Experimental Study on Recovery of Cyanide Tailings Slurry by Membrane Separation in a Gold Mine

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Abstract. In view of the difficulty in recovering valuable metals and cyanides from cyanide tailings pulp in gold mines, the laboratory exploratory test of recovering gold and silver from the tailings pulp produced by a CIP process was carried out by using the technology of "solid-liquid separation + membrane separation and purification + adsorption and recovery of gold and silver by activated carbon". The results showed that the cyanide tailings slurry was separated by solid-liquid in the laboratory and stabilized by chemicals, and the dry slag was identified as a general solid waste according to the results of the identification standard for hazardous waste leaching toxicity GB5085.3-2007. The screened reverse osmosis membrane test showed that 95% of the permeate water recovery rate were obtained. The concentration of cyanide in membrane concentrate water reached 807.9 mg/L, the concentration of copper, gold and silver reached 0.43 mg/L and 3.91 mg/L respectively after being concentrated from below the detection limit, and the concentration was 19.9, 14.3 and 18.6 times respectively. The adsorption test of membrane concentrate water by activated carbon showed that gold, silver and copper were absorbed in membrane concentrated water, the adsorption rates reached 99.76%, 96.16% and 9.09% respectively, which facilitated the subsequent selective recovery of gold and silver. The recovery of valuable metals and cyanide from cyanide tailings slurry by the process of "solid-liquid separation + membrane separation and purification + adsorption and recovery of gold and silver by activated carbon" had a good effect.

1. Introduction

With the rapid development of gold production technology in China, the number, scale and output of gold mines are increasing day by day, the mining intensity is increasing day by day, and the amount of tailings is also increasing substantially. At present, most tailings pulps produced by gold production enterprises are discharged into tailings ponds after simple oxidation cyanide breaking (e.g. alkali chloride method). The discharged tailings contain not only a large amount of residual cyanide, but also other valuable metals and minerals which can be comprehensively recovered, such as copper, gold and silver. Using direct cyanide breaking treatment the cyanide and valuable metals in tailings pulp cannot be recovered, it’s a waste of resources.

At present, the mature treatment technology of cyanide-bearing tailings pulp by comprehensive recovery method is relatively simple, mainly acidizing stripping to recover cyanide and acidizing
precipitated copper, while the recovery of gold, silver and low-content copper is very little, because the content of gold and silver in cyanide lean liquor is very low, the traditional method is difficult to recover, and acidizing stripping process is very difficult and the stripping recovery efficiency of low concentration cyanide-containing waste liquor is not high. Membrane separation technology is a practical technology which integrates separation, concentration and purification. It can realize the concentration of low concentration gold and silver and the purification of cyanide at the same time. Membrane treatment technology is used to treat cyanide-containing wastewater from gold mine and to recover low concentration gold and silver and cyanide comprehensively. It has been widely used in engineering both in China and abroad. In 2004, Yanacocha Gold Mine Peru successfully built a treatment station for cyanide-containing wastewater using membrane system, cyanide and precious metals were recovered from the wastewater, and the treatment capacity reached 2383 m$^3$/h. The system significantly reduces the cost of water treatment, improves the recovery rate of precious metals and alleviates the pressure of environmental protection. There are also engineering application practices of membrane separation in China to treat cyanide lean liquor and recover gold, silver and cyanide, such as Hubei Silver Mine and Axi Gold Mine. With the continuous improvement of membrane treatment technology and the continuous improvement of national environmental protection requirements for gold extraction enterprises, the application of membrane treatment technology to comprehensive recovery and treatment of cyanide-containing tailings slurry will become an inevitable trend.

In this paper, the process of "solid-liquid separation + membrane separation and purification + activated carbon adsorption to recovery of gold and silver" was used to recover the tailings slurry produced by a Full-slime cyanide carbon pulp process, and a good recovery effect was obtained.

2. Raw Ore material properties
The gold deposit is located in Hebei Province, it belongs to fracture filling metasomatic medium-low temperature hydrothermal deposit. The ore is gold-bearing pyrite quartz vein and fine quartz vein disseminated type. The ore multielement analysis is shown in Table 1.

| Element name | Au(g/t) | Ag(g/t) | Cu     | S   | Pb  | Zn   | As    | SiO$_2$ | Fe   |
|--------------|--------|--------|--------|-----|-----|------|-------|--------|------|
| content(%)   | 4.40   | 4.95   | 0.042~0.05 | 0.31~0.60 | 0.017 | 0.014 | 0.0015~0.03 | 65.8  | 1.72 |

The ore material composition is simple, the main metal mineral is pyrite, and other metal minerals are very few, metal minerals are mainly natural gold, with a small amount of silver and gold deposits and natural silver. Gangue minerals are mainly quartz and feldspar, followed by sericite, kaolin and carbonate minerals. The concentrator adopts All-sliming cyanidation CIP process, the mineral process flow is "crushing - grinding - all slime cyanide carbon leaching - desorption electrolysis - smelting purification". The existing processing capacity is 1200 t/d ore, and the cyanide-bearing tailings slurry is about 2200 m$^3$/d. The cyanide-bearing tailings pulp is treated by alkali-chlorine method, the oxidant is calcium hypochlorite. After treatment, the tailings are transported to the tailings reservoir by plunger pump, and the supernatant of the tailings are returned to the grinding section of the concentrator for further use. The tailings slurry treatment process is as follows:
Figure 1. Treatment process of cyanide-bearing tailings pulp in a gold concentrator

The basic conditions of cyanide tailings slurry before treatment are shown in Table 2.

| Items       | Value | CN₁ (mg/L) | Au (mg/L) | SCN (mg/L) | COD (mg/L) | Ammonia nitrogen (mg/L) | As (mg/L) |
|-------------|-------|------------|-----------|------------|------------|-------------------------|-----------|
| pH          | 11.3  | 96.27      | 401.7     | 39~42      | ~          | ~                       | ~         |
| Conductivity (mg/L) | 3120-3431 | 2-10     |            |            |            |                         |           |
| COD (mg/L)  | 106   |            |           |            |            |                         | <0.05     |
| Au(mg/L)    | 0.02L | 0.017~0.07 |            |            |            | ~                       | ~         |
| Pb(mg/L)    | 0.05L | 0.05L      |            |            |            |                         | <0.05     |
| Zn (mg/L)   | 0.25  | 0.01L      | 0.014     |            |            |                         |           |
| Ag (mg/L)   | 0.07~0.5 | 2.95~6.83 |            |            |            |                         |           |
| Cu(mg/L)    | 2.2   |            |           |            |            |                         |           |
| As (mg/L)   | 9.30  | 0.007L     | 0.038     |            |            |                         |           |
| Cd (mg/L)   | 143.11| 0.02L      | 22.37     | 152.8      | 9.30       |                         |           |
| Pb (mg/L)   | <0.05 |            |           |            |            |                         |           |
| Sulfate (mg/L) | 500~600 |          |           |            |            |                         |           |
| Chloride (mg/L) | 400~500 |        |           |            |            |                         |           |
| Chloride (mg/L) | 400~500 |        |           |            |            |                         |           |
| Chloride (mg/L) | 400~500 |        |           |            |            |                         |           |
| Chloride (mg/L) | 400~500 |        |           |            |            |                         |           |
| Chloride (mg/L) | 400~500 |        |           |            |            |                         |           |

After the cyanide tailings slurry was obtained from the gold concentrator, the water quality of the supernatant of the slurry was analyzed, and the results were shown in Table 3.

| No. | Items       | Value | No. | Items       | Value |
|-----|-------------|-------|-----|-------------|-------|
| 1   | pH          | 9.5-9.8 | 11  | Ca(mg/L)    | 150-250 |
| 2   | Conductivity (mg/L) | 3120-3431 | 12  | Mg(mg/L)    | 2-10   |
| 4   | COD (mg/L)  | 106   | 13  | As(mg/L)    | <0.05  |
| 5   | Au(mg/L)    | 0.017~0.07 | 14  | Hg(mg/L)    | <0.05  |
| 6   | Ag(mg/L)    | 0.07~0.5  | 15  | Sulfate(mg/L) | 500-600 |
| 7   | Cu(mg/L)    | 2.95~6.83 | 16  | Chloride(mg/L) | 400-500 |
| 8   | Total Fe(mg/L) | 11.52  | 17  | Nitrate (mg/L) | 40-50  |
| 9   | Zn(mg/L)    | 2.2   | 18  | Total CN(mg/L) | 80-100  |
| 10  | Pb(mg/L)    | <0.05 | 19  | Free CN(mg/L) | 60-80  |
According to the data of Table 2 and Table 3, the cyanide, copper, COD and pH in the tailings pulp exceed the first-class standard of "Comprehensive Wastewater Discharge Standard" (GB8978-1996). Cyanide seriously exceeds the standard and contains low concentration of gold, silver and copper ions, which has a certain recovery value.

3. Bench test proposal
The bench test process is shown in the following figure:

![Bench test process diagram]

Firstly, cyanide tailings slurry was treated by solid-liquid separation and stabilization, the solid waste property of the filtrate was evaluated, the filtrate was concentrated and purified by reverse osmosis membrane, and the concentrated water obtained by membrane separation was then adsorbed by activated carbon to investigate the recovery effect of activated carbon on gold, silver and copper in concentrated water of membrane, the water quality of membrane permeate water and production water are compared to determine whether the permeate can be used for production.

4. Test results and discussion

4.1. Characterization of Dry Slag from Pressure Filtration of Solid-liquid Separation
In this experiment, the solid-liquid separation of tailings pulp was carried out by a laboratory filter press. After that, the heavy metals in the filter residue were stabilized by adding compound stabilizers. After that, the total cyanide, copper, lead, As, Cr and Cd in the filter residue were identified according to the "Hazardous Waste Identification Standard Leaching Toxicity Identification GB5085.3-2007". Toxicity leaching experiment was carried out. According to the test results, the dry residue of press filtration is a general solid waste.
4.2. Membrane Separation Test

4.2.1. Membrane Separation Test process. Membrane separation test process as below:

![Membrane bench test process diagram]

4.2.2. Membrane Separation Test Description. Each 100 liter sample was placed in a feed tank, at a nominal pressure of 1.2Mpa permeate was removed from the batch tank until 5 liters remained in feed tank as concentrate. The concentrate was left overnight to precipitate.

4.2.3. Water Quality Analysis of Membrane Separation Test samples. In this experiment, an anti-pollution reverse osmosis membrane was determined through membrane screening test. 95% of the water recovery rate was obtained, and the volume of concentrated water only accounted for 5% of the raw water. The water quality analysis of the test is shown in the table below.

| No. | Name             | pH  | TDS mg/L | Conductivity μS/cm | Total CN mg/L | Free CN mg/L | Cu mg/L | Fe mg/L | Au mg/L | Ag mg/L |
|-----|------------------|-----|----------|--------------------|---------------|--------------|---------|---------|---------|---------|
| 1   | Raw Feed         | 11.98 | 3491    | 4502               | 60            | 33.29        | 18.65   | 0.83    | 0.03    | 0.21    |
| 2   | Permeate water   | 11.78 | 408.4   | 594                | 13            | 7.37         | 0.34    | 0.081   | <0.005  | <0.005  |
| 3   | Concentrate water| 11.46 | 50510   | 47170              | 807.9         | 304.94       | 371.4   | 14.6    | 0.43    | 3.91    |

It can be seen from the above table that the anti-pollution reverse osmosis membrane used in this experiment has a good rejection rate of 61% on cyanide, and can partly concentrate cyanide. The concentration of cyanide in concentrated water is 807.9 mg/L, which is convenient to improve the efficiency of the subsequent recovery process of concentrated water resources. At the same time, the membrane has a good concentration effect on copper ion, the rejection rate is ~98%, the copper content in the concentrated water side is 371.4 mg/L, the copper ion content in the produced water is reduced to 0.34 mg/L, and the copper was concentrated about 20 times; the RO membrane also has a good rejection rate of 90.24% for iron ion, and the iron ion content in concentrated water is about 18 times as much as that in raw water. The permeate water has low concentration of sodium cyanide and sodium hydroxide which are easy to be reused in gold ore production process, test samples picture as below:
4.3. Water quality comparison between permeate water and reused water produced by enterprises

Comparing the water quality of the comprehensive water produced by laboratory bench test with that of the production water reused from the tailings pond by the gold concentrator at present, see the table below.

**Table 5.** Water quality comparison between membrane water production and recycled water production in concentrator

| NO. | Items          | Permeate water | recycled water in concentrator |
|-----|----------------|----------------|--------------------------------|
| 1   | pH             | 11.56          | 11.78                          |
| 2   | TDS, mg/L      | 84.43          | 1694                           |
| 3   | Conductivity, mg/L | 112.87      | 2640                           |
| 4   | ORP, mV        | 90             | 78                             |
| 5   | Ca, mg/L       | 46.7           | 315.2                          |
| 6   | Mg, mg/L       | <0.002         | 21.8                           |
| 7   | K, mg/L        | 1.9            | 43.6                           |
| 8   | Na, mg/L       | 4.30           | 236.6                          |
| 9   | Cu, mg/L       | <0.01          | <0.05                          |
| 10  | Fe, mg/L       | <0.03          | 0.26                           |
| 11  | Zn, mg/L       | <0.006         | <0.05                          |
| 12  | Pb, mg/L       | <0.001         | <0.05                          |
| 13  | Total CN, mg/L | 22.6           | 50.4                           |
The membrane used in the experiment is a reverse osmosis membrane, which can reject most of the pollutants. From the table above, it can be seen that the water quality of the permeate water produced by the membrane is much better than that of the existing recycled water produced by the enterprise. It can be used as a supplement for new water reuse and will not affect the production index of mineral processing.

4.4. Activated carbon adsorption test of membrane concentrate water

Take the concentrated water of 1000ml membrane test, put it into beaker, add 5g activated carbon, stir slowly for 12h with agitator, take the supernatant sample after the experiment, and analyze the content of gold, silver and copper.

The experimental results are shown in the table below.

**Table 6. Contents of Au, Ag and Cu before and after Activated Carbon Adsorption**

|                       | Au/mg/l | Ag/mg/l | Cu/mg/l |
|-----------------------|---------|---------|---------|
| before Activated Carbon Adsorption | 0.43    | 3.91    | 371.4   |
| after Activated Carbon Adsorption    | 0.001   | 0.15    | 337.7   |
| Adsorption Rate        | 99.76%  | 96.16%  | 9.09%   |

It can be seen from the above table that activated carbon has a good adsorption effect on gold and silver in membrane concentrate water. The adsorption rates of gold and silver reach 99.76% and 96.16% respectively. Activated carbon has a very low adsorption rate on copper, which is conducive to the selective adsorption and recovery of gold and silver by activated carbon method.

5. Conclusion

(1) The cyanide tailings slurry of the gold mine is separated by solid-liquid in laboratory and stabilized by chemicals. The dry slag is identified according to the "Leaching Toxicity Identification Standard for Hazardous Waste GB5085.3-2007". The test results show that the pressure filter dry slag is a general solid waste, not a hazardous waste;

(2) The results of membrane test show that the recovery rate of permeate water produced by membrane test is 95%, the volume of concentrated water is reduced to 1/20 of raw water, and the volume of permeate water is 95% of raw water. The quality of permeate water is much better than the existing recycled water of enterprises;

(3) The concentration of cyanide in concentrate water is 807.9 mg/L, and the concentration of copper, gold and silver reached 0.43 mg/L and 3.91 mg/L respectively after being concentrated from below the detection limit, the concentration was 19.9, 14.3 and 18.6 times respectively;

(4) Activated carbon adsorption test on concentrate water showed that the adsorption rates of gold, silver and copper reached 99.76%, 96.16% and 0.09% respectively, which facilitated the subsequent selective recovery of gold and silver;

(5) The experimental results show that the process of "solid-liquid separation of slag water + membrane separation and purification filtrate + activated carbon adsorption and recovery of gold and silver" has a good effect on recovery of valuable metals and cyanide in cyanide tailings pulp.

Acknowledgments

This work was financially supported by National key research and development program (2018YFC1903105).

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