

HUANG ZHONGSHENG^{①,2,3*}, YANG TIANZU^①**GOLD RECOVERY FROM CYANIDATION TAILINGS USING FLOTATION PROCESS**

The gold recovery from cyanidation tailings was only 4.01% with the general flotation process, the surface analyses of flotation products were performed, and the results showed that the poor gold recovery with general flotation process was due to the passive films covering the surface of the gold bearing pyrite. These films are mainly hydrophilic hydroxides of Ca, Fe and Mg, at the same time, the depression of CN⁻ to pyrite flotation in the flotation slurry was also a main contributing factor. With the surface repair regeneration procedures, it was proven that sulfuric acid pretreatment plays a dominant role in the removing and cleaning of passive films, while destroying free cyanides in the slurry. Sodium carbonate was then used as a buffering pH modifier and as a slurry dispersant after sulfuric acid pretreatment. The gold recovery was as high as 93.41%, compared to the original gold recovery of 4.01%.

Keywords: Gold; cyanidation tailings; surface repair regeneration; flotation; bio-oxidation.

1. Introduction

Bio-oxidation pretreatment is one of the main pre-oxidation technologies for refractory gold concentrates and there are more than 20 processing plants globally that are using this technology [1-2]. The total output of cyanidation tailings is about 1.5 million tons/year. There are about eight bio-oxidation plants operating in China, with a total gold concentrate bio-oxidation capacity of 0.5 million tons/year, the output will be approximately 0.3 million tons/year from cyanidation tailings.

The content of gold in cyanidation tailings, produced by refractory gold concentrate bio-oxidation and cyanidation process, is in the range of 2-6 g/t because of incomplete bio-oxidation [3-5], therefore, the recovery of gold from cyanidation tailings is not only valuable but also necessary.

Gold extraction research on cyanide slags from roasting-CIL and other process are very popular, the main gold extraction processes are flotation [6-8], hydrometallurgy [9-12], roasting [13-14], or a combination of these technologies [15]. Nonetheless, research on cyanidation tailings of the bio-oxidation process has rarely been investigated. The cyanidation tailings from one refractory gold concentrate bio-oxidation plant (XinJiang province, China) contains 7.40 g/t Au, 6.45% S, and 24.96 g/t Ag, with the Na₂CO₃ + Na₂S as regulators, CuSO₄ as an activator, and isoamyl xanthate and ammonium butyl aerofloat as collec-

tors. The gold and silver recovery is merely 61.30% and 47.47% respectively [3], likewise, cyanidation tailings from another gold plant (JiLin province, China) contains 4.87 g/t Au, with the sodium carbonate and sodium silicate (water glass) as regulators, amyl xanthate and ammonium dibutyl dithiophosphate as collectors, and copper sulfate as an activator, the gold recovery was just 65.12%, with the 26.03 g/t concentrate Au grade [7].

The feed for this study was the cyanidation tailings produced by refractory gold concentrate bio-oxidation and CIL process. The tailings contained gold which was mainly enclosed in pyrite, however, the cyanidation tailings had the following features, bringing about much difficulty to the recovery of gold:

- 1) The product of the bio-oxidation reaction produced lots of films, which covered the surface of cyanidation tailings, seriously affecting the flotation recovery rate.
- 2) The presence of cyanide species in the cyanidation tailings significantly affect the flotation of gold bearing pyrite and liberated gold.
- 3) The cyanidation tailings are very fine, thus, detrimental to flotation process.

Based on the discussion above, a new process, floatability, surface repair and regeneration for increasing gold recovery was established in this article. The gold recovery increased dramatically through this new process compared to the conventional flotation process.

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2. Experimental

2.1. Materials

The cyanidation tailings used in the study were obtained by bio-oxidation and cyanide leaching of refractory gold concentrate originally sourced from the Long-nan Zijin gold mine site in Gansu province, China. Particle size analysis of the samples showed that 90% of the particles passed through a sieve of mesh 0.045 mm. The chemical composition and major minerals composition are presented in Table 1, Figure 1, respectively. Chemical phases for gold and sulfur are listed in Table 2.

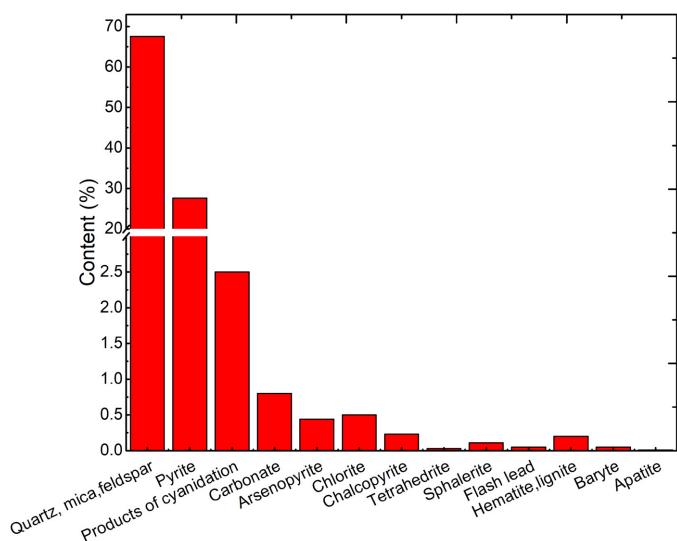


Fig. 1. Mineral composition of cyanidation tailings

From Table 1 and Figure 1, the pyrite, quartz, mica, and feldspar were the major minerals in the cyanidation tailings. The valuable metal was gold, and its content was as high as 5.47 g/t.

From Table 2, 87.75%, 4.02%, and 0.92% of gold in the cyanidation tailings were enclosed in sulfide, silica, carbonate

and oxide respectively, with the total being 92.69%. The sulfur species analysis shows that sulfides are the main components, accounting for 84.88% of the total sulfur in the samples. Theoretically, it is possible to recover the gold in the tailings by the flotation process.

2.2. Equipment and procedure

The floatability repair and regeneration of cyanidation tailings were studied to increase the flotation performance. Sulfuric acid (AR, Jilong Chemical Co., Ltd., China) and sodium carbonate (AR, Xilong Chemical Co., Ltd., China) were used as the pretreatment reagent and regulator, respectively, in this study. A 250 g sample of cyanidation tailings was added to a 1.5L flotation cell and the mixing slurry density was brought to 20wt% solids using domestically supplied water. The original pH of the slurry was approximately 10. Different dosages of sulfuric acid, sodium carbonate, SNBX (sodium n-butylxanthate, Hainan Zhongxin Chemical Co., Ltd) + ADD (Ammonium dibutyl dithiophosphate, Y&X Beijing Technology Co., Ltd) (SNBX:ADD ratio = 2:1), and terpenic oil (Jiangxi Xuesong Natural Medicinal Oil Co., Ltd) were studied for their effect on gold recovery. The flowchart for the test is shown in Fig. 2.

2.3. Analysis

The elemental composition and mineralogy were analyzed with an atomic absorption spectrophotometer (AAS, iCE3400, Thermo Fisher, USA) and a mineral liberation analyzer (MLA, MLA650, FEI, USA) respectively. A combination of analytical techniques were used for the mineralogical characterization of the samples, which were performed with a scanning electron microscope (Quanta 650, FEI, USA) and an energy dispersive X-ray detector (EDX APOLLO X, USA).

TABLE 1
Element analysis of the cyanidation tailings

Content	Au*	Ag*	As	S	Fe	SiO ₂	Al ₂ O ₃	C	MgO	CN	Others	Total
wt/%	5.47	9.8	0.38	19.05	19.35	35.62	8.62	1.58	1.14	0.02	12.94	100

* Au and Ag contents are expressed in g/t.

TABLE 2
Gold and sulfur chemical phase of cyanidation tailings

Au phase	Item	Free gold	Enclosed in sulfide	Enclosed in carbonate and oxide	Enclosed in Silicate	Total
	Content/g.t ⁻¹	0.40	4.80	0.05	0.22	
	Proportion/%	7.31	87.75	0.92	4.02	
Sulfur species	Item	Sulfide sulfur		Sulfate sulfur	Other sulfur	Total
	Content/g.t ⁻¹	16.17		0.58	2.3	
	Proportion/%	84.88		3.05	12.07	

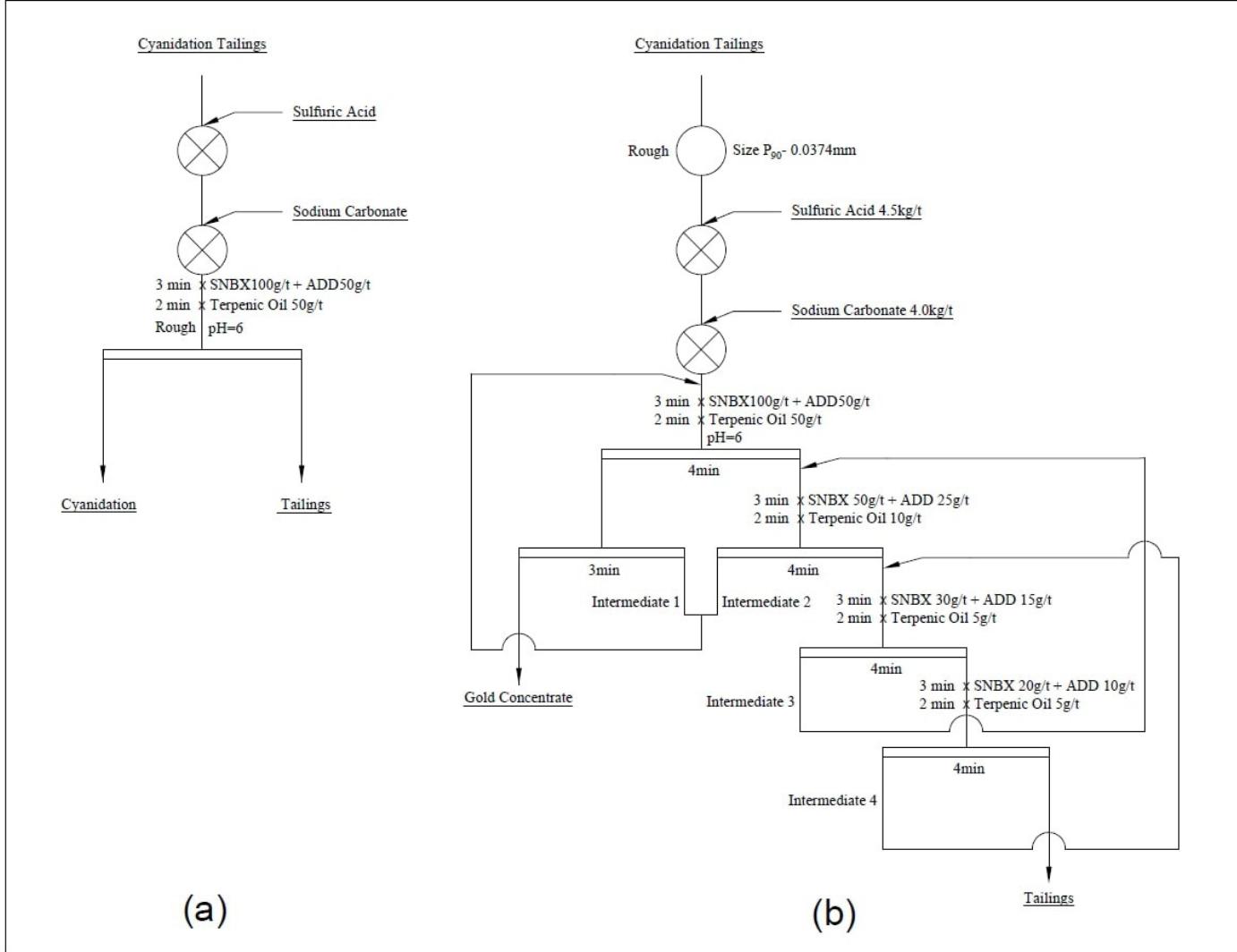


Fig. 2. Flowchart for gold recovery; (a) rough flotation, (b) closed-circle flotation

3. Results and discussion

3.1. Influence of sulfuric acid

The sulfuric acid pretreatment test results are shown in Figure 3. The gold recovery was only 4.01% with the absence of sulfuric acid pretreatment. It can be seen that the gold recovery increased as the sulfuric acid dosage increased; however, when the dosage is higher than 4.5 kg/t the recovery decreased. The gold recovery was 60.31% when sulfuric acid was 4.5 kg/t. This phenomenon can be explained by three assumptions.

Firstly, it can be seen from SEM and EDX in Fig. 4(a) and Fig. 4(b), that there are lots of hydrophilic films on the surface which was generated in the system of high alkalinity with lime during cyanide leaching of gold. These hydrophilic products involving $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$, lead to poor floatability. Sulfuric acid can dissolve these hydrophilic films, liberating the ions, except for Ca which forms insoluble CaSO_4 on the freshly exposed pyrite surface. The mechanism of sulfuric acid dissolving hydrophilic films is shown in Fig. 6(a).

The fresh surface is exposed resulting in gold bearing pyrite having good floatability when using sulfuric acid as an activator. The flotation reagent can now easily contact with target minerals, gold bearing pyrite and increase gold recovery effectively. It can be seen from EDX of flotation concentrate and tailings in Fig. 4(a) and Fig. 4(b), that, there are more kinds of impurity elements and the content of Ca, Al, Mg, O, K, and Si etc. were higher when sulfuric acid was absent. Also, it can be seen from EDX of flotation concentrate shown in Fig. 5(c), that there is only S and Fe, when sulfuric acid dosage was 4.5 kg/t, the surface is very clean and films are removed, meanwhile, it can also be seen from EDX of flotation tailings products when sulfuric acid dosage was 4.5 kg/t, shown in Fig. 5(d), that there are only Si, Mg and Al. Element content and variety decreased effectively, as opposed to Fig. 4(b), EDX content when sulfuric acid activator was absent.

Secondly, the concentration of CN^- was 4.68 mg/L, $\text{Cu}(\text{CN})^{2-}$ was 1.89 mg/L and $\text{Zn}(\text{CN})^{3-}$ was 0.06 mg/L in the flotation slurry. Of all the sulfide minerals studied so far, the depression of pyrite by free cyanide is the best understood [16-17].

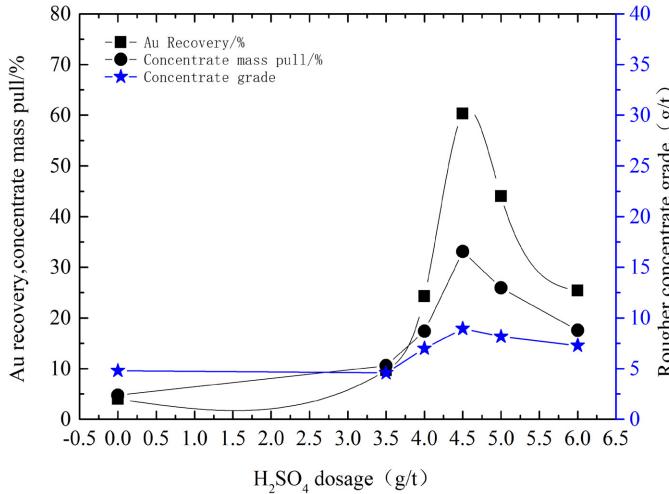


Fig. 3. Influence of sulfuric acid on the flotation

Free cyanide is preferentially absorbed on pyrite surfaces as iron cyanide compounds, therefore inhibiting the chemisorption and oxidation of SNBX and ADD. Cu(CN)²⁻ is not believed to be a depressant for the flotation of pyrite [18]. Interaction of Zn(CN)³⁻ with pyrite minerals needs to be further examined, however, the Zn(CN)³⁻ influence was limited because of its low concentration. The destruction by sulfuric acid resulted in a CN⁻ concentration below 0.1 mg/L as per mechanism and reaction shown in Fig. 6(c).

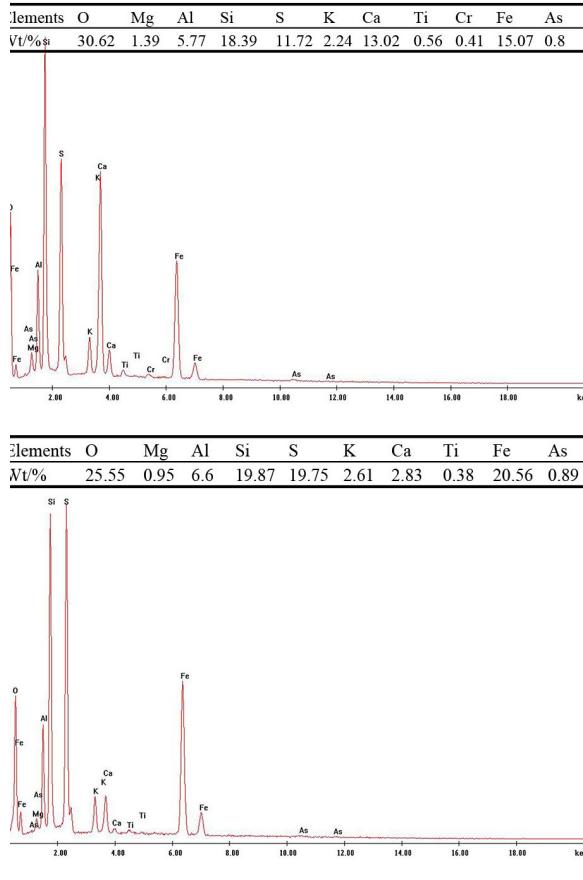
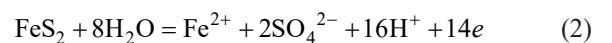
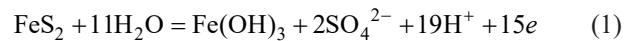


Fig. 4. SEM and EDX of concentrate and flotation tailing when sulfuric acid dosage was 0 (a) concentrate, (b) flotation tailing

Finally, the original flotation slurry pH is approximately 10. In alkaline system the oxidation reaction of pyrite may occur as reaction equation (1), and the pyrite floatability will decrease, however, equation (1) will be suppressed with the increased sulfuric acid dosage, resulting in better flotation; hence increasing gold recovery effectively. Nevertheless, with the increased sulfuric acid dosage the slurry environment transforms from alkaline to acidic system gradually. When sulfuric acid dosage is higher than 4.5 kg/t the oxidation reaction of pyrite in acid system may start as equation (2), with hydrophilic products, SO₄²⁻ was produced on the surface of pyrite, so the floatability of pyrite is decreased. The mechanism and reactions occurs as outlined in Fig. 6(b).



3.2. Influence of sodium carbonate

The experimental results of sodium carbonate dosage were shown in Fig. 7. The roughing gold recovery, mass pull and concentrate grade increased as the dosage increases for sodium carbonate. The highest gold recovery was observed at 4.0 kg/t sodium carbonate dosage, with the gold recovery 60.74%, mass pull 37.84% and concentrate grade 9.4 g/t. However, when the

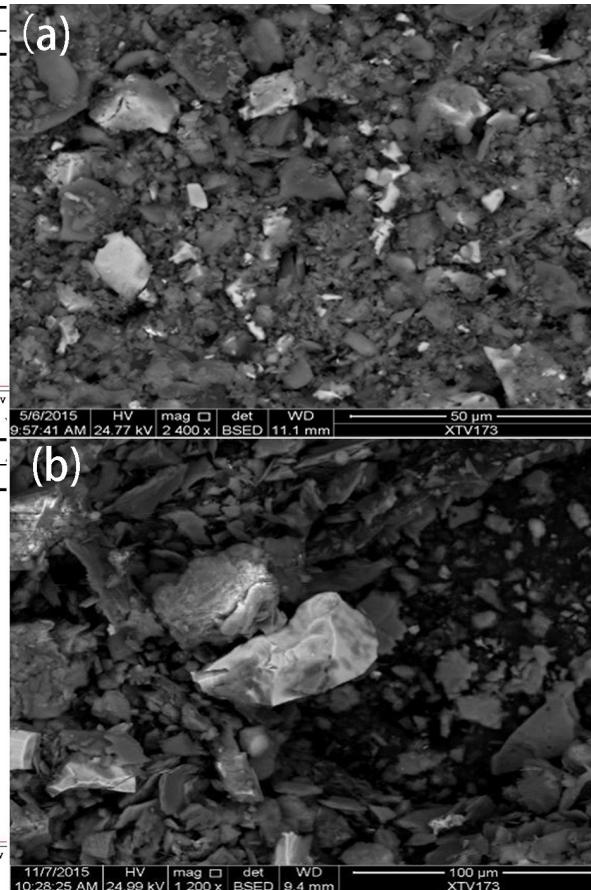


Fig. 4. SEM and EDX of concentrate and flotation tailing when sulfuric acid dosage was 0 (a) concentrate, (b) flotation tailing

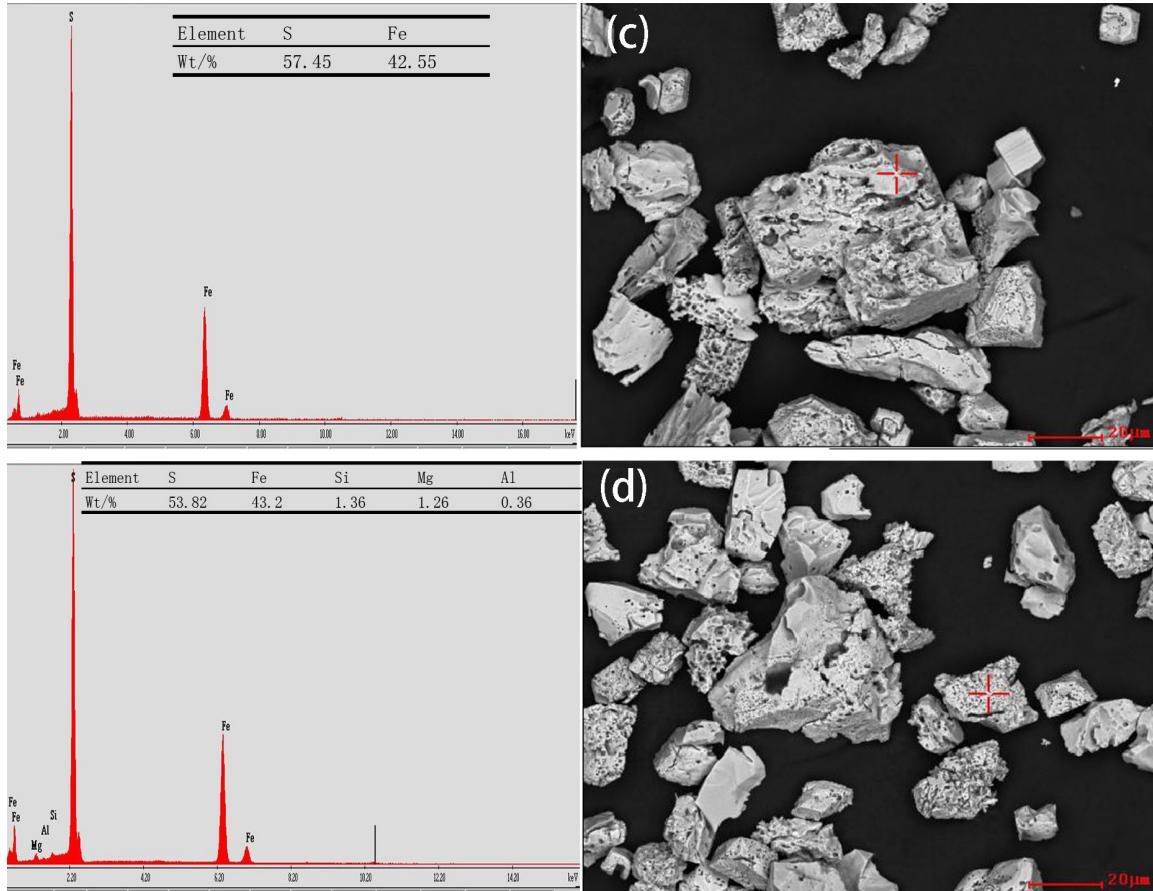


Fig. 5. SEM and EDX of concentrate and flotation tailing when sulfuric acid dosage was 4.5 kg/t; (c) concentrate, (d) flotation tailing

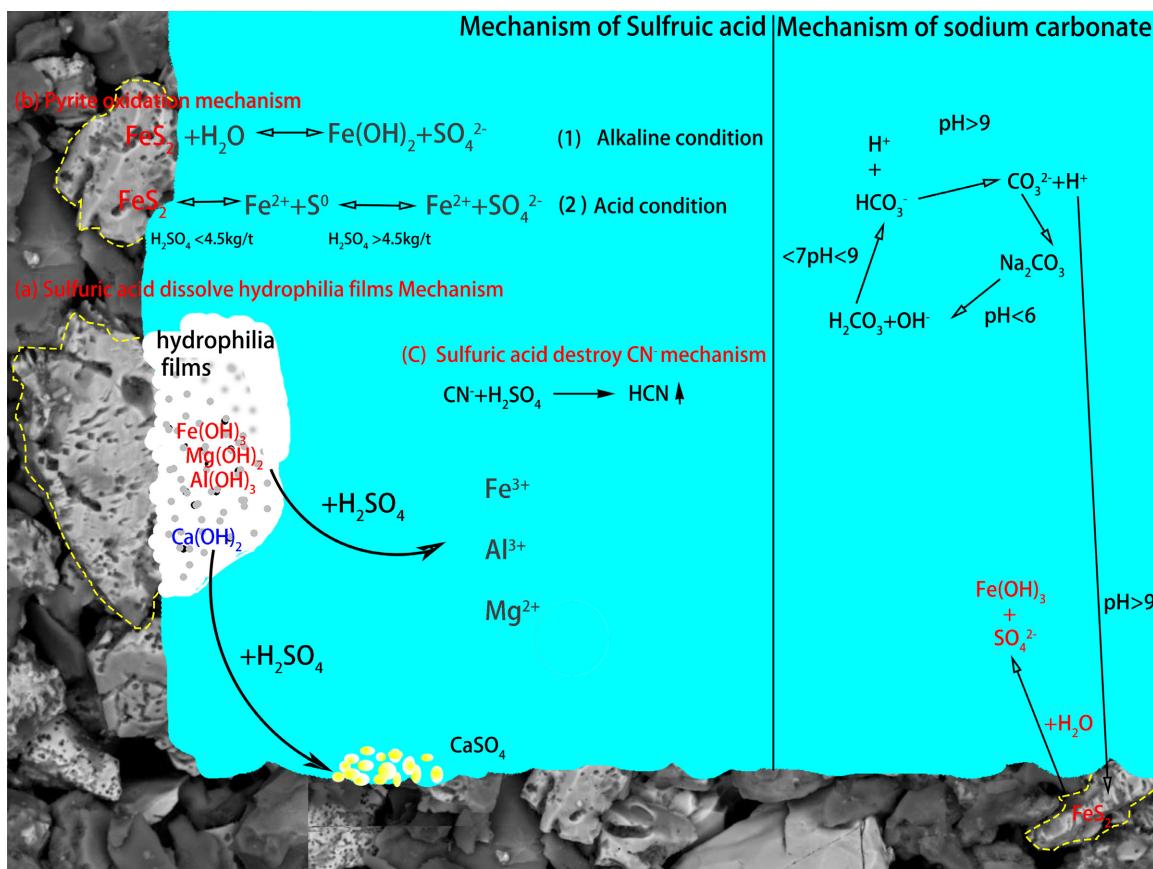


Fig. 6. Mechanism of surface repair regeneration using sulfuric acid

dosage was higher than 4.0 kg/t, the gold recovery, rough concentrate mass pull and gold grade decreased with the increase of sodium carbonate dosage. This phenomenon can be explained by two assumptions. Firstly, sodium carbonate can increase flotation system pH by neutralizing excess sulfuric acid, and keeping acid and alkali balanced during flotation. The sodium carbonate mechanism and reaction was shown in Fig. 6 it's a buffering pH modifier and keeps flotation pH between 7-9. Sodium carbonate starts hydrolysis reaction when slurry flotation pH < 6. When slurry flotation pH > 9 the reactions occur as outlined in equation (1), and the pyrite floatability will decrease. Secondly, sodium carbonate is a slurry dispersant, it can reduce the adverse effect of slime on flotation by depressing the slime during flotation.

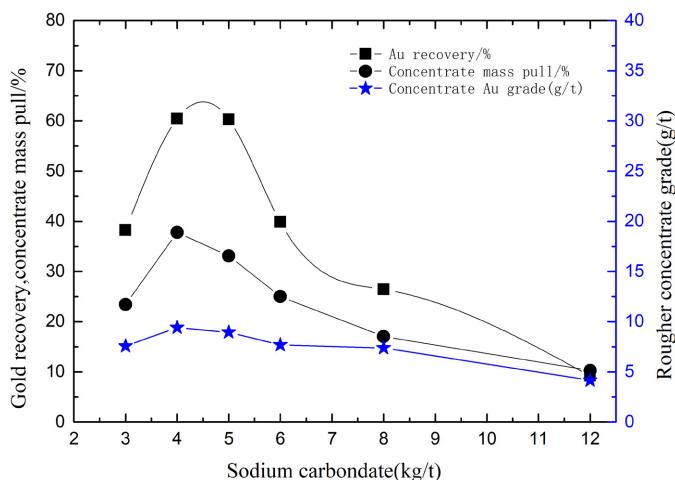


Fig.7. Influence of sodium carbonate

3.3. Influence of synergetic collector

Fig. 8 represents the influence of combined collector, it can be seen that the roughing gold recovery followed similar trends, first increased and then decreased with the dosage of SNBX + ADD increasing from 90 g/t to 180 g/t and reached a maximum of 69.23% as the dosage of SNBX + ADD increases. When the dosage was higher than 180 g/t, the recovery decreased, while the

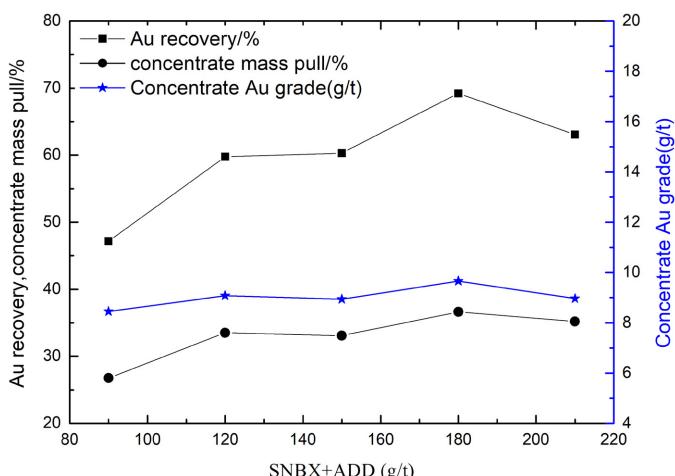


Fig. 8. Influence of synergetic collector

rough concentrate, mass pull and gold grade were not significant. SNBX and ADD are usually used as combined collectors to improve flotation recovery from complex refractory gold material.

3.4. Results of closed-circle flotation

The closed-circuit test results are shown in Table 3, it can be seen that the gold recovery was 93.41%, and the content of gold in the flotation tailings decreased to 0.55 g/t from 4.72 g/t in cyanidation tailings.

TABLE 3
Closed-circuit test results

Products	Mass pull/%	Grade		Recovery/%	
		Au/g.t ⁻¹	S/%	Au	S
Flotation Concentrate	43.48	10.14	43.67	93.41	99.67
Flotation tailings	56.52	0.55	0.11	6.59	0.33
Cyanidation tailings	100.00	4.72	19.05	100.00	100.00

4. Conclusions

The gold recovery from cyanidation tailings obtained from refractory gold concentrate of the bio-oxidation pretreatment is only 4.01% by traditional flotation process. SEM and EDX analysis of the flotation products shows that the mineral's original properties were destroyed by films which covered the surface of gold bearing pyrite, these films are consisted of hydrophilic $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$, which lead to poor floatability. Sulfuric acid can dissolve these hydrophilic films, and the fresh surface is exposed for gold bearing pyrite to have a good floatability. Furthermore, the depression of gold bearing pyrite floatability due to CN^- in the flotation slurry was also the main reason for bad flotation performance and gold recovery. CN^- was destroyed when using sulfuric acid as activator, hence increasing gold recovery.

Sodium carbonate is a buffering pH modifier, which can also neutralize the excess acid after sulfuric acid pretreatment. Also, it is a slurry dispersant, which eliminates the effects of slime during flotation.

The present study demonstrates that floatability repair and regeneration on cyanidation tailings by sulfuric acid pretreatment, and sodium carbonate pretreatment can increase gold recovery effectively. The gold recovery can increase from 4.01% under direct flotation to 93.41% under the new process presented by this study.

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REFERENCES

- [1] A.H. Kaksonen, N.J. Boxall, Y. Gumulya, H.N. Khaleque, T. Bohu, K.Y. Cheng, K.M. Usher, A.M. Lakaniemi, *Hydrometallurgy* **180**, 7-25 (2018).
- [2] M.Z. Mubarok, R. Winarko, S.K. Chaerun, I.N. Rizki, *Hydrometallurgy* **168**, 69-75 (2017).
- [3] S.L. Yu, Y.H. Wang, J.M. Wang, Y. Zhang, S.L. Yu, *Non-ferrous metals (mineral processing part)* **6**, 35-39 (2013).
- [4] Z.S. Huang, C. Wang, D.P. He, Z.W. S.P.Z, *Gold Science and Technology* **22**, 99-102 (2014).
- [5] J. Liu, W.J. Wu, X. Zhang, M.L. Zhu, W.S. Tan, *International Journal of Mineral Processing* **160**, 39-46 (2017).
- [6] C.S. Luo, *Materials Research and Application* **3**, 181-184 (2012).
- [7] M.J. Yu, F. Jiao, *Mining and Metallurgical Engineering* **38**, 66-69 (2018).
- [8] Y. Sun, J.J. Wu, C. Su, *Mining & Metallurgy* **27**, 11-13 (2018).
- [9] X.J. Yu, H.M. Li, Y.L. Zhang, *Non-Ferrous Metals* **5**, 30-32 (2012).
- [10] W.L. Chen, J. Wang, K.H. Yang, Z.G. Li, *Journal of Kunming University of Science and Technology (natural science edition)* **42**, 93-97 (2017).
- [11] F. Zhang, Experimental researches on recovering gold and silver from cyanide residue. Master's Thesis, Xi'an University of Architecture and Technology, Xi'an, December (2010).
- [12] Y.C. Liu, B.J. Peng, Q.Q. L, J.G. Fu, Y. Chen, J. Wu, *Precious Metals* **37**, 11-14 (2016)
- [13] J. Ding, S.F. Ye, *Gold Science and Technology* **22**, 113-117 (2014).
- [14] Y.L. Zhang, H.M. Li, X.J. Y, *Trans. Nonferrous Met. Soc. China* **23**, 1165-1173 (2013).
- [15] C. Gong, Process Study on Iron and Gold Recovery from Cyanide tailings, Master's Thesis, Central South University, Changsha, April, 2014.
- [16] K.L. Sutherland, I.W. Wark, *Principles of Flotation*, Australasian Institute of Mining and Metallurgy Melbourne, 1955. Articles in press.
- [17] J.R.D. Wet, P. C. Pistorius, R.F. Sandenbergh, *Int. J. Miner. Process.* **49**, 149-169 (1997).
- [18] I.W. Wark, *Principles of flotation*. Australian Institute of Mining and Metallurgy (Inc.), Melbourne, 1938. Articles in press.