

Oxidation-free thiourea leaching of gold with sulphur dioxide

Ikromjon Boboev^{1*}, Abubakr Pirov², Rahim Saidzoda, Turaboi Turayev¹, and Dilbar Khakimova

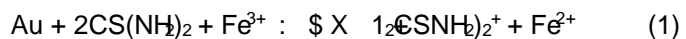
¹Dushanbe branch of the National University of Science and Technology "MISIS" (NUST "MISIS"), Dushanbe, Tajikistan

²Ministry of Industry and New Technologies of the Republic of Tajikistan, Dushanbe, Tajikistan

Abstract. The paper summarizes research on gold recovery by the Carbon in Leach (CIL) process using thiourea by feeding sulphur dioxide by a hydroacoustic emitter. It was found that the use of such a device favors the formation of the radical OH^{*}. The latter is the strongest oxidizing agent. One of the main regulated parameters of the plant is the pressure of pulp supply to the inlet device, which was studied. According to the results of the study, it was found that a high degree of gold recovery is achieved under the following conditions: initial concentration of H₂SO₄ 0.5%, thiourea loading ±1.5 kg/t, coal loading 10 g/kg, sulphur dioxide feed 0.13 kg/t*min, ratio L:S ±1:3, slurry supply pressure to the inlet 1.5 atm, CIL process time ±60 min. Thiourea consumption amounted to 0.57 kg/t, and sulphur dioxide ±8 kg/t. Gold recovery reached 93.5%.

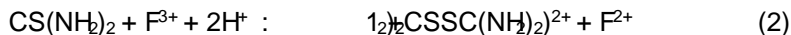
1 Introduction

Application of thiourea (chemical formula CS(NH₂)₂) for the processing of gold-bearing raw materials has recently gained considerable research interest [1]. Compared to cyanidation technology, which is used to extract 85% of the world's gold from ores, thiourea leaching is characterized by low environmental impact, easier handling of the reagent, high selectivity towards gold, faster leaching kinetics, the possibility of uncovering gold and silver included in acid-soluble minerals, lower dependence of efficiency on the presence of impurity ions. Dissolution of gold in thiourea solutions proceeds in the presence of an oxidizing agent [2], by the following reaction:

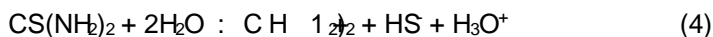
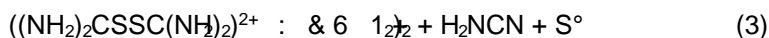


At the same time, there are negative aspects of this process application. Thiourea is more expensive than cyanide due to its high consumption and acid [7]. In addition, thiourea decomposes under oxidizing conditions to formamidine disulfide (FD), which is associated with high consumption of this reagent.

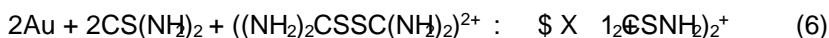
* Corresponding author: bobevi@mis.ru



FD decomposition by irreversible reaction proceeds with formation of adverse products



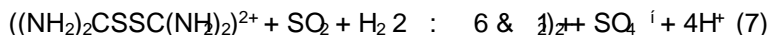
A positive point in FD formation is the fact that, as the strongest oxidizing agent, it accelerates the dissolution of gold by the following reaction:



and on the other hand, the decomposition product is elementary sulphur and partially hydrogen sulphide anion (when interacting with water) [8].

Elemental sulphur, by passivating the gold surface, reduces its dissolution rate, and the presence of hydrogen sulphide may determine the deposition of gold in the form of insoluble gold compounds Au_2S , AuHS , and AuS

A search of the literature revealed that one promising area is the recovery of the FD to thiourea in the leaching process by introducing such an effective reducing agent as SO_2



About the application of SO_2 as a stabilizer in thiourea leaching was first reported by Schultz R.G. [9]. The results of his study showed [10] that the introduction of SO_2 significantly reduces thiourea consumption. It is noted in the paper that SO_2 is a selective reducing agent of DF. In general, in the literature on the application of SO_2 as a stabilizer only a few works reported above. This is obviously due to the complexity of the process due to possible gas leakage into the work area and the lack of proper equipment.

We have developed an installation, using hydroacoustic emitters, which allows effective operation in a gas-liquid environment, including the intensification of the process of cyanidation of gold-containing raw materials to increase the concentration of dissolved oxygen [11-13]. This unit can be applied for effective feeding of SO_2 to the leaching process.

One of the advantages of using hydroacoustic emitter is the possibility of formation of hydroxyl radicals as a result of excitation of water molecule due to cavitation, which increases the potential of pulp by the following reaction



An electronically excited water molecule dissociates to form OH^* and H^* radicals by the following reactions:



These radicals can undergo recombination reactions to form molecular products such as H_2O_2 or H_2 or H_2O .



The primary radical H^{*} is a reducing agent. But a small content of dissolved oxygen in the solution leads to its instantaneous transformation into radicals, which makes it very unstable



The most stable radicals are the radicals OH^{*} [14].

OH^{*} radical is the strongest oxidising agent due to its huge reduction potential (2.81 eV). The intensity of OH^{*} radical formation increases with decreasing pH of the medium (acidic medium) and the recombination rate decreases and in the process of dissolution of gold in thiourea solution can replace the expensive oxidant SO₂·xH₂O.



The aim of the work is to optimize thiourea consumption in gold leaching with feeding SO₂ using a hydroacoustic transmitter unit. One of the adjustable parameters of this unit is the slurry supply pressure at the inlet of the hydroacoustic transmitter.

2 Methods and materials

For the study we used the samples of lead tailings represented by finely dispersed material of light grey color with yellowish tinge. The fineness of the sample grain is microns, 58.11 %.

According to the data of chemical composition (Table 1) the valuable component of the sample is gold and silver. It was found that the gold content in the sample is 2.4 g/t, and silver content is 7 g/t, respectively.

Table 1. Chemical composition of the sample.

Components	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	P ₂ O ₅	S _{gen}	K ₂ O	CaO
Content, %	80.76	0.300	0.560	7.900	0.049	0.100	2.800	0.730
Components	TiO ₂	MnO	Fe ₂ O ₃	Ag, g/t	Au, g/t	Li, g/t	Cr, g/t	Cu, g/t
Content, %	0.260	0.081	2.600	7.000	2.400	67.7	59.6	81.90
Components	Zn, g/t	Rb, g/t	Sr, g/t	Zr, g/t	Ba, g/t	Pb, g/t	Others *	Total, %
Content, %	58.40	102.00	71.60	25.30	477.00	87.60	3.860	100

For leaching with sulphur dioxide supply, a laboratory unit was set up (Figure 1), in which a fan-type hydroacoustic emitter was mounted (Figure 2).

A jacketed reactor consisting of a six-neck glass flask equipped with tubes for sucking sulphur gas from both the cylinder and the top of the reactor, a tube for pumping out the slurry, two electrodes for measuring pH and ORP immersed in the slurry and a tripod for holding the sorbent mesh, was filled with slurry and the desired pH of the medium was set using sulphuric acid. Reagents were then fed through feed tubes 15. The temperature was controlled by the thermostat 14. Then switched on the discharge pump 1, which pumped the pulp from the reactor 4 and pressurized it into the inlet of the hydroacoustic emitter 3 at a rate of 3 m³/h. Additional mixing of the pulp was not required. Due to a distinctive feature of the emitter, when the pulp is fed into the resonator chamber, a vacuum is created, which leads to the suction of sulfur dioxide 7 with subsequent dispersion into tiny bubbles. Inlet pressure values of pulp were controlled by manometer 2. pH and Emf were monitored during each experiment. A barometer was installed inside of the tank to measure the

gas pressure. When the gas pressure above the pulp in the tank increased, the gas pumping screw was manually opened and thus the gas pressure above the pulp was kept constant and equal to 1 atm.

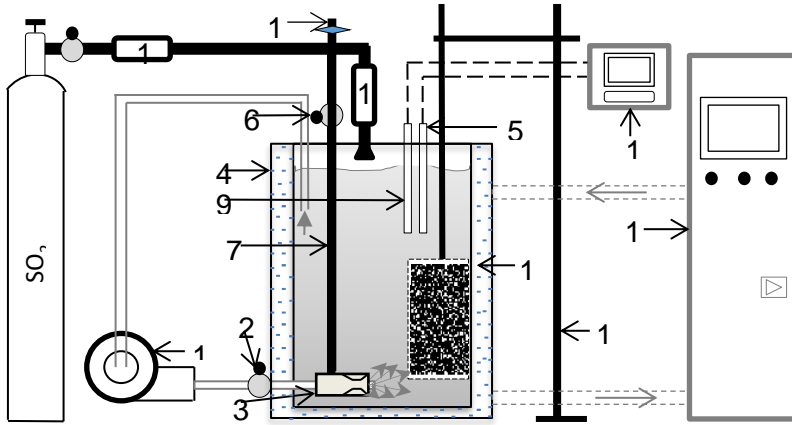


Fig. 1. Installation for laboratory testing: 1-Centrifugal Pump (TH1.5x1B Small Slurry Pump); 2 pressure gauge; 3-hydroacoustic radiator; 4-closed jacketed reactor consisting of a thick glass flask; 5 - electrode ORP; 6 manovacuum gauge; 7-tube for sucking sulphur dioxide into the resonator chamber; 8-crane; 9- electrode for pH measurement, 10-grid for sorbent content, 11-tripod, 12- gas flow meter, 13 pH/ORP meter [Mettler Toledo], 14-thermostat 15- reagent supply tube.

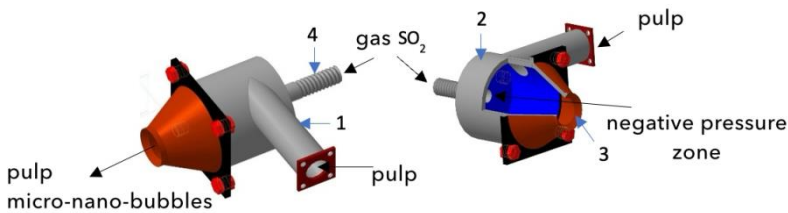


Fig. 2. Hydroacoustic radiator: 1 pulp supply connection; 2 resonator chamber; 3 output connection; 4 suction connection SO_2 .

Water-soluble iron (III) sulphate at a frequency of 100% or ferrous sulphate was used as the injected oxidant ($F_2(SO_4)_3 \cdot xH_2O$), and sulphuric acid was used as a medium regulator (H_2SO_4) with a frequency of 96% and a density of 1.84 g/cm³.

After leaching, the pulp was filtered on a Buechner funnel connected to a vacuum pump via a Bunsen flask. The filtrate volume was measured with a measuring cylinder. The cake was washed with distilled water and dried at 80 °C. They were then weighed and abraded using an agate mortar. The samples were sent for analysis.

The residual amount of thiourea in the filtrate was determined by titrimetric method in accordance with GOST 63473. Thiourea was also determined by titration using potassium iodate (KIO_3) with starch as an indicator based on the methodology proposed by Singh and Verma [15].

If necessary, the concentration of trivalent iron was determined by titration with ethylenediaminetetraacetic acid in the presence of indicator sulfosalicylic acid. The concentration of divalent iron was determined by potassium dichromate titration in the presence of indicator phenyl anthranilic acid.

Gold content in the cakes was estimated by assay smelting, as well as by the method of tsarvodka dissolution followed by sorption and x-ray phase analysis of the sorbent on an ElvaX Standart spectrometer (manufactured by Elvatech LLC, Ukraine).

3 Results and discussion

Comparative studies on the scheme of direct CIL and CIL process with acid pretreatment and addition of formamiddin disulphide as a reducing agent have been carried out. The results are presented in Table 2.

Table 2. Comparative results of the thiourea leaching study

Parameters	Direct CIL ¹ process	CIL ¹ process acid pretreated
	SO ₂ ³	SO ₂ ³
ORP(beginning/end), mV	208/594	230/611
Residual ThiO content according to titration results, %	0	0
Residual ThiO content after zinc titration, %	4.3	5.7
ThiO consumption (including recovered FD), kg/t	1.91	1.89
Extraction Au, %	61.3	63.4
¹ CIL process conditions: L:S 1:3; initial concentration H ₂ SO ₄ - 0.5% or pH- 1.95 (with acid pretreatment); iron (III) sulphate loading 7 kg/t; thiourea loading 2 kg/t; charcoal loading- 10 kg/t; time- 2 hours. ² Acid pre-treatment conditions: T:L 1:3; initial concentration H ₂ SO ₄ - 0.5% (initial pH- 1.72, final pH- 1.95); time- 1 hour. ³ The sulphur dioxide supply is 20 kg/t (0.17 kg/t *min). Slurry supply pressure to hydroacoustic transmitter inlet is 3 bar.		

Gold recovery from CIL process using SO₂ is low. No free thiourea was found in the solution and the irrecoverable loss of thiourea is low and is about 6 %. There is little difference between the results of acid treatment and direct CIL process and therefore further studies were carried out according to the scheme of direct CIL process.

The absence of FD should have resulted in a decrease in pulp ORP, but a significant increase in ORP equal to 561 mV is observed (Figure 3). The ORP increases steadily with increasing time of the CIL process. It is obviously connected with formation of hydroxyl radicals in the results of cavitation bubbles collapse, which being the strongest oxidising agents increase ORP of the pulp.

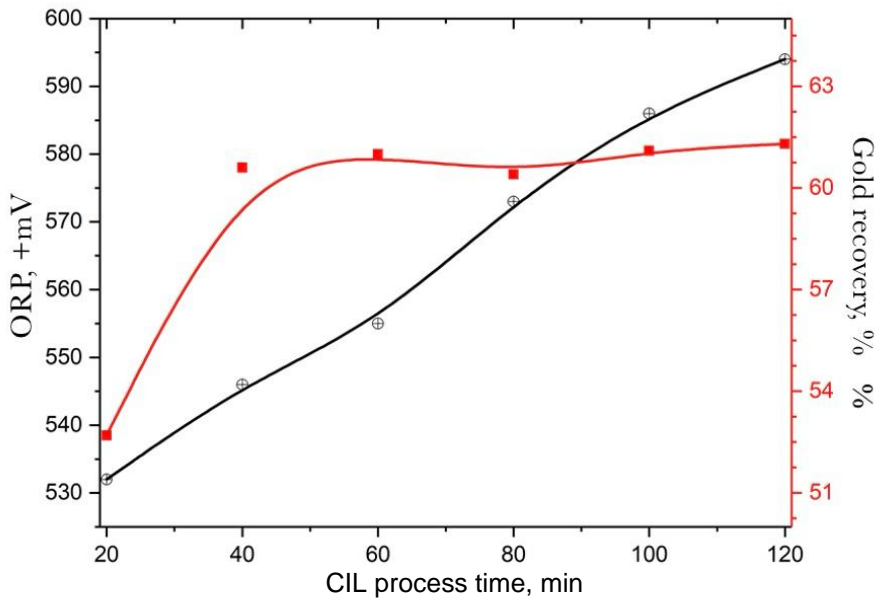


Fig. 3. Slurry potential and gold recovery as a function of the time of the direct CIL process with SO feeding: L:S- 1:3; initial concentration of FeSO_4 - 0.5%; iron (III) sulphate loading 7 kg/t; thiourea loading- 2 kg/t; coal loading 10 kg/t; slurry supply pressure to the hydroacoustic transmitter inlet bar, sulphur dioxide supply 20 kg/t (0.17 kg/t *min), time 2 hours.

Low gold recovery (see Fig. 3), which reached its maximum already at 20 min, is obviously due to the absence of free thiourea in the pulp, which was established by titration. It can be assumed that thiourea in this case is mainly irreversibly oxidized. This is a confirmation of the fact that in the solution after 2 hours (see Table 2) FD is contained in a minimum amount of 4.3 %. Thus, along with the concentration of thiourea and oxidant ORP of the pulp plays an important role both in the issue of thiourea consumption and reduction of gold recovery due to surface passivation due to elemental sulphur. It follows that the formation of OH^* radicals in an amount that excessively increases the ORP of the pulp is not desirable. The latter is confirmed by the state diagram pH for the $\text{Au}-\text{SC}(\text{NH}_2)_2-\text{H}_2\text{O}$ [16] system where it is shown that at pH thiourea is stable at a potential $E_{\text{HORZ}} \leq P9 \text{ DQG W KCSNFR}_2$ is stable at a potential below 450 mV. This was also reflected in the works [17].

The effect of ferrous sulphate concentration was studied. The results are presented in Table 3. It can be seen that with the decrease of iron sulphate loading, gold recovery increases and thiourea consumption decreases. These results indicate that the amount of OH^* radicals formed is sufficient for the gold dissolution reaction to proceed.

Table 3. Results of the study on the effect of FS loading on thiourea consumption and gold recovery

Loading $Fe_2(SO_4)_3$, kg/t	ORP (final), mV	Residual ThiO content according to titration results, %		Total ThiO* consumption, kg/t	Au recovery, %
		direct	zinc		
0	392	33.5	36.2	1.28	93.4
1	422	14.7	18.4	1.63	93.5
2	437	12.3	21.7	1.57	87.2
3	482	0	4.2	1.92	62
4	503	0	4.3	1.91	60.7
7	594	0	4.3	1.91	61.4

*including recovered FD.
 L:S - 1:3; initial concentration of $FeSO_4$ - 0.5%; thiourea loading 2 kg/t; coal loading 10 kg/t; pulp supply pressure to the hydroacoustic transmitter inlet 3 bar, sulphur dioxide supply 20 kg/t (0.17 kg/t *min), time 2 hours.

The effect of pulp feed pressure in the inlet of the plant on gold recovery and ThiO consumption was studied in the absence of ferrous sulphate. The results are presented in Table 4.

Table 4. Results of research on the influence of pulp feeding pressure into the inlet device of the hydroacoustic emitter on gold recovery and ThiO flow rate

Slurry supply pressure, bar	ORP (final), mV	Residual ThiO content according to titration results, %		Total ThiO* consumption, kg/t	Au recovery, %
		direct	zinc		
1	267	67.4	68.2	0.64	91.6
1.5	271	66.2	66.3	0.67	93.1
2	293	39.3	41.5	1.17	93.5
2.5	317	35.6	37.9	1.24	93.2
3	392	33.5	36.2	1.28	93.4

*including recovered FD.
 L:S - 1:3; initial concentration of $FeSO_4$ - 0.5%; thiourea loading 2 kg/t; coal loading 10 kg/t, sulphur dioxide feeding 20 kg/t (0.17 kg/t *min), time 2 hours.

At a slurry feed pressure of 1.5 bar, the minimum thiourea flow rate is achieved. At the same time ORP decreases, apparently, in proportion to the decrease in the degree of oxidation of thiourea to FD. The gold recovery does not change in this case. Thus, at a feed pressure of 1.5 bar, a minimum thiourea flow rate of 0.67 kg/t is achieved.

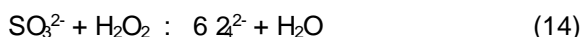
The effect of sulphur dioxide on gold recovery and thiourea consumption was studied. Detailed results are presented in Table 5

Table 5. Detailed results of the effect of sulphur dioxide on gold recovery and thiourea consumption

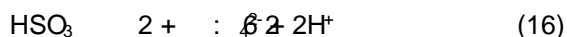
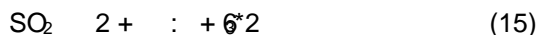
SO_2 flow rate, kg/t	ORP (final), mV	pH (final)	Residual ThiO content after zinc titration, %	Total ThiO* consumption, kg/t	Au recovery, %
10	685	1.8	2.7	1.95	12.8
12	603	1.5	3.1	1.94	11.5
14	462	1.4	14.3	1.71	35.3
16	385	1.2	64.1	0.72	93.5
18	310	0.7	65.7	0.69	92.8
20	271	0.3	66.3	0.67	93.1

22	172	0.1	68.3	0.25	44.7
*inclusive of recovered FD.					
L:S - 1:3; initial concentration of H ₂ O ₂ - 0.5%; thiourea loading 2 kg/t; coal loading 10 kg/t; pulp supply pressure to the inlet of the hydroacoustic emitter 1.5 bar, time 2 hours.					

The results show that sulfur dioxide has a significant effect on the process performance. A decrease in ORP with increasing sulfur dioxide consumption is observed. This phenomenon is probably due to a decrease in the amount of hydrogen peroxide in the interaction with SO₂, which is formed by partial recombination of radicals [14]. In this case, the decrease in the concentration of oxidant occurs due to the following reaction



ORP drop can also occur due to the interaction of OH* radicals with SO₂ the following reaction



The formation of sulfuric acid according to equations-(15) is confirmed by a decrease in the final pH of the medium (see Table 5). Therefore, reducing the consumption of sulfur dioxide in this case negatively affects not only the consumption of thiourea due to its shortage as a result of its consumption during reaction with hydrogen peroxide and OH* radical, but also on the degree of gold recovery.

Determining the volume of thiourea to be loaded is an important factor in the applicability of this reagent in industry. It is of particular economic importance, affecting the cost of processed raw materials. In this regard, a study was carried out to establish the optimum loading volume of thiourea. The detailed results are presented in Table 6.

Table 6. Results of the study to establish the optimal volume of thiourea to be loaded

Thio load, kg/t	Potential (final), mV	Residual ThiO content according to titration results, %		ThiO consumption, kg/t	Au recovery, %
		direct	zinc		
1	362	17.4	17.7	0.82	81.7
1.25	365	38	38.2	0.77	84.2
1.5	377	41.8	45.2	0.82	93.4
2	385	64.2	64.1	0.72	93.5
2.25	394	65.7	65.70	0.77	93.7
L:S - 1:3; initial concentration of H ₂ O ₂ - 0.5%; coal loading 10 kg/t; pulp supply pressure to the hydroacoustic emitter inlet - 1.5 bar, sulphur dioxide supply 16 kg/t (0.13 kg/t *min) time - 2 hours.					

The table shows that the most optimal is the volume of thiourea loading at 1.5 kg/t, which achieves a high gold recovery rate of 93.4 % at a thiourea consumption of 0.82 kg/t. Changing the volume of thiourea loading does not significantly affect the ORP of the slurry and thiourea flow rate.

Kinetic studies were carried out to establish the optimum of the CIL process at different sulphur dioxide feed volumes with thiourea loading of 1.5 kg/t. The results are summarised in the Table 7.

Table 7. Results of kinetic studies of CIL process with sulphur dioxide

CIL process time min	Change in gold recovery and ORP at different feed rates sulphur dioxide, kg/t*min							
	0.08		0.10		0.12		0.13	
	Au, %	E, mV	Au, %	E, mV	Au, %	E, mV	Au, %	E, mV
20	8.6	451	8.8	418	34.2	319	83.7	312
40	8.2	584	8.7	596	34.6	437	88.3	384
60	8.4	647	9.1	612	33.7	432	93.5	376
80	8.5	673	8.6	604	32.3	453	93.6	352
100	8.1	681	8.9	607	31.1	445	92.5	383
120	8.3	682	8.7	606	31.2	449	93.4	377
ThiO consumption, kg/t	1.5		1.5		1.43		0.82	
L:S - 1:3; initial concentration of FeSO_4 - 0.5%; thiourea loading 1.5 kg/t, coal loading 10 kg/t, pulp supply pressure to the inlet of the hydroacoustic emitter 5 bar, time 2 hours.								

The table shows that increasing the consumption of sulfur dioxide leads to an increase in gold recovery, and at the same time the ORP of the pulp decreases, reaching the area most favourable for the gold dissolution reaction. Thus, the most optimal time is of 60 minutes. At this time the consumption of thiourea was 0.57 kg/t, and sulphur dioxide kg/t.

4 Conclusion s

Our results show a decrease in thiourea consumption when sulfur dioxide is introduced into the pulp during the CIL process using a device with a hydroacoustic emitter. A significant increase in the final ORP was observed, probably due to the formation of OH^* radicals during cavitation. In the CIL process using the hydroacoustic emitter device, the pH of the medium is maintained around 2, which favors cavitation and OH^* radical formation. In addition, the recombination of OH^* radicals with a weaker oxidant such as CS_2 is slower in this pH range of the medium. The cavitation effect is significantly influenced by the slurry pressure at the inlet of the hydroacoustic emitter. Higher inlet pressure results in an increase in the slurry potential due to the abundant formation of OH^* radicals. It is important to note that the use of the hydroacoustic emitter unit in the CIL process eliminates the need to use ferrous sulfate as an oxidizing agent for gold dissolution.

For example, using an HC reactor to feed sulfur dioxide in the CIL process reduces thiourea consumption to 0.57 kg/t. Gold recovery increased to 93.5% with a process time of 60 minutes and a feed of 0.13 kg/t.

References

1. R. Sousa, M. João Regufe, A. Fiúza, et al., *The Extractive Industries and Society* 101018 (2022)
2. G. Mishra, R. Jha, M. Dhanunjaya Rao et al., *Environmental Challenges* 100073 (2021)
3. M.G. Aylmore *Alternative lixivants to cyanide for leaching gold ores. Developments in Mineral Processing. Volume 15, 2005, Pages 509,*

4. Z.-W. Liu, X.-Y. Guo, Q.-H. Tian, L. Zhang *Journal of Hazardous Materials* **410**, 129778(2022)
5. Y. Guo, X. Guo, H. Wu, et al., *Hydrometallurgy* **171**, 213-221 (2017)
6. J. Li, J. D. Miller, *Hydrometallurgy* **89**(3-4), 279-288 (2007)
7. N. Gönenç *Hydrometallurgy* **69**(1-3), 169-176(2003)
8. L. F. Kozin, E. O. Bereznoi *Theoretical and Experimental Chemistry* **38**(6), 388-392 (2002)
9. R. G. Schulze *Journal of Metals* **36**(6), 62-65 (1984)
10. P. Lacoste Bouchet, G. Deschenes, E. Ghali, *Hydrometallurgy* **47**, 189-203 (1998)
11. L. S. Strizhko, I. R. Boboev, K. G. Gurin, et al. *Pat. RU 2522921 C1*, Int. Cl. C22B 11/08. Gold extraction from ores and concentrates. \$ S S O L F D W L R Q
14.03.2013; Publication: 20.07.2014. Bull. < 20 (2014)
12. L. S. Strizhko, I. R. Boboev, K. G. Gurin, et al. *Pat. RU 2522873 C1*, Int. Cl. C22B 3/02. Plant for gold extraction from ores and concentrates.
Application: 14.03.2013; Publication: 20.07.2014. Bull. < 20 (2014)
13. I. R. Boboev, A. Skozlovskiy, R. P. Khabiev, E. S. Shigin, *Patent utility model RU 167219 U1*, Int. Cl. BO1F 3/04, BO1F 5/00, BO1F 13/02. Device for oxygenation of cyanide solutions/ \$ S S O L F D W L R Q 3 X E O L F D
27.12.2016. Bull(2016)
14. K. Fedorov, K. Dinesh, X. Sun, et al., *Chemical Engineering Journal* **432**, 134-191 (2022)
15. D. Calla Choque, F. Navarro Alonso, *Revista Mexicana de Ingeniería Química* **19**(1), 275-284(2020)
16. L. Tremblay, G. Deschênes, E. Ghali, et al., *International Journal of Mineral Processing* **48**(3-4), 225-244 (1996) DOI:10.1016/S0307-516(96)00029-4
17. D.A. Ray, M. Baniasadi, J. E. Graves, et al. *Journal of Sustainable Metallurgy* (Received: 26 July 2021 / Accepted: 17 January 2022)