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Faculty of Technology

Process and Product Development

**COMPARISON OF CYANIDE AND THIOSULPHATE LEACHING
FOR GOLD PRODUCTION
(A Literature Review)**

by

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TABLE OF CONTENTS

1 INTRODUCTION	5
2 GOLD ORES	6
2.1 Complex Ores and Carbonaceous (Preg-Robbing) Ores	7
2.2 Classification of Gold Ores	8
3 PRETREATMENT OF CONCENTRATE	9
4 LEACHING CHEMISTRY	10
4.1 Cyanidation	10
4.1.1 Gold Dissolution.....	10
4.1.2 Cyanide Consumption	11
4.1.2.1 Cyanide Consumption in Competitive Reactions.....	12
4.2 Thiosulphate Leaching	13
4.2.1 Thiosulphate Consumption.....	15
4.2.2 In Situ Generation and Regeneration of Thiosulphate	17
5 LEACHING KINETICS	19
5.1 Factors Affecting Gold Cyanidation Phenomena	19
5.1.1 Effect of Pretreatment.....	19
5.1.2 Effect of Oxygen	19
5.1.3 Effect of Cyanide Concentration	20
5.1.4 Effect of pH	20
5.1.5 Effect of Temperature.....	21
5.1.6 Effect of Particle Size	21
5.1.7 Effect of Agitation	22
5.1.8 Effect of Pressure	22
5.1.9 Effect of Slurry Density.....	22

5.1.10 Effect of Foreign Ions	22
5.1.10.1 <i>Effect of Sulfide Minerals</i>	22
5.1.10.2 <i>Effect of Copper Ions</i>	23
5.1.10.3 <i>Effect of Lead Ions</i>	23
5.2 Factors Affecting Thiosulphate Gold Leaching Phenomena	24
5.2.1 Effect of Pretreatment.....	24
5.2.2 Effect of Thiosulphate	24
5.2.3 Effect of Ammonia	25
5.2.4 Effect of Copper	25
5.2.5 Effect of Oxygen	25
5.2.6 Effect of pH	26
5.2.7 Effect of Temperature.....	26
5.2.8 Effect of Agitation Speed	26
5.2.9 Effect of Pulp Density	27
5.2.10 Effect of Impurities.....	27
5.2.10.1 <i>Effect of Sulfite, Manganese, Sulfur, Lead and Zinc</i>	27
5.2.10.2 <i>Effect of Hematite and Pyrite</i>	27
6 GOLD RECOVERY FROM LEACHING LIQUORS.....	30
6.1 Carbon Adsorption	30
6.2 Precipitation	31
6.3 Solvent Extraction.....	32
6.4 Electrowinning	32
6.5 Resin Adsorption.....	32
7 ENVIRONMENTAL AND SAFETY ASPECTS	34
7.1 Environmental Impacts of Cyanide.....	34
7.1.1 Cyanide Spill Accident in Baia Mare, Romania	34

7.2 Treatment, Recovery and Destruction of Cyanide from Mine Waters	37
7.2.1 Activated Carbon Adsorption.....	37
7.2.2 Ion-Exchange Resins	37
7.2.3 Alkaline Chlorination	37
7.2.4 Biological Treatment	38
7.2.5 Caro's Acid.....	38
7.2.6 INCO Process	39
7.2.7 Aqueous Discharges to Receiving Waters from Cyanidation Process	39
7.3 Safety Aspects of Cyanide	41
7.3.1 Cyanide Poisoning and First Aid.....	41
7.4 Environmental and Safety Aspects of Thiosulphate	42
8 CONCLUSIONS	44
REFERENCES	45

1 INTRODUCTION

The conventional cyanidation process in gold leaching has been used since 1887. It is currently the main gold leaching process in the world. However, gold cyanidation process has serious environmental risks if an accident occurs in the process because of the toxicity of cyanide. After some serious cyanide accidents some countries have campaigned to ban cyanide in gold mining industry. Political alignments and concern about environment have been the reasons to find good and less-toxic alternatives to cyanide. In this literature review one promising alternative lixiviant, thiosulphate, has been considered along with cyanide for gold leaching. These two lixiviants have been compared based on the information available in scientific literature.

Thiosulphate leaching can be considered as a non-toxic process. It has its own pros and cons which have been discussed in this work. The topics of this work are gold ores and their suitability for leaching processes, pretreatment of concentrate, leaching chemistry and reagent consumption, leaching kinetics, gold recovery from leaching liquors and environmental and safety aspects.

2 GOLD ORES

The chemical element gold is a noble metal and its symbol is Au. Gold belongs to the same group as silver and copper in the periodic table. It is usually found to be associated with these metals in rocks. The average concentration of gold in earth's crust is 0.005 g/t, for silver it is 0.07 g/t and for copper 50 g/t (Mardsen and House, 1992).

According to Vaughan (2004) there are about 30 gold minerals. However, most of these have only little or no value in gold processing. The principal gold minerals are the native metal gold, electrum (Au-Ag tellurides), aurostibite (AuSb_3), maldonite (Au_2Bi), and auricupride (AuCu_3). Except gold and electrum, these other minerals in gold ores cause severe processing problems and gold losses.

Gold ores can be divided into free milling and refractory types. The former are easy to treat by cyanidation process and they give good gold recoveries without pretreatment, over 90%, whereas the latter are difficult to treat and give gold recoveries less than 90% and in some cases less than 50% in cyanidation process. There are also two other terms to describe gold ores that are difficult to treat, i.e. are preg-robbing ores and complex ores.

Refractory ores can be categorized as follows:

- (a) non-refractory or free milling, with over 95% gold recovery,
- (b) mildly refractory, with 85-95% recovery,
- (c) moderately refractory, with 50-80% recovery and
- (d) highly refractory, with under 50% recovery.

Research on refractory gold ores has shown that existence of submicroscopic gold particles is the main cause for refractory ores. However, submicroscopic particles is not the only cause. Gold ores that contain high levels of Au-Ag tellurides have poor solubility in cyanide. Very finely grained inclusions of native gold in sulfides, where the size of gold particles is less than about 10 μm and gold is therefore difficult to liberate, are often refractory. Some ores have more than one cause for their refractory behavior. For all of these refractory ores gold is locked within the ore in the sense that cyanide solution is unable to access the gold chemically or physically.

2.1 Complex Ores and Carbonaceous (Preg-Robbing) Ores

According to Vaughan (2004) complex ores are ores in which the gold is readily available for leaching but the gangue mineralogy in some way interferes with cyanidation process. The gangue minerals consume cyanide and oxygen in solution or they re-adsorb gold from solution. Ores that contain cyanide and oxygen consumers are mostly in practice copper-gold ores. The most difficult copper-gold ores to treat are near-surface oxide and supergene ores, which contain copper oxides, carbonates, metallic copper and secondary copper sulfides.

Many gold ores contain pyrrhotite which is easily oxidized and thereby consumes oxygen from leach solution. Besides copper minerals and pyrrhotite, other minerals that consume cyanide, oxygen or lime are arsenopyrite, realgar, orpiment and stibnite. The two last ones are the most reactive and may cause considerable processing problems.

Carbonaceous ores are difficult to treat because fine-grained carbonaceous material in ores adsorbs gold from pregnant leach solution. A major problem of such ores is to determine how much gold recovery is lost because of preg-robbing and how much is lost because of refractory sulphides. According to Nanthakumar *et al.* (2007) when both sulphides and carbonaceous matter are present then the ore is classified as a double refractory ore and it requires pretreatment before leaching.

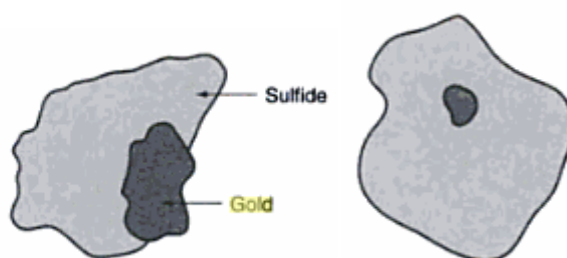


Figure 1 On the left readily liberated free milling gold ore particle and on the right gold grain enclosed in pyrite or sulfide (Mardsen and House, 1992).

2.2 Classification of Gold Ores

Oraby (2009) classifies gold ores in seven categories as presented below:

1. Free milling ores: from which cyanidation can extract 95% of the gold when the ore is ground to a size of 80% under 75 μm . For example palaeoplacer and quartz vein gold are the two main classes of free milling ores.
2. Oxidized ores: the ore material is in oxidized form in these ores. The degree of gold liberation is increased by oxidation degree. For example iron oxides ores such as hematite, magnetite, goethite and limonite are the most common oxidized ores.
3. Iron sulfides: these sulfides hinder liberation of gold in leaching. The behavior of the iron sulfides affects process selection and operation conditions. Pyrite, pyrrhotite and marcasite are the most common iron sulfide minerals.
4. Arsenic sulfides: if gold is associated with arsenic sulfide it belongs to this class. Arsenic sulfides such as arsenopyrite have a negative effect in gold leaching.
5. Copper sulfides: ores that contain gold associated with copper sulfide minerals belong to this class. Chalcopyrite and chalcocite are the main copper minerals and they have a detrimental effect in gold leaching.
6. Tellurides: these are gold minerals that have economic significance as metallic gold and gold-silver alloys. The most important tellurides are calverite, petzite, hessite, krennerite and maldonite.
7. Carbonaceous ores: these are gold ores that contain carbonaceous components. They adsorb dissolved gold during cyanidation and therefore reduce gold extraction. Oxidative pre-treatment methods are needed prior to cyanide leaching.

According to Grosse *et al.* (2003) in most of the refractory ores, cyanidation is unable to leach significant quantities of gold without consuming excessive quantities of reagents. Thiosulphate is a more effective lixiviant of preg-robbing and high-copper ores than cyanide because ammoniacal thiosulphate leaching is less sensitive than cyanidation to contamination by unwanted cations.

3 PRETREATMENT OF CONCENTRATE

Many minerals have a detrimental effect on gold leaching. These minerals may dissolve in alkaline cyanide or thiosulphate solution and consume reagent and oxygen. Certain sulfide minerals are characteristically associated with gold, and the most important are pyrite, chalcopyrite, pyrrhotite, galena and arsenopyrite (Habashi, 1999). All sulfide minerals contain sulfide (S^{2-}) anion.

Before leaching the gold, ore must be crushed and grinded into small particles, usually particle size varies between 30 and 180 μm . Free milling ores are ready for leaching after crushing and grinding whereas refractory ores need pretreatment. It is important to pretreat a refractory ore before leaching to achieve better gold extraction. Pretreatment methods are for example chemical blanking, roasting, chlorination, bio-oxidation, pressure oxidation, chemical oxidation and ultrafine grinding (Nanthakumar *et al.*, 2007; Celep *et al.*, 2011).

If gold ore contains pyrite, the pyrite should be oxidized before leaching. Li *et al.* (2006) reported that pre-oxidation of pyrite containing gold ore increased gold recovery from 20% to 70%. At the same time cyanide consumption decreased from 2.5 kg/t ore to 1.5 kg/t ore.

Nanthakumar *et al.* (2007) tested microwave pretreatment with conventional roasting for a double refractory gold ore where both sulphides and carbonaceous matter were present. Roasting temperatures of 650°C or over were required to convert the pyrite to hematite and to eliminate the organic carbon. For both conventional and indirect microwave roasting preg-robbing was eliminated and gold recoveries of over about 98% were achieved after cyanide leaching in 2 hours. The relatively low specific energy consumption for microwaving indicates that this method has considerable potential.

Feng and van Deventer (2010) studied oxidative pretreatment in thiosulphate leaching of sulphide gold ores. The sulphide minerals were partially decomposed in the pretreatment process and thiosulphate consumption was reduced during leaching. Gold extraction in 0.8 M ammonia and 0.1 M thiosulphate solution after 24 h increased from 69% without pretreatment to 81%, 84%, 90% and 94% after 1, 3, 7 and 22 h of pretreatment.

4 LEACHING CHEMISTRY

4.1 Cyanidation

Gold cyanidation is the main gold leaching process and it has been used over century. Cyanide is relatively low cost and effective lixiviant for gold dissolution; gold is dissolved in a very dilute solution of sodium cyanide (NaCN). The main concern of cyanidation is its high toxicity.

Cyanide salts, like sodium cyanide, potassium cyanide (KCN) and calcium cyanide [Ca(CN)₂] are used as sources of cyanide in leaching. Cyanide salts dissolve in water and form metal cation and free cyanide ions (CN⁻) as presented in Eq. (1):

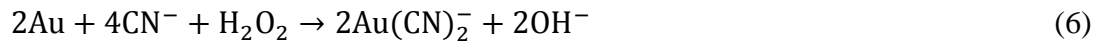
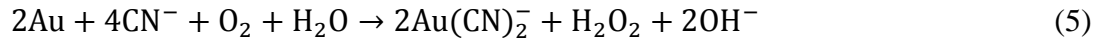


Cyanide ions hydrolyze in water and form hydrogen cyanide (HCN) and hydroxyl (OH⁻) ions. In alkaline solution at pH about 9.3, cyanide exists both as hydrogen cyanide and as free cyanide ions, half as hydrogen cyanide and half as free cyanide ions. Higher pH than 9.3 increases the amount of free cyanide in solution. Hydrogen cyanide and free cyanide can be oxidized with oxygen to form undesirable cyanate (CNO⁻) which does not dissolve gold and hence reduces the free cyanide concentration (Srithammavut, 2008).

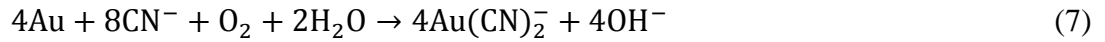


4.1.1 Gold Dissolution

The dissolution of gold is an oxidation-reduction process in which cyanide ion forms a strong complex with Au⁺ ion. The stable complex ion is [Au(CN)₂]⁻. The overall reaction, where oxygen is reduced and hydrogen peroxide is formed to be the oxidizing agent in the second step, is presented in Eq. (5):



Summation of these two equations is presented in Eq. (7):



4.1.2 Cyanide Consumption

As shown in the reaction equations above, for every mole of metal dissolved, 2 moles of cyanide is consumed, and for every 2 moles of metal dissolved, 1 mole of oxygen is consumed. According to this stoichiometry, 1 mole of oxygen and 4 moles of NaCN should be present in solution. At room temperature and atmospheric pressure, 8.2 mg O₂ is dissolved in 1 liter of water. This corresponds to oxygen concentration to 0.27×10^{-3} mol/L. Accordingly, gold dissolution should occur at a concentration of NaCN equal to $4 \times 0.27 \times 10^{-3} \times 49 = 0.05$ g/L or 0.005 %. Gold dissolves in very dilute sodium cyanide solutions.

The rate of gold dissolution grows linearly with increasing cyanide concentration until a maximum is attained. Increase of cyanide has no effect after the maximum is reached (Habashi, 1999).

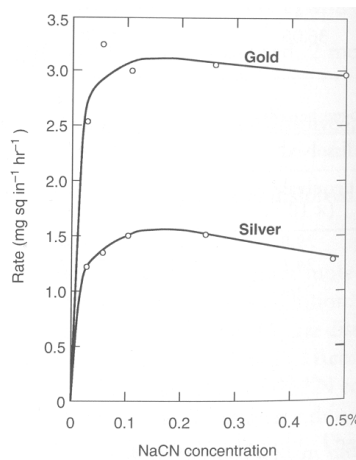


Figure 2 Effect of cyanide concentration on the rate of dissolution of gold in air-saturated solution (Habashi, 1999).

If excess cyanide is added while the oxygen content of the solution is below the theoretical value, this excess cyanide is wasted (Habashi, 1999). It is reported that high pH level results in lower cyanide consumption as shown in Figure 3.

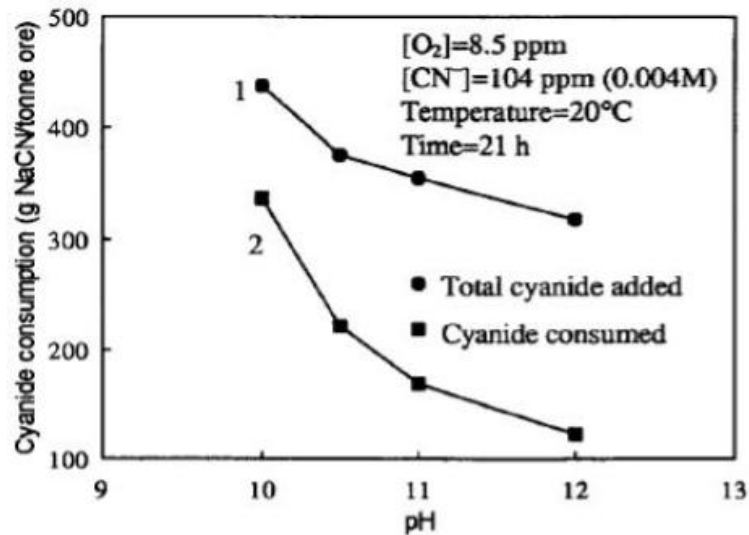


Figure 3 Effect of pH on cyanide consumption (Ling *et al.*, 1996).

In agitation leaching, cyanide consumption typically varies for free milling ores from about 0.25 to 0.75 kg/t and if there are cyanide consuming minerals then cyanide consumption varies from about 1 to 2 kg/t. In heap leaching cyanide consumption is lower than in agitation leaching. For non-refractory ores cyanide consumption typically ranges from 0.1 to 0.5 kg/t. Intensive cyanidation leaching consumes the most cyanide of these three leaching techniques. Cyanide consumption in this intensive leaching varies from 5 to 25 kg/t (Mardsen and House, 1992).

4.1.2.1 Cyanide Consumption in Competitive Reactions

Also other minerals and elements besides gold are dissolved in alkaline cyanide solution. Usually these competitive reactions consume cyanide and thus reduce the efficiency of gold leaching. For example iron and copper sulfides in solution have harmful effects because they are also dissolved and produce metal cyanide complexes and sulfur containing species which consume cyanide and oxygen.

For example, the most reactive iron sulfide, pyrrhotite, reacts with cyanide in alkaline cyanide solution and forms thiocyanate as presented in Eq. (8):



and further oxidation produces Fe(III) cyanide:



The $\text{Fe}[\text{CN}]_6^{4-}$ complex is stable in the pH range that is used in cyanidation.

Also copper minerals, such as chalcocite (Cu_2S) and cuprite (Cu_2O) have high solubility in cyanide solution whereas chalcopyrite (CuFeS_2) has lower solubility. Chalcocite and cuprite consume cyanide and oxygen less than sulfide but the formed species may affect precipitation reactions and overall process efficiency. Pretreatment methods such as pre-aeration, pressure oxidation and roasting are beneficial prior to cyanidation to reduce the cyanide and oxygen consumption (Srithammavut, 2008). Li *et al.* (2006) reported that pre-oxidation of pyrite containing gold ore increased gold recovery from 20% to 70%. At the same time cyanide consumption decreased from 2.5 kg/t ore to 1.5 kg/t ore. Kondos *et al.* (1995) reported that too fine grinding of ore increases cyanide consumption and does not improve gold extraction.

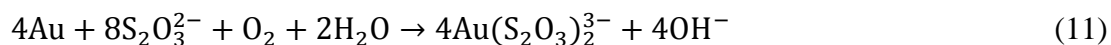
4.2 Thiosulphate Leaching

Because of high toxicity of cyanide good alternatives to cyanide have been searched. One seriously taken alternative is a non-toxic thiosulphate ($\text{S}_2\text{O}_3^{2-}$) (Aylmore and Muir, 2001). Thiosulphate is also kinetically and environmentally one of the most promising alternative to cyanide. Sodium and ammonium thiosulphate are the two main commercial sources of thiosulphate. They are the most common thiosulphate salt forms that are used in research on thiosulphate leaching of gold (Oraby, 2009).

Gold forms stable complex with thiosulphate in an aqueous solution as shown Eq. (10):



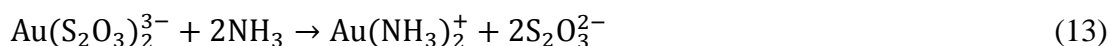
In alkaline thiosulphate solution where oxygen is as an oxidant, the complex redox reaction is shown in Eq. (11).



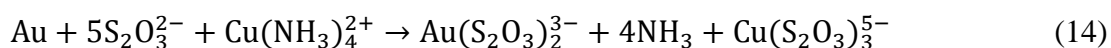
The thiosulphate leaching of gold in the presence of oxygen needs a suitable catalyst because otherwise leaching is very slow. A very efficient catalyst is copper(II) which is used with ammonia that stabilises the copper(II) in solution as the Cu(II) tetra-amine complex as shown in Eq. (12). According to Aylmore and Muir (2001) copper ions in solution can speed up the dissolution of gold even 20 times.



Gold forms stable complexes not only in thiosulphate solutions but also in ammonia solutions. Therefore in ammoniacal thiosulphate solution, both ammonia and thiosulphate can form complexes with gold.



The chemistry of the ammoniacal copper-thiosulphate system is complex and the exact mechanism of gold dissolution and the catalytic action of Cu(II) is not completely understood. The overall dissolution reaction of gold in ammoniacal copper-thiosulphate solution is presented in Eq. (14):



The presence of ammonia is important to stabilise Cu(II) in the solution as the Cu(II) tetraamine ion. The mechanism of gold dissolution in the ammoniacal copper-thiosulphate system is illustrated in Figure 4.

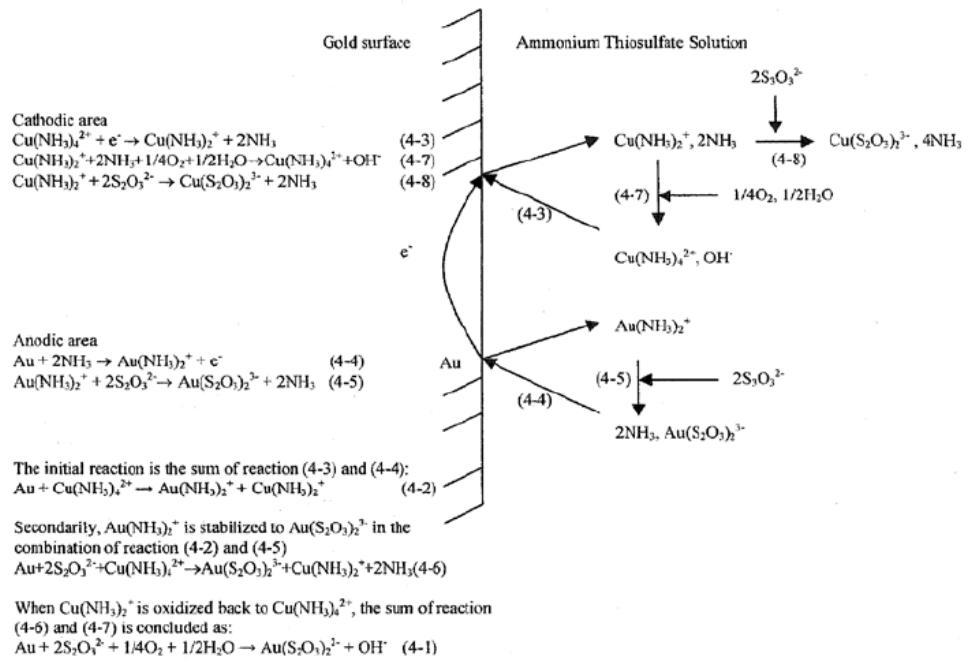


Figure 4 Schematic dissolution mechanisms in ammonium thiosulphate solution on gold surface (Aylmore and Muir, 2001).

4.2.1 Thiosulphate Consumption

Even though thiosulphate leaching has a potential in gold leaching, there is one major problem remaining and that is a high consumption of thiosulphate during gold leaching. Reagent consumption is one of the major factors affecting the feasibility of the process to the actual operation (Yen *et al.*, 2001). High consumption of thiosulphate is mainly caused by its decomposition in solution. Thiosulphate can also be lost with tailings by adsorption onto solids. Losses up to 50% of thiosulphate in ammoniacal thiosulphate solutions which contain copper have been reported (Aylmore and Muir, 2001).

In a research of Xia *et al.* (2003) the influence of pulp density on thiosulphate consumption was studied. It was noted that when pulp density increased from 28.6% to 61.5%, the thiosulphate consumption for 24 hours reduced from 77.9 to 17.4 kg/t.

Xia (2008) studied the effect of some associated minerals on thiosulphate leaching of gold. He used synthetic ore samples that had been prepared by mixing specific high purity minerals into a free-milling quartz gold ore. In the absence of associated minerals thiosulphate leaching of the quartz gold ore was quick. Xia reported that 93% of gold was leached within 3 hours and 7.1 kg/t of ammonium thiosulphate was consumed. The optimum reagent conditions were: 0.2 M ammonium thiosulphate, 0.9 M ammonia and 1.2 mM copper.

Thiosulphate leaching in the presence of iron oxides, such as limonite, magnetite and hematite had no significant impact on thiosulphate consumption. Pyrite, pyrrhotite and arsenopyrite have detrimental effects on gold extraction. Pyrite and pyrrhotite substantially increased the consumption of thiosulphate. Bornite, chalcocite and chalcopyrite have also detrimental effects on gold extraction and they resulted in higher consumption of thiosulphate. Galena and litharge were dissolvable in thiosulphate solution and the gold extraction was largely reduced in the presence of these minerals. Galena reduced thiosulphate consumption while litharge increased.

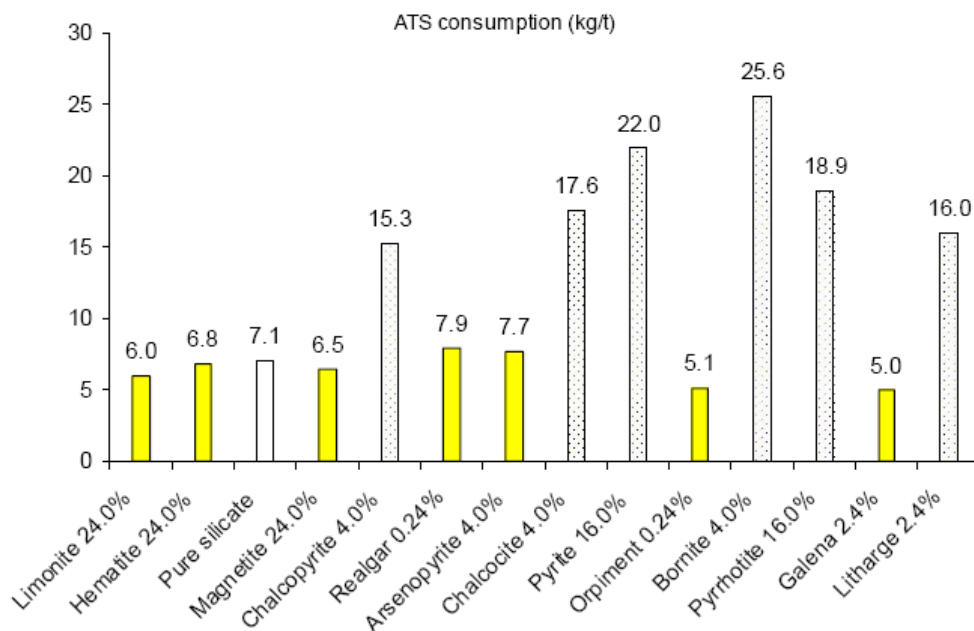


Figure 5 Effect of associated minerals on ammonium thiosulphate (ATS) consumption, the yellow bars represent the non-problematic minerals and the bars filled with dots represent the problematic minerals (Xia, 2008).

According to Feng and van Deventer (2010) oxidative pretreatment of sulphide gold ores partially decomposes sulphide minerals which reduces thiosulphate consumption during leaching. Oraby (2009) has reported that hematite and pyrite have catalytic effect on the decomposition of thiosulphate whereas sulfur species reduce thiosulphate decomposition.

According to Oraby (2009) the range of thiosulphate concentration in researches has varied from 0.05 to 2.0 M. Yen *et al.* (2001) listed leach conditions and thiosulphate consumption that were reported by several investigators.

Table 1 Thiosulphate Leach Conditions and Reagent Consumption (Yen *et al.*, 2001).

Ore Type	S ₂ O ₃ ²⁻ , M	NH ₃ , M	Cu ²⁺ , M	pH	% Au Recovery	S ₂ O ₃ ²⁻ kg/t Consum.	Investigator
S ²⁻ , Mn	1.21	0.57	0.02	7-9	95	4	Kerley et al. (1981)
Zn-Pb, S ²⁻	0.12-0.5	0.75		7-9	90	23	Block et al. (1985)
MnO ₂	2	4	0.1	10	90	50%	Zipperian et al. (1998)
Carbon	0.71	3	0.15	10.5	73	15-19%	Hemmati et al. (1989)
Copper	1-22%	1.4-8.9%	0.05-2%		93.9	40	Caixia et al. (1991)
S ²⁻ , Cu	0.2-0.3	2-4	0.047	10-10.5	95	4.8	Cao et al. (1992)
Copper	0.2	0.09	0.001	11	90	2	Langhans et al. (1992)
S ²⁻ , C	0.1	0.1	0.005	9	51-66	5.2-8.9	Wan et al. (1997)
Copper	0.3	3	0.01	9.7	90	17	Yen et al. (1999)

4.2.2 In Situ Generation and Regeneration of Thiosulphate

It is also possible to generate in situ or regenerate thiosulphate from sulfidic gold ores. Added sulfite reacts with elemental sulfur which is generated from sulfidic ore as a by-product and produces the thiosulphate ion. This thiosulphate is generated in situ and is available for leaching (Choi *et al.*, 2009, U.S. Pat. No. 7,572,317 B2). Thiosulphate can be

regenerated from spent thiosulphate solution reacting spent thiosulphate solution with sulfide to produce elemental sulfur and regenerated thiosulphate solution. After this elemental sulfur is separated from regenerated thiosulphate solution and biologically reduced to sulfide. Sulfide is returned back to spent thiosulphate solution (Buisman and Picavet, 2004, U.S. Pat. No. 0151657 A1).

5 LEACHING KINETICS

According Aylmore and Muir (2001) in thiosulphate leaching of gold the gold dissolution rates can be faster than in conventional cyanidation. It is reported that in preg-robbing ore types 73% of gold was extracted in 4 hours by thiosulphate leaching whereas cyanidation extracted gold only 10% in over 24 hours. In the case of leaching sulfide ore thiosulphate leaching required only 1 hour to achieve 90% gold recovery whereas cyanidation required at least 24 hours to extract 50% of the gold.

5.1 Factors Affecting Gold Cyanidation Phenomena

Many variables affect gold leaching and therefore leaching parameters have been studied by many researchers to optimize the cyanidation process. Variables such as concentrations of oxygen and cyanide, pH, particle size, temperature etc. affect on the gold dissolution rate, gold extraction and cyanide consumption (Srithammavut, 2008).

5.1.1 Effect of Pretreatment

A right pretreatment of refractory ore before leaching gives better gold extraction and decreases reagent consumption. Used pretreatment methods are for example chemical blanking, roasting, chlorination, bio-oxidation, pressure oxidation and chemical oxidation (Nanthakumar *et al.*, 2007; Celep *et al.*, 2011).

5.1.2 Effect of Oxygen

Oxygen is one of the key reagents in gold cyanidation because it is reduced in the cathode and reduction of oxygen is determined by the concentration of oxygen. Oxygen may be supplied to the system by air, pure oxygen or as enriched air bubbles. Small oxygen bubbles dispersed in the slurry give sufficient oxygen concentration for gold dissolution. With right amount of oxygen in the solution, higher gold recovery, shorter retention time and lower cyanide consumption can be achieved. Different mineralogical compositions need different amount of oxygen. Dissolved oxygen concentration has no significant effect on cyanide consumption, but faster leaching kinetics has been observed by using higher

dissolved oxygen concentrations (Srithammavut, 2008). Any side reactions in which the cyanide solution is deprived of its oxygen content will cause a decrease in the rate of gold leaching (Habashi, 1999).

5.1.3 Effect of Cyanide Concentration

Gold extraction increases with increasing cyanide concentration. When maximum is achieved the excess cyanide has no effect. Maximum cyanide concentration is 0.075% KCN or 0.06% NaCN, equivalent to 600 ppm (Srithammavut, 2008).

5.1.4 Effect of pH

The alkalinity of cyanide solutions is important to achieve high dissolution rates. pH usually ranges from 11 to 12 (Habashi, 1999). The right pH value is maintained by the addition of lime (CaO). Increasing pH reduces gold dissolution rate because the adsorption of OH^- ion onto gold surface decreases the surface available for cyanide leaching. In Figure 6 it is seen that gold extraction is reduced in high pressure system when pH increases. After all, every ore type and leaching system has the particular optimum pH (Srithammavut, 2008).

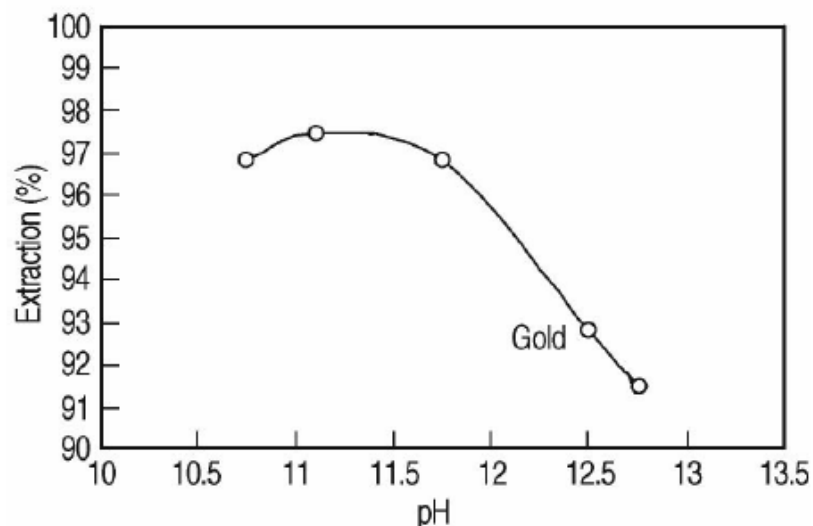


Figure 6 Effect of pH on gold extraction. Condition: 20% solid, 0.6 MPa, 300 min⁻¹, 80 °C, 1% NaCN, 1 h (Parga *et al.*, 2007).

5.1.5 Effect of Temperature

According to Habashi (1999) an increase in the temperature increases the rate of dissolution. On the other hand, increasing temperature decreases the oxygen content of the solution. As seen in Figure 7 the optimum temperature is approximately 85 °C.

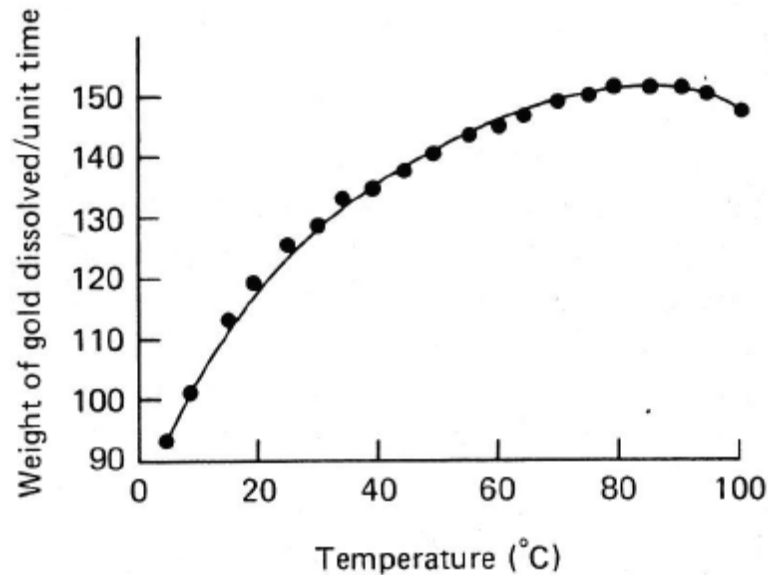


Figure 7 Effect of temperature on gold dissolution rate in aerated 0.25% KCN solution (Mardsen and House, 1992).

5.1.6 Effect of Particle Size

The average size of grinded ore particles is usually 30 - 180 μm . Ling *et al.* (1996) reported that smaller particle size can improve gold dissolution rate because smaller particle size provides larger contacting surface area between solid and liquid. Also the contrary has been reported by Kondos *et al.* (1995). In their research it was found that finer grinding increases cyanide consumption and does not improve gold extraction. The rate of dissolution may decrease with decreasing particle size due to the increased rate of reagent consumption and competing side reactions.

5.1.7 Effect of Agitation

According to Habashi (1999) gold leaching is a diffusion-controlled process. Therefore, the rate of dissolution increases with increased agitation. Gold dissolution rate depends on the diffusion layer thickness and mixing characteristics of the bulk solution. All the particles should be suspended in the slurry by sufficient agitation (Srithammavut, 2008).

5.1.8 Effect of Pressure

The solubility of gas increases when pressure increases. Hence, pressure can improve gold dissolution. High pressure with appropriate temperature improves gold extraction (Shrithammavut, 2008).

5.1.9 Effect of Slurry Density

Typical slurry density in leaching varies between 35% and 50% of solids. This depends on factors such as the specific gravity of solids, particle size and the presence of minerals affecting slurry viscosity, for example clay. Mass transfer is maximized when slurry density is low (Shrithammavut, 2008).

5.1.10 Effect of Foreign Ions

5.1.10.1 Effect of Sulfide Minerals

Most of sulfide ions have negative effect on gold dissolution since they passivate the surface of gold and consume cyanide and oxygen. An exception is galena which has increased gold dissolution under atmospheric condition at 8 ppm O₂. When the O₂ concentration increases to 32 ppm the gold dissolution rate is found to be almost zero, as seen in Figure 8 (Shrithammavut, 2008).

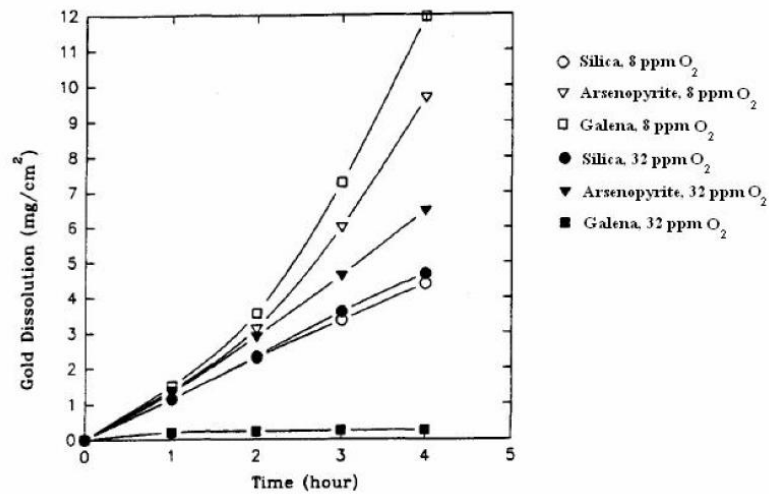


Figure 8 Effect of arsenopyrite and galena on gold dissolution (Lui and Yen, 1995).

5.1.10.2 Effect of Copper Ions

Copper minerals can dissolve and form a variety of copper cyanide complexes such as CuCN , $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ at convenient pH. Copper dissolution has detrimental effect on gold dissolution since it consumes cyanide and oxygen (Shrithammavut, 2008).

5.1.10.3 Effect of Lead Ions

Addition of lead solution for instance lead nitrate, $\text{Pb}(\text{NO}_3)_2$, can enhance gold leaching kinetics. It is observed that lead nitrate activates the surface of passivated gold particle and prevents the formation of passivation film on gold surface. In Figure 9 is illustrated the effect of adding lead nitrate on gold ore with pyrite, pyrrhotite and chalcopyrite (Shrithammavut, 2008).

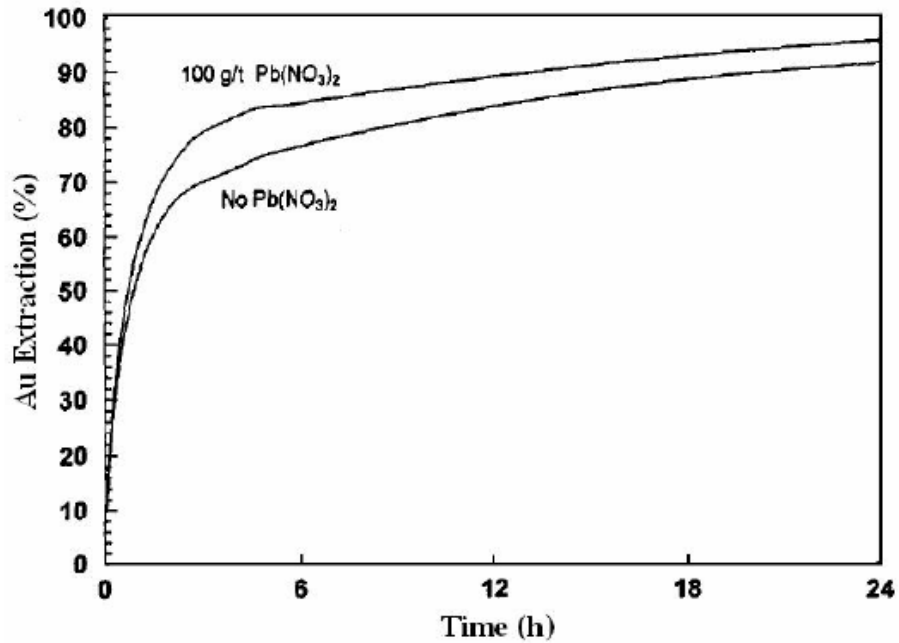


Figure 9 Effect of lead nitrate addition on the leaching of gold ore with pyrite, pyrrhotite and chalcopyrite (Deschénes *et al.*, 2000).

5.2 Factors Affecting Thiosulphate Gold Leaching Phenomena

Many variables affect thiosulphate leaching and its kinetics. The most studied variables are thiosulphate, copper(II), ammonia and oxygen concentration, agitations speed, temperature, pH and the effect of impurities (Oraby, 2009).

5.2.1 Effect of Pretreatment

It is important to pretreat a refractory ore before leaching to achieve better gold extraction. Feng and van Deventer (2010) have reported that oxidative pretreatment for sulphide gold ore reduced thiosulphate consumption during leaching.

5.2.2 Effect of Thiosulphate

Thiosulphate concentration is an important variable since increasing thiosulphate concentration increases the gold leaching rate. Only 10% gold extraction is reported in the absence of thiosulphate but in the presence of copper sulfate and ammonia. Too low

thiosulphate concentration reduces the rate of gold leaching due to both oxidation of thiosulphate and the reduction of copper(II) amine to copper(I) thiosulphate. The range of thiosulphate concentration is from 0.05 to 2.0 M in these researches. An optimum thiosulphate concentration depends on the type of gold ore (Oraby, 2009).

5.2.3 Effect of Ammonia

Ammonia is an important reagent in thiosulphate leaching of gold. Ammonia has two functions in thiosulphate solution. First it reacts with gold to form $\text{Au}(\text{NH}_3)_2^+$, which then reacts with $\text{S}_2\text{O}_3^{2-}$ to form $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ in the anodic reaction, as shown in Eq. (15):



Secondly, ammonia stabilizes the cupric ion by reacting with it to form a cupric amine complex. The cupric amine complex is a strong oxidizing agent.

It is reported only 9% gold recovery with thiosulphate in the absence of ammonia. Moreover ammonia prevents gold passivation and the dissolution of iron oxides, silica, silicates and carbonates which are the most common gangue minerals in gold ores (Oraby, 2009).

5.2.4 Effect of Copper

Copper(II) ion has an important role in the thiosulphate leaching of gold since it acts as an oxidant for gold and as a catalyst. Copper ions in solution can speed up the dissolution of gold by 20 times (Aylmore and Muir, 2001). It is reported only 34% gold extraction in the absence of cupric ion. When cupric ion was added, 76% extraction was achieved. Increasing copper(II) concentration enhances gold dissolution rates, but it also has a negative effect on thiosulphate oxidation (Oraby, 2009). In Arima's (2003) research the best gold leach rate was achieved when the copper sulfate concentration was 0.01 M.

5.2.5 Effect of Oxygen

Oxygen is required to convert copper(I) to copper(II) for further gold leaching (Aylmore and Muir, 2001). In the absence of oxygen copper(I) ions cannot return to the copper(II)

state. This causes copper sulfide precipitation from solution. Oxygen oxidizes thiosulphate, therefore oxygen concentration should be controlled in thiosulphate solutions to prevent decomposition of thiosulphate. It is noted that gold leaching is very slow without oxygen added to the leach solution and only small amounts of oxygen can enhance the gold dissolution rate (Oraby, 2009).

5.2.6 Effect of pH

The correct pH of thiosulphate solutions is important to ensure the presence and the stability of reagents and concentrations in the system. Thiosulphate leaching pH must be alkaline; pH has varied in different studies between 8.5 and 12. At low pH values thiosulphate decomposes into sulfur and polythionate components. Sulfur may coat the surface of gold and thus stop the process of gold dissolution. The dissolution of gold is very poor under pH 9.2 or above pH 12.0. Below pH 9 the Cu(I) triamine complex becomes prevalent and it makes the copper species less effective as a catalyst. The optimum pH value is 10.0 for high gold extraction and lesser thiosulphate consumption (Oraby, 2009).

5.2.7 Effect of Temperature

Temperature has a significant effect on the rate of a leaching process when reaction is chemically controlled as thiosulphate leaching of gold. It is reported that when temperature was increased from 25 °C to 35 °C the gold leach rate was doubled. At high temperatures (55 °C), almost 95% of the gold was leached in one hour. When temperature increases the volatilization of ammonia also increases. Therefore the temperature between 30 °C and 40 °C in thiosulphate system is indeed required to achieve the best results of gold dissolution and to minimize ammonia losses and copper(II) reduction (Oraby, 2009).

5.2.8 Effect of Agitation Speed

In the diffusion controlled reactions the agitation speed has effect, whereas in chemically controlled reactions it has not. Since the thiosulphate leaching of gold is not a diffusion controlled reaction but a chemically controlled one, the agitation speed does not increase the gold dissolution rate (Oraby, 2009).

5.2.9 Effect of Pulp Density

Pulp density is defined as the weight of ore in kilograms in the volume of solution in litres. Navarro *et al.* (2002) reported that 10% pulp density increased the percentage of gold extracted compared to 25 and 40%.

5.2.10 Effect of Impurities

Gold ore is associated with various minerals. These minerals act as impurities in thiosulphate leaching solutions. Most of them reduce gold dissolution rate and increase thiosulphate oxidation, but some can enhance gold dissolution rate (Oraby, 2009).

5.2.10.1 Effect of Sulfite, Manganese, Sulfur, Lead and Zinc

Sulfite has a positive effect in the thiosulphate leaching of gold. Sulfite substantially reduces thiosulphate consumption and inhibits the decomposition of thiosulphate. Free sulfite ions regenerate thiosulphate as shown in Eq. (16).



A small amount of manganese dioxide in the thiosulphate leaching of sulfide bearing gold ores improves both the kinetics and the gold extraction. The addition of manganese dioxide had only little impact on thiosulphate consumption.

Sulfur species have a significant effect on the thiosulphate leaching of gold. Sulfur species increase gold dissolution and reduce thiosulphate decomposition. Lead(II) and zinc(II) ions do not have effect on thiosulphate consumption, but the presence of these ions shows beneficial effects on gold dissolution.

5.2.10.2 Effect of Hematite and Pyrite

Hematite significantly reduces the dissolution of gold. It may be due to coatings which hematite forms on gold surfaces and which would prevent the leach solution from diffusing to the gold surface. Hematite also catalyses the oxidative decomposition of thiosulphate to polythionates in the presence of oxygen.

Pyrite has detrimental effect on gold dissolution in ammoniacal thiosulphate solutions. It is reported that pyrite has a catalytic effect on the decomposition of thiosulphate (Oraby, 2009).

Table 2 The optimum concentrations and leaching parameters in thiosulphate solutions according to various studies (Oraby, 2009).

Author	Optimum conditions	Type of gold
Arslan et al. (2008)	0.5 M $S_2O_3^{2-}$, 1 M NH_3 , 10 mM Cu(II), 20°C, S/L ratio 10%	Gold ore (6.4 g/t Au and 10.4 g/t Ag)
Arima (2003)	0.4 M $S_2O_3^{2-}$, 3 M NH_3 , 30 mM Cu(II), room temperature	Gold ore (16 g/t)
Xia et al. (2003)	0.3 M $S_2O_3^{2-}$, 3 M NH_3 , 30 mM Cu(II), pH 10.2	Copper-bearing ore
Aylmore (2001)	0.8 M $S_2O_3^{2-}$, 4 M NH_3 , 50 mM Cu(II)	Au-Cu sulfide
Jeffrey (2001)	Heap leaching: 0.2 M $S_2O_3^{2-}$, 0.4 M NH_3 , 5 mM Cu(II); Standard gold leaching circuits: 0.4 M $S_2O_3^{2-}$, 0.6 M NH_3 , 10 mM Cu(II)	Gold/Silver disc
Breuer and Jeffrey (2000)	0.2 M $S_2O_3^{2-}$, 0.09 M NH_3 , 1 mM Cu(II), 6.25 mM SO_3^{2-}	Gold disc
Chai (1997)	0.287 M $S_2O_3^{2-}$, 2 M NH_3 , 12 M Cu(II), 60°C, aeration	Gold ore
Muyunda (1996)	0.4 M $S_2O_3^{2-}$, 0.84 M NH_3 , 25 mM Cu(II), 35°C, pH 10.5	Pure gold disc
Abbruzzese et al. (1995)	2 M $S_2O_3^{2-}$, 4 M NH_3 , 0.1 M Cu(II), 25°C	Ore (51.6 g/t Au)
Langhans et al. (1992)	0.1 M $S_2O_3^{2-}$, 0.4 M NH_3 , 10 mM Cu(II), 30°C, pH > 11.4	Low-grade Ore

6 GOLD RECOVERY FROM LEACHING LIQUORS

There are several techniques to recover gold from conventional cyanide leach liquors. These are carbon adsorption, resin adsorption, precipitation, solvent extraction and electrowinning (Grosse *et al.*, 2003). Even thiosulphate is considered to be one of the most promising alternatives to cyanide, it is difficult to recover the gold thiosulphate complex (Oraby, 2009; Aylmore and Muir, 2001). The same processes that are used for cyanide leach liquors have also been applied to recover gold from ammoniacal thiosulphate leach liquors with varying degrees of success (Crosse *et al.*, 2003).

6.1 Carbon Adsorption

Carbon adsorption can be divided into two processes, namely the carbon-in-pulp (CIP) and the carbon-in-leach (CIL). CIP and CIL processes have been widely used since 1970s and they are the dominant gold recovery methods due to their high efficiency, relatively low costs and purity of product (Grosse *et al.*, 2003). The CIP process is more used than the CIL due to its lower costs and higher gold recoveries. Together they account for approximately 44% of world's gold production.

In cyanidation gold leaching the CIP consists of three stages. The first stage is adsorption where the dissolved gold in the pulp is loaded onto activated carbon. After adsorption follows elution where gold is removed from carbon into an alkaline cyanide solution. Lastly, in electrowinning gold is removed from the alkaline cyanide solution by an electrical process and it is deposited on electrodes (Srithammavut, 2008).

Aurothiosulphate $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ has significantly less affinity for carbon than aurocyanide $\text{Au}(\text{CN})_2^-$ anion (Aylmore and Muir, 2001). Carbon adsorption is not therefore as convenient for thiosulphate leaching as it is for cyanidation.

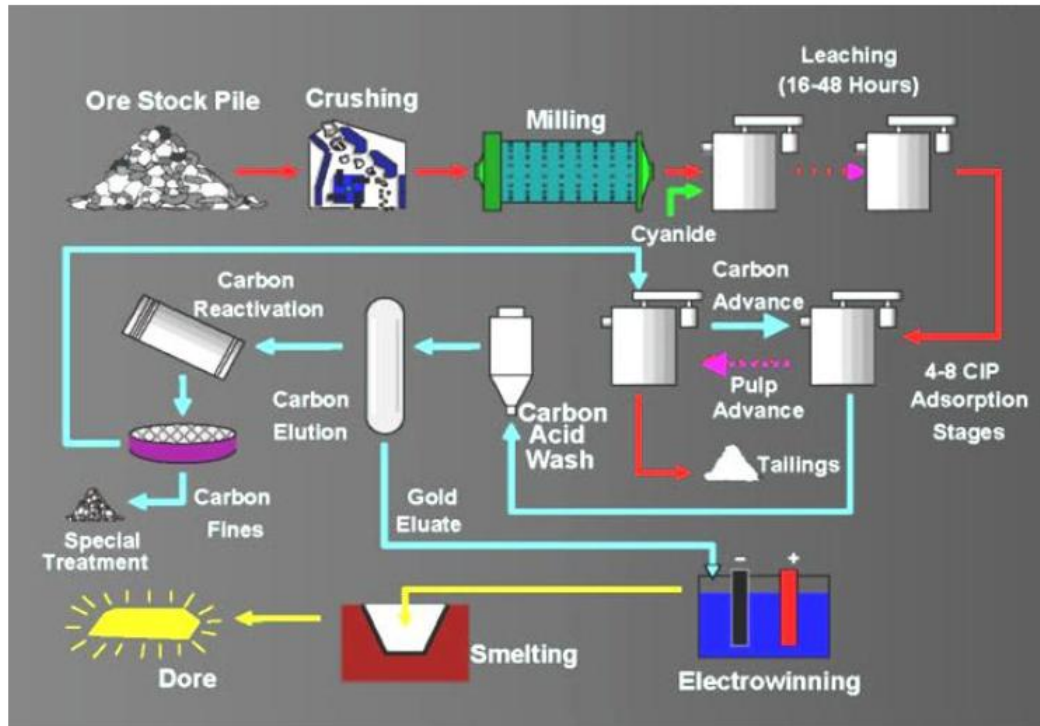
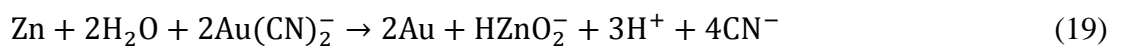
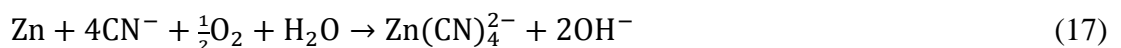


Figure 10 Flow sheet of a CIP plant (Fleming, 2004).

6.2 Precipitation

Precipitation, also known as the Merrill-Crowe process or cementation, is a recovery technique where gold can be recovered from pregnant leach liquor by adding a pulverized metal. The primary mechanism of this recovery technique is the redox reaction between the zero valent base metal grains and the target noble metal gold. The precipitant stoichiometrically displaces gold from the solution as shown in Eq. (17), (18) and (19). The common precipitants are zinc and copper, although iron or aluminium is also sometimes used. The precipitant particles with gold are removed from the solution using a plate and frame filter press (Grosse *et al.*, 2003; Parga *et al.*, 2007).



Many metallic precipitants often have detrimental effect on thiosulphate since they reduce thiosulphate ions and produce unwanted cations, thus complicating the recycling of the leach liquor. Copper is a reasonable choice for thiosulphate leaching since copper ions in thiosulphate liquors may be recycled as leach liquor.

6.3 Solvent Extraction

In solvent extraction, the leach liquor is contacted with a solution of extractant in a water-immiscible organic solvent. The gold complex is partitioned into the organic phase and the other metals remain in the aqueous phase. After this the organic phase may be separated, stripped of gold and returned to the extraction circuit. Diluents such as benzene, kerosene and 1- and 2-octanol have been tested in solvent extraction (Grosse *et al.*, 2003).

6.4 Electrowinning

When direct current is used to recovery gold ions from solutions it is known as electrowinning. Aurocyanide or aurothiosulphate ions in the leach liquor solution will migrate to the cathode and form a metallic deposit.

Copper ions in thiosulphate leach liquors are problematic for electrowinning because they may contaminate the metallic product. Also various oxidation and reduction reactions of thiosulphate take place at the anode and cathode. Therefore, electrowinning is not a viable option for recovery of gold from thiosulphate leach liquors (Aylmore and Muir, 2001; Grosse *et al.*, 2003).

6.5 Resin Adsorption

The use of resin adsorbents for the recovery of gold from leach liquors is a relatively underdeveloped area of hydrometallurgy because of abundance of cheap activated carbon

adsorbents. Resin adsorbents are more expensive than carbon and their application needs the installation of specialized apparatus. Resin adsorption can be divided into Resin-in-Leach (RIL) and Resin-in-Pulp (RIP) techniques (Aylmore and Muir, 2001). In RIL, the adsorbent is added to the ore at the same time as the leaching reagents, whereas in RIP the adsorbent is added after an initial leaching period. The ion exchange resins must be chemically stripped after separation from the leach pulp (Grosse *et al.*, 2003).

In thiosulphate leaching the sorption onto an ion exchange resin is considered to be the only appropriate technique for recovery of gold from commercial thiosulphate leach liquors. The principal difficulty is the competitive adsorption of unwanted anions such as trithionate and tetrathionate with the gold and copper complexes (Oraby, 2009).

7 ENVIRONMENTAL AND SAFETY ASPECTS

According to Oraby (2009) the major environmental problems caused by gold mining are acid mine drainage and air and water pollution from toxic chemicals. Cyanide is a highly toxic chemical and it has detrimental environmental impacts on soil, surface, groundwater and air if it is released to nature. Some severe cyanide spills and mine-related accidents have happened last decades. Because of high toxicity of cyanide there is a need to find less-toxic substitute for cyanide due to environmental and political factors. Thiosulphate is a less toxic alternative to cyanide and it is commonly used as a fertilizer and an indirect and direct human food ingredient.

7.1 Environmental Impacts of Cyanide

Since environmental awareness has increased and severe cyanide accidents happened there is much public concern about the use and toxicity of cyanide around the world. Some countries such as Czech Republic, Argentina, Turkey and some states of USA have campaigned to ban cyanide in mineral processing applications (Duffield and May, 2003).

Environmental monitoring of total cyanide levels in the environment is required in all the mines that utilize cyanide. Most of the hydrogen cyanide (HCN) which is emitted into the atmosphere stays in the lowest part of the atmosphere called troposphere. The environmental degradation of hydrogen cyanide from surface waters is usually occurred through volatilization, biodegradation, hydrolysis and sorption. Aeration and pH affect the volatilization rates of hydrogen cyanide, therefore the pH should be kept over 9.2 so that the free cyanide would not exist as hydrogen cyanide in the solution. Cyanide salts such as sodium and potassium may be lost from surface water through volatilization whereas the soluble metal cyanides are removed from water by sedimentation (Oraby, 2009).

7.1.1 Cyanide Spill Accident in Baia Mare, Romania

On January 30, 2000 happened cyanide tailings spill accident in Baia Mare, Romania. Prior to 30 January, 70 centimetre of snow and ice had accumulated in the tailings dam. 30th of

January it rained 30 mm water and snow and temperature rose above 0°C. This caused the snow and ice in the dam to melt. The rapid rise in water level caused the inner embankment to lose its strength and therefore to collapse. In the inner embankment formed a breach 23 meter wide and 2.5 meter deep. The area between the inner and outer embankments filled with water and slurry which then overtopped the outer embankment. About 100,000 m³ of water containing 100 tonnes of cyanide as well as heavy metals escaped into Tisza, Somes and Danube river systems (Duffield and May, 2003; Klemola, 2012).

As a result of the accident thousands of tons of fish died in the rivers where cyanide entered and drinking water of 24 towns and of 2.5 million people was contaminated. Luckily cyanide decomposed in nature quite fast thus environmental impacts were not long-term.



Figure 11 Dead fishes of the Tisza River (Duffield and May, 2003).

Table 3 Cyanide accidents and the environmental impacts (Oraby, 2009).

Mine/country	Year of occurrence	Impact
Placer Dome tailings disposal, The Philippines	1975-1991	Loss of aquatic life forms in Ajkwa River and Calancan Bay
Echo Bay's McCoy/Cove Gold Mine, Nevada USA	1989-1990	Eight cyanide leaks over a two-year period released almost 400 kg of cyanide
Galatic Resources Ltd.'s Summitville Mine, Colorado USA	1992	Severe environmental problems along a 17-mile stretch of the Alamosa River
Ghana •Bogoso Goldfields 1994 •Teberebie Goldfields 1996 •Ashanti Goldfields 1998 •Goldfields (S.A.) 2001 •2001 – second spill occurred in the same area after 2 weeks	1994-2001	Communities were re-located, waters polluted, there were reported cases of avian mortality, and crops were affected. There were serious health impacts including skin rashes.
Harmony mine, South Africa	February, 1994	10 miners killed by cyanide-laced mud.
Omai gold mine, Guyana	August, 1995	All aquatic life forms in a creek that runs into the Essquibo river were killed.
Grasberg Mine, Indonesia	1996	The spill affected aquatic life forms in Ajkwa River and surrounding communities.
Baia Mare, Romania	January, 2000	Thousands of tons of fish died in the Tiza and Danube Rivers. Rare Osprey, birds, river otters, fox and other mammals died from eating cyanide contaminated fish.

7.2 Treatment, Recovery and Destruction of Cyanide from Mine Waters

To minimize the environmental impact of cyanide, a variety of chemical, physical and biological processes have been developed for the treatment, recovery and destruction of cyanide from mine waters. Treatment processes are for instance activated carbon adsorption, ion-exchange resins, alkaline chlorination, biological treatment, Caro's acid and INCO process which are briefly presented in following chapters (Oraby, 2009; Duffield and May, 2003).

7.2.1 Activated Carbon Adsorption

Activated carbon adsorption can be used for cyanide removal from mine waters. Cyanide is first adsorbed and then oxidized to cyanate (OCN^-) and then partially to carbonate (CO_3^{2-}) and ammonium (NH_4^+) with copper catalyst. When using granular activated carbon without oxidation the addition of copper or nickel is necessary for the formation of cyanide complexes which then can be adsorbed onto the granular activated carbon.

7.2.2 Ion-Exchange Resins

Ion-exchange resins are synthetic materials which consist of an inert matrix and contain surface functional groups. Ion-exchange resins are widely used for the recovery of cyanide and cyanide complexes from leach liquors. This technology includes three steps: loading, elution and recovery. In the first stage cyanide is adsorbed and it can be done either using strong base resin or weak base resin. Strong base resins have high loading capacity and good kinetic. After adsorption cyanide is recovered by elution. When ion exchange resins are used to recover gold the third stage is the recovery of gold by electrowinning (Strangfeld, 2000; Mining & Metallurgy, 2012).

7.2.3 Alkaline Chlorination

According Oraby (2009) the alkaline chlorination is the oldest of the cyanide destruction processes and it is used to oxidize free and WAD (weak acid dissociable) forms of cyanide. Firstly in this process free and WAD forms of cyanide are converted to cyanogen chloride (CNCl) by chlorine (Cl_2) or hypochlorite (OCl^-) as shown in Eq. (20) and (21):



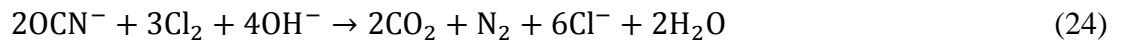
In this first stage the pH ranges between 10.5 and 11.5 to eliminate the volatilization of cyanogen chloride which occurs if pH is less than about 8.0. At convenient pH cyanogen chloride hydrolyses to yield non-poisonous cyanate as shown in Eq. (22):



In the second stage of the oxidation the cyanate is hydrolyzed in the presence of chlorine or hypochlorite to yield ammonia and carbonate according to the reaction represented in Eq. (23):



Habashi (1999) explains how the cyanate ion can further be oxidized to carbon dioxide and nitrogen by chlorine in pH over 11 as shown in Eq. (24):



7.2.4 Biological Treatment

Biological treatment of cyanide is relatively new technique in gold mining industry. Biological processes are effective in the treatment of elevated concentrations of cyanide. In the biological treatment a large number of micro-organisms remove constituents in mine waters. In this process the cyanide is converted to thiocyanate then about 90% of thiocyanate is decomposed into NH_4^+ , CO_2 and SO_4 (Oraby, 2009). Nelson *et al.* (1998) reported that the biological treatment methods have high capital costs but low operating cost.

7.2.5 Caro's Acid

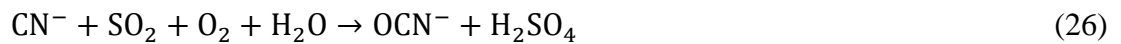
Caro's acid, also known as peroxymonosulphuric acid (H_2SO_5) can be used to oxidize cyanide in solutions. Caro's acid reacts with both free and WAD cyanides to produce cyanate and sulphuric acid as shown in Eq. (25):



Treatment of cyanide with Caro's acid is rapid it takes only few minutes (Oraby, 2009).

7.2.6 INCO Process

INCO sulfur dioxide (SO₂)/air process is a simple method that requires little supervision and does not interrupt gold recovery. Over 90 goldmines worldwide use INCO process to treat cyanide less toxic form. In this process sulfur dioxide in liquid or gaseous form acts with air to oxidize WAD cyanide to cyanate and sulfuric acid as shown in Eq. (26) while metals are released into solution. Copper sulfate is used as a catalyst during the process (Duffield and May, 2003; Wikipedia: Gold Cyanidation, 2012; Strangfeld, 2000).



7.2.7 Aqueous Discharges to Receiving Waters from Cyanidation Process

Biological oxidation, either naturally occurring or as a cyanide detoxification technique, causes transformation of cyanide to ammonia. Further microbial action will convert ammonia to nitrate and thiocyanates to sulfate. Nitrate causes eutrophication of water systems, therefore aqueous discharges should be kept minimal (U.S. Environmental Protection Agency, 1994). The cyanide cycle and its discharges to air, water and sediments are represented in Figure 12. Not only nitrogen containing compounds are present in aqueous discharges but also metals. Table 4 gives an example of metal concentrations in feed and discharge streams in INCO-SO₂ process.

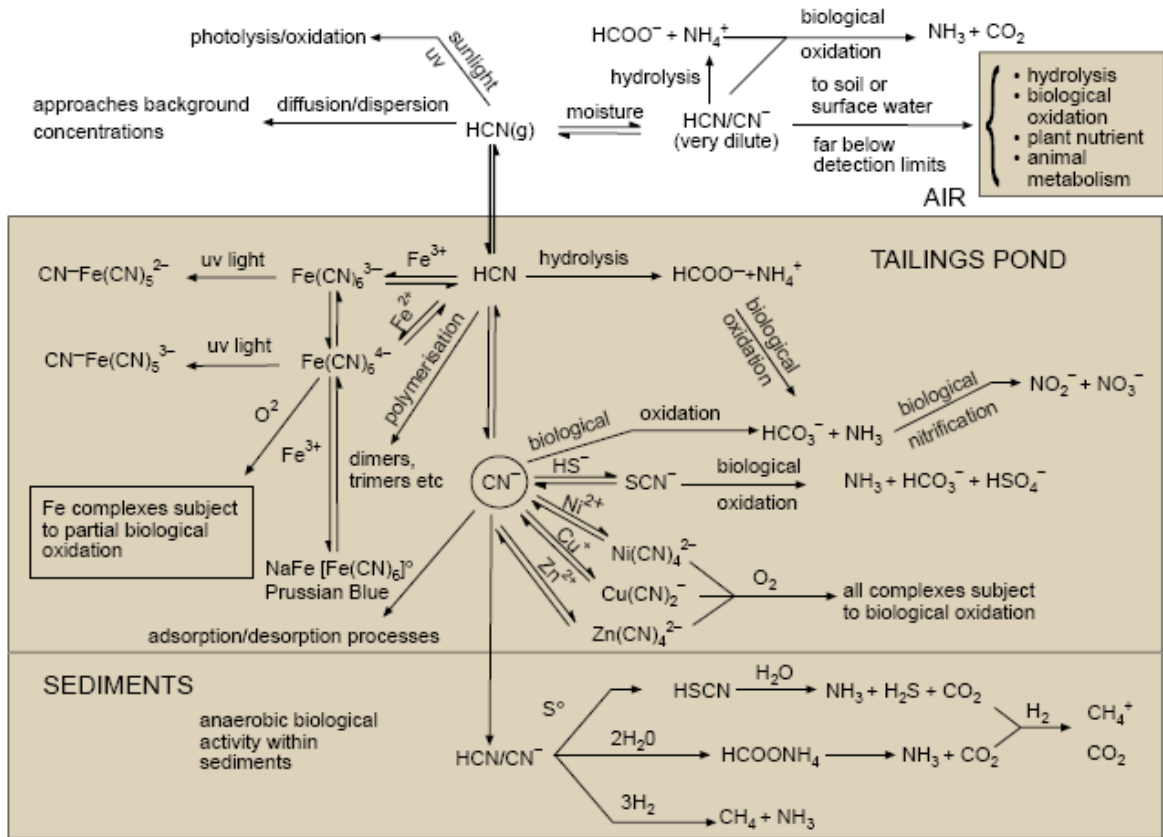


Figure 12 The cyanide cycle and its discharges to air, water and sediments (Smith and Mudder, 1991).

Table 4 Example of feed and discharge concentrations of selected species for the INCO-SO₂ detoxification process (Devuyst *et al.*, 1988).

	Barren Solution (mg/L)	Treated Barren Solution (mg/L)	Final Tailings (mg/L)	Tailings Overflow (mg/L)
Copper	35.45	1.21	7.70	3.10
Cyanate	44.60	324.20	52.90	20.50
Iron	45.82	0.26	0.51	0.32
Thiocyanate	100.70	82.50	18.90	8.30
Total cyanide	365.80	0.69	29.40	8.80
WAD cyanide	225.00	0.15	12.20	5.20
Zinc	62.00	0.20	0.00	0.00

7.3 Safety Aspects of Cyanide

After Baia Mare tailings spill accident in January 2000, a cyanide use and management workshop was organized. As a result of the workshop the International Cyanide Management Code was created. Experts from the United Nations Environment Programme and from the International Council on Metals and the Environment prepared the code. The International Cyanide Management Code includes instructions for safe manufacture, transport and use of cyanide. The code tries to protect workers, communities and the environment from adverse effects of cyanide (Duffield and May, 2003).

During cyanide leaching it is essential to keep the solution alkaline to prevent the formation of hydrogen cyanide (HCN) which is an extremely poisonous gas (Habashi, 1999). The concentration of hydrogen cyanide must be monitored and measured regularly. The occupational exposure standard for hydrogen cyanide is 10 ppm and for cyanide dust it is 5 mg/m³. Respirators must be used during lengthy maintenance work (Oraby, 2009).

7.3.1 Cyanide Poisoning and First Aid

According to the National Institute of Occupational Safety and Health of the USA for HCN gas in air for humans: content 270 ppm is immediately fatal, 180 ppm is fatal after 10 minutes, 135 ppm is fatal after 30 minutes, 110 ppm can be fatal, 45-55 ppm can be tolerated for up to 60 minutes without immediate effects and 18-36 ppm results in symptoms of poisoning several hours after exposure.

According to Oraby (2009) cyanide intoxication can happen through inhalation, ingestion or skin contact of cyanide. After exposure cyanide is readily distributed throughout the body via blood. As little as 200 mg of cyanide salts ingested may be deadly. According to Hilson and Monhemius (2006) toxicity of cyanide is based on its ability to bind the iron-carrying enzymes required for cells to use oxygen, thus inhibiting bodily tissues from extracting oxygen from the blood. After cyanide intoxication the body exhibits symptoms of oxygen starvation and suffocation. Other symptoms of cyanide poisoning include irregular heartbeat, convulsions, chest pain and vomiting.

When patient who has exposed to cyanide is conscious the route of exposure should be found out. When cyanide has been swallowed the patient should be induced to vomit and 100% oxygen should be given. In the case when cyanide has been inhaled 100% oxygen should also be given to the patient. When cyanide exposure has happened through skin contact all contaminated clothing must be removed and all contaminated skin must be washed with water and 100% oxygen must be given to the patient. After first aid the patient must be taken quickly to medical attention (Duffield and May, 2003).

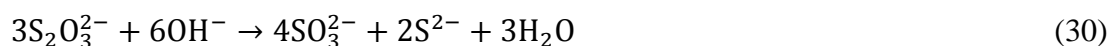
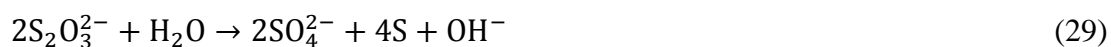
7.4 Environmental and Safety Aspects of Thiosulphate

Ammonium thiosulphate has been used as a fertilizer for many decades. Therefore it is known that high concentrations of ammonium thiosulphate in water systems cause eutrophication and algae growth in rivers and lakes (Aylmore and Muir, 2001).

Under oxidizing conditions thiosulphate will be oxidized to sulfate (SO_4^{2-}) or tetrathionate ($\text{S}_4\text{O}_6^{2-}$) as presented in Eq. (27) and (28).



Depending upon the conditions thiosulphate may be oxidized also into sulfate and elemental sulfur or into sulfite and sulfide ion as shown in Eq. (29), (30) and (31).



Thiosulphate and sulfate are not toxic but they have in excess amounts in environment harmful effects for water system, soil and groundwater.

Muir and Aylmore (2004) mention that ammonia which is a reagent in thiosulphate leaching poses environmental and toxic problems. Ammonia has detrimental effect in water systems and it may metabolise to nitrate, which has the potential to promote algal

growth and to pollute groundwater. Thus, it is even more important to control ammonia emissions than thiosulphate, and prevent release of ammonia into the environment.

According to Oraby (2009) thiosulphate is classified as GRAS (generally recognized as safe) since up to 12 g of thiosulphate can be taken daily by mouth with no ill effects. LD₅₀ (dose needed to kill 50% of a population) dosage to thiosulphate is 7.5 ± 0.752 g/kg for mice. Thus the difference between cyanide and thiosulphate in toxicity is huge.

Sodium thiosulphate may cause inhaled irritation of the nasal and respiratory passages. In contact with skin dust may cause irritation with itching and redness. Large doses ingested may cause diarrhea. First aid in exposure to sodium thiosulphate, when skin is exposed the contaminated clothing should be removed and skin washed with running water 5-10 minutes. If patient has inhaled sodium thiosulphate, oxygen should be given to patient. If patient has ingested sodium thiosulphate 2 to 4 glasses of water should be given to patient and not induce vomiting (Caledon, safety data sheet).

8 CONCLUSIONS

In this work cyanide and thiosulphate leaching for gold production has been compared. Cyanidation is a conventional process in gold leaching, whereas thiosulphate leaching is a relatively new process compared to cyanidation and is currently used just in pilot scale. Both processes have their own pros and cons. In cyanidation a very dilute cyanide solution can dissolve gold and gold is easy to recover from leaching liquors for example by carbon adsorption. The main disadvantage of cyanidation is the high toxicity of cyanide. One drop of cyanide in water of glass is fatal for human because cyanide binds iron-carrying enzymes required for cells to use oxygen. In addition cyanidation cannot dissolve very well refractory gold ores without pretreatment of ores.

Thiosulphate leaching is considered a non-toxic process and the gold dissolution rates can be faster than in conventional cyanidation. Thiosulphate leaching is a better choice for complex and carbonaceous-type ores since it is not as sensitive for interference of foreign cations. The disadvantages of thiosulphate leaching are high reagent consumption and the difficulties to recover gold from leaching liquors. The use of resins to recover gold from leaching liquors appears to show some promise. Thiosulphate leaching has potential to be an effective and less hazardous process for gold extraction from auriferous ores.

The concern of environment and the political alignments are the main driving forces to find less toxic alternatives to cyanide. Some countries are campaigned to ban the use of cyanide in the gold mining industry and many cyanide accidents have happened last decades. This has accelerated the research work to find good and less toxic alternatives to cyanide. It remains to be seen will thiosulphate substitute cyanide in the coming decades.

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