The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Study on New Process of Zero Discharge of Cyanide Wastewater

QIU Ting-sheng TANG Guan-zhong HAO Zhi-wei CHENG Xian-xiong
(Southern Institute of Metallurgy , Ganzhou, Jiangxi, China, 341000)

ABSTRACT: According to the requirement of cyanide precipitation—purification technology, adopt the acidized sulfate to precipitate cyanide. Studying the influence of acidity and the dosage of sulfate on precipitation rate of impurity ion in cyanide wastewater, and, on the basis of synthetic precipitation experiments, we obtain principle process of cyanide precipitation—purification technology.
Key words: gold, cyanide wastewater, zero discharge

Introduction

Gold and silver are typical noble metals. Besides currency, jewellery, decoration, They are widely used in electronic industry, spaceflight and aeronautic industry chemical industry medical field, etc. There are many ways of extraction for gold ,such as plate amalgamation ,cyanide leaching ,thiourea method, CIP(Carbon in the pulp) and so on. However, at present, cyanide leaching is the most principal internal and external method of extraction for gold, This way has a mature technology and higher technical economic index, but the main reagent of the cyanide leaching for gold has deadly poison. In the process of the cyanide leaching for gold, a great deal of water is needed, and the wastewater , which is containing the heavy metal ion or is cyanided, is produced. This kind of wastewater contains a good deal of simple cyanides, complex cyanides(such as Cu, Zn, Fe, etc.), rhodanates and other impurity. If the wastewater is drained directly , it could pollute environment and water resources. If it is used directly and circulatingly, it could influence the leaching rate in the leaching process, because there are a lot of heavy metal ions, such as Cu, Zn, Fe and so on, in the wastewater. So it only can be drained or used circulatingly when it has been teated.

For traditional methods of treatment for the cyanide wastewater can be classified into two categories summarily.

First, purification method: such as bleaching powder method, liquid chlorine method, ferrous sulfate—lime method, electrolytic method, ozonization method, hydrogen perdioxidation method, potassium permanganate method, ion exchange membrane method and so on. The bleaching powder method is often used in productive practice. The principle is to use the bleaching powder to oxidize the cyanides into CO_2 and N_2 in the alkaline medium(pH=8~9).

$$CN^- + HOCl = CNCl + OH^-$$
$$CNCl + 2OH^- = CNO^- + Cl^- + H_2O$$
$$2CNO^- + 3OCl^- + H_2O = 2CO_2\uparrow + N_2\uparrow + 3Cl^- + 2OH^-$$

As a matter of fact, this kind of method is destruct method, it is to destroy the deadly poison cyanides and change it into the wastewater with minimum toxic, then, it can be drained before meeting the drainage standard.

Second, reclaimation: this method, in fact, is to drain the lean cyanide solution in which the cyanides have been reclaimed . For example, use the sulphuric acid to make the wastewater acidized to turn the cyanide into hydrogen cyanide gas ,and then, use the sodium hydroxide or calcium hydroxide to absorb, the filtered decyano-solution was drained after diluting. From this ,we can see the greatest common property of this two kinds of methods is not to reclaim water. Although, the wastewater which is to be drained out doesn't meet the drainage standard, it contains poisonous impurity ,it cannot be used as industry water, nor as domestic water or irritated water, so the only method to eradicate pollution is to study on the technology of non-discharge, on the other word, the zero discharge, in addition, it can save a great deal of fresh water. In this study, the cyanide wastewater of one gold mine is used as a example. Under the condition that not too many cyanide ions will not be destroyed, we adopt precipitation—purification technology to remove the harmful heavy metal ions, such as Cu, Zn, Pb and so on, from the wastewater, which will have great influence on the leaching process, and then, make all of the wastewater recycle back for the use of gold leaching and smelting, what's more, we also could make the metal ,such as Zn ion, Cu ion etc, being used recyclabely.

The Properties and The Components of Cya nide Wastewater in The Gold Mine

In a gold mine, cyanide leaching for gold and displacing with Zinc dust technology are used, and 50~60 ton cyanide wastewater is produced everyday. There are lot of ions in the wastewater such as Cu ion, Zn ion, CN^- ion, SCN ion and so on. The main components be shown in table 1:

Table 1

Main on-the-spot components of cyanide wastewater

Components	Cu	Zn	CN^-
Content (g/l)	0.363	1.12	1.47

Decision of Rsearch Scheme

In order to looking for and deciding the most proper process and technique scheme of treating cyanide wastewater of the gold mine, we are doing the exploring experiments with the sulfate precipitation and solvent extraction. Although, according to introduction of the materials, heavy metal ions such as Cu ion, Zn ion etc, can be precipitated with sulfate precipitation method. But the results of the experiments show, after adding soluble sulfate the color of the cyanide wastewater changes from colorless into brown and precipitation is modicum and fine and cannot be separated. And because of drawing in more S^{2-} ions, they can make the solution complicated and bring difficulties to next treatment. But for solvent extraction, although the extractive rate of Cu ion ,Zn ion etc, can reach 97%, the conservation rate of CN^- ion can pass 80%, and the extractive speed is fast, the extractive effect is perfect, the backextractive and regeneration can be finished in one step. But in the experiments we can also find some problems following:

1) In the extraction process, the extractive volume of the organic phase is limited. Because in the cyanide wastewater, the complexes which have been extracted are comparatively g e ' be e ch e he e f he extractive phase. The phenomena of the experiments show that O/A=1:1 is the best, the demand for the organic phase is great. When in the backextractive process, although the ratio of the extractive phase is very small, for example O/A=0.5:1. As the organic phase is great, the backextractive solution is also great, it will become a new kind of cyanide wastewater, serious water expansion phenomenon will occur, water balance cannot be realized in the process, so a large of wastewater is drained as usual which is contradictive to the theme of this study—zero discharge.

2) Extractive solvent is easy to decay which will begin to show in the second circulation process, especially, the bachextraction of the Cu is much more difficult which need the special extractive solvent, if doing by this way, there will be more new complex wastewater.

3) We still don't know, if the organic phase which is lost in the remained extractive solution will have effect on the gold leaching or not. But it's estimated that there will not be good influence. Another complex procedure is added if we want to get rid of the organic phase.

So we decide to adopt cyanide precipitation—purification technology, considering the shortcoming of the sulfate precipitation method and extraction. The principled process of purification method that use the acidized sulfates to precipitate the cyanides and use the $Ba(OH)_2$ to remove SO_4^{2-} ions is shown in chart 1:

Results and Discussion

1. The conditional experiment of precipitation cyanide

1.1 Influence of acidity on precipitating cyanides

Acid is a kind of important reagent which is easy to destroy the complex cyanide ions, when the H_2SO_4 is added into the cyanide wastewater, it will make the complex ions disggregated, the major reaction are as following:

$2CN^- + H_2SO_4 = SO_4^{2-} + 2HCN\uparrow$

$2Cu(CN)_3^{2-} + 2H_2SO_4 = Cu(CN)_2\downarrow$

$Zn(CN)_4^{2-} + 2H_2SO_4 = ZnSO_4 + SO_4^{2-} + 4HCN\uparrow$

$2Na_3Cu(CNS)(CN) + 3H_2SO_4 = 2CuCNS\downarrow + 3Na_2SO_4 + 6HCN\uparrow$

$Cu_2(CN)_2 + 2NaCNS = 2CuCNS\downarrow + Na_2SO_4 + 2HCN\uparrow$

These reactions are influenced greatly by the acidity, they are the major reaction when reclaiming cyanide in the traditional treatment—sulfuric acid method. Under the condition that sulfate is remained unchangeable, we change the adding dosage of H_2SO_4, the results of the experiment show as table 2:This study is trying to avoid the production and volatile of HCN, so we add very little H_2SO_4 and, at the same time, add proper sulfates, if the system is still under the alkalic condition, we get the cyanide precipitation.

Table 2 The influence of acid on the precipitation rate

Item	pH	The components of the solution after precipitating (g/l)			Precipitation rate		
		Cu	Zn	CN^-	Cu	Zn	CN^-
ZC-21	10.1	0.360	1.10	1.38	0.8	1.8	6.8
ZC-11	9.8	0.320	1.01	1.24	11.8	9.8	15.6
ZC-14	9.1	0.092	0.26	0.409	74.1	76.8	63.5
ZC-18	8.6	0.050	0.17	0.253	86.2	84.8	82.8

We can see from the table that under the condition that the dosage of sulfate is fixed precipitation rate of the cyanide will increase as the increase of the acidity. In order to increase the precipitation rate, the acidity can be little higher, but it cannot be increased endlessly, there is a limit to the acidity. If the acidity is so high that a lot of HCN is produced and excessive SO_4^{2-} ions are drawn in, which will bring unconvenience to the next step.

1.2 The influence of the dosage of sulfate on the precipitation

If the sulfate solution is acidic, it can replace a small deal of H_2SO_4. It is also a kind of reagent used to destroy the complex ions. The precipitation reactions are as following:

$$2CN^- + MSO_4 = M(CN)_2\downarrow + SO_4^{2-}$$

$$Zn(CN)_4^{2-} + MSO_4 = Zn(CN)_2\downarrow + M(CN)_2\downarrow + SO_4^{2-}$$

$$Cu(CN)_3^{2-} + 2MSO_4 = Cu_2(CN)_2\downarrow + 2M(CN)_2\downarrow + 2SO_4^{2-}$$

When the MSO_4 is added into the wastewater, it change the acidity and the alkalinity, so the acidity and the alkalinity of the wastewater is decided by MSO_4 and H_2SO_4 together, on the other word, there is a matching relation between the dosage of MSO_4 and the dosage of H_2SO_4. The proper matching point must be decided by experiments. The results of the experiment which shows the influence of dosage of MSO_4 on the precipitation rate are shown in the following table 3:

Table3 The influence of the dosage of MSO_4 on the precipitation rate

Item	pH	The dosa--ge of the sulfa--te	The components of the solution after precipitat--ing (g/l)			Precipitation rate		
			Cu	Zn	CN^-	Cu	Zn	CN^-
ZC-20	8.5	0	0.075	0.29	0.172	79.3	74.1	88.3
ZC-17	8.0	1	0.025	0.13	0.293	93.1	88.4	80.1
ZC-13	9.1	2	0.049	0.17	0.192	86.5	84.8	86.9
ZC-8	6.2	5	0.058	0.83	1.111	84	25.9	24.4
ZC-6	6.7	12	0.028	1.133	1.232	92.3	-1.16	16.2
ZC-7	6.8	15	0.028	1.43		92.3	-27.7	

We can know from the table 4 that the dosage of sulfate should be limited, in the theory, we should add sulfate about 2.4g per liter wastewater. Because of the adding of H_2SO_4, the dosage of sulfate is reduced. The experiment shows we should add sulfate about 1g per liter wastewater.

Deserve to point out that this technology get the ions, such as Cu^{2+}, Zn^{2+}, etc, out of the wastewater in the form of sulfate and become a kind of byproduct. So the sulfate which used as precipitation reagent is only a part of byproduct.

2 Synthetic experiment of cyanide precipitation

Table 3 shows that under the ordinary temperature, the condition of the precipitation of cyanide wastewater is:

PH=7~8, the dosage of sulfate is about 1kg/M^3 (wastewater)

According to this, in order to know the popularity of this technology, we enlarge the scale of experiment into 4000ml and, at the same time, in the system of HNO_3 doing contrastive experiments, the results of the experiments are

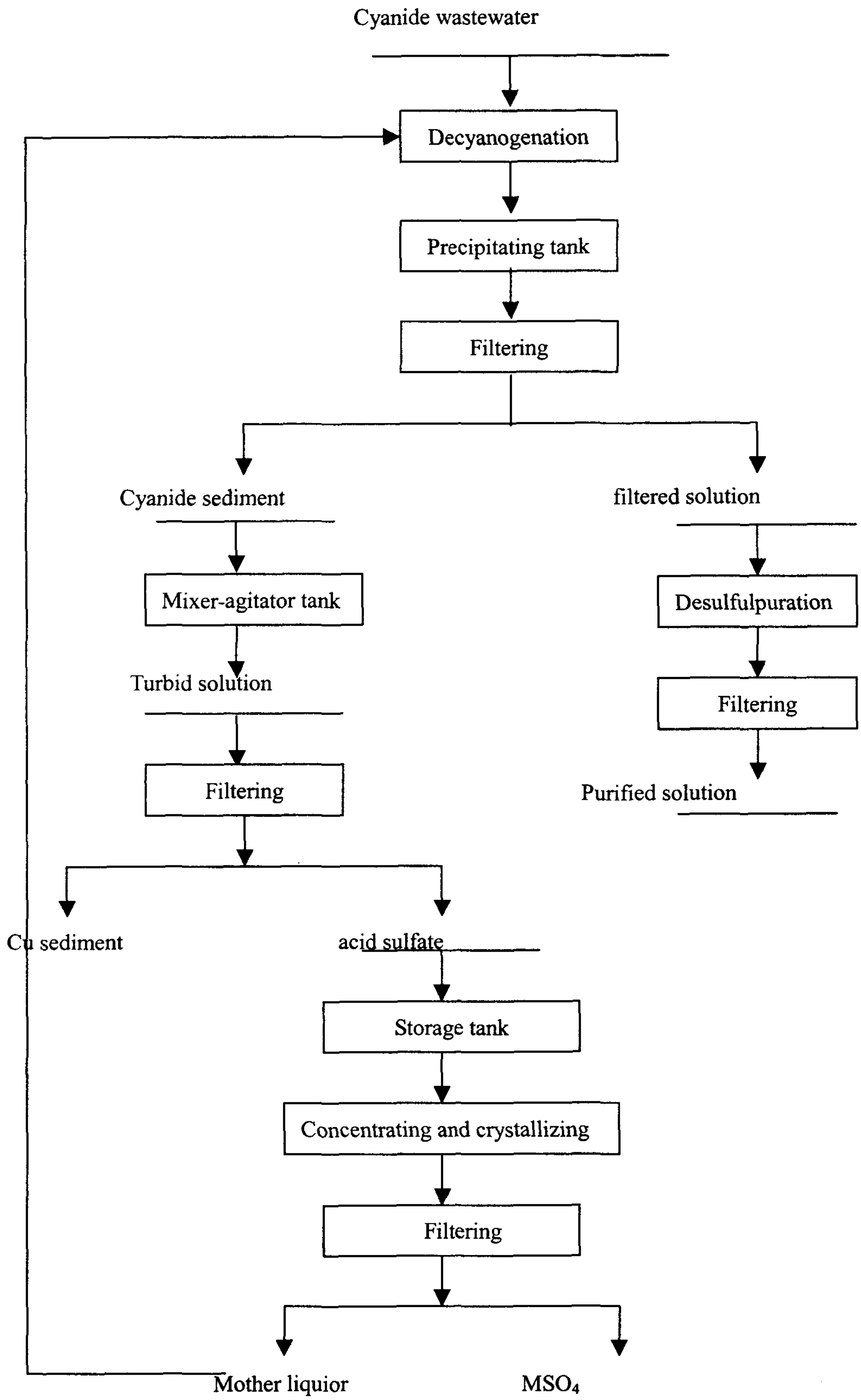

Chart 1:the principled process of the treating technology of the cyanide wastewater

shown in the table 4:

Table 4 The results of the synthetic experiments (Volume of the wastewate is 4L)

Item	Acidity	The components of the solution after precipitat- -ing (g/l)			Precipitation rate		
		Cu	Zn	CN^-	Cu	Zn	CN^-
ZC-20	H_2SO_4	0.019	0.058	0.05	94.8	94.8	96.6
ZC-17	H_2SO_4	0.008	0.166	0.11	97.8	85.2	92.5.
ZC-13	HNO_3	0.073	0.464	0.22	79.9	58.6	85.0
ZC-8	HNO_3	0.042	0.494	0.17	88.4	55.9	88.4

We can see from the results of the experiments:

1). In the H_2SO_4 system, PH=7~8, the precipitation condition is ideal if the dosage of sulfate is $1kg/M^3$(wastewater). To the original pH value(pH =10.8) of the experimental wastewater, when it decline to 7~8, the dosage of H_2SO_4 (98%) is about $2L/M^3$(wastewater).

2). In the HNO_3 system, it may have its own precipitation condition, we have not discussed the best condition deeply. If the precipitation effect is not as good as the effect in the H_2SO_4 system, we need to explore further to advance the. effect of precipitation.

Conclsions

1. The results show, it's reasonable and feasible to adopt the reclaiming firstly and then purifying technology which is the cyanide precipitation—purification technology. Under the ordinary temperature, PH=7~8, if the dosage of sulfate is $1kg/M^3$(wastewater), the removal rate of Cu^{2+} is over 90% and the removal rate of Zn^{2+} is over 85%.

2. This process really is a whole closed cycle, no wastewater drained, not only the reagent is saved but also the valuable materials are reclaimed, and deserve to point out is that the precious water is reclaimed. What's more, this process has no special equipment and easy to be industrialized, especially for the factories which used the sulfuric acid method to treat the wastewater in the past time. If they choose to use this process they will invest small capitals and see desired result early. So it has obvious economic and social benefit.

3. If the SO_4^{2-} ions which are drawn in have influence on the process of gold leaching, we can use baryte to remove them.