NEW METHOD OF EXTRACTING GOLD AND SILVER FROM HIGH SILVER-GOLD CONCENTRATES①

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ABSTRACT Laboratory tests have been carried out to develop the new method of extracting silver by chloride leach and gold by sulphur-ammonia leach. Results showed that by the method recovery efficiency of gold and silver from the concentrate was more than 95%.

Key words extraction of gold and silver chloride leach sulphur-ammonia leach cementation

1 INTRODUCTION

The high silver-gold concentrates used in tests contain 3.7～5.9kg/t of silver and about 40 g/t of gold. Chemical composition of the concentrate in Hebei Silver Mine is given in Table 1.

Table 1 Chemical analyses of concentrate

Component	$Ag/g\cdot t^{-1}$	$Au/g\cdot t^{-1}$	Cu%	Zn%	Pb%
1#	3770	24.95	0.06	0.41	0.64
2#	5959	40.80	0.07	1.66	3.10
Component	**Fe%**	**S%**	**As%**	**SiO_2%**	**CaO%**
1#	8.83	7.61			
2#	13.99	13.99	0.101	46.8	1.80

The concentrates failed to respond to ordinary cyanidation techniques and showed poor efficiency of silver extraction. Pretreatment on desulphurization would cause pollution and cost increase. After compared with many techniques, the processes of extracting silver by chloride leach and gold by sulphur-ammonia leach were chosen.

2 EXTRACTION OF SILVER

2.1 *Principles of Chloride Leaching*

Silver ion Ag^+ and chlorine ion Cl^- in chloride solution will form complex such as $AgCl_{aq}$, $AgCl_2^-$, $AgCl_3^{2-}$ and $AgCl_4^{3-}$ in addition to AgCl precipitate. Thermodynamical data of AgCl and the complexes are given in Table 2.

Table 2 Themodynamical data of AgCl and the complexes

Temperature /℃	AgCl pK_{sp}	$AgCl_{aq}$ pK_1	$AgCl_2^-$ pK_2	$AgCl_3^{2-}$ pK_3	$AgCl_4^{3-}$ pK_4
25	9.55	3.31	5.52	5.52	5.51

Total concentration of Ag^+ in the solution can be calculated by the following equation[1]:

$$[Ag]_T = [Ag^+] + [AgCl_{aq}] + [AgCl_2^-] + [AgCl_3^{2-}] + [AgCl_4^{3-}] = K_{sp}\cdot 10^{pCl}\cdot a$$

where K_{sp} — solubility product of AgCl;
$pCl = -\lg[Cl^-]$;
$a = 1 + 10^{pK_1 - pCl} + 10^{pK_2 - 2pCl} + 10^{pK_3 - 3pCl} + 10^{pK_4 - 4pCl}$

The effect of pCl on $[Ag]_T$ in aqueous solution is shown in Fig. 1. In the ranges of chloride ion concentration, $[Cl^-] = 10^{-2} \sim 10^{-3}$ (pCl = 2～3), $[Ag]_T$ in the solution is minimum, about 10^{-6} mol/L, and then, it will increase with the increase of $[Cl^-]$ and

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reach 0.32 mol/L as $[Cl^-]=5$ mol/L. Accordingly, Ag in the concentrate will be oxidized and become soluble in solution if high $[Cl^-]$ presents. Maximum concentration of Ag^+ in the solution is 0.32 mol/L or 34.517 g/L.

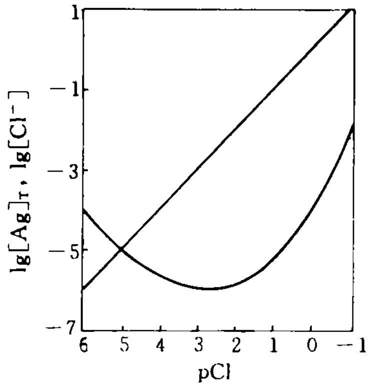

Fig. 1 Effect of pCl on $[Ag]_T$

2.2 *Experiment of Leaching*

The chloride leaching was conducted in a glass reactor under the condition of agitation and constant temperature. All runs were performed according to a three level orthogonal test design which involved the variables, such as $[Cl^-]$, reaction time, reaction temperature, liquid-solid ratio and additives. The purpose of the tests was to obtain the effect of the variables on silver extraction. Experimental results are given in Table 3.

It was indicated by experimental results in Table 3 that the best leaching efficiency of silver extraction was 94.4%, and the order of the effects was temperature>$[Cl^-]$>time>liquid-solid ratio. The object analysis of the orthogonal test is shown in Fig. 2, which shows the silver extractions increase with the increase of $[Cl^-]$, time, temperature and liquid-solid ratio. It should be noted, however, that the increase of $[Cl^-]$ will be restricted by solubility of chloride and the increase of liquid-solid ratio will decrease $[Ag^+]$ in leach solution. In addition, efficiency of silver extractions would not increase significantly if temperature rise above 42 ℃ and reaction time is more than 4 h. As mentioned above, optimum conditions obtained are that $[Cl^-]$ is 4 mol/L, reaction time is 4 h, reaction temperature is 42

Table 3 Effect of variables on silver extraction

Run No.	$[Cl^-]$ /mol·L^{-1}	Time /h	Temperature /℃	Liquid-solid ratio	Silver extraction /%
1	2	3	27	4	44.4
2	2	4	42	5	90.74
3	2	5	57	6	93.74
4	3	3	42	6	88.90
5	3	4	57	4	89.30
6	3	5	27	5	85.50
7	4	3	57	5	92.74
8	4	4	27	6	92.80
9	4	5	42	4	94.40
K	76.29	75.35	74.20	76.06	
K	87.90	90.95	91.35	89.66	
K	93.34	91.21	91.95	91.82	
Differences	17.05	15.86	17.73	15.76	

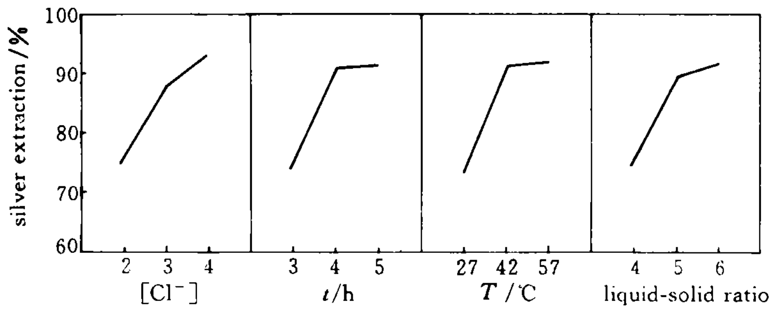

Fig. 2 Object analysis of the orthogonal test

℃ and liquid-solid ratio is 6∶1. The check test using 2# sample was done with the optimum conditions and silver extraction was 96%.

2.3 *Extracting Silver and Regeneration of Leach Solution*

Silver was extracted from leaching solution by zinc dust cementation. The amount of zinc dust added was two times as much as that of silver in solution. The gold was also precipitated in the cementation process and could be separated from silver in the next refine process.

After cementation, the leaching solution which becomes NaCl solution must be regenerated and recycled for reducing costs. Purpose of regeneration process is to remove Fe^{2+} and Zn^{2+} ions remaining in solution by precipitation of iron and zinc hydroxides with inexpensive neutraliser.

3 EXTRACTION OF GOLD

3.1 *Principles of Sulphur-Ammonia Leaching Gold*

Sulphur oxide, sulphur and ammonia in a right proportion can form the mixture solution of $(NH_4)_2S_2O_3$ and $(NH_4)_2SO_3$ with certain concentrations in the presence of catalyzer at room temperature. Both gold and silver in the concentrates will be oxidized to monovalent ions, by which soluble $Au(S_2O_3)_2^{3-}$ and $Ag(S_2O_3)_2^{3-}$ complexes will be formed respectively. Solubilizations of gold and silver belong to electrochemical catalysis process and can be carried out in the following equations[2]:

$$2Au+4S_2O_3^{2-}+1/2O_2+H_2O = 2Au(S_2O_3)_2^{3-}+2OH^- \quad (1)$$

$$2Ag+4S_2O_3^{2-}+1/2O_2+H_2O = 2Ag(S_2O_3)_2^{3-}+2OH^- \quad (2)$$

$$Au+2S_2O_3^{2-}+Cu(NH_3)_4^{2+} = Au(S_2O_3)_2^{3-}+Cu(NH_3)_2^{+}+2NH_3 \quad (3)$$

$$Ag+2S_2O_3^{2-}+Cu(NH_3)_4^{2+} = Ag(S_2O_3)_2^{3-}+Cu(NH_3)_2^{+}+2NH_3 \quad (4)$$

Thermodynamical calculations indicate that free energy changes of above reactions are −95.00, −125.97, −275.80 and −290.80 kJ/mol respectively at 25℃. Thus the reactions are spontaneous. It can be seen from the free energy changes that the oxidations of gold and silver occur more easily in the presence of $Cu(NH_3)_4^{2+}$. $Cu(NH_3)_2^{+}$ formed in reactions (3) and (4) can be easily oxidized to $Cu(NH_3)_4^{2+}$ and be generated. AgCl and Ag_2S in residue from chloride leach will solve in the following reactions:

$$AgCl+2S_2O_3^{2-}=Ag(S_2O_3)_2^{3-}+Cl^-$$

$$Ag_2S+4S_2O_3^{2-}+2O_2=2Ag(S_2O_3)_2^{3-}+SO_4^{2-}$$

Disproportionation of $S_2O_3^{2-}$ takes place easily in basic solution:

$$3S_2O_3^{2-}+6OH^-=4SO_3^{2-}+2S^{2-}+3H_2O$$

The presence of SO_3^{2-}, therefore, is favourable fo. the stability of $S_2O_3^{2-}$. For the above reasons, leach solution should contain some SO_3^{2-} and Cu^{2+} ions.

3.2 *Experiments of Leaching Gold*

The raw material for sulphur-ammonia leaching gold process was the residue obtained from chloride leach. Effects of the variables on the leach of gold and silver were investigated based on a series of experiments with 20 g residue and 3.3∶1 liquid-solid ratio. The variable elements include the concentrations of $(NH_4)_2S_2O_3$, $(NH_4)_2SO_3$ and Cu^{2+} in solution, the reaction time and the reaction temperature. It is indicated by the results that the concentrations of $(NH_4)S_2O_3$, $(NH_4)_2SO_3$ and Cu^{2+} are 0.62~0.90 mol/L, 0.20~0.29 mol/L and 0.10~0.18 mol/L respectively, and the temperature is 40~50℃, the time is about 7 h, and the extraction efficiency is more than 93% for gold and more than 68% for silver. Total extraction efficiency for gold and silver in two stages are 94% and 96% respectively.

3.3 *Check Tests of Sulphur-Ammonia Leach*

Check tests using 100 g concentrate with the optimum conditions in two stages were conducted. Two group tests of sulphur-ammonia leaching gold were done, 1# test without active carbon, 2# test with 5 g of active carbon. The results of check test were given

Table 4 Check Test Results

Test	Amount of raw material /g	Amount of residue /g	Au amount in residue /g·t⁻¹	Ag amount in residue /g·t⁻¹	Au extraction /%	Ag extraction /%
Leaching Ag	100	98.60	33.16	624.10	19.79	89.17
Leaching Au 1#	30	27.50	2.68	303.00	92.60	55.50
Leaching Au 2#	30	26.70	1.99	340.00	94.66	51.50
Total Extraction 1#					94.06	95.35
Total Extraction 2#					95.72	95.00

in Table 4.

From Table 4 it can be seen that:

(1) The efficiency of silver and gold extractions were 89.17% and 19.79% respectively in the first leaching stage, 55.50% and 92.60% in the second stage, and the total efficiency of silver and gold extractions were 95.35% and 94.06% respectively.

(2) Efficiency of gold extraction with carbon-in-pulp process in the second stage is higher than that without carbon-in-pulp process, reaching 94.66%, and efficiency of total extraction is 95.72%.

(3) It is difficult to treat high silver-gold concentrates using one stage leaching, whereas it is feasible to treat the concentrates using two stage leaching, in which the silver leaching is mainly in the first stage and gold mainly in the second one.

3.4 *Treatment and Regeneration of Leaching Solution*

Gold and silver were extracted from leaching solution by copper cementation. Cu^{2+} resulted from the cementation process is advantageous to regeneration and reuse of leaching solution. During every leaching operation, 40% of $(NH_4)_2S_2O_3$ and 45% of $(NH_4)_2SO_3$ were consumed, which can be replenished by mixing SO_2, S and NH_4OH in the presence of catalyzer at room temperature.

4 CONCLUSIONS

(1) A new method of extracting gold and silver without pollution has been developed, which can treat the high silver-gold concentrates, and efficiency of gold and silver extractions are more than 94% and 95% respectively.

(2) A method of preparing directly leach reagent of extracting gold and silver has been studied. This method is practical for the extraction of gold and silver.

(3) This method has a great advantage because of its good effectiveness, inexpensiveness as well as availability of raw materials.

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