac{\rho_{Au}}{M_{Au}} \frac{R_{in}^2}{D_{Cl_2} C_T \ln(1 - y_{Cl_2})} \quad (23)$$

In the lixiviation experiments the liquid: solid ratio is 1:1.5; working temperature is 50 °C, liquid phase containing NaOCl 6% and HCl 3M. In such conditions, the value of total molar concentration is evaluated to  $C_T = 30 \text{ kmol/m}^3$  and the value of  $\text{Cl}_2$  diffusion coefficient is  $D_{Cl_2} = 2.03 \times 10^{-9} \text{ m}^2/\text{s}$  [10]. Concerning the value that the molar fraction of free chlorine could have in the attack solution, it has to be considered the data of its solubility in NaCl and HCl containing solutions.

Thus, figure 7, shows that the chlorine solubility depends on hydrochloric acid concentration and solution temperature, this being modified from 0.01 mol/l to 0.08 mol/L, which is inducing the following molar fraction expression  $0.0003 < y_{Cl_2} < 0.0024 \text{ kmol Cl}_2/\text{Kmol mixture}$  [11].

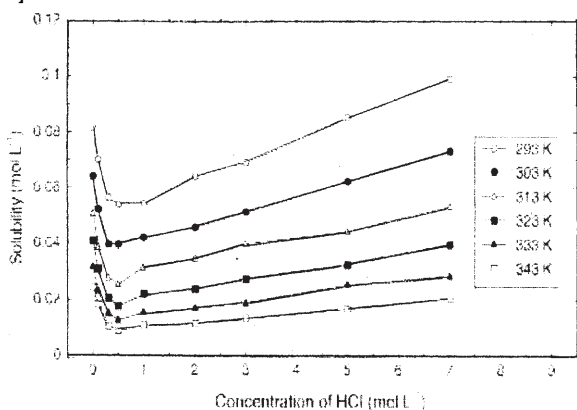


Fig. 7. Chlorine solubility on temperature and hydrochloric acid concentration in the attack solution [11]

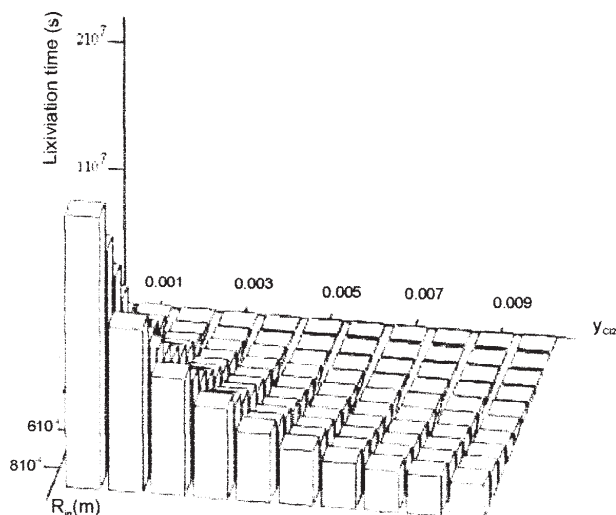


Fig. 8. Variation of lixiviation times of gold particles as a function of particle radius ( $y$  axis) and molar fraction of active chlorine ( $x$  axis)

Figure 8 presents the estimation of lixiviation time starting from the following parameters: the initial radius of particle ( $0.0002 < R_{in} < 0.002 \text{ m}$ ) and molar fraction of chlorine from solution ( $y_{Cl_2}$ ). It is interesting to mention that the estimated lixiviation times using the proposed computing model are according 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.

## Conclusions

Chloride/hypochlorite leaching system at room temperature was used to recover gold from gravitational concentrates from alluvial sands. To find the optimal operating conditions, the effect of many factors, including: liquid: solid ratio; temperature; time; stirring speed; chlorine and chloride ion concentration; redox potential were investigated.

The chlorine was obtained « in situ » by the reaction of NaClO and HCl. The dissolution time is 4h at 50°C and 900 mV (vs. AgCl/Ag(KCl sat.)) redox potential, at a liquid: solid ratio 1.5:1. The amount of 0.150 l NaClO/kg conc. is necessary for ensuring the gold dissolution. Under optimal leaching conditions, the dissolution yield of gold is higher than 99 %.

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 ( $y_{Cl_2}$ ).

Although this computing model for lixiviation time is relatively simplified (it considers that the gold particle is spherical, accepts that the surface reaction is fast related 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, being it intended to be only estimative.

## Nomenclature

- $C_T$  - global molar concentration in the system,  $\text{kmol/m}^3$ ;
- $D_{Cl_2}$  - diffusion coefficient of chlorine,  $\text{m}^2/\text{s}$
- $M_{Au}$  - gold molecular weight,  $\text{kg/kmol}$ ;
- $n_{Cl_2}$  - chlorine mass flow,  $\text{kg/h}$ ;
- $N_{Cl_2}$  - chlorine flow rate,  $\text{kg/m}^2/\text{s}$ ;
- $N_{HCl}$  - HCl flow rate,  $\text{kg/m}^2/\text{s}$ ;
- $N_{HAuCl_4}$  -  $\text{HAuCl}_4$  flow rate,  $\text{kg/m}^2/\text{s}$ ;
- $R$  - gold particle radius,  $\text{m}$ ;
- $R_{in}$  - initial radius of particle,  $\text{m}$
- $\rho_{Au}$  - gold density,  $\text{kg/m}^3$ ;
- $V_p$  - volume of particle,  $\text{m}^3$ ;
- $y_{Cl_2}$  - molar fraction of chlorine;
- $y_{Cl_2\infty}$  - molar fraction of chlorine from solution;
- $\tau$  - time,  $\text{s}$

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