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REMEDIATION BY ION FLOTATION TECHNIQUE OF CONTAMINATED WATERS WITH CYANIDE

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ABSTRACT

The substances which are containing cyano (CN) group are called cyanide. There are two types of cyanide substances: organic cyanides and inorganic cyanides. Inorganic cyanides have negatively charged ions, like sodium cyanide, copper(i) cyanide and ferrocyanide, on the other hand, like methyl cyanide, organic cyanides includes covalent cyano group (MacLennan and Moiemen, 2015). Main purpose of production of cyanide is for the mining of silver and gold. Cyanidation process purpose is to extract gold from ores which are low graded by a hydrometallurgical technique which basically is a conversion process of gold into a complex that can be soluble in water. In range of gold extraction processes, gold cyanidation is the most used leaching technique (Gail, Gos, Kulzer, Lorösch, Rubo, Sauer, Kellens, Reddy, Steier, and Hasenpusch, 2011). It is also used generally in silver extraction process in the end of the froth flotation step (Etris, 2000).

In this graduation thesis, for the remediation of the water from mining contaminations with cyanide, ion flotation experiments are used. Flotation is a technique used in mineral processing which allows to separate and concentrate ores depending on their surface properties, such as hydrophobic or hydrophilic condition, it defines the repulsion or attraction of water. Ion flotation can be considered as a preference option since it has a high recovery rate and provides selective separation, also it is a quick and respectively low-cost method that can be applied to recover or remove many low-concentrated metals (Yenial, and Bulut, 2017).

Ion flotation technique is a very basic process for ion concentration in dilute solutions. Addition of surfactant lets the adsorption at the surface where the bubbles are formed and becomes the froth product in the dilute solution. For the selection of the optimal ion flotation process, many types of conditions and reagents are experimented. In the end, most suitable condition and reagents are understanded for remediating the contaminated waters by cyanide.

ACKNOWLEDGEMENTS

This project is a result of nearly a year of work, and I really enjoyed while I was searching, learning, experimenting and creating the project. Throughout this project I learned a lot of things about ion flotation technique, cyanidation processes, importance of cyanide in mining, how crucial cyanide contamination is and how important it is to remediate properly. First of all, I would like to thank my advisor Assoc. Prof. Paola Marini from Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino and Prof Dr. Gülay Bulut from Department of Mineral Processing Engineering, Istanbul Technical University for giving me chance to do this thesis and for the great guidance and support. While I was creating this project Assoc. Prof. Paola Marini and Prof. Dr. Gülay Bulut was always with me and helped me with their strong knowledge.

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1. INTRODUCTION

Cyanide is a very important matter in mining industry. Especially in modern gold mining industry it is essential. Since 1970 cyanide leaching or in other words, "cyanidation" has made the biggest impact on gold extraction technologies. Much remarkable scientific research has been conducted over the years but none of them were as successful both economically and environmentally in recovering precious metals. There are many concerns about the toxicity and management of the cyanide, because it is a fatal matter. Mostly cyanide is used as a solution in the processes therefore it is possible to contaminate the waters (SME, 2021).

There are many possible treatment methods for safe management of the reagent. Ion flotation can be considered as one of the useful approaches for safe management of this matter. Flotation method is a very common and easily applicable mineral processing method. Precipitation, oxidation or reduction, filtration, ion-exchange, reverse osmosis, membrane technology, evaporation and electro flotation can be considered as useful methods to remove heavy metals from aqueous solutions. Although, certain amount of these techniques is not sufficient or expensive when metal concentrations are between 1 to 100 mg/L. These techniques also cause occurrence of secondary wastes that requires another purification or removal process. On the contrary, with the high recovery rates, separation selectivity ion flotation offers rapid and financially rewarding method that can be applied to recover or remove metals with low concentrations (Yenial, and Bulut, 2017).

The purpose of this project is to remediate the water from mining contaminations with cyanide, ion flotation experiments are used.

2. WHAT IS CYANIDE

The substances which are containing cyano (CN) group are called cyanide. There are two types of cyanide substances: organic cyanides and inorganic cyanides. Inorganic cyanides have negatively charged ions, like sodium cyanide, copper(i) cyanide and ferrocyanide, on the other hand, like methyl cyanide, organic cyanides includes covalent cyano group (MacLennan and Moiemen, 2015).

2.1. Cyanide Usage in Mining

Many things that are used by people regularly are made thanks to cyanide. Production of plastics, adhesives, fire retardants, cosmetics, pharmaceuticals, food processing, metal processing, the production of organic chemicals, photography, insecticides and in anti-caking additives for both table (food) and road salts are the areas where most of the cyanide are used yearly which is around over 1.1 million tons. The usage of cyanide in the mining sector is about six percent of the total production of cyanide. Cyanide can be naturally found approximately 0-700 ppm in plant families, such as cassava, lima beans and almonds, pits and seeds of common fruits such as apricots, apples and peaches (SME, 2021).

Cyanidation process which is also called cyanide leaching always has been the most used technique in gold processes. Basically, the method starts with sodium cyanide in a solution which is diluted between 100 ppm to 500 ppm, or 0.01 percent to 0.05 percent of cyanide can be applied to particularly extract gold from ore. Generally, heap leaching and milling are used for gold recovery, which can also be called as carbon-in-leach (CIL). After many experiments it has been decided that cyanide is the most efficient chemical reagent in precious metal recovery process considering its economic, environmental advantages. For safety and financial stability, it is better to use few amounts of cyanide in mining operations.

After the physical beneficiation processes such as crushing and grinding, cyanide leaching technique can be applied. Before the recovery of the gold, it must be dissolved in the solutions, in the end smelting process begins which resulted into bullions of gold. For removing away the residual cyanide there are alternative physical and chemical techniques which are applied to the tailings slurries and leached material holding solutions before releasing into the tailings facility (SME, 2021).

Moreover, for recovering and reusing purposes of residual cyanide in the process flows there are various types of scientific methods are applied.

The stored solutions which are containing cyanide in the tailings facilities are mostly not harmful to living species. According to the International Cyanide Management Code, for preserving the wildlife cyanide concentrations must be less than 50 ppm, this rate is generally lower in most of the mining operations which is even less than 10 ppm in their tailings dam. Natural processes lead to the significant dilution and destruction of the residual cyanide. For example, oxidation and UV- catalysis caused by the sunlight. There are legal limitations to regulate the release of cyanide into the tailing dams (SME, 2021).

2.2. Gold Cyanidation Process

In order to extract gold from ores there is one method that stands alone with its importance in the industry which is called gold cyanidation process. There are many reasons for considering this method as the most important, such as economic and metallurgical advantages. Recovery rates of cyanidation is higher and offers easy operation when it is compared with other methods such as, plate amalgamation and chlorine/bromine processes. Gold cyanidation method is preferred more also because in the end it produces almost pure metal. This final product also eases the transportation, which is only possible by planes or mule trains because of the inaccessible location of gold mines. As an auxiliary gold treatment process amalgamation and flotation can be used with cyanide processes by the metallurgists. With the aim of analyzing cyanidation process, the properties of gold should be well studied. To dissolve gold, it is better to use aqua regia (a mixture of nitric and hydrochloric acid) or chlorine/bromine compounds; it would have no use to dissolve gold in sulphuric, nitric or hydrochloric acids also it does not tarnish at standard temperatures. The reaction which was based on bromo-cyanide technique applied on some refractory ores in gold mining as well (911Metallurgist, 2016).

Gold dissolves in mercury solution, together they form amalgam. Nevertheless, cyanide solutions are preferred primarily when gold must be dissolved in. Mainly because of economic reasons. Dissolving fine sized particles of metallic gold and silver with the weak potassium or sodium cyanide solutions is the main principle of the cyanide process. Generally, sodium cyanide is considered when cyanide is planned to be used. Nevertheless, nowadays for cyanidation potassium cyanide is mostly considered. CN part has the dissolving ability the alkaline base such as potassium, calcium or sodium only provides adequate chemical stability to the compound. According to the Eisner’s equation, the gold and the cyanide reaction as follows: 4 Au+ 8 KCN + O2 + 2H2O = 4 KAu (CN)2 + 4 KOH. This reaction happens in an aqueous solution with a free oxygen and in the end gold cyanide compound and hydroxide (alkaline) occurs. Solutions with high levels of strengths usually treats concentrates of gold sulphides which are collected from flotation. Potassium cyanide per ton of solution in pounds is the expression of the strength of a solution. Such as, 1 lb. CN to 1 ton of H2O equals to 0,05% solution. Another critical factor for preserving efficient dissolving activity is the solution’s temperature. Generally, in cold weather solution heated up to 22° C. When this temperature is exceeded, CN is decomposed, and situation becomes critical. In theory, at temperatures around 59° C dissolving of gold becomes faster. It is generally recommended to preserve the utmost densities in the mill circuits in order to keep the highest capacity and the lowest loss of precious contents in the mixture. Additions and removal of water must be in an equilibrium in the mill circuit. The released solution contains both lime and cyanide reagents with the dissolved gold. The density of the feed and the capacity of the agitator is related to each other; they are both increase and decrease together. Free oxygen is a primary necessity in a cyanidation process. Atmospheric air is financially more beneficial than to use pure oxygen. There are also some studies are experimented on using Ozone, but it still has time to apply it for commercial purposes. Physical contact between air and gold is essential for an efficient dissolving practice. The distribution of the gold particles is very rare that is why it is necessary for air bubbles dispersion to be surrounding the entire pulp. Sodium peroxide, potassium permanganate or manganese dioxide can be used as oxidizing agents. These oxidizers can speed-up the dissolution of gold and harmful impurities' oxidation consist in ore or solution. Increase in aeration is required when tonnage rates get higher or the ore modificates in specific types of mills. Numerous techniques are applied for this, such as surrounding the circumference of the agitators by inserting ring of air jets on them, on the other hand flow of the pulp can be dispersed when it gets in the vessels in one vast wide flow, numerous flows of pulp transit the screens are tossed in the vessel in very fine sized particles, when the aeration starts, this method is better for the aeration of the pulp (911Metallurgist, 2016).

Reagents' Decomposition Stage

Portion of reagents which are necessary for gold dissolution are not very much. Nevertheless, rapidly the reagents' portion is definitely more than the necessary portion. There are particular reasons for this, which are water impurity, cyanicides, and mechanical loses. Water impurity is a very critical matter in both quality and quantity. For contaminated waters by soluble salts and organic materials additional lime remediation is recommended and required before this water gets into mill return stream. In order to precipitate the soluble salts, lead nitrate solutions can be useful also potassium permanganate or a chemical oxidizer like this can be useful. If a material naturally exists and has ability to demolish cyanide, it is called as a cyanicide which might be found in the ore. Pyrrhotite can be given as a great example, it produces ferro-cyanide and sulpho- cyanide with cyanide. Experiments shows that stibnite needs to stop its solubility in solution which must be under low alkalinity conditions. The opposite situation can apply for the sphalerite, in this situation to reducing zinc solubility high limes are used. Sometimes copper, antimony, arsenic, cobalt or nickel sulphides contents can be seen in ores which are taken to the solution with the effect of the cyanide. In spite of the fact that, control over the dissolution rate of these contents can be managed at some point, but because of re-cycling the solutions will lose their strength. Relieving the pressure from the failed solution is required, and re-balance the solution by adding new materials. Positive aeration is critical before the re-use when the dearation and precipitation stages completed. Regularly aeration is done by letting flow of the solution drop vertically into an open solution vessel. In this stage aeration both regenerates cyanide and reinstate free oxygen to the solution. In these processes sometimes mechanical losses happens, these are: accidental and inherent losses. Spills and leaks are the main cause of the accidental losses, sometimes it may require dumping agitators, classifiers or thickener tanks. These are mainly consequences of failures because of insufficient power supply or some other struggles with the mechanics of the system. On the other hand, there are two points of views for the inherent losses: the ones seen only in new circuits and the ones constantly seen. Inherent losses which are seen only in new circuits, are because of wetted solutions inside the fresh wood vessels and happens in a time span of two or three months. Moreover, constantly seen inherent losses are mainly because of filter discharge failures. In order to prevent this re-pulpings and second filtrations are advised. In all scenarios cost analysis should be done for sure (911Metallurgist, 2016).

How pH affects Cyanidation?

In order to obtain and keep holding a “protective alkalinity” lime addition to the solution is required which reduces the amount of demolished cyanide. Alkalinity level should be kept around 0,5 to 1,5 lbs. per ton of solution. Some particular unwanted substances precipitates and the thickeners which are holding finally ground rock or slimes accelerating the settlement. All because of lime usage which affects this project advantageously. As a protector lime will be effective in the ball mill at the same time when the ore is fed into it. Adding lime dry or wet are both possible. It is recommended that in the dissolving process mill solutions should be sampled periodically at different types of fixed points. It is easier for the operator to monitor the strength of lime and cyanide and maintenance requirements according to this strength. Newly aerated solution, which is sent to the grinding process by pumps, generally has a cyanide addition before the pumping. Nevertheless, time to time at dissolution process some of the cyanide kept away to treat internal issues (911Metallurgist, 2016).

Cyanidation Throughout Grinding Stage

There are various mechanical processes, and when it is analyzed financially most critical one is the grinding process which takes around the %40 to %70 of the expenses. This action generally takes place in a ball mill in order to decrease the ore to adequate size for gold particles to dissolve in a solution of cyanide. This process can be initiated both in ball mill and in the agitators. Cyanide solution is where the grinding stage is completed before. Around %30 to %85 of the gold generally has a dissolving action at this stage when the metallurgical conditions are provided. At high temperatures metals have exposures with the cyanide solution when all conditions are in standards. Nevertheless, in alkaline water grinding action may required by some ores which holds cyanicides that require pre-liming. In this case thickening is necessary to get rid of harmful particles prior to adding cyanide, which is also done in the remediation of the concentrates. The main practice between the size and grinding of the gold states that level of the fineness of the gold correlates with the level of necessary grinding action. This is specifically used on ores which are sulphide related gold. High rate of grinding results in finer materials and increased level of extraction. Nevertheless, financial equilibrium should be sustained in grinding processes because of the rapid raise of the finer materials make it difficult to grind further which is also causes fine slimes that is not easy to contain in thickeners. On the other hand, it helps to coat gold with an external material crushed into them by ball mill. Slightly in ore portion gold found with high sulphide rate. Sharply excessive level of fine grinding sometimes required to release the gold from the surrounding sulphides. Particularly for this matter if the feed is totally ground, price of the work will be increased. Sulphides should be removed from the initial mill system and a separate mill should be assigned for them. Jig is run with a constant releasing rate, when it is required to re-grind the feed of sulphides. In order to help the dissolution of the gold in a refractory material super-agitators can be inserted into the newly enclosed system which has the function of high-level agitation and aeration. The discharge of this circuit added into the primary cyanide system. At this moment it is difficult to use flotation because cyanide depresses the sulphides in the circuit. The primary overflow which includes mostly gangue minerals can have larger sizes when separate mills are used in the circuit. Golds in finer sizes which are linked to the pure quartz rapidly dissolves, and exposure span lowers to the bottom. Concentrated care is applied on golds which are connected with the sulphides that needs fine sized grinding action. Nevertheless, grinding feed is only a tiny part of this individual system, price of the equipping and working would be reduced in case of comprehensive treatment to the entire tonnage. Wet process is used in grinding circuits because of the desired efficiency rates which are not reachable in dry circuits, and the effect of dissolution of the solution. Rake or spiral type classifiers sustain the control of the size of the completed materials. Rate of the completed material which goes through a typical screen states the grind's fineness generally. For instance, %70 -200 mesh. 2.83 power of the diameter of the ball of the mill shows the capacity of it. When measuring the capacity, it is critical to notice if the length of the diameter of the ball mill is inside the core or not because the effective diameter is related with the inner measurements (911Metallurgist, 2016).

Classification

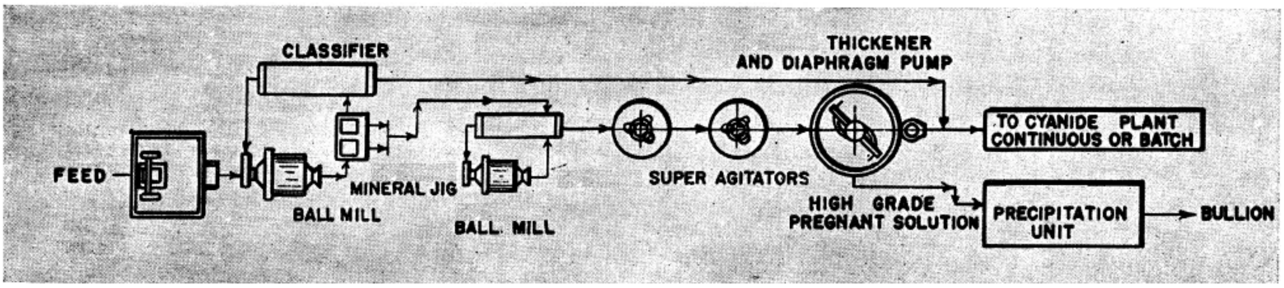
In order to monitor the size of the material that enters to the dissolution or agitation system, classification is done. Classifiers split the released material which comes from the ball mill and enters itself into the sand and slime; when the sand particle sent to the ball mill through mechanically, fixed fine sized materials overspill from the release end of the classifier and prepared for the agitation stage. The definition of this stage is, 'grinding in closed circuit' and sharply raises the productivity of the whole system. The reason for that is to be grinding the coarse particles more and the removal of the fine sized particles from the pulp. The energy saving through this method is highly remarkable in the milling circuit (911Metallurgist, 2016).

Cyanide Concentration in Grinding Circuit

Firstly, it is crucial to prevent the gold which is coarse sized from the milling system instantly when it is discharged, to avoid obstacles for a productive operation, or else, the coarse sized particles would stuck inside the ball mill and it would be difficult to recover. Sometimes it may stuck inside the classifier and thickener tanks as well, which will cause a huge trouble if the case is about a tiny high-grade mill. In addition, the dissolution of coarse sized gold particles is not easy, that is why generally these large particles avoid dissolving and released with tailings. Moreover, the discharge of this system which is proceeded by blankets, traps, concentrating tables or the jig, raises the capacity of the grinding process (911Metallurgist, 2016).

Effect of Agitation in Cyanidation

Main purpose of agitation, for dissolving the gold with cyanide solution in a circular vessel which has an adequate capacity to manage the equilibrium of the gold by creating a mixture of air and pulp mechanically. Mainly agitators consist of two groups. These are airlift types, and the merge of air and mechanical blending type. Brown or Pachuca vessels which has a great height even more than the three times of its own diameter can be given as a great example for the airlift type agitators. Bending action is the deciding factor where the air comes from the core of the cone. On the other hand, for elevating and aerating the pulp, surplus of air is used by the mechanical agitators which are also keeping the pulp hanging at the bottom by mechanical blending tools. It is suggested that minimum two agitators should be adopted in series, in order to avoid short-circuiting. Moreover, it is also suggested that the strong cyanide solution to be replaced with the fresh one to help the slow dissolution process by installing new thickeners with some ores that have refractory properties to the agitation system. The introduction technique of the air is a determining factor for the productivity of an agitator. For instance, when the quick dissolution is required, air bubble dispersion is critical. For decreasing the agitator volume and to block undue sand settlement it is advised that the dilution of the pulp should be hold at lowest levels (911Metallurgist, 2016).



With this flowsheet entire tonnage is given coarse grind sufficient to re-lease sulphides; jig concentrate reground and cyanided separately . . gives low grinding cost and increased recovery.

Figure 1: Flowsheet of the cyanidation circuit of gold (911Metallurgist, 2016).

Clarification

Main requirement is to remove the impurities and hanging solids prior to the precipitation process and following the removal of the solution that carries gold, from the thickeners, which is generally defined as clarification process. For an efficient precipitation process chain, clarification is needed. There are many alternative tools are ready to use for this process. Nevertheless, absorption of the solutions by a filtering medium which suits for the coarse sized materials in a solution vessel is the general application of these systems. In order to help the filtration stage and the discharge of the slimes which are fine sized, the filtering medium covered by inorganic material regularly. For example, diatomaceous earth. Following the clarification process, it is necessary for the solutions to be completely clear. Also following the clarification and de-aeration processes, it is urgent for precipitation to be completed, or else, contamination risk for the solution could occur. In order to have a productive clarification, apart from helping for the slime coagulation by the addition of the lime into the thickeners, some extra work must be done. For instance, caustic starch usage in the processes which helps to develop the settlement of the slime and complete a smooth precipitation in a longer period of time (911Metallurgist, 2016).

According to the Mining Magazine (London), “In the Raub Australian Gold Mining Company, in thickeners starch is used, but while thickening the concentrate of the flotation they faced a problem, and it is treated with the addition of the starch. Five gallons of water is required to mix with 40 pounds of tapioca flour to get a slurry that does not contain lumps, and it should be blended with water, which is boiling and should be 35 gallons, after that sodium hydrate which is about 1.2 pounds must causticize the mixture in order to obtain a useful caustic starch. For each ton of concentrate in the thickeners it is necessary to put 2 pounds of caustic starch.” (911Metallurgist, 2016).

Zinc Process For The Precipitation Of Gold

When the clarification process ends, precipitation process follows right away which is required to get rid of the oxygen in the solution which is dissolved in it. At this stage process of de-aeration is employed which is founded by Merrill-Crowe Process. Removal of gold is done with the dust of zinc by precipitating. Technique basically states that, by the electro-negativity between gold (or silver) and zinc, process of precipitation is obtained (911Metallurgist, 2016).

Reaction is showed below:

$$KAu\ (CN)2+2KCN+Au+H2O=K2Zn\ (CN)4+Au+H+KOH$$

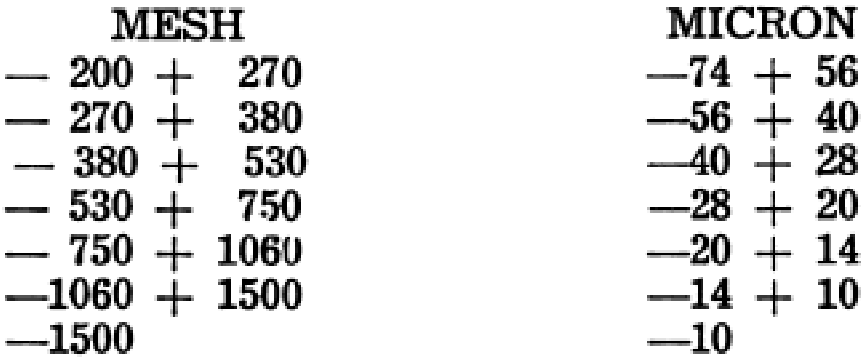
In case of over consumption of the zinc, the reaction below is obtained:

$$Zn+4KCN+2H20 = K2Zn\ (CN)4 + 2KOH + H2$$

Sometimes into the solutions of cyanide, dissolving lead is inserted in order to obtain zinc-lead compound for a better action of precipitation. Also, regularly solution of strong cyanide’s drop is included with the zinc. When a problem occurred while precipitating, process of clarification and process of de-aeration should be re-analyzed. In case of an air leak precipitation may fail (911Metallurgist, 2016).

Screen Analysis — Microns

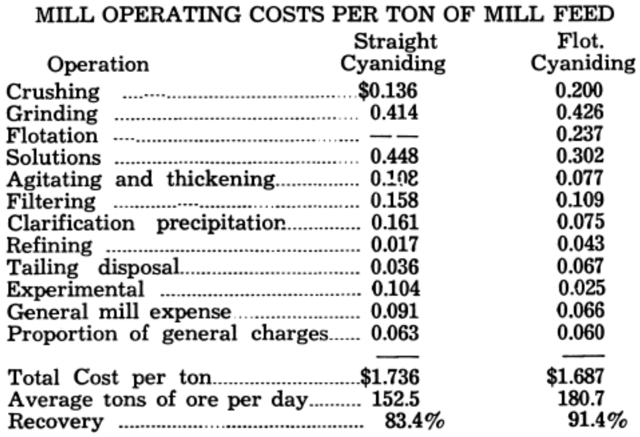
The conventional laboratory screening is not sufficient to determine the finest fractions of a pulp of gold that is why using alternative techniques are needed sometimes. For example, in Canada mostly for these cases Haultian infrasizer and superpanner are used together. Micron unit system is used for analyses of screen (1 mm=10^3 microns). Tyler Screens have 75 micron opening with a 200 mesh (911Metallurgist, 2016).



MESH	MICRON
— 200 + 270	—74 + 56
— 270 + 380	—56 + 40
— 380 + 530	—40 + 28
— 530 + 750	—28 + 20
— 750 + 1060	—20 + 14
—1060 + 1500	—14 + 10
—1500	—10

Table 1: Mesh- micron relation for finer sizes (911Metallurgist, 2016).

Flotation and Cyanidation



MILL OPERATING COSTS PER TON OF MILL FEED

Operation	Straight Cyaniding	Flot. Cyaniding
Crushing	$0.136	0.200
Grinding	0.414	0.426
Flotation	— —	0.237
Solutions	0.448	0.302
Agitating and thickening	0.108	0.077
Filtering	0.158	0.109
Clarification precipitation	0.161	0.075
Refining	0.017	0.043
Tailing disposal	0.036	0.067
Experimental	0.104	0.025
General mill expense	0.091	0.066
Proportion of general charges	0.063	0.060
Total Cost per ton	$1.736	$1.687
Average tons of ore per day	152.5	180.7
Recovery	83.4%	91.4%

Table 2: Comparison of mill operating costs per ton of mill feed between flotation and cyanidation at each operation (911Metallurgist, 2016).

Re-grinding the concentration of flotation and fine sized feed of the ball mill causes raises in cost of size reduction. From a metallurgical point of view, it is stated that from a combination circuit each ton of the product will cost less, nevertheless it is believed that it will be more economical to run a direct cyanide circuit which is under 100 tons a day. Moreover, ores at the surface are easier to treat with a direct cyanide system. Generally, in the grinding stage jigs are used to liberate the gold away. To obtain primary gold- holding sulfides, ore character regularly changes. For the expansion of the mill, adequate tonnage is prevented. After this stage, to get rid of the sulfides which are in the starting cyanide mill, cyanided, it is best to build up flotation circuit with cells. In order to elevate the mill capacity to the next level fresh circuit of grinding with the flotation machine is necessary. Most critical part is the concentration and the tailing of the flotation process which may lead to maximum raise according to the process outcome ratio which is between 2:1 to 35:1. It would be a mistake to financially reject the tailing that comes from the flotation process. For instance, a hydroclassifier is fed with a tailing of a flotation process by a concentrator which does not cost much. In this process the exceeded slime is thrown away and agitators are fed with sand fractions in a 4-hour span and because of the fast-settling ability thickeners which has 0.3 sq. ft. per ton capacity works properly, and in relation to this compact sized cyanide mill is built (911Metallurgist, 2016).

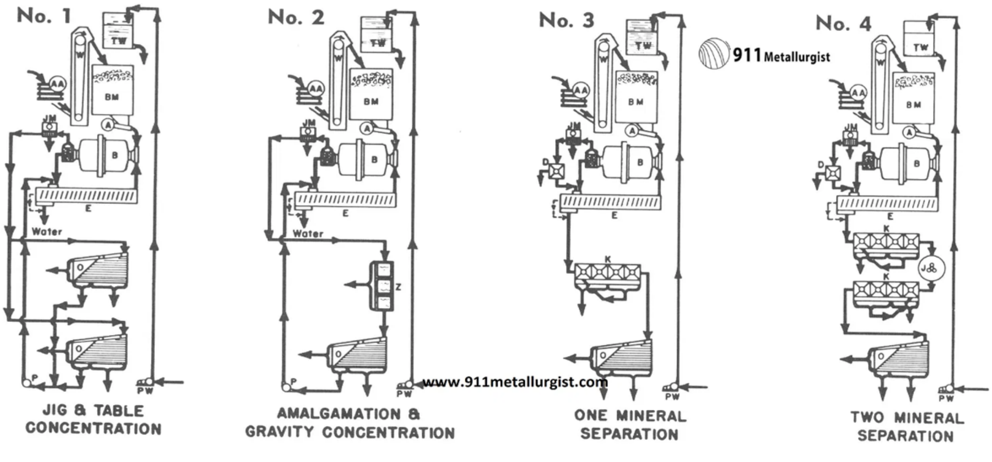


Figure 2: Flowsheets for each operation in cyanidation process (911Metallurgist, 2016).

Batch Cyanidation of Gold

This process is generally used on two separate mils which are not identical, and the remediated materials quantity is not very much. In some qualities the type of the processed material is very irregular that is why batch cyanidation is used in order to have highest level of extraction. Until the ultimate analyze of the residue is adequate in terms of the standards that has been set, agitation of the material continuous in company of various type of solutions. In the end, from the vessels the agitated material is released. Generally, in these processes there are three type of machines that are essential and these are: super agitators, float decantation, and bottom discharge machines (911Metallurgist, 2016).

Cyanidation—Sand Leaching

In today's world, ore sizes are reduced to uniform fineness which is the consequence of the brand-new type of crushing and grinding technologies which are highly consumed by Americans and Canadians cyanide experiments. Deciding whether to use the sand leaching or not is very critical, peculiarly on gold ores which are graded shortly. Having a grinding operation at coarse sizes benefits when it is on a simple plant. Primarily, most of the gold has to be able to go through a dissolution at that size. Productivity in classification phase is crucial for a well-working leaching facility. Porosity of the sand bed can be affected badly even with a low level of slimes. Particle size must be granular for not to face any trouble. In slime circuit the overflow of the released material processed individually or thrown away depending on the profit after classification. Empty vessels with bottoms that has porosity receive sands by pumping. With a mechanical distribution, sand is dispersed evenly in the vessel. Feeding of the solution of cyanide can be from down and let it move to upper parts or vice versa. Addition order of the cyanide solution is strongest to weakest solution after these additions it is washed by water. In every permeation break, sand movement should let it happen for leading air to get to the disintegrated gold from the dissolution process. Tailing bulk is removed by the belt conveyors which receives the released sand from the downward of the vessel after the permeation ends. Classifiers are chosen for end phase washing when the cyanidation stage ends in the vessel. The tonnage capacity for necessary situations determines whether there will be more permeation or not. Up to 10 days leaching and washing may take and it may change with the type of the ore (911Metallurgist, 2016).

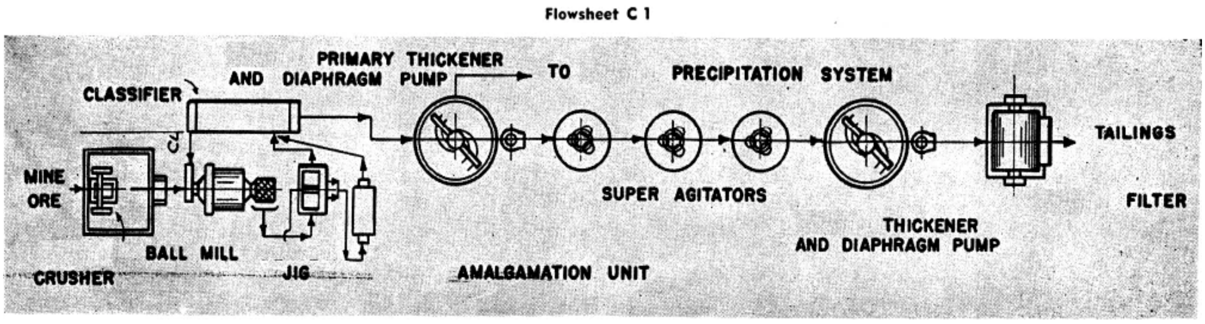


Figure 3: Flowsheet of treating a medium grade ore where the main focus is on recovering fine gold in grinding phase in mineral jig (911Metallurgist, 2016).

The figure shows jig in grinding stage where the most of the gold’s dissolution occurs, this system is suitable for grade level medium and recovery rate on top. Primary thickener sends the solution to the precipitation when the solution has an adequate level of grade increasement. After these, in order to start the dissolution of the rest of the gold, agitators treat the newly aerated solutions. In figure three agitators can be seen, they are all together required to harshly decrease the pulp’s risk of short circuiting which is very crucial to remediate the pulp which has increased grade. Filtration receives agitated pulp without additional thickening has applied sometimes. It won’t cause a problem when it is applied on to the pulp with a reduced grade, at increased density levels agitators can be employed. Nevertheless, for stabilization between the load and the filter additional thickener is recommended, which decreases the feed that can dissolve into the filter by letting variable actions of agitators and reduced dissolvable waste in weight and in concentration. Double filtration is a concept that widely preferred in mills. For providing fresh water and the released cake together from the main filter or agitator which is mechanical can be added in order to supply comprehensive blending, re-pulper is the right option. Remediated ore determines the flow of the solution (911Metallurgist, 2016).

Continuous Counter-Current Decantation

The rational evolution of the initiation of decantation of the cyanide’s batch method and the constant slime thickener is the Continuous Counter-Current Decantation system (CCD system) for cleaning the pulps of cyanide. The thickeners which are used as series in the system is fed by pulp and water from separate ends of it. For this reason, the flow directions of the pulp and water are different from each other. In relation to this, when pulp set to release from the system dissolving substance decreases. Contrarily, from the ejection end addition of water is done which continue to flow through, and its strength raises in lime, cyanide and gold which went through dissolution. Filtration is boosted or replaced by CCD system in the past. Cleaning with weighty water for the filtration generally lower than the dissolution waste. Mill needs much more space. Although, the expenses coming from the operations generally less than others. With the help of simultaneous equations wastes of dissolution from the CCD system can be measured (911Metallurgist, 2016).

Using Charcoal/Carbon In Precipitation

It is beneficial to use charcoal because of its property to absorb dissolved gold in a solution of cyanide. For extraordinary types of gold ores, the Chapman Process (U. S. Patent 2,147,009) can be considered for future studies. Carbon as charcoal, lime, cyanide, and gold ore are added into the ball mill where there is also an existing classifier. Outpouring of the classifier is taken into thickeners and agitators respectively. Solution of cyanide dissolves the gold in itself, after this, charcoal absorbs the mixture of gold-cyanide. After this stage charcoal is obtained by the flotation method. The Chapman Process (U. S. Patent 2,147,009) which applied to a gold ore which has an upper-level grade states that, tailing which came from the main flotation unit taken into the scavenger unit, and the outcome is transferred into a grinding unit which is fed by concentrate that its grade is reduced (911Metallurgist, 2016).

According to The Chapman Process (U. S. Patent 2,147,009), "for decreased-level grade tailing two lb. of charcoal per ton, and three to seven lbs. for analyzed ore up to 0.4 oz. gold per ton is used for sufficient suction."

Thin pulps do not have successful outcomes as thick pulps. Treating gold is more productive when it is compared with silver. Charcoal is more efficiently floated than the sulfides. Some processes have to be done for the charcoal respectively, filtration of the concentrate, dewatering, and transferring for smelting. Generally, suction rate of gold is between 65% to 85% and the carbon is retrieved around 90% to 99% (911Metallurgist, 2016).

Graphitic Gold Ore Treatment

Early precipitation is a consequence when carbon being in an ore as graphite, it is a natural precipitant for gold particles. Feeding the ore with kerosene shows that decreases the ability of precipitation. After that as a froth, graphite is separated from the upper surface of the thickeners. The graphite can be both floated or depressed when its ores are taken into the flotation process (911Metallurgist, 2016).

2.3. How Harmful is Cyanide

Numerous symptoms can be occurred with chronic low-level exposure to cyanide. Causes like loss of appetite, headache, weakness, nausea, dizziness, and symptoms of irritation of the upper respiratory tract and eyes are because of subject to a little quantity of cyanide compound for long term periods. Tropical ataxic neuropathy associated with chronic cassava consumption is a very common pathologic condition which is assigned to cyanide. This neurological disease is diffuse degenerative which also has peripheral and central signs. In numerous tropical areas cassava is a well-known food which includes cyanogenic glycoside (linamarin) highly. Moreover, in time tropical neuropathy increases by resuming ingestion. Sensory spinal nerve involvement causes optic atrophy, nerve deafness, and ataxia which is affected by this syndrome. In addition to these effects, scrotal dermatitis, stomatitis, glossitis, ultrastructural changes of heart muscle thyroid may be affected due to enhanced formation of thiocyanate and this causes thyroid goiter, and cretinism may occur. Cyanide also may transfer to the fetus (Cai, 2005).

There were many accidents worldwide includes cyanide in mining industry can be given in the last decade, such as (Wikipedia, 2024): Eagle Gold Mine (Canada, 2024), Çöpler Gold Mine, İliç, Erzincan (Türkiye, 2024), Gbomblora (Burkina Faso, 2022), Kondago Village (Niger, 2021), Kamituga Mine, Kamitung Town, South Kivu (Democratic Republic of the Congo, 2020), Kampine Mine, Kampine Town, Maniema ((Democratic Republic of the Congo, 2019), Veladero Mine, San Juan Province (Argentina, 2015), Gold King Mine (USA, 2015).

3. WHAT IS ION FLOTATION

Developments and growth in industrial sectors are in relation with the increasing population, this is also related with the industrial waste growth. From industries such as, mining, metal plating, fertilizer, paper and dye many same kinds of contaminants which are heavy metals are produced. There is a great need of productive applications to remediate this subject. These heavy metals are mostly toxic and harmful for nature and health; however, these products may contain precious metals which may be very hard to find. These wastes should be recovered if it is possible, because it may affect more industries to remediate their possible valuable rare metal holding wastes which can be valorize in time that may cause increasement waste remediation. Mainly chemical precipitation can be considered as the most conventional remediation method for cleaning aqueous waste streams from heavy metals which is regularly used because of being basic and economically reliable. Nevertheless, the settling time of the process is too much, to operate it needs wide spaces, and causes downstream treatment problem which is because of generating too much sludge. Considering its productivity, the limitations are restrictive and the purification of the water that is produced is not sufficient. There are some other processes that can take place of the precipitation, but these are not very recommended due to their financial instability, energy needs, additional pollutant generation or restricted productivity which also restricts the execution of it. For instance, ion exchange, membrane filtration, adsorption and reverse osmosis. These remediation techniques results in waste precipitates that hardly remediated for valuable metals and waste handling corporations left them out in landfills. Remediation of these contamination is a serious matter, and possible recoveries might have remarkable values when they are processed. There are new techniques appear for metal extraction in literature, for instance, metal–organic frameworks (MOFs) which have adsorbent features, molecularly imprinted polymers (MIPs) which is highly recommended for selective and stable extraction, and finally, another significant method is biofiltering, which basically filters the contaminants. Nevertheless, shared problems for these methods are being too expensive, difficult to operate the system, and possible additional contamination occurrence. On the other hand, there is a cheap and highly productive method for metal extraction to remediate contaminations, and it is flotation. It is the most basic technique to separate ions from aqueous solutions, there are various types of flotation methods exists such as ion flotation, precipitative flotation, sorptive flotation, dissolved air flotation, and foam fractionation. Nevertheless, the technique, should be determined according to chemical properties of the solution. Ion flotation is highly productive on concentrations which are dilute and does not create a lot of mud (Schlebusch, Pott, and Tadie, 2023).

3.1.Process Steps of Ion Flotation

In ion flotation, modifications of the hydrodynamic features of the processed substant can only be done by the specifically required collectors. Collectors that are charged reversely holds the wanted colligends from the solution and include them in a complex which is hydrophobic that sticks into the bubble surface in ion flotation liquid. Collecting and frothing is handled by the surfactants. Solution chemistry and froth features decides the needed surfactant type. In the recent works, sodium dodecyl sulphate (SDS) is used mostly as a surfactant which is synthetic, nevertheless disturbing consequences regarding with the environment can occur because of using these chemicals. In order to, decrease the environmental effects of the ion flotation, unharmful collectors and frothers should be used. Various of microorganisms produces the biosurfactants which are suitable for this purpose and produced by various types of microorganisms that produces amphiphiles. These surfactants are biodegradable and renewable carbon sources that can make these surfactants. When biosurfactants are compared with the synthetic chemical ones the obvious advantages can be observed. At high levels of pH, temperature the stability and activity of the biosurfactants are remarkable, also their versatility is significant which has resulted by their ionic strength. SDS has less capacity for foaming and foam capacity when it is compared to a liopeptide biosurfactant that having a suface activity which is significantly strong which is called surfactin. Metal-surfactin complexes are made by these biosurfactants which has binding properties. Hydrophilic heptapeptide which is a part of the surfactin has a carboxylic acid group that has an acidity between 5.4 and 5.8 pKa with a pH value higher than 5 when they are at anionic conditions. Surfactins tie up metals while precipitating which is let by clawlike structure that is made by the carboxylate anions. This results in the formation of metal-surfactin complexes which are stable. Metal-surfactin complexes fractionating away from aqueous solution and this can be used to form foams by the strong activity of surface of the surfactin. Surfactin is useful in both sorptive and ion flotation, it used as frothing reagent and collecting reagent respectively in these processes. Accomplishing the task, which is to remove almost all the ions, can be done by surfactins which they previously proved for the characteristic separations of the ions of the watery concentrations. Removing the heavy metal ions from contaminated waters can lead to reuse of these ions and this helps to overcome the harming and unknown properties of these heavy metals. Fractioning of foam is affected by air flow rate, molar ratio, and pH while operating (Schlebusch, Pott, and Tadie, 2023).

Recovery and removal of metal ions from watery solutions are done by ion flotation. Non-surface-active materials are transported by ionic collectors and these materials are oppositely charged from the solution-vapor interface. Sparging gas may supply large solution-vapor interface zone adequately, colligends can be captured and used with a collector in foam process. Ion flotation currently holds a lot of opportunities for remediating watery solutions (Doyle, 2003).

3.2.Treatment of Flotation Reagents

Water consumption approximately millions of cubic meters in mining operations per annum. One of the most important phase in mineral processing is flotation which consumes serious quantities of water. The treatment of these wastewaters in mining not only helps to save more water for the system and create a closed-loop circuit which helps the operation economically as well, but also it helps to prevent the negative effects of the reagents that resides such as poor concentration of the separation and environmental damages. Specifically, xanthates and amine derivatives are considered as the main contaminants among the surfactants in wastewaters. For treating these contaminants there are effective applications, such as adsorption, biodegradation, ozonation, Fenton reaction, and photocatalysis, together with electrochemical treatments (Falconi, Junior, Baltazar, Espinosa, and Tenório, 2023)

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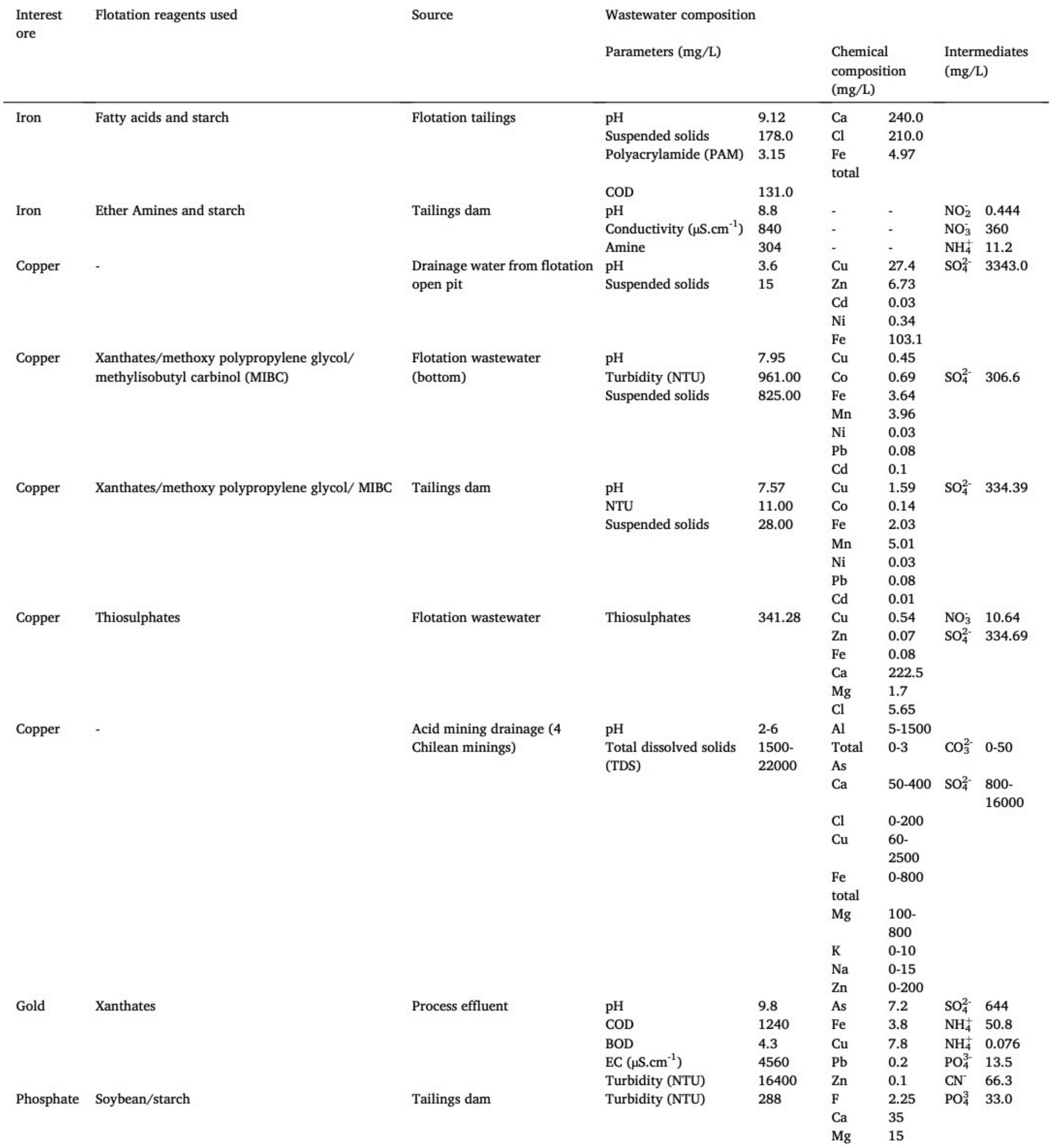
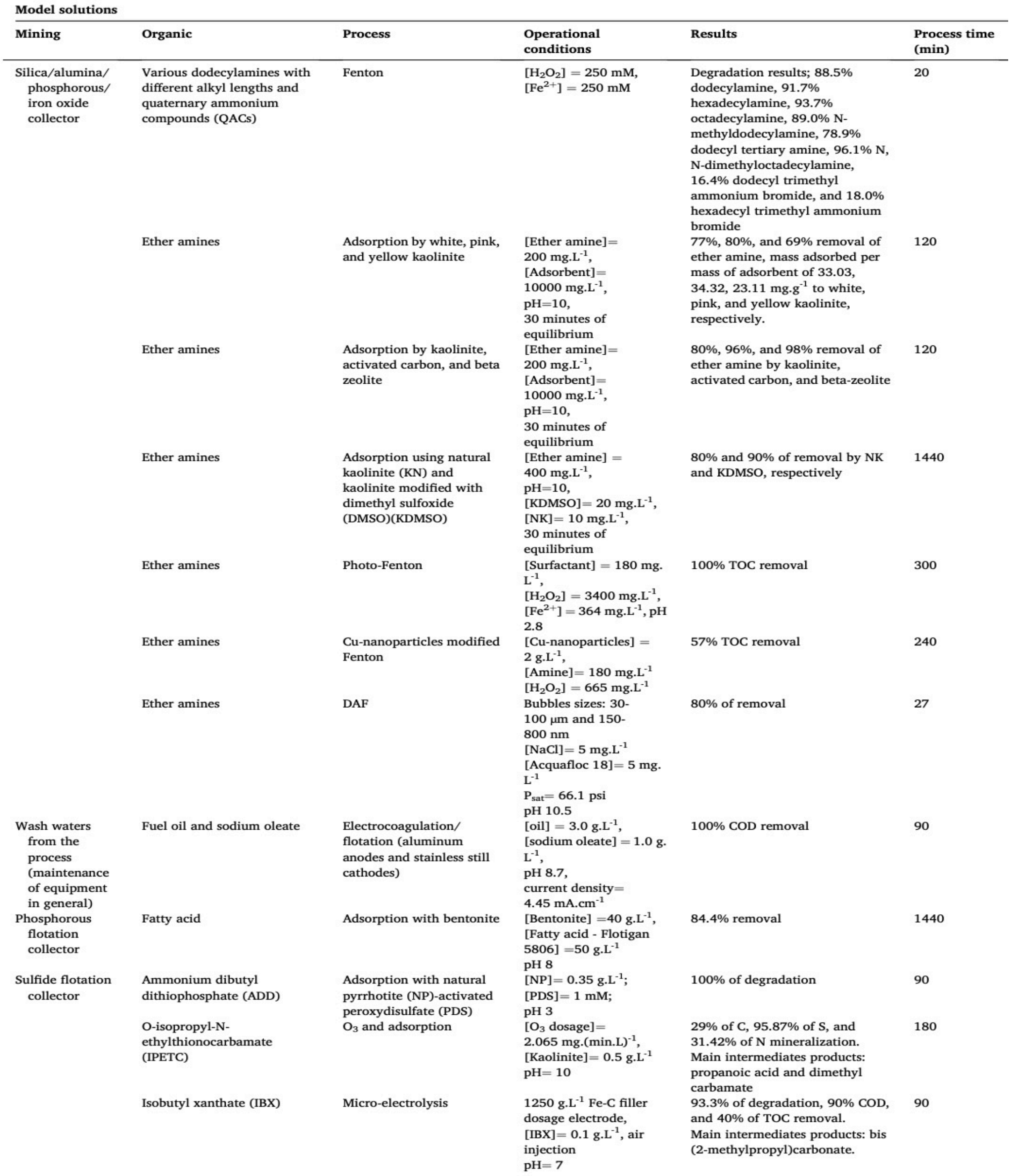


Interest ore	Flotation reagents used	Source	Wastewater composition					
			Parameters (mg/L)		Chemical composition (mg/L)		Intermediates (mg/L)	
Iron	Fatty acids and starch	Flotation tailings	pH	9.12	Ca	240.0		
			Suspended solids	178.0	Cl	210.0		
			Polyacrylamide (PAM)	3.15	Fe total	4.97		
			COD	131.0				
Iron	Ether Amines and starch	Tailings dam	pH	8.8	-	-	NO_2^-	0.444
			Conductivity (μS.cm^{-1})	840	-	-	NO_3^-	360
			Amine	304	-	-	NH_4^+	11.2
Copper	-	Drainage water from flotation open pit	pH	3.6	Cu	27.4	SO_4^{2-}	3343.0
			Suspended solids	15	Zn	6.73		
					Cd	0.03		
					Ni	0.34		
					Fe	103.1		
Copper	Xanthates/methoxy polypropylene glycol/ methylisobutyl carbinol (MIBC)	Flotation wastewater (bottom)	pH	7.95	Cu	0.45		
			Turbidity (NTU)	961.00	Co	0.69	SO_4^{2-}	306.6
			Suspended solids	825.00	Fe	3.64		
					Mn	3.96		
					Ni	0.03		
					Pb	0.08		
					Cd	0.1		
Copper	Xanthates/methoxy polypropylene glycol/ MIBC	Tailings dam	pH	7.57	Cu	1.59	SO_4^{2-}	334.39
			NTU	11.00	Co	0.14		
			Suspended solids	28.00	Fe	2.03		
					Mn	5.01		
					Ni	0.03		
					Pb	0.08		
					Cd	0.01		
Copper	Thiosulphates	Flotation wastewater	Thiosulphates	341.28	Cu	0.54	NO_3^-	10.64
					Zn	0.07	SO_4^{2-}	334.69
					Fe	0.08		
					Ca	222.5		
					Mg	1.7		
					Cl	5.65		
Copper	-	Acid mining drainage (4 Chilean minings)	pH	2-6	Al	5-1500		
			Total dissolved solids (TDS)	1500-22000	Total As	0-3	CO_3^{2-}	0-50
					Ca	50-400	SO_4^{2-}	800-16000
					Cl	0-200		
					Cu	60-2500		
					Fe total	0-800		
					Mg	100-800		
					K	0-10		
					Na	0-15		
					Zn	0-200		
Gold	Xanthates	Process effluent	pH	9.8	As	7.2	SO_4^{2-}	644
			COD	1240	Fe	3.8	NH_4^+	50.8
			BOD	4.3	Cu	7.8	NH_4^+	0.076
			EC (μS.cm^{-1})	4560	Pb	0.2	PO_4^{3-}	13.5
			Turbidity (NTU)	16400	Zn	0.1	CN^-	66.3
Phosphate	Soybean/starch	Tailings dam	Turbidity (NTU)	288	F	2.25	PO_4^3	33.0
					Ca	35		
					Mg	15		

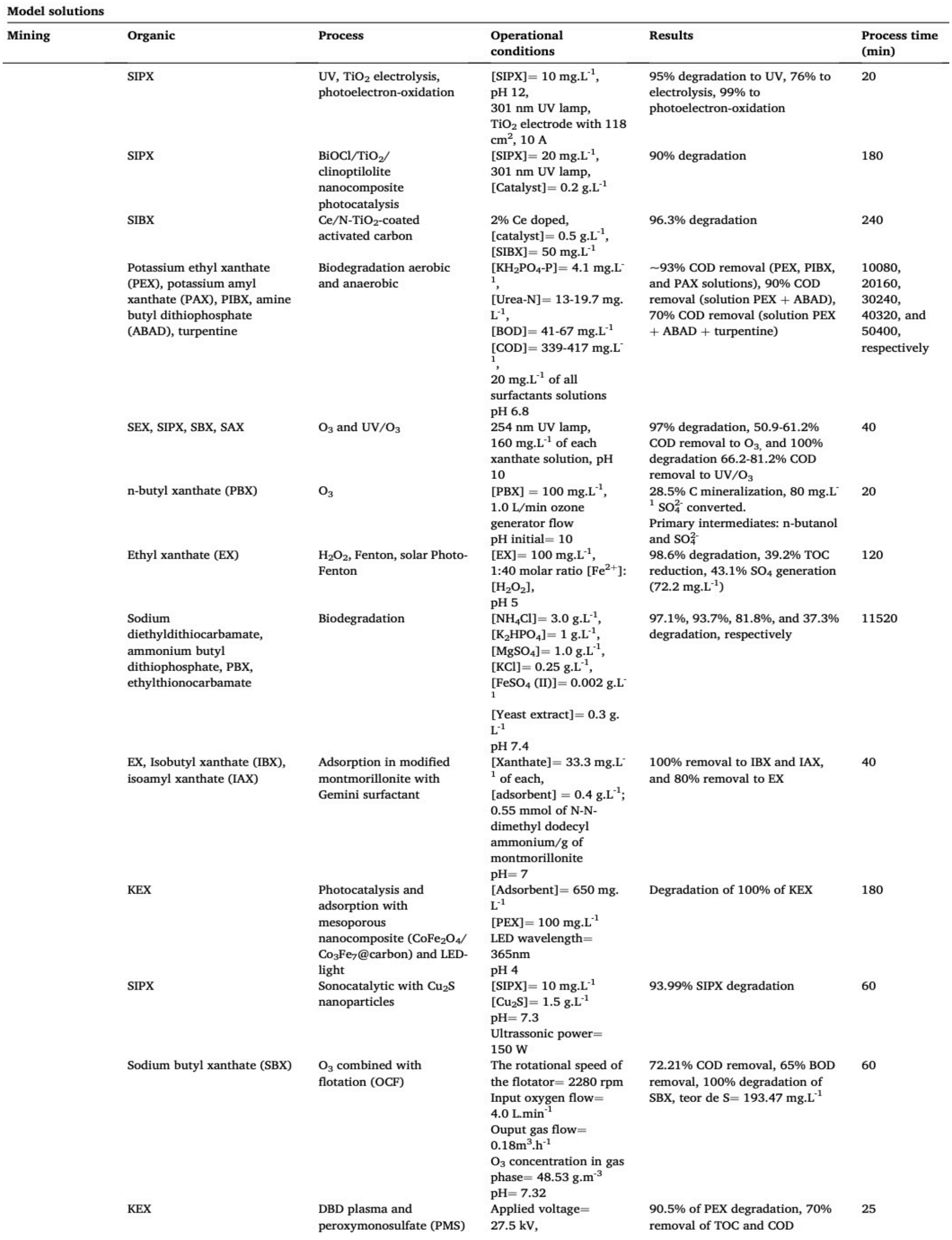
Table 3: Various types of wastewaters from operations of mining industry (Falconi, Junior, Baltazar, Espinosa, and Tenório, 2023).



Model solutions

Mining	Organic	Process	Operational conditions	Results	Process time (min)
Silica/alumina/ phosphorous/ iron oxide collector	Various dodecylamines with different alkyl lengths and quaternary ammonium compounds (QACs)	Fenton	$[H_2O_2] = 250$ mM, $[Fe^{2+}] = 250$ mM	Degradation results; 88.5% dodecylamine, 91.7% hexadecylamine, 93.7% octadecylamine, 89.0% N-methyldodecylamine, 78.9% dodecyl tertiary amine, 96.1% N, N-dimethyloctadecylamine, 16.4% dodecyl trimethyl ammonium bromide, and 18.0% hexadecyl trimethyl ammonium bromide	20
	Ether amines	Adsorption by white, pink, and yellow kaolinite	[Ether amine]= 200 $mg.L^{-1}$, [Adsorbent]= 10000 $mg.L^{-1}$, pH=10, 30 minutes of equilibrium	77%, 80%, and 69% removal of ether amine, mass adsorbed per mass of adsorbent of 33.03, 34.32, 23.11 $mg.g^{-1}$ to white, pink, and yellow kaolinite, respectively.	120
	Ether amines	Adsorption by kaolinite, activated carbon, and beta zeolite	[Ether amine]= 200 $mg.L^{-1}$, [Adsorbent]= 10000 $mg.L^{-1}$, pH=10, 30 minutes of equilibrium	80%, 96%, and 98% removal of ether amine by kaolinite, activated carbon, and beta-zeolite	120
	Ether amines	Adsorption using natural kaolinite (KN) and kaolinite modified with dimethyl sulfoxide (DMSO)(KDMSO)	[Ether amine] = 400 $mg.L^{-1}$, pH=10, [KDMSO]= 20 $mg.L^{-1}$, [NK]= 10 $mg.L^{-1}$, 30 minutes of equilibrium	80% and 90% of removal by NK and KDMSO, respectively	1440
	Ether amines	Photo-Fenton	[Surfactant] = 180 $mg.L^{-1}$, $[H_2O_2] = 3400$ $mg.L^{-1}$, $[Fe^{2+}] = 364$ $mg.L^{-1}$, pH 2.8	100% TOC removal	300
	Ether amines	Cu-nanoparticles modified Fenton	[Cu-nanoparticles] = 2 $g.L^{-1}$, [Amine]= 180 $mg.L^{-1}$ $[H_2O_2] = 665$ $mg.L^{-1}$	57% TOC removal	240
	Ether amines	DAF	Bubbles sizes: 30-100 μm and 150-800 nm [NaCl]= 5 $mg.L^{-1}$ [Acquafloc 18]= 5 $mg.L^{-1}$ P_{sat}= 66.1 psi pH 10.5	80% of removal	27
Wash waters from the process (maintenance of equipment in general)	Fuel oil and sodium oleate	Electrocoagulation/ flotation (aluminum anodes and stainless still cathodes)	[oil] = 3.0 $g.L^{-1}$, [sodium oleate] = 1.0 $g.L^{-1}$, pH 8.7, current density= 4.45 $mA.cm^{-1}$	100% COD removal	90
Phosphorous flotation collector	Fatty acid	Adsorption with bentonite	[Bentonite] =40 $g.L^{-1}$, [Fatty acid - Flotigan 5806] =50 $g.L^{-1}$ pH 8	84.4% removal	1440
Sulfide flotation collector	Ammonium dibutyl dithiophosphate (ADD)	Adsorption with natural pyrrhotite (NP)-activated peroxydisulfate (PDS)	[NP]= 0.35 $g.L^{-1}$; [PDS]= 1 mM; pH 3	100% of degradation	90
	O-isopropyl-N-ethylthionocarbamate (IPETC)	O_3 and adsorption	[O_3 dosage]= 2.065 $mg.(min.L)^{-1}$, [Kaolinite]= 0.5 $g.L^{-1}$ pH= 10	29% of C, 95.87% of S, and 31.42% of N mineralization. Main intermediates products: propanoic acid and dimethyl carbamate	180
	Isobutyl xanthate (IBX)	Micro-electrolysis	1250 $g.L^{-1}$ Fe-C filler dosage electrode, [IBX]= 0.1 $g.L^{-1}$, air injection pH= 7	93.3% of degradation, 90% COD, and 40% of TOC removal. Main intermediates products: bis (2-methylpropyl)carbonate.	90

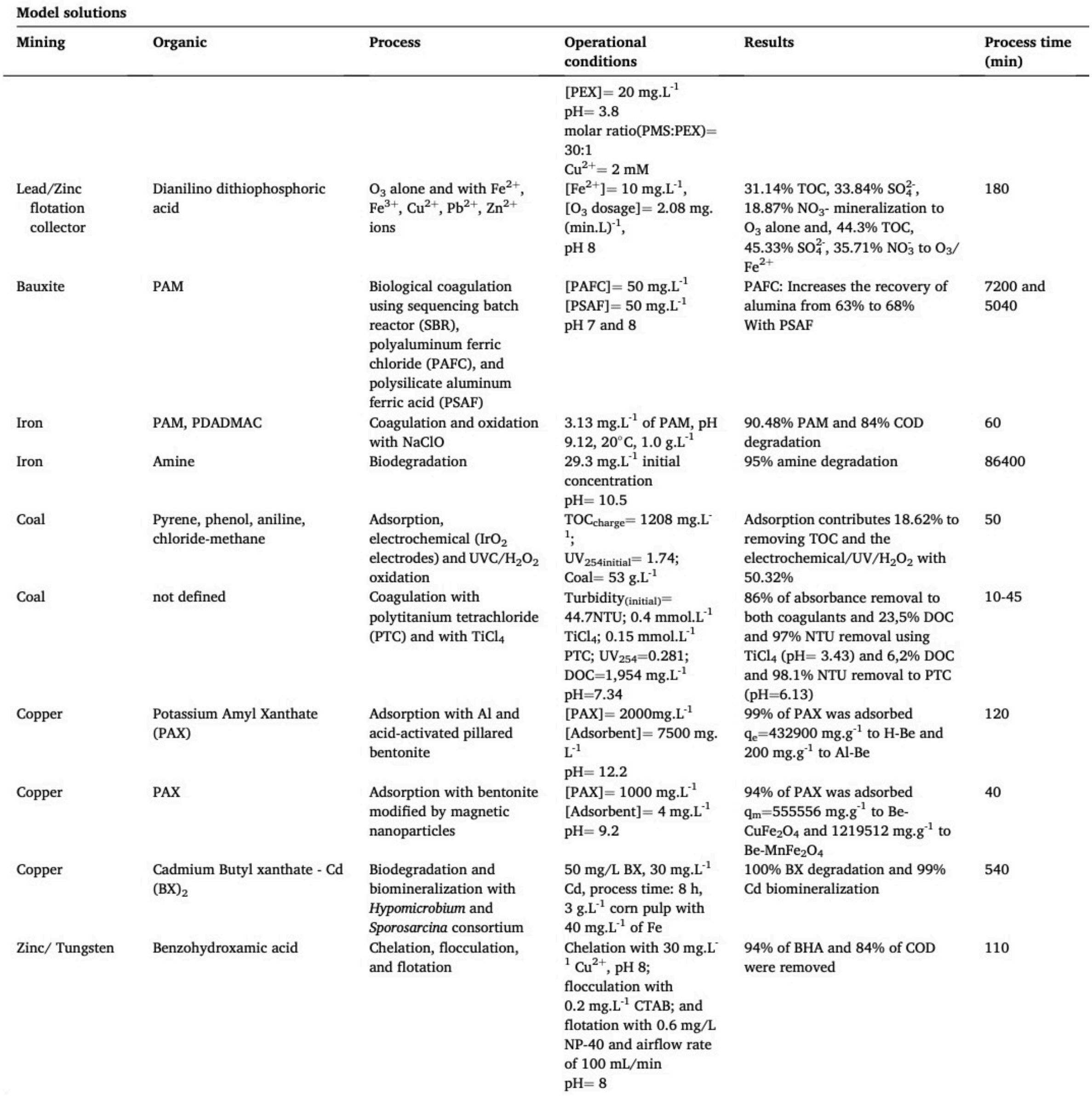
Table 4: Obtained results after wastewaters are remediated (Falconi, Junior, Baltazar, Espinosa, and Tenório, 2023).



Model solutions

Mining	Organic	Process	Operational conditions	Results	Process time (min)
	SIPX	UV, TiO_2 electrolysis, photoelectron-oxidation	[SIPX]= 10 $mg.L^{-1}$, pH 12, 301 nm UV lamp, TiO_2 electrode with 118 cm^2, 10 A	95% degradation to UV, 76% to electrolysis, 99% to photoelectron-oxidation	20
	SIPX	$BiOCl/TiO_2$/ clinoptilolite nanocomposite photocatalysis	[SIPX]= 20 $mg.L^{-1}$, 301 nm UV lamp, [Catalyst]= 0.2 $g.L^{-1}$	90% degradation	180
	SIBX	Ce/N-TiO_2-coated activated carbon	2% Ce doped, [catalyst]= 0.5 $g.L^{-1}$, [SIBX]= 50 $mg.L^{-1}$	96.3% degradation	240
	Potassium ethyl xanthate (PEX), potassium amyl xanthate (PAX), PIBX, amine butyl dithiophosphate (ABAD), turpentine	Biodegradation aerobic and anaerobic	[KH_2PO_4-P]= 4.1 $mg.L^{-1}$, [Urea-N]= 13-19.7 $mg.L^{-1}$, [BOD]= 41-67 $mg.L^{-1}$ [COD]= 339-417 $mg.L^{-1}$, 20 $mg.L^{-1}$ of all surfactants solutions pH 6.8	~93% COD removal (PEX, PIBX, and PAX solutions), 90% COD removal (solution PEX + ABAD), 70% COD removal (solution PEX + ABAD + turpentine)	10080, 20160, 30240, 40320, and 50400, respectively
	SEX, SIPX, SBX, SAX	O_3 and UV/O_3	254 nm UV lamp, 160 $mg.L^{-1}$ of each xanthate solution, pH 10	97% degradation, 50.9-61.2% COD removal to O_3, and 100% degradation 66.2-81.2% COD removal to UV/O_3	40
	n-butyl xanthate (PBX)	O_3	[PBX] = 100 $mg.L^{-1}$, 1.0 L/min ozone generator flow pH initial= 10	28.5% C mineralization, 80 $mg.L^{-1}$ SO_4^{2-} converted. Primary intermediates: n-butanol and SO_4^{2-}	20
	Ethyl xanthate (EX)	H_2O_2, Fenton, solar Photo-Fenton	[EX]= 100 $mg.L^{-1}$, 1:40 molar ratio [Fe^{2+}]:[H_2O_2], pH 5	98.6% degradation, 39.2% TOC reduction, 43.1% SO_4 generation (72.2 $mg.L^{-1}$)	120
	Sodium diethyldithiocarbamate, ammonium butyl dithiophosphate, PBX, ethylthionocarbamate	Biodegradation	[NH_4Cl]= 3.0 $g.L^{-1}$, [K_2HPO_4]= 1 $g.L^{-1}$, [$MgSO_4$]= 1.0 $g.L^{-1}$, [KCl]= 0.25 $g.L^{-1}$, [$FeSO_4$ (II)]= 0.002 $g.L^{-1}$ [Yeast extract]= 0.3 $g.L^{-1}$ pH 7.4	97.1%, 93.7%, 81.8%, and 37.3% degradation, respectively	11520
	EX, Isobutyl xanthate (IBX), isoamyl xanthate (IAX)	Adsorption in modified montmorillonite with Gemini surfactant	[Xanthate]= 33.3 $mg.L^{-1}$ of each, [adsorbent] = 0.4 $g.L^{-1}$; 0.55 mmol of N-N-dimethyl dodecyl ammonium/g of montmorillonite pH= 7	100% removal to IBX and IAX, and 80% removal to EX	40
	KEX	Photocatalysis and adsorption with mesoporous nanocomposite ($CoFe_2O_4$/Co_3Fe_7@carbon) and LED-light	[Adsorbent]= 650 $mg.L^{-1}$ [PEX]= 100 $mg.L^{-1}$ LED wavelength= 365nm pH 4	Degradation of 100% of KEX	180
	SIPX	Sonocatalytic with Cu_2S nanoparticles	[SIPX]= 10 $mg.L^{-1}$ [Cu_2S]= 1.5 $g.L^{-1}$ pH= 7.3 Ultrassonic power= 150 W	93.99% SIPX degradation	60
	Sodium butyl xanthate (SBX)	O_3 combined with flotation (OCF)	The rotational speed of the flotator= 2280 rpm Input oxygen flow= 4.0 $L.min^{-1}$ Ouput gas flow= 0.18$m^3.h^{-1}$ O_3 concentration in gas phase= 48.53 $g.m^{-3}$ pH= 7.32	72.21% COD removal, 65% BOD removal, 100% degradation of SBX, teor de S= 193.47 $mg.L^{-1}$	60
	KEX	DBD plasma and peroxymonosulfate (PMS)	Applied voltage= 27.5 kV,	90.5% of PEX degradation, 70% removal of TOC and COD	25

Table 5: Obtained results after wastewaters are remediated (continued) (Falconi, Junior, Baltazar, Espinosa, and Tenório, 2023).



Model solutions

Mining	Organic	Process	Operational conditions	Results	Process time (min)
			[PEX]= 20 mg.L^{-1} pH= 3.8 molar ratio(PMS:PEX)= 30:1 Cu^{2+}= 2 mM		
Lead/Zinc flotation collector	Dianilino dithiophosphoric acid	O_3 alone and with Fe^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+} ions	[Fe^{2+}]= 10 mg.L^{-1}, [O_3 dosage]= 2.08 mg.(min.L)$^{-1}$, pH 8	31.14% TOC, 33.84% SO_4^{2-}, 18.87% NO_3- mineralization to O_3 alone and, 44.3% TOC, 45.33% SO_4^{2-}, 35.71% NO_3^- to O_3/Fe^{2+}	180
Bauxite	PAM	Biological coagulation using sequencing batch reactor (SBR), polyaluminum ferric chloride (PAFC), and polysilicate aluminum ferric acid (PSAF)	[PAFC]= 50 mg.L^{-1} [PSAF]= 50 mg.L^{-1} pH 7 and 8	PAFC: Increases the recovery of alumina from 63% to 68% With PSAF	7200 and 5040
Iron	PAM, PDADMAC	Coagulation and oxidation with NaClO	3.13 mg.L^{-1} of PAM, pH 9.12, 20°C, 1.0 g.L^{-1}	90.48% PAM and 84% COD degradation	60
Iron	Amine	Biodegradation	29.3 mg.L^{-1} initial concentration pH= 10.5	95% amine degradation	86400
Coal	Pyrene, phenol, aniline, chloride-methane	Adsorption, electrochemical (IrO_2 electrodes) and UVC/H_2O_2 oxidation	TOC_{charge}= 1208 mg.L^{-1}; $UV_{254initial}$= 1.74; Coal= 53 g.L^{-1}	Adsorption contributes 18.62% to removing TOC and the electrochemical/UV/H_2O_2 with 50.32%	50
Coal	not defined	Coagulation with polytitanium tetrachloride (PTC) and with $TiCl_4$	$Turbidity_{(initial)}$= 44.7NTU; 0.4 mmol.L^{-1} $TiCl_4$; 0.15 mmol.L^{-1} PTC; UV_{254}=0.281; DOC=1,954 mg.L^{-1} pH=7.34	86% of absorbance removal to both coagulants and 23,5% DOC and 97% NTU removal using $TiCl_4$ (pH= 3.43) and 6,2% DOC and 98.1% NTU removal to PTC (pH=6.13)	10-45
Copper	Potassium Amyl Xanthate (PAX)	Adsorption with Al and acid-activated pillared bentonite	[PAX]= 2000mg.L^{-1} [Adsorbent]= 7500 mg.L^{-1} pH= 12.2	99% of PAX was adsorbed q_e=432900 mg.g^{-1} to H-Be and 200 mg.g^{-1} to Al-Be	120
Copper	PAX	Adsorption with bentonite modified by magnetic nanoparticles	[PAX]= 1000 mg.L^{-1} [Adsorbent]= 4 mg.L^{-1} pH= 9.2	94% of PAX was adsorbed q_m=555556 mg.g^{-1} to Be-$CuFe_2O_4$ and 1219512 mg.g^{-1} to Be-$MnFe_2O_4$	40
Copper	Cadmium Butyl xanthate - Cd $(BX)_2$	Biodegradation and biomineralization with *Hypomicrobium* and *Sporosarcina* consortium	50 mg/L BX, 30 mg.L^{-1} Cd, process time: 8 h, 3 g.L^{-1} corn pulp with 40 mg.L^{-1} of Fe	100% BX degradation and 99% Cd biomineralization	540
Zinc/ Tungsten	Benzohydroxamic acid	Chelation, flocculation, and flotation	Chelation with 30 mg.L^{-1} Cu^{2+}, pH 8; flocculation with 0.2 mg.L^{-1} CTAB; and flotation with 0.6 mg/L NP-40 and airflow rate of 100 mL/min pH= 8	94% of BHA and 84% of COD were removed	110

Table 6: Obtained results after wastewaters are remediated (continued) (Falconi, Junior, Baltazar, Espinosa, and Tenório, 2023).

3.3.Flotation Reagents, Equipments and Machinery

- Reagents: CTAB (Cetyltrimethylammonium Bromide), HTAB (Hexadecyltrimethylammonium Bromide), OTAB (Octadecyltrimethylammonium Bromide), MIBC (Methyl Isobutyl Carbinol)
- NaOH (to stabilize pH), pH meter, DI water
- $AgNO_3$, Rodanin, and titration apparatus for sample analyses.
- NaCN, KCN, $K_3[Fe(CN)_6]$
- Denver Type Flotation Machine (911Metallurgist, 2016): It has an arm that is capable of moving up and down on a vertical support that can be locked in any needed level. Single phase, ½ HP of motor that can work on 110 V and 220 V, 50 Hz or 60 Hz current, a v-belt drive with digital frequency inverter, cord and plug, toggle switch, digital display of RPM, and drive guard are available. The machine has CE Mark and the tank that it has can carry out flotation processes with materials that weight 250 to 2000 grams. The other features that the Denver Type Flotation Machine has are the propeller that is used for mixing the solution in the cell and the attrition scrubber kit for scrubbing the surface and liberating the materials.

Figure 4: An image of Denver Type Flotation Machine (911Metallurgist, 2016).

3.4.Other Ion Flotation Examples Beside Cyanide

For the purpose of remediating wastewaters by removing Ni(II) and Zn(II) cation, ion flotation is used. In the experiment for frothing, the reagents were: Dowfroth259 and methyl isobutyl carbonyl (MIBC); and for the collecting, the reagents were: Ethylhexadecyldimethylammonium bromide (EHDABr) and sodium dodecyl sulfate (SDS). DX7 software was used for analyzing the parameters by using two-level factorial technique and formulation of 6-level variables with 16 tests were completed. Primarily, a Hallimond tube was used to start the experiment. The findings from the elimination of Ni(II) and Zn(II) ions were used for conclusion at 10 ppm concentrations initially where pH was 3, air flow rate was 1.8 ml/min and the concentrations of SDS and Dowfroth250 reagents were 300 ppm and 90 ppm respectively. Furthermore, in a flotation cell which is mechanical was where the assessments are done according to the previous phase's records. Regaining rate of Ni(II) was %88 and for the Zn(II) it is%92 at a time span of 60 min and at ideal state. The results showed that, it takes shorter time for the Zn(II) to be recovered. In summary, it is understood that the method of ion flotation is very useful for this removal process industrially (Hoseinian, Irannajad, and Nooshabadi, 2015).

4. EXPERIMENT DEVELOPMENT

4.1. Principles of Preparing the System

Main principles in ion flotation of cyanide that must be followed are: for floating anionic cyanide complexes, cationic collector is needed to be neutralized electrostatically and to become hydrophobic; on the other hand, for smaller, monovalent anions, quaternary ammonium is needed generally, for example CTAB. Finally, for heavily charged poli-anions double chain or cationic polymer (polyelectrolyte) is needed, because when the positive charge increased the bond strength must be more, and it is hard to break the hydrate shell.

4.2. Process Flowcharts

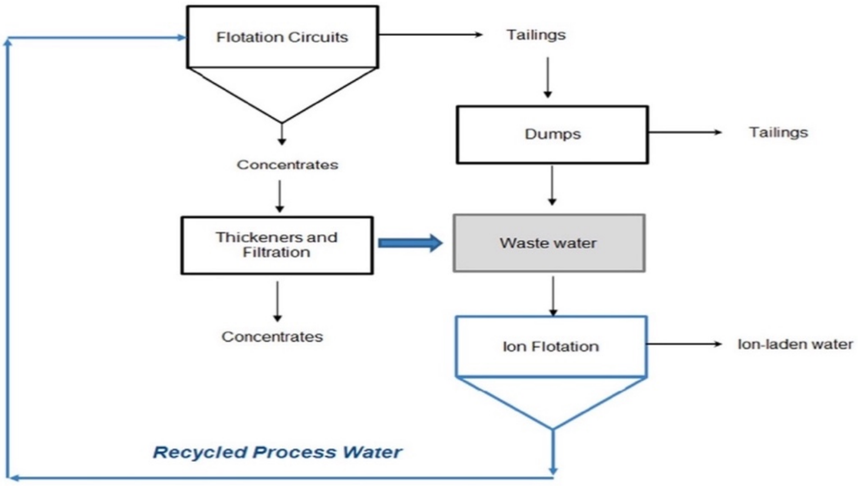


Figure 5: Flowsheet of how the water is re-used in an ion flotation circuit (Yenial, and Bulut, 2017).

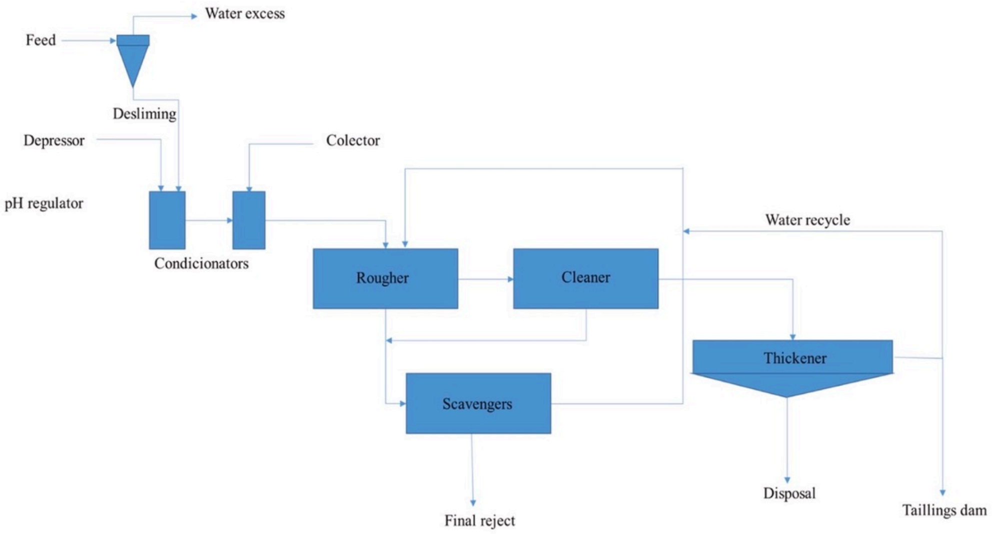


Figure 6: Flowsheet of the standard froth flotation circuit that generally used in the plants (Falconi, Junior, Baltazar, Espinosa, and Tenório, 2023).

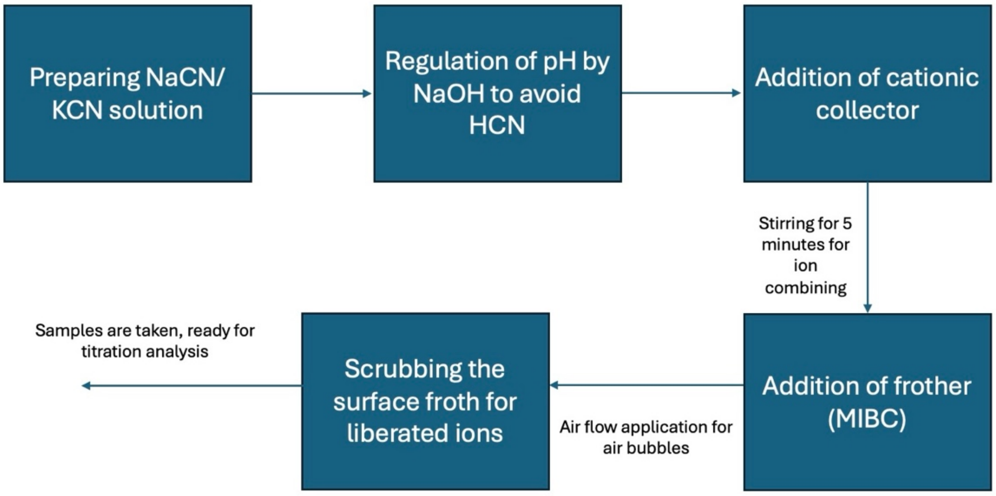


Figure 7: Flowsheet of ion flotation of NaCN and KCN.

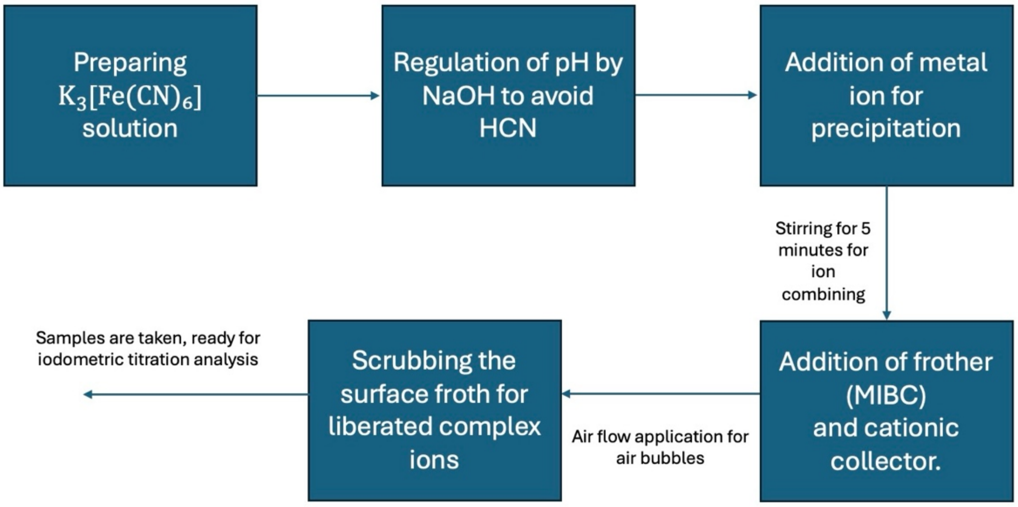


Figure 8: Flowsheet of ion-precipitate flotation of ferricyanide.

4.3.Methodology

In flotation laboratory, Denver type flotation machine is used for the experiments. In the each experiment the tank is filled with 1150 mL water and 575 mg NaCN. After adding the reagents and starting the flotation process; 10 mL of aliquots are taken later to be analyzed for determining the CN concentration in each step of the flotation process. For CN analyzing, titration method is used. Flotation time is 5 minutes, pH is between 10-10,5, 40 mg/L MIBC is used for frother, and 3 types of collectors are used separately in each experiment. These are: Cetyltrimethylammonium Bromide (CTAB), Hexadecyltrimethylammonium Bromide (HTAB), and Octadecyltrimethylammonium Bromide (OTAB). Amount of collector's effects are tested. Respectively 1,45 mg, 2 mg, and 3 mg of collector is used for each experiment. Samples from each experiment are analyzed with titration method. In titration method 3 drops of rodanin solution ($2x10^{-5}$ mol (0,01 g) dissolves in 50 ml acetone) added into the sample then 0,02 M $AgNO_3$ solution is titrated with the rodanin-CN sample. Rodanin-CN sample is yellow; while adding the $AgNO_3$ solution the moment the sample color turns into red, it means all the CN bonded with the $AgNO_3$. 1 cc $AgNO_3$, bonds with 2,5 mg CN, with this ratio it is possible to measure the CN amount in the samples from the $AgNO_3$ decrease.

Moreover, methodology for the ion flotation of KCN is just same as the NaCN, both technique, reagents and the amount of the contents. The purpose is to bond ionically the cationic surfactant with the CN^- in the solution and carry them to the froth. For safety pH is between 10-10,5 as always to avoid HCN occurrence, for frother 40 mg/L MIBC is used and again same 3 types of collectors applied to the circuit. Finally, again the titration method with $AgNO_3$ is repeated for analyzing the amount of CN.

Figure 9: The yellow color of Rodanin before changing color.

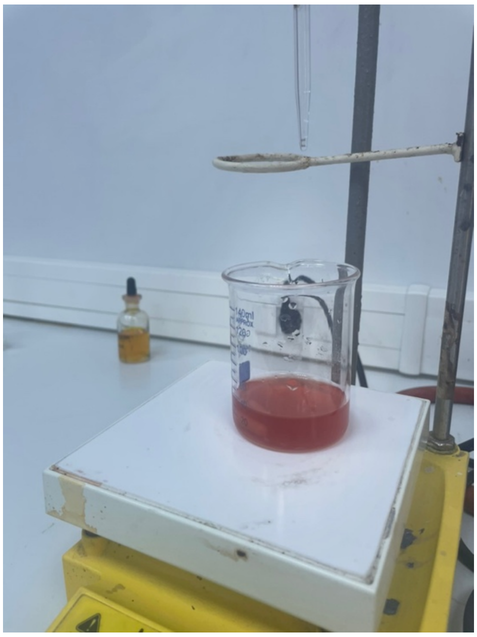


Figure 10: In titration process rodanin sample changes colors when the process is completed.

On the other hand, for ferricyanide a different kind of ion flotation is applied which is also include a precipitation step that is why this method is called ion-precipitate flotation. The purpose of this experiment is to remove the $\mathrm{Fe(CN)_6}^{3-}$ complexes away from the solution by floating them to the froth phase. However, these complexes are negatively balanced and chemically stable, that is why it is hard to carry them with classic "ion + surfactant" technique. To fix this problem, $\mathrm{Fe(CN)_6}^{3-}$ ions are bonded with positive metal ions such as Cu^{2+}, $\mathrm{Fe}^{2+}, \mathrm{Zn}^{2+}$ to form a complex which is not capable of dissolving in water. Then, these precipitants are covered with cationic surfactants and connects to the bubbles of the froth and collected there. The system that is applied in here starts with preparing 1150 mL water and 575 mg $K_3[\mathrm{Fe(CN)_6}]$ which will be dissolved in it. pH has to be kept around 10-11 to avoid HCN occurrence. After this stage, to precipitate ferricyanide, addition of $\mathrm{FeSO_4.7H_2O}$ is done for Fe^{2+} requirement. The required Fe^{2+} mol equals to 1,92 mmol (stochiometric calculations: $K_3[\mathrm{Fe(CN)_6}]$ (M = 329,24 g/mol). n(ferricyanide) = 0,575 g / 329,24 $\mathrm{g{\cdot}mol^{-1}}$=

1.746×10^{-3}mol. C = 1,746 mmol / 1,150 L=1,52 mM $Fe(CN)_6{}^{3-}$ 1,746 mmol x 1,1= 1,92 mmol). And the amount of the $FeSO_4.7H_2O$ is 0,53 g (M=278,01 g/mol). After this addition it has to be stirred for 5 minutes, and 3 types of collectors are used separately in each experiment.

These are: Cetyltrimethylammonium Bromide (CTAB), Hexadecyltrimethylammonium Bromide (HTAB), and Octadecyltrimethylammonium Bromide (OTAB). Amount of collector's effects are tested. Respectively 1,45 mg, 2 mg, and 3 mg of collector is used for each experiment, and for frother 40 mg/L MIBC is used and again (Zhang, Cao, Peng, Tian, Barvor, 2020; Bucsh, Spottiswood, and Lower, 1980). This time titration method for CN analysis must be different from the previous experiments, because ferricyanide can not directly titrated with $AgNO_3$. The reason for that is, $AgNO_3$ can only connects with free CN^- ions. However, in ferricyanide bonds with CN^-ions inside the complex, it has to be liberated. For this experiment, iodometric titration without acid is more suitable. Ferricyanide makes I_2 from reacting with I^-. After that by titrating the I_2 with $Na_2S_2O_3$, the result shows the mol of ferricyanide from the stochiometric calculations.

Reactions are:

1. $2(Fe(CN)_6)^{3-} + 2I^-$ -> $2(Fe(CN)_6)^{4-} + I_2$
2. $I_2 + 2S_2O_3^{2-}$ -> $2I^- + S_4O_6^{2-}$

It is clearly seen that, the mol of thiosulfate is equal to the ferricyanide's mol.

4.4.Test Results

	NaCN	KCN	$K_3[Fe(CN)_6]$
1,45 mg CTAB	61,4%	65,8%	51,3%
2 mg CTAB	70,1%	73,7%	66,2%
3 mg CTAB	76,35%	76,45%	72,4%
1,45 mg OTAB	45,25%	53,5%	35,35%
2 mg OTAB	61,4%	68,3%	54,85%
3 mg OTAB	68,65%	71,2%	58,15%
1,45 mg HTAB	62%	65,5%	70,5%
2 mg HTAB	70,5%	74%	73,5%
3 mg HTAB	75,2%	76,3%	79,6%

Table 7: Recovery rates of cyanide for each experiment.

- Recovery (%) = ((Cinitial-Cfinal)/Cinitial) x 100.
- Cfinal is measured from the float.

5. CONCLUSION

In summary, it is undeniable that mining industry does have wastes like all the other industrial processes. In this thesis, the main focus is on the wastewaters which includes cyanide, and the proposed solution is ion flotation. Beside ion flotation conventional precipitation techniques are often used reliably, but in particular concepts ion flotation can be considered as an innovative option comparing to the other methods. Considering the process duration, efficiency, simplicity, and financially suitability this technique very significant among others. In this thesis work, different types of cyanide combinations (NaCN, KCN, $K_3[Fe(CN)_6]$) are experimented with different types of collectors (CTAB (Cetyltrimethylammonium Bromide), HTAB (Hexadecyltrimethylammonium Bromide), OTAB (Octadecyltrimethylammonium Bromide)) in ion flotation circuit and samples are taken from each experiment analyzed by titration method. The results clearly show remarkable recovery rates of the cyanide ions. That is why ion flotation method can be considered as an effective technique for remediating waste waters in mining plants, especially in gold mining, because cyanide is a major part of gold processing as it is explained before in this thesis work.

Figure 11: Ion flotation process scenes from Istanbul Technical University laboratory.

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