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Leaching behavior of butanedionedioxime as gold ligand ①

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Abstract: Butanedionedioxime, a small organic compound with low-toxicity and good chemical stability, has been proposed as an effective gold ligand in gold extraction. The result of experiment shows that: 1) highly effective gold lixiviant can be composed of butanedionedioxime (BDM) with many oxidants, especially potassium permanganate; 2) in the leaching system of BDM-$KMnO_4$ the suitable Ox/Lig (ratio of oxidants to gold ligands) range is 0.20 ~ 0.50, optimally 0.25 ~ 0.45 at the pH range of 7 ~ 11; 3) BDM-$KMnO_4$ extraction of gold from an oxide ore is similar to cyanide (cyanide-O_2) extraction, but the leaching rate of gold by BDM-$KMnO_4$ is faster than that by cyanide-O_2; 4) gold may readily be recovered by carbon adsorption and zinc precipitation.

Key words: gold; leaching; lixiviation **Document code:** A

1 INTRODUCTION

There are two types of orbitals in outer electron orbitals of gold and its lixiviants[1,2]. One is called HOEO (higher occupied electronic orbitals), such as π-type HOEO of both $5d^2_{(x^2-y^2)}$ and $5d^2_z$ of gold, and σ-type HOEO of σ^2_{2px} of cyanide; and another called LUEO (lower unoccupied electronic orbitals), such as π-type LUEO of both π_y^{*0} and π_z^{*0} of cyanide, and σ-type LUEO of both $(sp)^0_i$ ($i = 1 \sim 2$, for sp hybridization in Au(Ⅰ)) and $(dsp^2)^0_i$ ($i = 1 \sim 4$, for dsp^2 hybridization in Au(Ⅲ)) of gold. The reaction between frontier orbitals of gold and gold lixiviants[3~5] (exactly speaking-gold ligands, labeled as Lig) can be illustrated in Fig.1, taking the symmetrical factors into consideration.

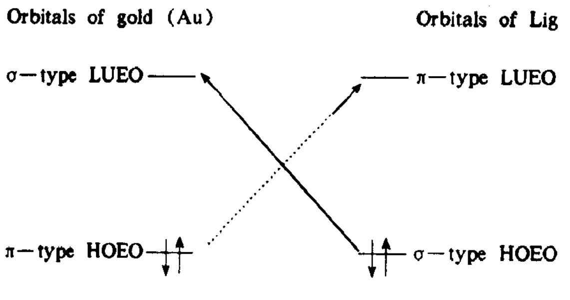

Fig.1 Illustration of electrons transferred between gold and ligands in leaching reaction

Obviously there are a simple coordination bond of Lig → Au and a π-back donating bond of Au → Lig in product ions of $Au(Lig)_m$ (here m represents coordination number)[3,6]. And it is easy to conclude that the outer electronic orbitals of an effective lixiviant of gold[7,8] (referring to gold ligand) should meet the following conditions: 1) there are σ-type HOEO and π-type LUEO in its electron structure; 2) the energy difference between σ-type HOEO and π-type LUEO of Lig is low and close to that between σ-type LUEO and π-type HOEO of gold; 3) the lower the energy difference between σ-type HOEO of Lig and σ-type LUEO of Au and between π-type LUEO of Lig and π-type HOEO of Au, the easier the leaching reaction. Among the compounds with above structural characteristics, butanedionedioxime (BDM) is low-toxic, soluble and stable in common hydrophillic solvents (including water, ethanol etc) and can be easily prepared from some primary materials such as butanone and butanedione[6]. The σ-type HOEO and π-type LUEO of BDM are σ^2_{2s} ($E = -9.594$ eV) and π^{*0} ($E = 0.084$ eV) respectively, and the energy level of them can be calculated by AM.1 method[1]. As chelating ligand BDM can form a stable cyclo-complex ions with Au and this leads to its application in gold extraction[1,6,9]. In this paper the leaching behavior of butanedionedioxime is reported, and several parameters including Ox/Lig (ratio of gold ligand to oxidant), operating pH and leaching time are discussed.

2 EXPERIMENTAL

The leaching experiments were carried out at room temperature in an XJT-type agitation machine with the agitating speed of 600 ~ 900 r/min. Samples (500 g for each test) were taken from the bottle and analyzed for gold over a certain time, and fresh water was added to the leach bottle to compensate solution

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loss due to sampling. At the end of each test, the leach slurry was filtered and washed, and the filter cake was dried at 105 ℃ for 4 h. Samples of the filtrate, the washings, and the residue were analyzed for gold. Gold grade in the solid (including feed and tailings) was measured by chemical analysis method and that in the leaching solution by atom-absorption spectrometer. The gold recovery was calculated from the gold content in the residue. The chemicals used, such as sodium hydroxide, butanedionedioxime and potassium permanganate etc were chemically pure. The feed, containing 4.6 g/t gold, was an oxide ore and was obtained from gold mine in Zhengzuo, Hunan, China. It was ground to particle size about 0.073 mm before testing, and in such a particle size range the comparison tests with direct cyanidation were also performed. Carbon adsorption and zinc cementation tests were conducted to investigate the recovery of gold from the pregnant solution[2,6,8].

3 RESULTS AND DISCUSSION

3.1 Effects of oxidants

The reaction process and mechanism of gold leaching reaction may be different from each other widely, fixing a gold ligand but altering the oxidants[9,10]. The processing tests were conducted to evaluate the cooperative relationship between gold and leaching oxidants. The leaching behavior of butanedionedioxime in different oxidants is shown in Table 1. The testing condition was w(BDM) = 0.1 %, w(Ox) = 0.1 % (Ox represents oxidants), L/S = 4 (ratio of liquid mass to solid mass), pH = 8, leaching time t = 10 h.

Table 1 Relationship between gold and leaching oxidants

Oxidant	Au in residue/($g\cdot t^{-1}$)	Extraction ratio/ %
H_2O_2	2.3	50
NaOCl	2.0	57
Na_2O_2	2.5	46
$KMnO_4$	0.6	87

The result (Table 1) demonstrates that potassium permanganate may be a suitable oxidant of gold for BDM leaching. Possible explanation can be given only after quantity calculation of the leaching reaction is made and the kinetic mechanism is clear.

3.2 Effects of Ox/Lig ratio on gold leaching

Because the side-reaction is inevitable[4,9] between Lig and Ox, the optimum Ox/Lig (mole ratio between oxidants and gold ligands) under a fixed ligand concentration can be ascertained in order to restrict the above side-reaction to minimum extent and keep a better leaching speed. As a matter of fact, the Ox/Lig reflects the coordinating behavior between gold ligands and leaching oxidants in a given leaching system. The leaching tests were carried out by using $KMnO_4$ as the oxidant and the experimental result is listed in Table 2.

Table 2 Effects of Ox/Lig on gold leaching

Ox/Lig mole ratio	Gold recovery/ %
0.10	45
0.15	67
0.20	83
0.25	89
0.30	90
0.35	92
0.40	91
0.45	90
0.50	88

It can be seen from Table 2, that the suitable Ox/Lig range is 0.20 ~ 0.50 (especially 0.25 ~ 0.45). The leaching speed will be too low if Ox/Lig is too small, but the side-reaction will be serious if Ox/Lig is too great, leading to a high consumption of the lixiviant and a sharp decrease in the effective concentration of BDM.

3.3 Effects of leaching pH

Table 3 shows the leaching result of BDM at different pH. The test condition was w(BDM) = 0.1 %, Ox/Lig = 0.30, L/S = 4, leaching time t = 10 h.

Table 3 Effects of pH on leaching results

pH	Au recovery/ %
4	56
5	72
6	78
7	89
8	90
9	91
10	92
11	91
12	87

Evidently the combination of BDM and potassium permanganate can leach gold in a wide range of pH, especially at pH = 7 ~ 11.

3.4 Effects of leaching time

The suitable leaching time was investigated by measuring the gold content in the pregnant solution in different times, as listed in Table 4. The test condition was w(BDM) = 0.1 %, Ox = $KMnO_4$, Ox/Lig = 0.30, L/S = 4.

Obviously 9 h is the satisfactory time to extract

Table 4 Dependence of leaching time on gold content in pregnant solution

Leaching time/h	Au in pregnant solution/(g·m^{-3})
6	0.7
7	0.8
8	1.0
9	1.1
10	1.1
11	1.1
12	1.1
14	1.1

gold effectively from this kind material, however under similar conditions ($L/S = 4$, $w(NaCN) = 0.1\%$, $pH = 10 \sim 11$), the leaching time and recovery of direct cyanidation are 20 h and 92 %, respectively. No doubt, the oxidant concentration in the BDM-$KMnO_4$ system is higher than that in the NaCN-O_2 system and this results in a kinetic difference (i.e. the difference of leaching speed) between them.

3.5 Gold recovery from pregnant solution

Carbon adsorption and zinc precipitation tests were conducted to investigate the recovery of gold from BDM pregnant solution. The procedures are described as below.

1) Carbon adsorption

500 ml BDM pregnant solution was mixed with 1 g active carbon (produced by Beijing Guanhua Woods Factory) in a bottle. After agitating for 4 h the sample was filtered and assayed.

2) Zinc precipitation

BDM pregnant solution was placed into zinc precipitation apparatus. The solution was purged with nitrogen for 30 min. After deaeration, $Pb(Ac)_2$ solution was added, followed by the addition of zinc dust. After allowing a contact time of 1 h, the solution was filtered and assayed. The results are summarized in Table 5.

Table 5 Gold recovery from pregnant solution

Method	ρ(Au)/(g·m^{-3})		Recovery of Au /%
	Feed solution	Barren solution	
Carbon adsorption	1.1	0.05	96
Zinc precipitation	1.1	0.06	95

Considering the results listed in Table 5, any one of these methods is a viable option for gold recovery from BDM pregnant solution.

4 CONCLUSIONS

1) The gold ligand-butanedionedioxime (BDM) can be combined with many oxidants, especially potassium permanganate, to form highly effective gold lixiviant.

2) In the leaching system of BDM-$KMnO_4$, the suitable Ox/Lig (ratio of oxidants to gold ligands) range is $0.20 \sim 0.50$, optimally $0.25 \sim 0.45$ at the pH range of $7 \sim 11$.

3) Both BDM-$KMnO_4$ and cyanide-O_2 give similar extractions of gold from oxide ores, but the leaching rate of gold by BDM-$KMnO_4$ is faster than that by cyanide-O_2.

4) Gold may readily be recovered by carbon adsorption and zinc precipitation from BDM pregnant solution.

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