Study on the properties and gold leaching kinetics of a new organic leaching agent

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Abstract. A new organic leaching agent (3YL) was applied the process of leaching gold in our recent research project. Compared to conventional cyanidation method, studies show that 3YL can serve as an alternative and non-toxic leaching agent, which has several advantages over cyanides including leaching speed, environmental effect, and other aspects. In this paper, the temperature and the acidity of the dissociation process for 3YL were investigated. The results show that within a certain range, the temperature and acidity have significantly positive effect on the dissociation. Meanwhile, the dynamic process of gold leaching was also studied. The experimental data are consistent with the existing model, and the results show that the process is controlled by external diffusion.

1. Introduction
Various methods have been used in the recovery of gold from ores and concentrates, including cyanide gold leaching, halide gold leaching, thiourea gold leaching, thiocyanate gold leaching, thiosulfate gold leaching, etc.[1]. Among them, the most widely studied leaching reagent is cyanide, thanks to its mature technique, ideal economic and technical indicators, and strong adaptability[2]. However, cyanide-based leaching agents face several challenges. On one hand, the recovery rate of the refractory gold ore is poor. On the other hand, the leaching speed is slow, and cyanide is highly toxic[3,4]. Taking the economic, feasibility, and environmental issues into account, it is necessary to develop an equally effective, faster, non-toxic, and degradable leaching reagent. Among all the promising candidates, 3YL organic chlorinated leaching agent may solve the above problems efficiently.

The 3YL leaching agent, which can be represented by R-Cl, consists of an organic group and chlorine. Many experiments have proved that 3YL leaching agent has a high leaching rate for refractory gold concentrates. Ya-nan Hou et al. studied the multi-metal recovery from a mine in Jilin, China, with 3YL as leaching agent. The optimized technological route and leaching conditions were obtained. However, some properties of 3YL have not been understood. The author mainly studies the influence of some parameters on the leaching efficiency, which has a guiding role in industrial practice. At the same time, the leaching mechanism of the dynamic process is discussed based on the existing data, and the control steps of the leaching process were preliminarily determined.

2. Materials and methods

2.1. Instruments and reagents
Instruments: Automatic potentiometric titrator, Magnetic stirrer, UV-visible spectrophotometer
Major reagents: 3YL, sodium chloride, silver nitrate, potassium iodide, sodium hydroxide. All solutions were prepared using deionized water. All chemicals were analytical grade.

2.2. Experiment procedures

2.2.1. The solubility of 3YL.
1.2000 g 3YL and 100.00 mL deionized water were added into a beaker and agitated at 500 rpm and 15°C for 2 h. After filtering, the pH of the filtrate was measured. The filter paper and residue were dried in an oven at 120°C, and the mass is measured after drying and cooling down to room temperature. The solubility of 3YL is then calculated.

2.2.2. Determination of chloride ion and chlorine in aqueous samples.
0.5000 g 3YL and 250.00 mL deionized water were added to conical flask and agitated at 450 rpm. 200 mL 5 M sodium hydroxide solution was transferred into absorption bottles. The concentrations of chloride and chlorine were measured at various time points at temperatures of 25°C, 35 °C, 45°C, 55 °C, 65°C, and 75°C. The concentration of sodium hypochlorite (same as chlorine concentration) in the absorption liquid was determined by the Iodometric method, and the concentration of chloride ion was determined by the Mohr method.

The acidity of the solution was adjusted to [H]=10⁻⁴M, 10⁻³M,10⁻²M, 10⁻¹M, 1 M, 2 M, with hydrochloric acid at temperature of 25°C. The above experiment was repeated for three times.

2.2.3. The leaching kinetics of gold nanoparticles.
In order to study the leaching kinetics of gold, we chose gold nanoparticle (the average particle size is 12 nm) solution as the gold source. 20.00 mL of leachant solution containing 0.5 g/L 3YL and 8% sodium chloride in 1M hydrochloric acid solution were transferred into a beaker. Next, 10 mL gold nanoparticle solution was added to the beaker and the contents were agitated. The stirring speed and temperature were adjusted by a magnetic stirrer. Every one hour apart, 1 mL of the leachate was withdrawn and analyzed by a crystal violet spectrophotometry. The blank reagent was used in a control experiment as reference.

3. Results and Discussions

3.1. Properties of 3YL
The solubility of 3YL is 0.88 g, and the pH of the solution is 2.87 at 15°C.

The variation of chloride ion and chlorine content in 3YL solution at different temperatures is shown in figure 1 and figure 2.
According to figure 1, in the range of 25°C to 75°C, the chlorine dissolved from 3YL increases with temperature, because elevated temperature increases the dissociation capacity of the 3YL reagent. When the temperature is between 25°C and 55°C, the chlorine content increases significantly, whereas when the temperature is higher than 65°C, the increment is not obvious, indicating that most of the chlorine contained in the 3YL solution has dissociated at this temperature. Thus, theoretically, when the reagent is used in factory practice, higher temperature and more chlorine concentration in the solution can lead to high possibility of leaching the metal element. Furthermore, studies have shown that leaching at room temperature can also meet the industrial requirements. Therefore, leaching conditions can be selected at room temperature.

The concentration of chloride ion in 3YL solution as a function of time is shown in figure 2. The constant variation of the concentration may be due to the presence of various forms of chlorine in the 3YL solution, such as Cl⁻, Cl₂, ClO⁻ and ClO₂. The following reactions can occur in the solution:

\[
\begin{align*}
Cl_2 + H_2O & \rightarrow HClO + HCl \\
3OCl^- & \rightarrow 2Cl^- + ClO_3^- \\
2HClO \xrightarrow{hv/\Delta} & 2HCl + O_2 \uparrow \\
2ClO_2 + Cl_2 + 2H_2O & \rightarrow 2Cl^- + 2ClO_3^- + 4H^+ \\
6ClO_2 + 3H_2O \xrightarrow{hv} & Cl^- + 5ClO_3^- + 6H^+ \\
5Cl^- + ClO_3^- + 6H^+ & \rightarrow 3Cl_2 + 3H_2O \\
2Cl^- + 2ClO_3^- + 4H^+ & \rightarrow 2ClO_2 + Cl_2 + 2H_2O \\
7Cl^- + 3ClO_3^- + 10H^+ & \rightarrow 2ClO_2 + 4Cl_2 + 5H_2O
\end{align*}
\]

The change of chloride ion and chlorine content in 3YL solution at different acidity is shown in figure 3 ~ figure 8.

![Figure 3. The relationship between chloride ion concentration and time at different acidity.](image)

![Figure 4. The relationship between chlorine release and time at different acidity.](image)

It can be seen from figure 3 and figure 4 that when the acidity is less than 1 M, with the increase of acidity, the amount of chlorine and chloride ions rises substantially. However, when the acidity is over 1 M, the amount of chloride ions and chlorine was reduced. The reason is that as too much chlorine ions is added, the common ion effect plays a leading role, inhibiting the dissociation of the chlorine in 3YL.
Figure 5. The relationship between the potential and the time at different acidity.

It can be concluded from figure 5 and figure 6 that when the \([H]\) is below \(10^{-2}\)M, the potential of the solution increases with the acidity, but the potential change is not significant during this process. When the \([H]\) is over \(10^{-2}\)M, the potential of the solution declines with the increase of acidity, and within this range of acidity, greater acidity leads to faster potential reduction. At \([H]=10^{-2}\)M, the potential of the solution is highest, i.e., the oxidation of the solution is the strongest.

In figure 7 (the following), we can see that at \([H]=10^{-2}\)M, the amount of chloride ions is reduced due to the possible reasons as below:

The experimental data show that in the solution with excessive hydrochloric acid, Cl\(^-\) will be oxidized to Cl\(_2\) by ClO\(_3^-\), and the chemical reaction is equation (4). If the concentration of hydrochloric acid is low, Cl\(_2\) and ClO\(_2\) are generated, and the corresponding chemical reaction is equation (7). In the intermediate acidity range, the above of two reactions occur simultaneously. At the same time, the oxidation of the solution is very strong, and the chemical reaction is equation (8).

Thus, \([H]=10^{-2}\)M is "an intermediate acidity" (mentioned above) that will consume a large amount of chloride ions, while a certain amount of chlorine is generated. The chlorine content is increased compared to low acidity solution, which explains the phenomenon in figure 8. At the same time, the solution composed of the substances produced by reaction equation (8) is more oxidizing than the solutions at other acidity. Therefore, when the \([H]=10^{-2}\)M, the solution has the highest potential value, which is consistent with the data in figure 6.

Figure 7. The relationship between chloride ion concentration and acidity at the first hour.  
Figure 8. The relationship between Chlorine release and acidity at the first hour.

3.2. Kinetics analysis of gold leaching process

In heterogeneous solid–fluid reactions, the following three sequential steps may occur: (a) diffusion of reactants to the surface of the gold particles, (b) chemical reaction on the gold surface, (c) the product scatters from the gold particle surface into the liquid\(^6\).
Determining whether a reaction is under diffusion, chemical, or mixed control is the primary step to understand the hydrometallurgical process. There are several mechanistic kinetic models developed to study the rate-controlling steps in the leaching process\cite{7,8}.

If the leaching process is governed by internal diffusion, the rate equation is:

\[
1 - \frac{2}{3}x - (1-x)^{2/3} = k_1t 
\]  

(9)

If the leaching process is governed by external diffusion, and the reaction does not produce a solid film, the rate equation is:

\[
1 - (1-x)^{2/3} = k_2t 
\]  

(10)

If the reaction produces a solid film, the rate equation is:

\[
x = k_3t
\]  

(11)

If the leaching process is governed by surface chemical reactions, the rate equation is:

\[
1 - (1-x)^{1/3} = k_4t
\]  

(12)

where \(x\) is the rate of gold extraction, and the parameter \(k\) is the overall reaction rate constant, which is temperature dependent\cite{9}.

The relationship between the concentration of gold leachant and time is shown in figure 9, which can be fitted with the developed model and is presented in figure 10 to figure 12. In these figures, it
can be seen that the leaching of gold is dominated by external diffusion, as the coefficient of regression for the model was 99.7%.

4. Conclusions
(1) The results show that at 15°C, the solubility of 3YL is 0.88 g/L, and the aqueous solution of the reagent is weakly acidic.
(2) The dissociation ability of 3YL increases with the increase of temperature.
(3) With the increase of the acidity, both the dissociation ability of 3YL and the potential of the solution increased first then decreased, and reached maximum at acidity of 1M and [H]=10^{-2}M, respectively.
(4) According to the kinetics of leaching reaction, it is determined that the leaching rate of gold is controlled by external diffusion.

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