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HYDROMETALLURGY OF PRECIOUS METALS: EFFECTS ON THE ENVIRONMENT

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ABSTRACT. Factors which affect the release of toxic substances to the environment during the hydrometallurgical processing of precious metals bearing ores are discussed. The experimental work and industrial results on the following aspects of the cyanidation process, having environmental notions, are surveyed.

- Chemistry of cyanidation and generation of an environmentally hazard compounds.
- Process selection and preparation of leach pads.
- Methods for treatment of process solutions.
- Effluent characteristics with a view of wastewater treatment options selection.
- Long and short term fate of cyanide in environment - regeneration and destruction.
- Environmental impact and risk assessment procedures.

The review of new work, in the field of alternative gold lixiviants is also presented and attention is drawn on the degree of toxicity of these lixiviants.

1. Introduction

Environmental impact of mining has existed since mining activities began centuries ago. As the scale of mineral workings increase, so did the degree of pollution. Coupled with this, came changes in processing techniques, involving the use of chemical reagents and the transport of ores and concentrates over greater distances. All these operations had as a consequence an ever increasing environmental impact. Whilst this impact did not cause serious concerns until the second half of our century, these issues have now being changed and the environmental aspects of mining are paramount, especially in the developed countries.

Ever since mining began, gold extraction has been the brighter spot; in recent years however, with the decline of mineral-based natural resources, it has become a central area of industrial activity world-wide, which has led to immense environmental pressure. A persistent feature of this activity is the involvement of

a wider variety of ores, characterized by progressively lower grades. Treatment of these ores is characterized by a concomitant increase in the generation of different waste products, in the form of gases, solids and mixtures of them, which must be disposed of responsibly, in compliance with stringent environmental regulations and as economically as possible. Some of these, like dusts from blasting or crushing, or solid waste from mining, are controlled, disposed of, or removed mainly by physical means without any chemical treatment. However, most of the other waste may contain components that require chemical treatment.

This situation is a real challenge for gold metallurgists, to select the most appropriate technology to suit a given need and to comply with varied environmental regulations and legislation. Indeed, although through increased gold recovery the new generation flowsheets are justified economically, it is really the environmental problems that have been the driving force, behind the development of improved gold recovery technologies. Any environmental impact, whether regulated or not, should be minimized by good process design, effective waste management and reclamation requirements.

It is known that the majority of gold recovery flowsheets employ hydrometallurgical techniques, which themselves are reactions in an aqueous system. The basic sequence of hydrometallurgical processes for gold extraction, from the principal resources to end products, is shown in Figure 1.

While the two key areas attracting interests among researchers are the development of effective methods for cyanide recovery and its destruction in process wastewater and/or the on-going search for an alternative non-cyanide lixivants, for the industry the most important yet techniques remain to be: leaching, solutions purification/concentration and recovery of gold. Depending on the ore type, pre-treatment operations could be involved as part of a complex flowsheet, mainly with the aim to increase overall gold recovery in the leaching stage, by liberating encapsulated gold and by rendering interfering components less reactive. Common interfering components are the highly reactive sulphide minerals. The most important methods used in this regard are: pre-aeration, roasting, chemical oxidation, pressure oxidation and bacterial oxidation. More exotic approaches studied, involve pyrolysis of refractory gold arsenopyrite ore in N_2 , CO_2 and SO_2 atmospheres, instead of oxidizing roasting [2] or anodic electroleaching in chloride media of the concentrate for releasing the fine gold grains [3].

This paper intends to review the environmental notions associated with the hydrometallurgical processing of different gold ores. Since cyanidation is the most universally known process and is considered a major environmental "headache", its environmental aspects are discussed in greater details. At the same time, environmental advantages and limitations reported for the main alternative to cyanide reagents are reviewed as well.

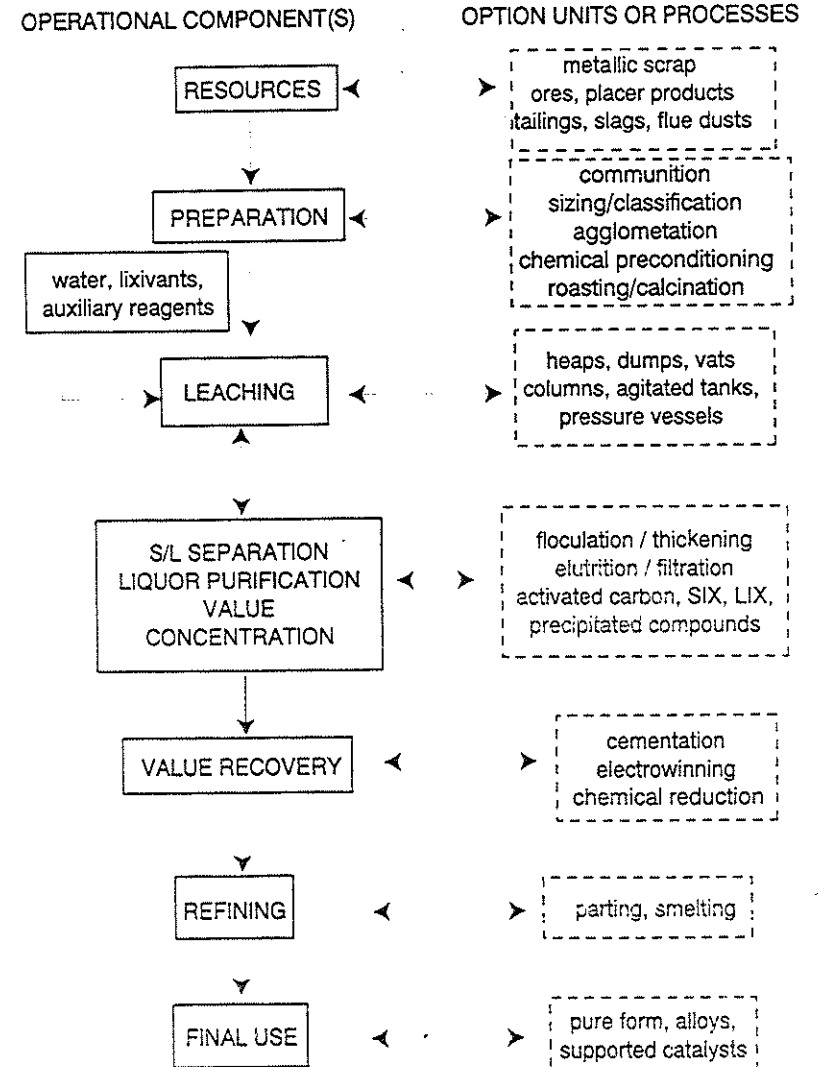
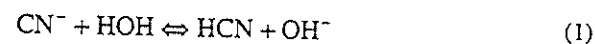


Figure 1. Technological sequence in hydrometallurgical processing of gold with related operation and unit processes (from J.P. Rosso and P.J. Woodward (eds.) IPMI [1]).

2. Cyanidation

2.1. BASIC CHEMISTRY OF PRECIOUS METALS LEACHING

The cyanidation process is the most widely used industrial hydrometallurgical method for gold extraction from ores and concentrates. Simple cyanide salts, such as sodium, potassium and calcium cyanides, dissolve and ionize in water to form their respective metal cation and free cyanide ions. The term free cyanide relates to two categories, the cyanide ion (CN⁻) and hydrocyanic acid or hydrogen cyanide (HCN). The relative proportion of these two forms depends upon the pH of the system. The reaction between cyanide ion and water could be given as:



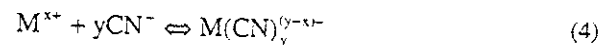
At any given pH and temperature, the system is in equilibrium and the relative amounts of each can be determined from the equilibrium constant:

$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} \quad (2)$$

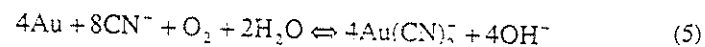
Hydrogen cyanide is a weak acid, which incompletely dissociates in water as follows:



Free cyanide complexes with many metal species, principally with the transition metals, which vary widely in stability and solubility:



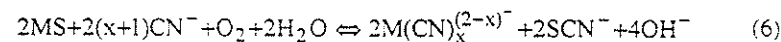
The main chemical reaction involved in gold solubilisation, known as Elsner equation, is as follows:



Relatively weak solutions can be used, because of the strong complex formed between cyanide and gold. For instance, in the absence of other metal cyanide complexes, a 100 mg/L solution of NaCN can provide the maximum rate and extent of dissolution. The silver cyanide complex is weaker than the gold one and hence, it requires stronger cyanide solutions and/or longer contact times for dissolution.

2.2. REACTIONS OF OTHER MINERALS

In spite of the relative specificity of the gold-cyanide reaction, other metals and metal sulphides decompose quite well in the leaching solutions, to form metal ions, metal oxides or metal cyanide complexes and various sulphur-containing species. This is accomplished by minerals reaction both with cyanide and to a given extent, with hydroxide, which must be present to maintain cyanide in its ionic form. Also, the need for more severe conditions in the presence of silver, facilitates additionally the attack on metallic minerals present in the ore, leading to increased cyanide consumption, decreased selectivity and higher concentrations of metals in solution. The reactions with iron minerals, pyrite and pyrrhotite are of utmost importance in many cases, since these minerals are known as the highest cyanide-consuming minerals in gold ore. Thus, cyanide and oxygen are consumed and a variety of solution species are produced, reducing the efficiency of gold leaching and the subsequent recovery processes. The cyanide consumption is considered as a direct reagent cost and could inhibit gold dissolution. Besides, the elevated cyanide and metal-cyanide concentrations in the leach liquors significantly increase the complexity of wastewater characteristics and the cost of its neutralization and treatment. The main reaction for a sulphide, containing a divalent metal cation could be given as follows:



All sulphide minerals, except lead sulphide, are capable of generating thiocyanate in cyanide solutions; the exact mechanism of thiocyanate formation during cyanidation is not clear. Primary requirement is the formation of compounds containing labile sulphur atoms in solution. Such compounds include elemental sulphur micelles (S₈) and alkali or alkaline earth polysulphides, thio-sulphates or polythionates [4]. It is believed that thiocyanate does not result from the direct reaction of the cyanide ion, but merely of its metallic complexes, with these sulphur atoms which usually originate from the attack of alkalis on reactive sulphides such as pyrrhotite. Sulphur atoms can also form via oxidation of sulphide ions released by dissolution of sulphide minerals. Thiosulphate and polythionate species may also contribute to thiocyanate generation. To minimize thiocyanate formation, a complete oxidation of sulphides to sulphates should be maintained. This could be accomplished by addition of lead salt, under vigorous agitation and lead must be present at time the sulphide ions first appear in solution. The production of thiocyanate is highest for ores with free sulphur or pyrrhotite containing minerals. When such ore is treated directly with cyanide solution, formation of thiocyanate proceeds continuously with both these minerals

and is accelerated under conditions, which combine partial or inadequate aeration with high alkalinity.

The formation of ferro- or ferri- cyanide ions, like $\text{Fe}(\text{CN})_6^{4-}$, or $\text{Fe}(\text{CN})_6^{3-}$ (i.e. the hexacyanoferrates), is often of greater concern from operational and environmental view points, mainly because of their extreme stability in the absence of light and their tendency to dissociate when light is present. They are formed relatively rapidly under conditions of low alkalinity and reduced aeration, particularly if pre-oxidation of the ore has led to the presence of ferrous ion. This is mainly due to a drop in pH, caused by incomplete precipitation of ferrous hydroxide. Much controversy exists over the relative toxicity of the iron cyanides due to photolysis. Although these complexes resist natural degradation until free cyanide and the more readily degradable metal cyanides, they tend to release toxic levels of hydrogen cyanide, when exposed to intense ultraviolet radiation [4].

It should be noted that the conditions for the formation of thiocyanate and ferrocyanide from iron sulphide minerals are to some extent mutually restrictive, since the conditions chosen to minimize one may promote formation of the other. This is of particular importance from a wastewater treatment viewpoint, since thiocyanate creates an oxidant demand, is potentially toxic itself and breaks down forming ammonia, a cause of further concern. However, their chances of contaminating the aquifer are less dramatic compared to cyanide. The mobilities of thiocyanate and ferrocyanide are dependent on soil conditions and it is known that they are attenuated by a number of soil types.

2.3. PROCESS SELECTION

Cyanide leaching of gold-bearing materials is accomplished by a variety of methods which are summarized as follows, in order of decreasing economic importance:

- agitation leaching,
- heap or dump leaching,
- intensive leaching,
- vat leaching and
- *in situ* leaching.

The choice between these options depends primarily on the relationship between particle size and recovery, capital and operating costs, and the dissolution rate in each case.

The preparation of leach pads, in case of heap or dump leaching, is of primary importance to provide environmental protection and avoid gold losses in leach solutions. Careful and precise engineering and lining installation are required. The surface is first cleared of all growth, and the top soil is removed and stock-

piled for later restoration/remediation use. A compacted soil/clay liner, about 300-mm thick, is then prepared and a VLDPE plastic liner is placed on top of the liner. A 300-mm layer of crushed rock is placed as a protection, on top of the liner. Above, an approximately 300-mm coarse-rock layer is provided for drainage. Ore is loaded on top of this sequence [5]. A typical cross section of a leach pad is shown on Figure 2.

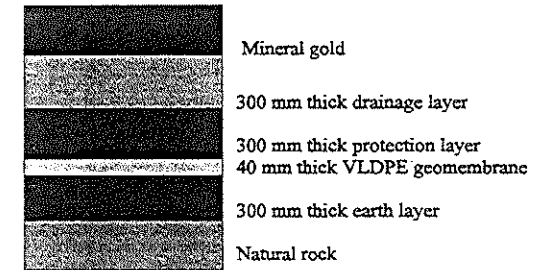


Figure 2. Cross section of leach pad lining

After completion of the leach cycle, i.e. when the ore body is exhausted, the heap is washed with water to remove the remaining of the dissolved metal. This procedure can ultimately detoxify the heap, for final site closure. The barren leach solutions ponds should be also rendered harmless and therefore, ponds are similarly carefully prepared and lined with a triple-layer HDPE plastic. It is reported that PVC has the potential of replacing HDPE as lining material and that the so called "geofastners" are gaining popularity for stabilization of the liner [6]. Geoneting is applied to assist with solution drainage between liners, and geofabrics - to protect liners from rock damage.

2.4. EFFLUENT CONTROL - ENVIRONMENTAL CONSIDERATIONS

Cyanide leaching produce definite amounts of liquid effluents in solution and slurry form. In some cases, economic and environmental necessities may justify the involvement of subsequent flowsheets, aiming to the treatment of these effluents for their detoxification, reagents recycle and metal values recovery. Thus, effluent treatment operations seem mandatory as part of the whole flowsheet. For many effluents, however, the above factors may not apply and the effluents can be disposed in a satisfactory manner without treatment. When treatment is envisaged, the major targets are the various cyanide species, toxic metal ions and extreme pH values. The cyanide compounds are divided into four major groups, which include:

- free cyanide, CN^- and HCN ,
- iron cyanides,
- weak acid dissociable (denoted hereafter as wad) cyanides and
- cyanide related compounds.

The long-term fate of any solid portion of the waste may be also under special consideration. Generally, the effluents arising from the hydrometallurgical processing of gold ores are divided into two main categories - contained effluents and those that require discharge.

2.4.1. Contained effluents.

They present materials that are stored on place, with little or no release to environment. The main characteristic of this type of wastes is that there is an impermeable, or semi-permeable barrier between the material and the ground on which it is laid. This is done to avoid any degradation of surface or ground water. Barriers may present:

- tailings impoundment,
- lined heap leach pads,
- lined solution ponds,
- steel tanks and
- concrete vats and sumps.

If necessary, the contained effluents can be treated *in situ* for reagent or metal recovery, prior to disposal in the containment facility. Besides, precaution measures might be required depending on the actual threat these effluents present to the wildlife, the possibility of a release to the environment and the risk of contaminating surface/ground water. The following procedures are applied to reduce the risks mentioned:

- minimizing the exposed surface area of solution, which reduces the attractiveness of the water body, especially to wild life;
- preventing wildlife access to toxic solutions, by fencing around open cyanide solution storage facilities. Some operating plants use floating plastic pond covers, which reduce cyanide losses by volatilization;
- minimizing the concentration of toxic components in solution by optimal process design and cyanide control.

2.4.2. Discharge effluents.

The need to discharge effluent into the surrounding environment depends on the overall water balance of the operation (Figure 3). Water balance itself is a function of various factors, like the processing method, the local climate, the amount of process water generated and the method of effluent disposal. The need for solutions discharge into the environment is more acute in plants located in regions with positive water balance. However, under certain circumstances, like

periods of heavy rainfalls or equipment failure, some operations with large negative balance might require discharge.

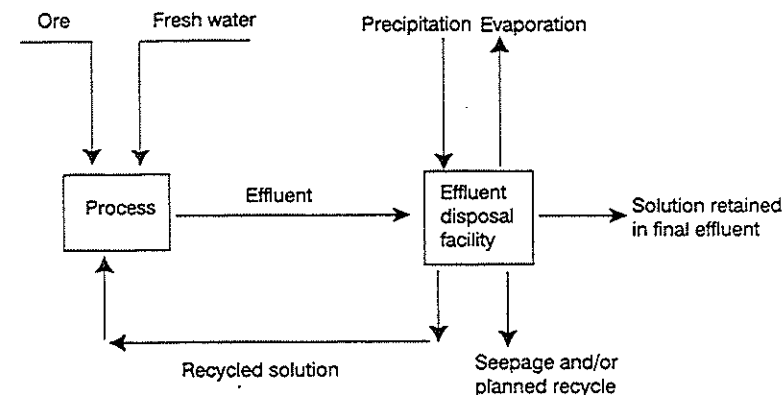


Figure 3. Water balance scheme of process flowsheet involving effluent recycle (from Mardsen and House, 1992 [7]).

2.5. EFFLUENT TREATMENT

The effluent potential to contaminate surface or ground water could stipulate the need to be treated, to meet certain regulatory standards prior to discharge. Therefore, to avoid serious legal consequences many industrial operations should seek quick solutions for detoxification. A detailed understanding of wastewater sources and characteristics is essential in the selection and design of reliable and efficient treatment systems to meet environmental standards. The chemical characteristic of gold mine wastewater is a result of the complex interactions occurring between metallurgical processes and reagents, ore geochemistry and site hydrology. The selection of a treatment system depends on wastewater chemistry and the level of effluent control limits, developed for many solution species, based on their measured, perceived or projected toxicity. A listing of parameters of concern and representative ranges of concentrations are given in Table 1. For the sake of comparison the World Health Organization drinking water standards, giving an indication of acceptable limits is shown on Table 2. These could be used only as an approximate estimation, since data deviate in different countries.

TABLE 1. Characteristics of cyanidation effluents

Parameter	Range in concentrations in mg/L
Arsenic	< 0.02 - 10.0
Cadmium	< 0.005 - 0.02
Chromium	< 0.02 - 0.1
Copper	0.1 - 400.0
Iron	0.50 - 40.0
Lead	< 0.01 - 0.1
Manganese	0.1 - 20.0
Mercury	< 0.0001 - 0.05
Nickel	0.02 - 10.0
Selenium	< 0.02 - 6.0
Silver	< 0.005 - 2.0
Zinc	0.05 - 100.0
Total Cyanide	0.5 - 1000.0
WAD Cyanide	0.5 - 650.0
Free Cyanide	< 0.01 - 200.0
Ammonia-N	< 0.1 - 50.0
Thiocyanate	< 1.0 - 2000.0
pH	2 - 11.5
Hardness (as CaCO ₃)	200 - 1500
Sulphate	5 - 20000
Temperature (°C)	0 - 35
Flow (in gpm)	1 - 6000

TABLE 2. Selected water drinking standards/guidelines

Chemical constituent	WHO International (1958)			WHO European (1961)	
	Permissible limit	Excessive limit	Maximum limit	Recommended limit	Tolerance limit
	concentrations in mg/L				
Ammonia (NH ₄)	-	-	-	0.5	-
Arsenic	-	-	0.2	-	0.2
Cadmium	-	-	-	-	0.05
Calcium	75	200	-	-	-
Chloride	200	600	-	350	-
Chromium (VI)	-	-	0.05	-	0.05
Copper	1.0	1.5	-	3.0	-
Cyanide	-	-	0.01	-	0.01
Fluoride	-	-	-	1.5	-
Iron	0.3	1.0	-	0.1	-
Lead	-	-	0.1	-	0.1
Mg + Na sulphates	500	1000	-	-	-
Manganese	0.1	0.5	-	0.1	-
Nitrate (NO ₃)	-	-	-	50	-
Selenium	-	-	-	5.0	-
Sulphate	200	400	-	250	-
Total solids	500	1500	-	-	-
Zinc	5.0	15	-	5.0	-

Data suggest that the most significant, in toxicological sense, are the free cyanide compounds and the weak acid dissociable complexes, like zinc, copper and nickel. The toxicity of these complexes is mostly due to the concentration of free cyanide that is in equilibrium with the metal complex. Hence, the strong complexes are essentially non-toxic. The co-existence of the two species CN⁻ and HCN is very dependent on solution pH and their relative proportion will vary with the pH value for the equilibrium reaction. The relationship between both forms and pH is shown on Figure 4.

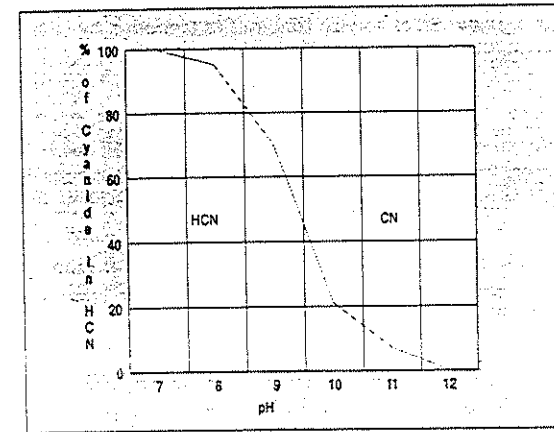


Figure 4. HCN and Cyanide ion existence as a function of pH.

The most commonly used, first-choice method for detoxification of cyanide takes advantage of natural decay processes in tailing ponds, lagoons and soil barriers. These processes include: complexation (chelation), volatilization, atmospheric oxidation, adsorption onto other minerals, hydrolysis, biodegradation and cyanide complex precipitation. It is known that twenty-eight elements (among them numerous transition metals) are capable of forming seventy-two different cyanide complexes, which are less toxic than free cyanide. Some are, however, not very stable and will decompose back to free cyanide. Volatilization of HCN is accomplished by lowering the pond pH by means of natural uptake of carbon dioxide from air and by addition of low pH rainwater, that is relatively saturated with carbon dioxide. The pH drop induces change in the CN⁻/HCN balance increasing HCN volatilization. During atmospheric oxidation, dissolved oxygen from the process solutions oxidizes cyanide to cyanate, when there is no catalyst. When as little as 20 g/L activated carbon is present, the reaction is accelerated. The method of cyanide removal by adsorption on other minerals is important in

the long-term fate consideration of cyanide in slurry tailings and heap leach pads. It is based on the known ability of some materials with carbonaceous structure to act as effective adsorbents. Other natural methods, resulting in precipitation and co-precipitation of solution species, account for varying degree of cyanide destruction, depending on the various conditions. The rate of degradation in natural systems depends upon factors such as pH, temperature, exposure to sunlight and depth of the pond. The microbial-assisted degradation is supported by the ability of certain bacteria to convert the immobilized (by soils) cyanide salts, to less toxic and further dissociable nitrates under anaerobic conditions.

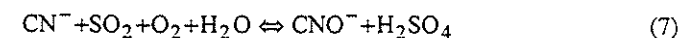
In many cases, however, residence time in the lagoon is too short, for ensuring adequate destruction of the cyanide, thus mandating involvement of chemical treatment operations. One traditional technique, used in this regard, involves chlorination. It is capable of destruction of total cyanides, except iron-cyanide complexes, thiocyanate, cyanate and ammonia. Depending upon the amount of chlorine or hypochlorite added to solution, these compounds can be oxidized to nitrogen gas and bicarbonate through "breakthrough chlorination". However, its popularity has recently declined, due to a number of operational disadvantages, as:

- alkalinity must exceed pH 11 prior to the addition of chlorine, in order to avoid the risk of discharging toxic cyanogen chloride into water or air;
- presence of thiocyanate in the waste water causes very high consumption of chlorine;
- chlorine oxidizes ferrocyanide to soluble ferricyanide, preventing this portion of the total cyanide from precipitating out of solution;
- use of chlorine causes additional salting in the discharge to waterways, and without proper control and monitoring, may lead to formation and release of hypochlorite, which is highly toxic to fish;
- organic substances present in the wastewater produce environmentally undesirable toxic chlorinated compounds;
- chlorine demands great care in shipping and handling.

One other known method called Cyanisorb, utilizes the volatility of HCN at a neutral pH to recover WAD cyanides from slurries or clear solutions [8]. Unit operations include agitated acidification tanks, to lower the pH to approximately 8.0, packed-bed stripping tower(s) to strip HCN from solution, adsorption tower(s) to recover stripped HCN in a hydrated lime slurry and a neutralization tank to raise the pH to approximately 10-11 prior to disposal. WAD cyanide recovery is assumed to be 90%, with recovered cyanide returning to leaching operations as calcium cyanide. Reagents used in this process are sulphuric acid, to lower the pH and lime, to recover stripped HCN and to neutralize acidified tailings. For a reduced consumption of reagents, there is a need for solutions to be cleared prior to treatment, which makes the flowsheets more sophisticated.

The two leading contemporary processes, incorporating chemical treatment schemes, are based on oxidation of cyanide with: SO₂-air mixtures (INCO process) and hydrogen peroxide (Degussa process) [9].

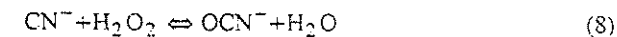
The SO₂ assisted oxidation has been used extensively in various forms. The process is based on the ability of SO₂-air mixtures to oxidize rapidly free cyanide and WAD metal cyanide complexes in the presence of Cu(II) as catalyst. Although details of its process chemistry are not fully understood, oxidation of weak cyanide take place according to the reaction:



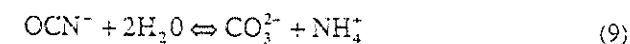
The reaction works at optimum pH of 9, but it will proceed to a sufficient extent between pH 7.5 and 9.5. Sulphur dioxide can be supplied as gas or liquid or by burning elemental sulphur. The INCO process posses also certain disadvantages among which are:

- the need for ultimate mixing of SO₂ and air with solid/liquid pulps makes them difficult to treat;
- SO₂ is a toxic gas and as such, requires delicate handling;
- to keep the operation under control, a very close parameter-regulation is required, when the process exceeds control limits, it can take long time to re-establish equilibrium;
- as with chlorination, the SO₂-air process produces large amounts of neutral salts, and any excess of SO₂ leads to discharge of sulfite, which is highly toxic to aquatic life.

The Degussa process is among the most popular ones, and is claimed to be effective at producing final effluent containing less than 1 mg/L weak acid dissociable cyanide, within practical time scales. The process has an advantage that no foreign ions are introduced into process solutions and the only by-products being oxygen and water. Besides, the oxidation kinetics is fast enough, that effective oxidation could be accomplished in a period of few minutes. Cyanide reacts with H₂O₂ in a single step, forming no toxic intermediates, as it produces cyanate following the reaction:



The cyanate then hydrolyzes, to form carbonate and ammonium ions (both of which are found in the environment):



Although dissolved molecular ammonia (NH₃) can be toxic to fish, at high enough levels of concentration, it is transformed to the almost non toxic ammo-

mium form at the neutral pH of open waterways:



Excess H_2O_2 remains in the wastewater after treatment and then, it decomposes to produce only water and oxygen:



These final compounds present no environmental threat and unlike other cyanide-treatment chemicals, H_2O_2 does not contribute to total dissolved solids in the effluent.

Ferrous and ferric sulphates are other possible reagents, used to convert free cyanide to less toxic iron cyanide complexes, but without reaching limits below 2.5 mg/L. Therefore, this is a simple, low-cost method for crude detoxification.

The ability of certain bacteria to decompose a variety of forms of cyanides and ammonia lies in the bio-method of cyanide detoxification. Although a highly effective one, it is considered a rather costly yet, having problems claimed to be mechanical, rather than biological. The process was first applied on a large scale for the treatment of gold cyanide leaching effluent at the Homestake Lead plant (South Dakota, USA) in 1984 and has been operating successfully since then. The process requires gradual acclimatization of mutant strains of bacteria to the concentration of free cyanide, thiocyanate and heavy metals, present in the process streams to be treated. The flowsheet of this system is given in Figure 5.

None of these oxidants, however, is known to be sufficiently strong to decompose thiocyanate, whose concentration in mill effluents varies depending on the ore type and operating conditions. A normal range would be 40 mg/L to 600 mg/L, but it may reach up to 2000 mg/L in the barren bleed of certain Merrill-Crowe operations. Thiocyanate is considered to be non-toxic and its concentration in mining effluents is not regulated at the present time. Whilst it is known that UV light decomposes thiocyanate to form cyanide, it could be presumed that sun light could liberate cyanide levels toxic to aquatic life from effluents rich in thiocyanate. In view of this consideration, restrictions are likely to be imposed regarding the concentration of thiocyanate in cyanidation effluents. In recent studies, *Soto et al* have successfully tested ozone to treat effluents for cyanide regeneration, by oxidation of thiocyanate to cyanide in mildly acidic conditions [10]. To avoid decomposition of the regenerated cyanide, it was found necessary to keep copper concentration below 10 mg/L and pH below 7. Both the oxidation of thiocyanate to cyanide and the oxidation of cyanide to cyanate are fast and are probably mass transfer controlled.

The recycling of reagent and metals from process wastewater is a factor having both economic and environmental advantages. The simplest method

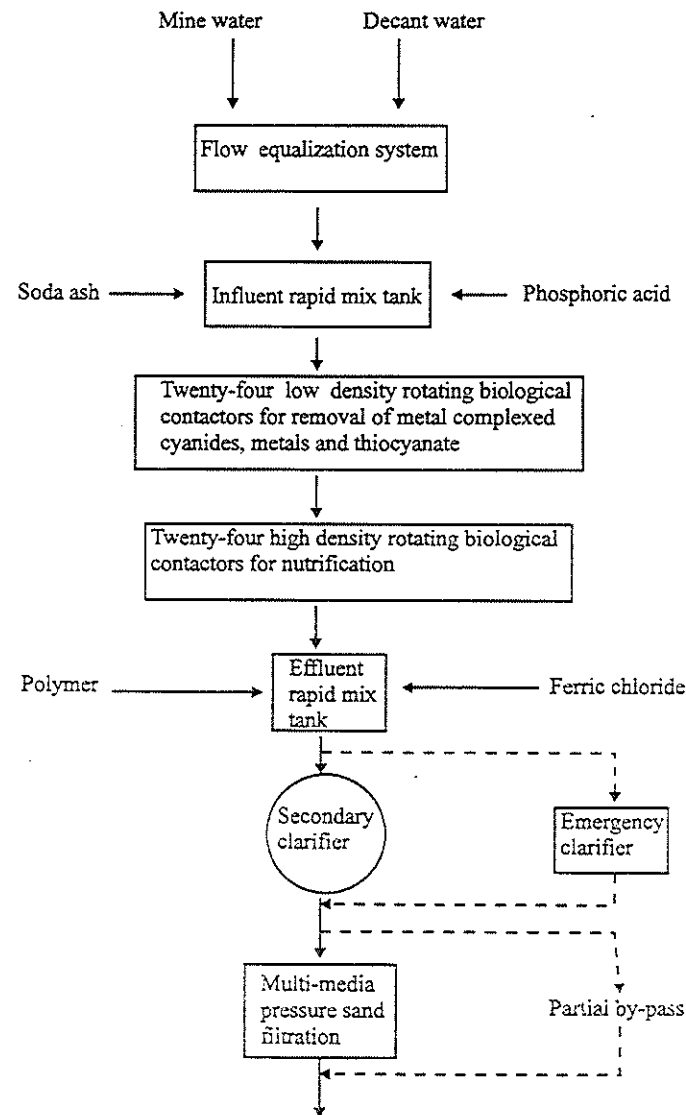


Figure 5. The Homestake biological treatment process [7].

used is the direct solution recycle, which contributes to significant savings. Generally, two flowsheets are used. In the first option (shown in Figure 3) the solution is returned directly from the process tailings stream to the process. The alternative option, requires recovering of solutions from tailings slurries prior to disposal, as illustrated in Figure 6, by the use of suitable solid-liquid separation equipment.

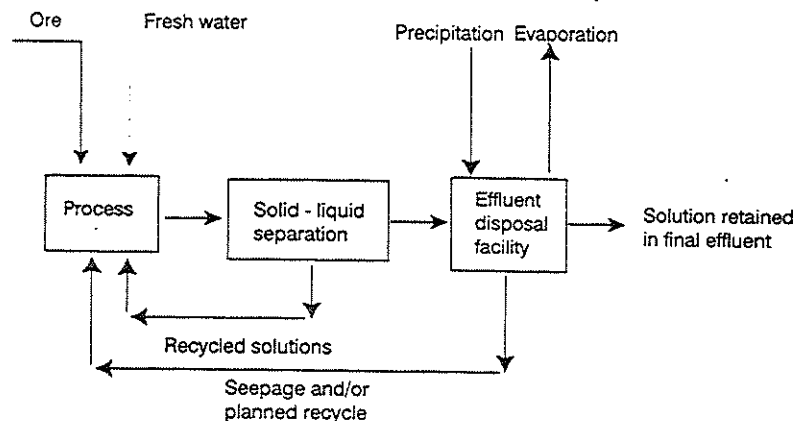


Figure 6. Scheme of process flowsheet involving solid-liquid separation for immediate recovery and recycle of effluent (from Mardsen and House, 1992 [7]).

Another possible option is the acidification, volatilization and re-neutralization process (AVR). It is an old, well proven technology that has been reinvented and applied on industrial scale. This system not only allows the cyanide to be recovered and recycled, but detoxifies cyanide and precipitates heavy metals as well. Its concept is a simple and elegant one: alkaline cyanide leach solutions are acidified, the hydrogen cyanide produced is removed by volatilization in a steam of air, and finally the gaseous hydrogen cyanide is re-absorbed back into an alkaline solution. This approach is claimed to be economically applied towards effluents containing > 150 mg/L total cyanide. However, it is unlikely to be suitable for producing a final solution, for discharge from the mill, due to the high cost of reducing cyanide concentrations down to required control levels. Main advantage of this technology is its possibility for treatment of slurry streams directly, without the need for solid/liquid separation. The scheme of AVR process is shown in Figure 7.

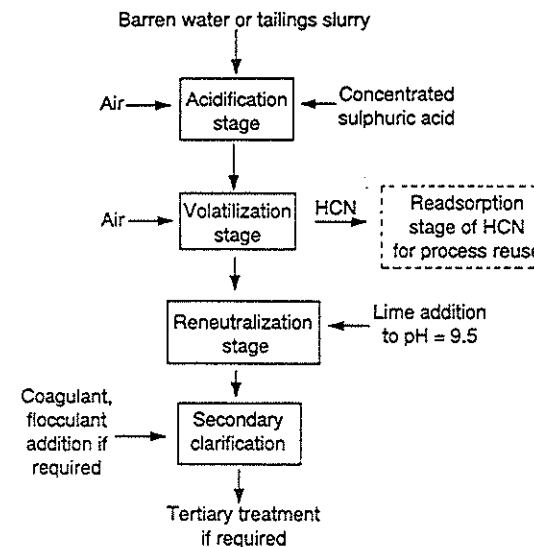


Figure 7. Scheme of the AVR process.

Other known methods, aimed mainly for value recycle, are: ion exchange, activated carbon, electrolytic treatment and ion or precipitate flotation. All these, however, are with less commercial significance, and perhaps of academic interest only.

It should be noted, that during reagent recycle operations, good safety practice must be employed for dealing with the hazardous HCN vapors released.

2.6. ENVIRONMENTAL IMPACT ASSESSMENT

As part of the feasibility study of a gold mining project an environmental planning stage must be incorporated. This stage begins with the production of an environmental impact assessment (EIA) which consists of a formal approach to evaluating the environmental effects of a project and to minimizing environmental degradation in the most cost effective manner. It can detect problems at the very beginning stage or minimize spending on mitigatory measures.

The established procedures for EIA involve:

- an assessment of existing environmental conditions;
- a review of the impact on the environment of proposed actions;

- an evaluation of the quality of this impact;
- a definition of appropriate mitigatory and remedial measures;
- monitoring to ensure the effectiveness of control measures.
- An environmental impact assessment is approached in the following manner:
- existing environmental conditions (locations, topography, climate, hydrology, flora) are defined;
- the aspects of the project with potential environmental impact are defined, e.g. movement of men and machinery, structures, waste disposal, aesthetics, changes to storm runoff, changes to the groundwater regimes;
- the significance of the impact of each aspect is assessed.

An important point is to quantify the key environmental parameters. In this context, a multidisciplinary and diverse approach is required, to identify the scope of environmental impacts for decision makers.

2.7. RISK ASSESSMENT

The reclaimed heaps, after mine operations cease, are subject of long-term attention and maintenance. In the USA, the Life-of-Mine Environmental Assessment (EA) stresses two important issues, related to long-term conditions within reclaimed heaps [11]. The amount of seepage generated and the concentration of metal and cyanide in seepage are of concern, in establishing closure criteria for the given facility. In addition, the fate of metals and cyanide in released solutions (e.g. attenuation, dissociation of complexes, etc.) is also an issue in the EA. In a similar way, a risk assessment model quantifies the perceived risk, posed to the defined "receptors" by a proposed action. A risk assessment normally consists of four distinct steps:

- Hazard identification.
- Exposure assessment.
- Toxicity assessment and
- Risk characterization.

Hazard identification involves the characterization of potential contaminants, their relative mobility, and relative toxicity, and identifies target contaminants of concern. Several potential contaminants may exist within solution, retained from the heaps at closure. Among them are the metal complexed WAD cyanides of copper, zinc and arsenic, which usually could be found in active heaps at such levels, that could be an environmental or human threat.

Exposure assessment consists of conceptual modeling of contaminant fate and transport, and its potential exposure for a given case. The concentration of target compounds within a "contaminant source" is also to be identified. Specific "migration routes" are defined depending on waste and environmental characteristics. Typically, one or more media (e.g. surface water, groundwater,

air or soil) may be affected by migrating contaminants. The conceptual model of migration routes and the environmental fate of cyanide and metals in heaps, after closure, are shown in Figure 8.

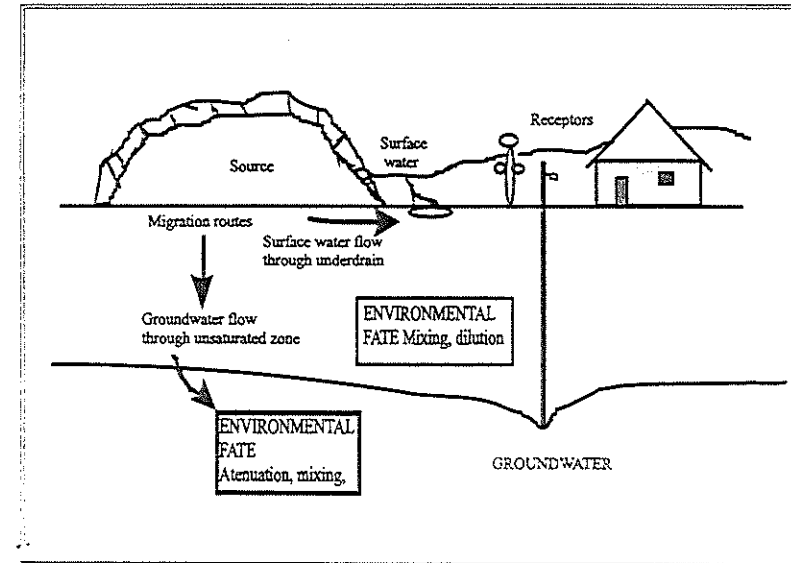


Figure 8. Model of migration routes and environmental fate of cyanide in heaps after heap operation closure [11].

Toxicity assessment deals with the determination of the dosage of target contaminants at a point of exposure to potential receptors and compares this information to known toxicological ones. For the case of handling and usage, a toxicity problem arises from the potential of digesting fatal doses of its compounds (1 to 3 mg per kg of human body are fatal) or inhaling of hydrogen cyanide (fatal exposure: 100 to 300 mg/L). An important characteristic of the dose-response behaviour of organisms is that it is difficult to identify the effects of chronic exposure. For example, cyanide does not accumulate in human body, it is regularly excreted by the urine. Therefore, the dose-response data for chronic effects are uncertain and conservative. The metals bound to cyanide can bioconcentrate or bioaccumulate, resulting in permanent physiological damage or rendering the organism unsuitable for consumption by humans or other animals.

As concerns heap leaching operations, free cyanide is noticed as the major target contaminant, since it is known that it manifests itself in either acute or

chronic manner. Acute toxicity is associated with immediate lethal effects to most organisms (after short-term exposure). The common measure of acute toxicity is expressed in the term LC_{50} , i.e. the lethal concentration of a toxic substance, that cause death in 50 percent to a given population, exposed for a specified time period. Although direct visual demonstration of acute toxicity is dramatic, there are serious toxicity problems associated with long-term exposure, to sub-lethal concentrations of a toxicant. These chronic effects include not only death, but also certain impairments and physiological abnormalities. However, long term toxicity of cyanide is a less definite problem, since CN^- is highly liable to decomposition by UV radiation, oxidants, weak acids in the environment, catalytic and bacterial actions, and readily converts to less toxic complex ions or compounds.

Risk characterization summarizes the overall environmental risk and the results from the exposure assessment model.

3. Non-cyanide operations

Although cyanide leaching remains the overwhelming option for treating gold ores, due to its economy and process simplicity, appreciable interest could be found in alternative non-cyanide reagents. Investigations have been motivated by the following considerations:

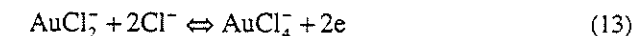
- environmental concerns and in some cases, restrictions could make the use of cyanide problematic in certain locations, especially those close to suburban and water supply areas;
- some of the alternative lixivants have faster leaching kinetics;
- most of them work in acidic media, which is more suitable for refractory ores treatment. Because of this, high neutralization costs, required by alkaline cyanidation, could be eliminated;
- some are more selective for gold and silver, over other metals present in the ore.

Among the reagents that have been pointed out as potential alternatives to cyanide, chlorine, thiourea, thiosulphate and halogens appear to have attracted the most serious attention [12-17]. At this point, their prevailing technological and environmental constraints are summarized below.

Chlorination was widely used for the leaching of gold during the second half of the nineteenth century. The process is based on the anodical dissolution of gold in acidic chloride solutions, with formation of gold(I) and gold(III) complexes depending on the relative rates of the two consecutive reactions:



and

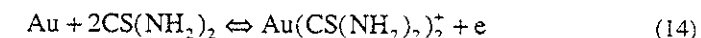


Nowadays however, chlorination finds only limited application in the field of gold refining. Different operational problems are hindering large scale commercial application, the most important of which are:

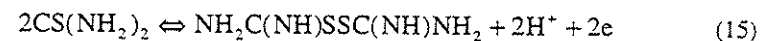
- leaching media is highly corrosive and requires special materials of construction;
- chlorine gas must be contained to allow optimum gas utilization and to avoid potential health risks;
- difficulties in electrorefining of gold from chloride media are leading to the production of poor quality cathodes.

As a consequence, chlorination requires high environmental controls and is characterized by unfavourable economics as a whole.

A number of studies shows that thiourea possesses a good potential for application, in treating not amenable to cyanidation ores or for locations, where environmental concerns make the use of cyanide problematic [12-15]. The leaching reaction of gold in acidic thiourea solutions could be presented as:



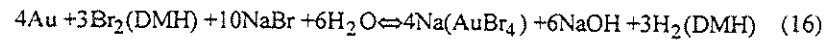
The oxidants used for facilitating gold dissolution also oxidize thiourea, the first product being the formamidine disulphide, which is formed rapidly according to:



Maintaining the acidic solutions potentials well below those required for the formation of oxide films on the gold surfaces, keeps the gold free of oxide films and therefore, the extraction rate of gold in thiourea solutions is generally very fast. Besides this advantage, one other motivation for on-going research in this field is the always highlighted low toxicity of thiourea compared to cyanide. This impression is due to the fact that thiourea behaves as a fertilizer in the environment. There is, however, a certain level of toxicity in the effluent streams from thiourea solutions after leaching. Moreover, there are suspicions in connection with damage to the thyroid glands of mice and some cancerous growths in those mammals. The most important technological drawbacks are the high reagent consumption, the non-well established routes for gold recovery from solutions and the production of a definite amount of sulphur as a byproduct, which hinders the leaching process.

The ability of gold to form stable complexes in the form of $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ with thiosulphate ions, has been exploited in the development of alkaline thiosulphate leaching methods. The rate of dissolution is dependent on thiosulphate and dissolved oxygen concentrations and temperature. It has been shown that leaching rates are enhanced in the presence of copper. Ammonium thiosulphate has been used for many decades as a fertilizer and as a consequence, from the environmental view point it has a definite advantage over cyanide.

Bromine has been recognized for many years as a strong gold extractant, but attention on its application to gold hydrometallurgy has been only recently paid. The overall reaction can be given as:



where DMH denotes dibromodimethyl hydantion [18]. The natural advantages claimed for bromine are rapid extraction, non-toxicity and adaptability to a wide range of pH values. Process costs are comparable to those for cyanidation. Disadvantage, as like with the thiourea process, seems to be the high reagent consumption. Similar high reagent consumption is observed in case iodine is applied, instead of bromine, although it forms the most stable gold complexes of all halogens and thus, it leaches gold at low concentrations.

For some of the reagents there is a wealth of accumulated laboratory data, available in the literature, but research on possible improvements in gold solubilization by these reagents still goes on [18]. Although at this moment none of them has a proven industrial utilization, the increase of restriction over cyanide plant implementation could turn them more attractive.

4. Conclusions

Although the theme of the paper is effects on the environment, it was considered worthwhile to discuss some technological aspects of modern gold hydrometallurgy. It is obvious that there can not be a panacea, either in a form of complete process or a newly invented chemical that would allow treating of every kind of gold resources with sufficient efficiency and environmental safety. The diversity of species present in the ores and the resulting process solutions makes the hydrometallurgical extraction of gold extremely complex. Individual process selection must consider as a first priority the environmental impact, which each process unit in the whole flow sheet possess. The following aspects of hydrometallurgical precious metals ores treatment are of utmost importance in this regard:

- the types and amounts of wastes generated;
- the short and long term stability of waste products;
- alteration of minerals and metals by the process;
- process water balance and need for discharge;
- methods of waste disposal and treatment.

Despite fears about immediate and long term toxicity of cyanidation process, this technology remains a proven one with an excellent safety record.

Technology for detoxification of cyanide compounds by natural degradation and oxidation by various agents is available. The long term fate of ions remaining in aquatic environment and soils after operations closure require further studies. Active research on alternative to cyanide reagents is in progress giving hope that the major restraints on their industrial scaling, like high consumption cost, will be eliminated in the not too distant future.

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NEW DEVELOPMENTS IN THE PROCESSING OF CHROMITE TAILINGS

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ABSTRACT. Shaking table, multi-gravity separator, high intensity wet magnetic separator, free jet and column flotation were applied for concentration of Üçköprü fine chromite tailings amounting about 1 million tons and occupying an area of approximately 50000 m². A flow-sheet was developed for the concentration of chromite tailings economically and a concentrate of about 48% Cr₂O₃ content could be obtained with a recovery of about 67.3%. Resultant tailings with 5.6% Cr₂O₃ can be transported to an environmentally suitable area.

1. Introduction

The Karagedik Chromite Concentrator, belonging to Etibank Üçköprü Chromite Mine, has been operating for almost 100 years. During the period of the plant operation, the resultant tailings have amounted about 1 million tons, occupying an area of approximately 50000 m². The tailings assay 12% Cr₂O₃ on the average and grain size is mostly below 1 mm [1].

Fethiye-Mugla region is one of the most spectacular touristic resorts in Turkey. However, the stockpiles of tailing dumps create ugliness to the eyesight, and disturb the natural panorama and more importantly, they lead to environmental pollution. On the other hand, one million tons of tailings with 12% Cr₂O₃ content can be considered as an ore reserve not to be neglected and can be beneficiated economically.

In chromite concentration, gravity methods have been generally used, based on difference between specific gravities of chromite and the gangue minerals, namely, olivine and serpentine. In coarse sizes, heavy medium separation and jigs; in fine sizes of minus 1 mm, shaking-table, spiral, magnetic separator and flotation are the usual methods to be taken into account, as explained by Onal and Guney [2]. Chromite grains below 0.1 mm have been beneficiated by slime tables, high intensity wet magnetic separation and flotation.