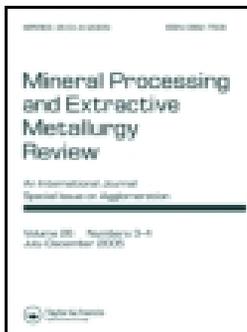


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# AN OVERVIEW OF RECLAIMED WASTEWATER REUSE IN GOLD HEAP LEACHING

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## Abstract

The intensive use of groundwater by the gold mining industry is an important sustainability concern, especially in arid and semiarid regions where groundwater is a scarce resource. Alternatives, such as water reuse, treatment and recycling, have been implemented to overcome this issue. The potential use of reclaimed wastewater in gold heap leaching, without decreasing the process efficiency, has not yet been considered. Hence, this review focuses on the physicochemical, biological and chemical features (organic matter, microbial loads, metal ions and anions) of reclaimed wastewater that may limit its use in gold heap leaching.

**KEYWORDS:** Sustainable mining; reclaimed wastewater; heap leaching; gold, cyanide biodegradation.

## 1. INTRODUCTION

Water quality and availability have become critical global concerns due to economic, social, technological and environmental variables. Approximately 3829 km<sup>3</sup> of water are consumed each year, mainly by the domestic (10%), industrial (20%), and agricultural (70%) sectors (UNESCO 2009).

Approximately 20% of total water used worldwide comes from groundwater. This ratio is rapidly increasing, particularly in dry areas where groundwater is often the only available water resource (UNESCO 2009). This groundwater reliance has led to groundwater depletion in many parts of the world, with the most affected regions located in countries such as India, the United States of America, Mexico, Saudi Arabia, and countries in northern Africa (Aeschbach-Hertig and Gleeson 2012).

Mining activities regularly occur in arid and semiarid regions (Kappes 2002) and are generally considered significant water consumers, which can sometimes arise as a social issue within the communities that are located around some of these mining operations. These operations include gold heap leaching operations, which are generally located in areas experiencing strong aquifer exploitation (Custodio 2002; Morris et al. 2003; Dunne 2012; ICMM 2012). Therefore, new, efficient development approaches must be created to manage water resources in arid/semiarid mining sectors.

This review focuses on the replacement of fresh water with reclaimed water in cyanide heap leaching operations associated with gold (Au) recovery, which represents a water management improvement that should be promoted. The features that characterize this type of water were

reviewed; specifically those that may affect the efficiency of the leaching process and pose an obstacle for use in gold heap leaching operations.

Water recycling is often used by mining operations, particularly for water intensive processes such as flotation, leaching, solvent extraction, electrowinning and dust suppression (Dudeney et al. 2012). The required water quality varies by case, although fresh water is the preferred choice when available. Fresh water access difficulties have prompted various actions. For instance, Chile reduced water consumption associated with mineral concentration processes, decreasing from 1.1 m<sup>3</sup> /Tms to 0.79 m<sup>3</sup> /Tms (Tons of mineral processed), and hydrometallurgical processing, which decreased from 0.3 m<sup>3</sup> /Tms to 0.13 m<sup>3</sup> /Tms (Brantes 2008). Dudeney et al. (2012) presented a thorough review that provides an integral perspective of waste and wastewater management for sulfide leaching. The authors note that wastewater recycling alleviates water consumption and environmental compliance issues and can generate revenue or offset the cost of treatment, as metals can often be recovered from the wastewater. Many gold operations currently practice water recycling. However, additional recycled fresh water is needed to offset losses due to evaporation (5 to 10%) and other factors (Bleivas 2012). This additional water can potentially be provided by reclaimed water.

Treated water can be associated with various sources, often creating variable compositions that require different treatment techniques. Hence, we highlight the possible effects that various biochemical factors, such as organic matter, microbial loads, metal ions, anions (nitrogen and phosphorus sources) and disinfectants, may have on gold recovery.

## **1.2. Gold mining**

Gold can occur in minerals, rocks and ores of different types in a variety of geological environments. An estimated 0.003 to 0.004 parts per million of gold (g Au/ton of ore) exist in the Earth's crust (EPA 1994a; Marsden and House 2006).

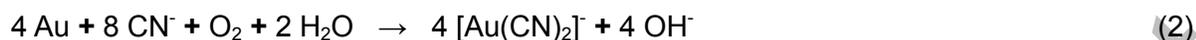
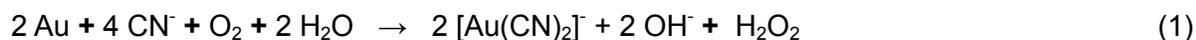
In general, three main processes are used for gold ore beneficiation: cyanidation, flotation and gravity concentration (EPA 1994a; Marsden and House 2006; Gül et al. 2012). The most common gold extraction process is cyanidation, which occurs in either vats or heaps. The method varies based on the mining operation, ore characteristics (gold grade) and economic considerations (operating costs). Mining methods are selected based on maximum ore recovery, efficiency, economic factors and ore body characteristics (including depth, size, shape and strength) (Whiteway and Loree 1990; EPA 1994a, Marsden and House 2006, Gül et al. 2012 ).

### **1.2. Heap leaching with cyanide: Process overview**

Gold heap leaching is a hydrometallurgical process designed to treat amenable low-grade gold ores that contain approximately 0.5 to 1.5 grams of gold per metric ton of ore (g Au/t); concentrations as low as 0.2 g Au/t have been considered attractive for gold recovery when gold prices are high. These low-grade ores are mixed with an alkaline source (e.g.,  $\text{Ca(OH)}_2$  or  $\text{CaCO}_3$ ) and stacked on an impermeable barrier. A water-based solution, or leachate, most often containing sodium cyanide (NaCN), is then applied to the surface of the stacked ore. The alkalinity additive keeps the pH above 10 to prevent the formation of hazardous HCN gas. Gold and other metals contained in the ore are dissolved to various degrees by the leachate as it percolates downward through the stack to the bottom of the heap, where a liner pad allows the recovery of any leached substance and prevents possible ground infiltration (Trexler et al. 1990, Bleiwas 2012). The pregnant solution, or metal-bearing leachate that contains the precious metals, is directed to facilities where the metals are extracted. The barren solution is then reapplied to the top of the stack. Depending on the ore characteristics, this solution can be treated prior to the leaching process. This pretreatment can include crushing, grinding and agglomeration.

The leaching is conducted by sprinkling or dripping a cyanide solution on the top of the heap

(100 to 600 mg/L NaCN) (Kappes 2002; Hilson and Monhemius 2006). According to the following reactions (equations 1 and 2), the cyanide ions form very stable complexes with gold:



These reactions correspond to the generally expected molar ratios  $\text{Au}/\text{O}_2 = 2$  and 4, respectively. A ratio of  $\text{Au}/\text{O}_2 = 4$  indicates the highest oxygen reduction efficiency, while 2 indicates 50% efficiency due to the formation of hydrogen peroxide (Senanayake 2008).

The pregnant leach solution is recovered at the bottom of the heap and is sent to a pregnant solution pond, which allows the suspended particles to precipitate over time. The supernatant is then transported to a recovery plant. The overall gold heap leaching circuit is illustrated in Figure 1.

**<Figure 1>**

Precious metals in the pregnant leach solution are recovered via adsorption on activated carbon or using the Merrill-Crowe zinc dust precipitation process. The choice between carbon adsorption or zinc precipitation is generally based on processing costs and on the gold/silver content of the pregnant solution. The zinc dust precipitation method is typically preferred by large operations where the silver/gold molar ratio exceeds two or where the concentration exceeds 2 mg/L. Carbon adsorption is the method of choice at smaller operations because it costs less (Muhtady 1985).

The carbon adsorption operation process involves precious metal loading from the pregnant solution onto the activated carbon. The gold/silver is then eluted, often using a hot caustic cyanide solution. The stripped carbon is regenerated using steam or thermal reactivation. The gold/silver is then recovered from the concentrated cyanide solution via electrowinning (although zinc dust precipitation can also be used), followed by fire refining to produce dore bullion (Hoye

1987; Mulan et al. 2002).

The Merrill-Crowe process is based on the addition of zinc powder to the pregnant solution, which causes zinc to replace gold ions in the cyanide complexes. This process proceeds according to the following reaction (Eq. 3):



However, two electron-consuming reactions are responsible for lowering the gold precipitation efficiency. These reactions include oxygen and water reduction (equations 4 and 5):



The first reaction is controlled by a deaeration operation. The second reaction is more difficult to control because it depends on an appropriate cyanide dosage to reach low free cyanide concentrations (Viramontes Gamboa et al. 2005). After the Merrill-Crowe operation, the precipitates are separated from the solution using mechanical filters. Concentrated solids are sent to a smelting and refining circuit, while the residual solution is sent to a barren pond where it is combined with natural water and cyanide, which is then sprinkled (or dripped) onto the heaps at the start of a new leaching circuit.

## 2. RECLAIMED WASTEWATER AS AN ALTERNATIVE TO REDUCE WATER USE DURING GOLD EXTRACTION

### 2.1 Water requirements of gold heap leaching

The amount of water used a gold heap-leach operation depends on various factors, such as the method used to apply the leachate; the surface area to be leached; the thickness of the lift; the ore characteristics, including the absorbency and the amount of fines that accompany the ore; the climate and the initial ore moisture when the ore is placed on the heap (Bleiwas 2012).

Kappes (2002) found that leaching solution application rates ranged from approximately 7 to 20 L/m<sup>2</sup>/h and averaged 11 L/m<sup>2</sup>/h based on a survey of 19 heap-leach mining operations that treated crushed ore. A modelled heap-leach gold operation with an annual treatment capacity of 5 Mt of gold ore was estimated to apply approximately 3.6 to 5.4 million m<sup>3</sup> of leachate during one year of operation. The associated makeup water (water used to compensate for evaporative losses from air passing through voids in the heap and losses caused by evaporation from barren and pregnant solution ponds) requirements ranged from approximately 0.18 to 0.54 million m<sup>3</sup> per year (Bleiwas 2012).

An advanced wastewater treatment plant possesses an average capacity of 38,000 m<sup>3</sup>/day (Tchobanoglous et al. 2003), which easily meets daily gold mining requirements. Wastewater treatment plant processes are characterized by numerous quality parameters, such as Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), heavy metals, nitrogen content, phosphorus content, pH, microorganisms and parasites as total coliforms, fecal coliforms and helminth eggs (Tchobanoglous et al. 2003).

### 3. EFFECTS OF IMPURITIES IN TREATED WASTEWATER FOR HEAP LEACHING

#### 3.1 Organic matter in treated wastewater

Wastewater reuse is currently considered the most critical element of sustainable water management worldwide. The organic matter present in biologically treated urban wastewater consists of a heterogeneous mixture of dissolved natural organic matter, soluble microbial products, endocrine-disrupting compounds, pharmaceuticals and personal care product residues, disinfection byproducts, metabolite/transformation products and others (Michael et al. 2015).

The chemical oxygen demand (COD) is commonly used to measure the organic matter present in water, a parameter widely used by wastewater treatment plants to determine if the wastewater has been properly treated (Tchobanoglous et al. 2003). The COD is the electron donating capacity of practically all the organic compounds in the water, including biodegradable or non-biodegradable elements (Duncan and Horan 2003; Tchobanoglous et al. 2003). Some microorganisms found in gold heaps are capable of degrading cyanide, but they are not a concern because their activity is diminished by the limited amounts of organic matter and nutrients in the heaps. Moreover, cyanide degradation is normally observed at pH 7 (Kao et al. 2003; Dash et al. 2009), and gold leaching is conducted at pH levels above 9. Additionally, the high cyanide concentration in the heap inhibits microorganisms (Baxter and Cummings 2006; Dash et al. 2009).

However, the microbial activity of cyanide-degrading microorganisms can increase if a high carbon source is introduced via reclaimed water, as these organisms use cyanide as a nitrogen source (Luque-Almagro et al. 2005; Baxter and Cummings 2006; Nallapan Maniyam et al. 2011;

Khamar et al. 2015, Landkamer et al. 2015). The COD contents of reclaimed water are generally low (Michael et al. 2015), with typical values between 10 and 30 mg/L (Al-Jasser 2011). Still, the COD concentration should be considered as a quality criterion when using reclaimed water.

It is also important to note that the presence of natural organic matter in treated water can drastically decrease the gold adsorption capacity of activated carbon. The organic matter blocks the adsorbent's pores, inhibiting the entrance of the adsorbate into the internal surface area of the activated carbon, which is where the majority of the adsorption sites are located.

### **3.2. Microbial load**

The microbial content in treated wastewaters is generally controlled by ozonation, chlorination or UV-disinfection; however, not all microorganisms are completely eliminated from the water. The potential microbial effects on the heap leaching process will be described and discussed in the following sections. Specifically, we introduce cyanide consumption as a possible occurrence because some microorganisms, such as *Pseudomonas* (Yi et al. 2015) and *Rhodococcus* (Kämpfer et al. 2014), and fungi, such as *Fusarium solani* (Mehl and Epstein 2007), are capable of degrading cyanide bacteria and have been found in wastewater and related processes.

#### **3.2.1 Cyanide consumption by microorganisms**

The presence of cyanide degrading microorganisms is always undesirable during precious metal beneficiation. Understanding the underlying biochemistry is the first step toward planning strategies to avoid cyanide consumption during gold extraction.

Microbial cyanide consumption takes place when microbial species convert free and/or cyanide-complexed metal ions to bicarbonate and ammonia, while free metal ions are either adsorbed onto cells or precipitated. Microorganisms involved in the biological treatment of cyanide and

thiocyanate typically include a heterogeneous mixture of commonly found indigenous soil bacteria and fungi which have adapted to the treatment of cyanide compounds due to continuous exposure (Mudder and Botz 2001; Dash et al. 2009).

Cyanide degradation is generally induced by the presence of cyanide in the media. Cyanide is then converted to a carbon and nitrogen source by various enzymes present in the microorganisms. The metabolic pathway (hydrolytic, oxidative, reductive and substitution/transfer; **Table 1**) (Dash et al. 2009) of cyanide conversion by microorganisms is influenced by the initial concentration, pH, temperature, availability of other energy sources required for cell maintenance and growth, oxygen level, ammonia content and various metal ion concentrations (Pereira et al. 1996; Adjei and Ohta 2000; Gupta et al. 2010). The first three pathways are degradation pathways in which enzymes catalyze the cyanide conversion into simple organic or inorganic molecules that then are further converted to ammonia, methane, CO<sub>2</sub>, formic acid and carboxylic acid. The last two pathways assimilate cyanide in the microbe as a nitrogen and carbon source (Baxter and Cummings 2006).

#### <Table 1>

More than fifteen different genera of bacteria involved in cyanide degradation processes have been identified in the literature. DNA data from these species were used to develop a phylogenetic tree via a basic neighbor-joining analysis of 16S/18S sequences taken from NCBI GenBank (National Center for Biotechnology Information) (**Figure 2**). The tree illustrates that *Pseudomonas* and *Rhodococcus* compose the largest groups of reported cyanide-degrading species. This observation is important because these strains can be found in wastewater (Kämpfer et al. 2014; Sun et al. 2015; Yi et al. 2015) and may be present in reclaimed water. An important difference worth noting is that *Rhodococcus* species possess a single metabolic pathway (nitrile hydratase), which suggests a high degree of specialization related to cyanide degradation (Nallapan Maniyam et al. 2013). Other species (e.g., *Pseudomonas*) display higher

metabolic diversities. In addition, fungi species only exhibited cyanide degradation capacities through the use of the cyanide hydratase enzyme. Other microorganisms, such as *Halomonas* (Khamar et al. 2015) and *Burkholderia* (Adjei and Ohta 2000), degrade cyanide via unidentified metabolic pathways. Some of these microorganisms have been isolated from wastewater treatment sources (Mehl and Epstein 2007, Nallapan Maniyam et al. 2014). This issue is important because the use of treated wastewater for heap leaching may introduce microbial inoculum, cyanide consumption and metallic complex instabilities to the heap.

#### <Figure 2>

Some instances of cyanide consumption by microorganisms have been reported under alkaline conditions ( $\text{pH} > 10$ ) (Dash et al. 2009) (**Table 2**). Although these studies seek to improve effluent treatment, the cyanide degradation potentials of the microorganisms mentioned above must be noted in the context of leaching. The effects of these microorganisms would certainly be highly undesirable, and therefore it is necessary to understand how to prevent them.

#### <Table 2>

Akcil et al. (2003) studied the effects of cyanide concentration and pH on cyanide treatment using aerobic heterotrophic *Pseudomonas* species. They tested pH values from 9.2 to 11.4, finding that a pH of 10.5 was optimal for cyanide degradation. In addition, cyanide was successfully removed at concentrations of 100, 200 and 300 mg/L and drastically reduced at 400 mg/L.

Dumestre et al. (1997) studied four microorganisms and their cyanide degradation capacities. The aerobic fungus *Fusarium solani* and three genera of bacteria (*Corynebacterium sp.*, *Rhodococcus sp.* and *Bacillus sp.*) were obtained from an alkaline soil contaminated with cyanide. Although the authors were able to isolate microorganisms within a very selective

medium, only *Fusarium solani* was able to consistently degrade cyanide at alkaline pH values. Moreover, they observed that fungus growth was only possible in the presence of a supplementary carbon source, i.e., *Fusarium solani* was unable to grow using cyanide as the sole carbon and nitrogen source.

Tiong and Mohd (2015) isolated a group of microorganisms, including *Pseudomonas pseudoalcaligenes*, from the tailings of a gold mining site in Malaysia. Microbial growth was recorded, with cyanide concentrations ranging from 2.6 to 39 mg/L, with lag phase variations contributing to the major differences between values. Complementary experiments identified cyanide degradation of approximately 58% for an initial cyanide concentration of 2.6 mg/L. Further analysis showed that the enzymatic mechanism corresponded to cyanide hydratase, an enzyme also found in fungi species. One of the most relevant findings of this study lies in the fact that other *Pseudomonas* species have been reported as cyanide producers, including *P. aeruginosa*, *P. fluorescence* and *P. plecoglossicida*. These species may play a complementary role when cyanide producers are present, such as *Chromobacterium violaceum*. Shin et al. (2015) demonstrated that *C. violaceum* is able to produce and accumulate enough cyanide to induce PGMs leaching in a batch system; however, no reports exist regarding the roles of these bacteria in heap leaching operations. Thus, these roles must be further evaluated during cyanide biogenesis or consumption.

### **3.2.2 Cyanide biogenesis by microorganisms present in treated wastewater**

Some microorganisms are capable of generating cyanide under certain conditions, which may improve the heap leaching process. Studies of gold bioleaching microorganisms have focused on species such as *Chromobacterium violaceum*, *Bacillus megaterium*, *Pseudomonas fluorescens* and *Pseudomonas plecoglossicida*, which are generally found in plants used to treat

wastewater and drinking water filters (Nishimori et al. 2000; Haselkorn 2003; Vary et al. 2007; Li et al. 2008; Stoimenova et al. 2009; Paes et al. 2012).

*Chromobacterium violaceum*, *Bacillus megaterium*, *Pseudomonas fluorescens* and *Pseudomonas plecoglossicida* are microorganisms capable of producing metabolic cyanide. Hence, these microorganisms can play an active role in gold extraction (Campbell et al. 2001; Tay et al. 2013). Among the aforementioned species, *C. violaceum* is noteworthy because of its remarkable cyanide production capacity, which can significantly affect gold extraction.

*C. violaceum* is a mesophilic, motile, gram-negative, facultative anaerobe that produces cyanide as a secondary metabolite. It is a saprophyte in soil and water and is common in tropical climates (Koburger and May 1982; Durán and Menck 2001; Garrity 2005). This microorganism can produce extracellular cyanide during mid- to late logarithmic phases and briefly during early stationary phases (Knowles 1976). *C. violaceum* is able to grow as a biofilm over gold coated surfaces and gold ore concentrates, solubilizing the precious metal (Campbell et al. 2001; Fairbrother et al. 2009). However, significant gold extraction has only been observed for ground (180  $\mu\text{m}$ ), low grade ores (Shin et al, 2013).

It remains unknown if *C. violaceum* can be isolated from wastewater; however, it has been isolated from soils, drinking water biofilters, various water bodies and stagnant water in tropical regions (Koburger and May 1982; Byamukama et al. 2005; Garrity 2005; Chang et al. 2007; Feng et al. 2013). A potentially useful approach for gold mining operations may be to biologically produce cyanide in relatively small quantities at the ore surface. These species can be used to enhance gold cyanidation process. However, the positive contribution of this species would be minimal in a conventional leaching process due to the lack of nutrients and heap conditions. Therefore, experiments must be conducted based on conditions similar to those in heap leaching operations.

Two potentially contrasting microbial load effects (cyanide production and cyanide consumption) can occur when using treated wastewater for heap leaching. These processes can even occur under extreme environmental conditions. *Bacillus megaterium*, *Chromobacterium violaceum*, *Pseudomonas fluorescens* and *Pseudomonas plecoglossicida* have already been found in different inoculum sources related to wastewater treatment (**Table 3**). In addition, Tiong and Mohd (2015) and Khamar et al. (2015) utilized microorganisms that were directly isolated from cyanide tailing ponds.

However, the impacts of the treated wastewater components and cyanide degraders must be directly studied. Cyanide heap leaching provides favorable conditions for the microorganisms, although the nutrient availability may affect the biodegradation of cyanide compounds (Baxter and Cummings 2006).

### <Table 3>

### **3.3 Effects of metal ions, anions and disinfectants in treated wastewater**

Cyanicide (substances that consume or destroy cyanide) treatments enhance the cyanide leaching efficiency and avoid higher cyanide consumption. Different authors (Trexler et al. 1990; Adams 2005) have reported that cyanicides chemically interfere with gold cyanidation, resulting in the formation of stronger cyanide complexes than are formed with gold. Additionally, cyanicides compete with gold in the consumption of dissolved oxygen (e.g., Ca, C, Mn and partially oxidized sulfides of Sb, Zn, Fe, Cu and As). The early identification of these species is necessary so that the appropriate corrective measures can be taken to minimize detrimental effects, either via a pretreatment option or adjusting operating parameters during leaching (Adams 2005). Carbonaceous materials prematurely adsorb the dissolved metal cyanide complexes, and organic substances consume the dissolved oxygen from the leach liquor (Kongolo and Mwema 1998).

### **3.3.1 Metal ions and their cyanide complexation**

In addition to gold, many other metals and minerals also dissolve in dilute alkaline cyanide solutions. These reactions consume cyanide and oxygen and produce a variety of solution species that can reduce the efficiency of gold leaching and subsequent recovery processes (Marsden and House 2006).

Metal ions are found in treated wastewaters (Chipasa 2003; Karvelas et al. 2003; Tchobanoglous et al. 2003; Üstün 2009) and some ions, such as  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ , form complexes with cyanide, which can deplete the leach liquor of free cyanide and retard gold dissolution (Fink and Putnam 1950; Mudder and Botz 2001). Copper, cobalt and zinc in the ore may preferentially take the place of gold and silver in the leaching reaction, reducing the extraction efficiency (Chamberlain and Pojar 1984).

Copper is generally undesirable during leaching because it can consume cyanide and dissolved oxygen, retard gold dissolution rates, interfere with subsequent recovery processes and contaminate the final product. When present in cyanide leach solutions, copper is predominantly present as a mix of three forms: copper dicyanide (II), copper tricyanide (II) and copper tetracyanide(IV) (Mudder and Botz 2001). Copper tricyanide(II) is the most common of these forms (Dai et al. 2012; Parga et al. 2013). The high copper concentration in solution requires a NaCN concentration of approximately 700 mg/L. Gold recovery significantly decreases when the average NaCN concentration is below 640 mg/L (Deschênes and Prud'homme 1997).

Cyanide reacts with iron (II) ions to form stable octahedral complexes within the pH range from 7.5 to 10.5 (Marsden and House 2006). These complexes include ferrocyanide/hexacyanoferrate(II), in which iron exists in a reduced oxidation state of +2. Ferrocyanide, the typical form in solution at ambient redox potentials, is readily oxidized to ferricyanide/hexacyanoferrate(III). In this case, iron is present in the oxidized ferric form, with an

oxidation state of +3 (Mudder and Botz 2001). Metallic iron is virtually insoluble in alkaline cyanide solutions. However, the formation of insoluble iron oxides and/or hydroxides is not desirable either prior to or during cyanide leaching because these products may coat gold particles and reduce the leaching efficiency, sometimes significantly (Rees and Van Deventer 2000).

Metallic zinc is used to recover gold from cyanide leach solutions during the Merrill-Crowe process. The behavior of zinc and its complexes in solution is of considerable interest. Zero-valent zinc readily dissolves in aerated alkaline cyanide solution to form a Zn(II) cyanide complex or zinc hydroxide depending on the solution conditions (Marsden and House 2006). Zinc can also take the place of gold and silver in the cyanide reaction (Chamberlain and Pojar 1984) and is thus undesirable in the leaching process.

The presence of other metal ions in the gold recovery liquor solution during the Merrill-Crowe process is also undesirable because these ions exhibit various detrimental effects on zinc cementation. Fleming (1992) reported that antimony and arsenic have the most negative effect on cementation. Early publications showed that concentrations of these ions as low as 1 ppm can reduce the cementation rate by 20 percent (Finkelstein, 1972). High concentrations of these ions can be decreased by treating the mill solution with sodium sulfide and filtering the resulting insoluble antimony and arsenic sulphides. However, silver would be lost from the mill solution. As previously mentioned, the presence of copper in cyanide solutions generally results in high cyanide consumption and decreases the precipitation efficiency due to zinc passivation. However, the use of powdered zinc exposes a fresh surface on a continuous basis. Hence, gold and silver precipitation is typically complete. Maintaining a higher free cyanide concentration in the precipitation circuit normally prevents the copper from precipitating, thereby reducing zinc surface passivation.

Low  $\text{Pb}^{2+}$  (Jeffrey and Ritchie 2000),  $\text{Hg}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Tl}^+$  concentrations can enhance gold leaching, as these metals depolarize gold surfaces and prevent or reduce passivation (Fink and Putnam 1950; Marsden and House 2006). In the case of lead is explained because it reduces the overpotential required for the oxidation of gold and it enhances the reduction of oxygen. Lead nitrate improved gold extraction and decreased cyanide consumption in batch leaching experiments (Deschênes and Wallingford 1995; Deschênes and Prud'homme 1997; May et al. 2005). The potential disadvantage of this method is that added metal species may be introduced to the final gold product or the tailings. Although lead ion additions have been proven beneficial and achieved concentrations of 1 to 10 mg/L, lead concentrations in excess of 20 mg/L have been found to retard gold dissolution (Marsden and House 2006). The addition of lead nitrate to sulphides in cyanide solutions can create a synergetic effect, which increases the gold dissolution rates of cyanide solutions. This increase is accompanied by a decrease in the gold corrosion potential and a significant decline in the thiocyanate and free sulphide concentrations (May et al. 2005).

Calcium ions are introduced into the cyanide pulp in the form of lime, which is the most commonly used protective alkali, and as calcium cyanide (Stanley 1987). The latter forms readily soluble complexes, such as the calcium aurocyanide complex. The adsorption of gold onto activated carbon is mainly dependent on the cation concentrations of the adsorption medium. The degree to which the aurocyanide complexes are adsorbed onto the activated carbon follows the series  $\text{Ca} > \text{Mg} > \text{H} > \text{Li} > \text{Na} > \text{K}$ , with calcium aurocyanide being the most stable complex and potassium aurocyanide the least (Davidson 1974). Activated carbon can load small quantities of calcium carbonate, cyanide, hydroxide and iron sulphide, which poisons the carbon, decreasing the gold adsorption capacity (Sheya and Palmer 1989). Calcium carbonate may eventually precipitate and reduce the heap permeability (Bartlett 1998).

Bahrami et al. (2007) compared Au, Ag and Hg recoveries when 500 g of a gold ore sample was placed in a glass reactor fitted with a mechanical stirrer at room temperature (the ore was from a deposit located near the Pouyazarkan gold processing plant and contained 3.8 g Au/t, on average). The pH was maintained at 10.2–10.4. The leaching was performed with fresh water, original process water and process water that had been either neutralized or treated with activated carbon to remove dissolved metals. The Au and Ag recoveries were 93 and 71.7% when leached with fresh water and 91 and 66.2% when leached with process water that had been treated with activated carbon for 1 hour, respectively. Cyanide consumption was substantially reduced when process water was used, indicating the feasibility of using process water. However, the authors did not measure the metal ion content in the process water that was used for the experiments. The amount of heavy metal ions present in municipal wastewater represents a very small amount compared to what is generally found in process water from leaching. Metal ion quantities are significantly reduced after wastewater treatment (**Table 4**). The relative abundance of metal ions in the wastewater samples followed the general order: [Cd] < [Cr] ≤ [Pb] < [Mn] < [Ni] ≤ [Cu] < [Zn] < [Fe] (Chipasa 2003; Karvelas et al. 2003).

**Table 4** shows the metal ion concentrations found in the influents and effluents from three treatment plants. The metal ion concentrations are minimal. However, the chemical equilibriums occurring in the solution should be established to evaluate the cyanide-consuming potential of metal ions in reclaimed wastewater (EPA 1994b; Kappes 2002).

#### <Table 4>

Chemical equilibriums, which can be simultaneously solved using Visual MINTEQ software, can be used to determine the cyanide complex concentration. A simple analysis was developed based on a total cyanide concentration of 200 mg CN/L (EPA 1994b; Kappes 2002) and a solution pH from 9 to 11. Metallic ions concentrations were fixed according to data from a San

Luis Potosi wastewater treatment plant (**Table 5**), which receives domestic and industrial wastewater. The reclaimed water is used as cooling water for energy generation. The data represent an average of the values obtained over 3 months of operation (CEASLP 2014).

#### < Table 5 >

The experiment revealed that, apart from free cyanide ( $\text{CN}^-$ ) and hydrogen cyanide (HCN),  $\text{Fe}^{2+}$  is the most important component of the system. In addition, the study suggests that metal ions in reclaimed water can be classified by importance as cyanide consumers as follows:  $\text{Fe} > \text{Zn} > \text{Ni} > \text{Cu}$ .

The software results suggest that the cyanide consumed by complexation of the metal ions in the water described in **Table 6** reached 0.09, 0.5 and 0.58 % at pH values of 9, 10 and 11, respectively. The percentages of cyanide lost as HCN were 60, 13.5 and 1.53%, respectively. Although metal ion complexes are numerous, they represent less than 0.6% of cyanide in solution. Thus, HCN represents a much broader cyanide pool compared with metal ion complexes at the evaluated pH levels. This result is significant when the system is open to atmosphere (as it is in gold heap leaching) because HCN can be easily volatilized and lost to the atmosphere and become an environmental hazard. This last is prevented by a careful control of alkalinity ( $\text{pH} > 10$ ).

Therefore, no considerable adverse effects on the cyanide concentration are foreseen because of metal ions (at the concentrations considered in this review) in reclaimed wastewater. Although, this does not consider the build-up effect associated with water recirculation.

### **3.3.2 Anions present in reclaimed water**

Wastewater contains nitrates, phosphates, carbonates and other anions, which can be reduced to low concentrations in wastewater treatment plant effluents via proper treatment techniques. The phosphate and nitrate contents should be minimal, preventing the eutrophication in water bodies in which the treated effluent is released (Conley et al. 2009; Al-Jasser 2011). **Table 7** shows the anion concentrations in treated wastewater.

**<Table 7>**

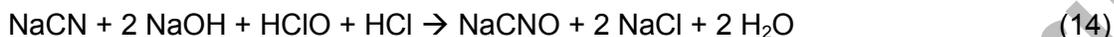
The concentrations of anions such as ammonium, nitrates and phosphates should be minimized, as they represent potential nutrient sources for both microorganisms that are indigenous to the heap and those that are introduced via the reclaimed water. As previously mentioned, microbial activity could lead to cyanide degradation and affect the gold recovery (Johnson 2015, Landkamer et al. 2015).

Nitrates form part of a lixiviate due to natural cyanide degradation and react with other chemical components within the system to form much less toxic concentrations (Logsdon 1999). The presence of anions in the leachate can affect the gold recovery using activated carbon. The gold-loading capacity of activated carbon decreases when the anion concentrations in solution increase in the order:  $\text{CN}^- > \text{S}^{2-} > \text{SCN}^- > \text{SO}_3^{2-} > \text{OH}^- > \text{Cl}^- > \text{NO}_3^-$  (Stanley 1987). Phosphate ions have been used to prevent the acid mine drainage and metal mobilization in mining waste (Mauric and Lottermoser 2011). However, specific studies of the impacts of phosphate and anionic compounds on heap leaching processes are necessary to establish the effectiveness of using reclaimed water.

### **3.3.3 Disinfectants used in wastewater treatment**

Treated wastewater is typically subjected to a disinfection process to eliminate harmful microorganisms. Various operations can be used, including ozone, UV radiation and chlorination (Naidoo and Olaniran 2013). Among these treatments, the chlorine introduced during

chlorination is the only compound that remains in the water after disinfection. In fact, residual chlorine concentrations (as HClO) in water generally range between 0.2 and 1.5 mg/L (WHO 2008). This may pose a problem, as a sufficient amount of the residual chlorine in a free alkaline medium (pH above 8.5) could provoke the oxidation of cyanide to cyanate:



This reaction is essentially instantaneous. In theory, it requires 1 mole of chlorine and 2 moles of caustic per mol of  $\text{CN}^-$  consumed.

Furthermore, further oxidation of cyanate to  $\text{CO}_2$  and  $\text{N}_2$  can proceed according to the following reaction if enough chlorine is present:



This reaction requires 3 moles of chlorine per 2 moles of  $\text{CN}^-$  and 4 moles of NaOH, although it proceeds much more slowly (Dobson 1947).

Taking both equations and the expected cyanide and free chlorine concentrations (7.7 mM  $\text{CN}^-$ , 0.0211 mM HClO) into account, it is expected that free chlorine would not significantly affect the cyanide concentration in the leaching solution (0.0211 mM of HClO is consumed by 0.0211 mM of  $\text{CN}^-$ ). It may be necessary to use other methods for disinfection, such as ultraviolet light or ozone, which reduce the formation of disinfectant by-products and avoid chlorine interference. However, these methods include major disadvantages, such as high costs (EPA 1999; Lazarova 1999).

## 4. SUMMARY

The microbial load is considered as an important factor in groundwater replacement by reclaimed wastewater, but it is not necessarily undesirable. Some microbial species found in wastewater may be useful for the pretreatment of refractory ores. Microorganisms naturally occur in heap leaching sites, are often adapted to demanding environments and can play relevant roles as cyanide consumers. However, knowledge of their natural characteristics and activity remains limited.

Equilibrium calculations have shown that the metal ion concentrations in reclaimed wastewater are not an important factor in cyanide consumption. Less than 0.6% of cyanide accounts for metal ion complexation in treated wastewater. In addition, the anions present in the treated wastewater do not seem to interfere with the leaching process, but additional studies involving leaching and gold recovery are necessary. Meanwhile, free chlorine, which is widely used as a disinfectant in treated wastewater, generates the oxidation of cyanide to cyanate,  $\text{CO}_2$  and  $\text{N}_2$ . It is unlikely that the free chlorine decreases cyanide concentrations, because chlorine is not overly abundant in treated wastewaters.

In summary, this theoretical analysis indicates that the replacement of groundwater with treated water is likely unproblematic at the process performance level. However, it is highly recommended that additional experiments are conducted prior to full-scale implementation, ensuring that no additional parameters (not considered in this review) could negatively affect the process.

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**Table 1.** Cyanide biodegradation pathways

Enzymes	Microorganism	Pathways	Reference
Hydrolytic reactions			
Cyanide hydratase	<ul style="list-style-type: none"> <li>• <i>Stemphylium loti</i></li> <li>• <i>Gloeocercospora sorghi</i></li> <li>• <i>Helminthosporium turcicum</i></li> <li>• <i>Aspergillus niger</i></li> <li>• <i>Aspergillus nidulans</i></li> <li>• <i>Setosphaeria turcica</i></li> <li>• <i>Leptosphaeria masculans</i></li> <li>• <i>Fusarium solani</i></li> <li>• <i>Neurospora crassa</i></li> <li>• <i>Thiobacillus plumbophilus</i></li> <li>• <i>Pseudomona pseudoalcaligenes</i></li> </ul>	$HCN + H_2O \rightarrow HCONH_2$	(Desai and Ramakrishna 1998; Basile et al. 2008; Dent et al. 2009; Woodward et al. 2008; Rinágelová et al. 2014; Barclay et al. 1998)
Nitrile hydratase	<ul style="list-style-type: none"> <li>• <i>Klebsiella oxytoca</i></li> <li>• <i>Rhodococcus erythro polis</i></li> <li>• <i>Rhodococcus borito lerans</i></li> <li>• <i>Rhodococcus rhodochrous</i></li> <li>• <i>Pseudonocardia thermophila</i></li> </ul>	$HCN + H_2O \rightarrow HCONH_2$	(Kang et al. 2014; Kao et al. 2006; Lin et al. 2012; Rucka et al. 2014)
Cyanidase	<ul style="list-style-type: none"> <li>• <i>Alcaligenes Xylosoxidans subsp. Denitrificans</i></li> <li>• <i>Pseudomonas fluorescens biotype II</i></li> <li>• <i>Pseudomonas stutzeri</i></li> <li>• <i>Klebsiella sp.</i></li> </ul>	$HCN + 2H_2O \rightarrow HCOOH + NH_3$	(Harris and Knowles 1983; Ingvorsen et al. 1991; Watanabe et al. 1998; Mak et al. 2005)
Oxidative reactions			
Cyanide	<ul style="list-style-type: none"> <li>• <i>Pseudomonas putida</i></li> </ul>	$HCN + O_2 + H^+ + NADPH \rightarrow HOCN +$	(Chapatwala et al.

monoxygenase	• <i>Pseudomonas fluorescen</i>	$NADP^+ + H_2O$	1998; Desai and Ramakrishna 1998)
Cyanide dioxygenase	• <i>E. coli</i> • <i>Pseudomonas fluorescens</i>	$HCN + O_2 + 2H^+ + NADPH \rightarrow CO_2 + NH_3 + NADP^+$	(Ebbs 2004; Figueira et al. 1996; Kunz et al 1998)
Reductive reactions			
Nitrogenase	• <i>Klebsiella oxytoca</i> • <i>Azotobacter vinelandii</i>	$HCN + 2H^+ + 2e^- \rightarrow CH_2NH + H_2O \rightarrow CH_2O$ $CH_2NH + 2H^+ + 2e^- \rightarrow CH_3NH + 2H^+ + 2e^- \rightarrow CH_4 + NH_3$	(Kao et al. 2003; Koksunan et al. 2013)
Substitution/transfer reactions			
Thiosulfate:cyanide sulfurtransferase (rhodanase)	• <i>Thiobacillus</i> • <i>Arthrobacter</i> • <i>Pseudomonas species</i> • <i>Roseobacter denitrificans</i>	$CN^- \rightarrow S_2O_3^- \rightarrow SCN^- + SO_3^{2-}$	(Conway et al. 2012; Paruchuri et al. 1990; Sorokin et al. 2001)

**Table 2.** Microorganisms capable of degrading cyanide at alkaline pH values

Microorganisms	Reactor	Cyanide Concentration (mM)	pH	Temperature	Reference
<i>Pseudomonas sp.</i>	Batch	3.8 - 15.4	9.2 - 11.4	30 °C	(Akcil et al. 2003)
<i>Pseudomonas pseudoalcaligenes</i>	Batch	0.1 - 1.5	10	30	(Tiong and Mohd 2015)
<i>Fusarium solani</i>	Batch	0.5 - 0.8	9.2 - 10.7	30 °C	(Dumestre et al. 1997)
<i>Rhodococcus UKMP-5M</i>	Batch	1 - 15; 15	8.4 - 9.5	30 °C	(Nallapan Maniyam et al. 2014)
<i>Halomonas BN1</i>	Batch co-culture	1.9	8.5 - 11.5	25 °C	(Khamar et al. 2015)
<i>Halomonas DNB</i>	Batch co-culture	1.9	8.5 - 11.5	25 °C	(Khamar et al. 2015)

**Table 3.** Type of inoculum sources related to wastewater treatment that could produce biogenesis or degradation of cyanide

Microorganism	Effect	Metabolism	Inoculum source	Water treatment process	Reference
<i>Chromobacterium violaceum</i>	Cyanide biogenesis	Facultative anaerobe heterotroph Alternative electron acceptors: nitrate and fumarate	Granular activated carbon and sand from drinking water filters	Drinking water filter.	(Haselkorn 2003; Feng et al. 2013)
<i>Bacillus megaterium</i>	Cyanide biogenesis	Aerobic heterotroph	Chlorine tank of the wastewater treatment station.	Wastewater treatment plant	(Paes et al. 2012; Vary et al. 2007)
<i>Pseudomonas fluorescens</i>	Cyanide biogenesis	Aerobic heterotroph	Wastewater samples	-	(Stoimenova et al. 2009)
<i>Pseudomonas plecoglossicida</i>	Cyanide biogenesis	Aerobic heterotroph	Wastewater treatment biofilms	Laboratory-scale nitrobenzene-compound wastewater treatment plant	(Li et al. 2008; Nishimori et al. 2000)

<i>Pseudomonas pseudoalcaligenes</i>	Cyanide degradation	Aerobic heterotroph	Heap leaching process	Tailing pond	(Tiong and Mohd 2015)
<i>Halomonas BN1</i>	Cyanide degradation	Aerobic heterotroph	Heap leaching process	Tailing pond	(Khamar et al. 2015)
<i>Halomonas DNB</i>	Cyanide degradation	Aerobic heterotroph	Heap leaching process	Tailing pond	(Khamar et al. 2015)

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**Table 4.** Comparison of heavy metal ions concentrations in effluents from three wastewater treatment plants

Parameter µg/L	Raw influent		Secondary effluent		
	California USA <sup>1</sup>	Thessaloniki Greece <sup>2</sup>	California USA <sup>1</sup>	Thessaloniki Greece <sup>2</sup>	San Luis Potosi Mexico <sup>3</sup>
Cd	3.6	ND	1.2	ND	ND
Cu	63	79	43	58	12.5
Cr	3	40	7	25	13
Hg	0.3	ND	0.1	ND	0.1
Ni	7	770	4	600	6
Fe	600	480	180	450	350
Pb	8	39	8	31	14
Zn	81	470	24	380	15

1. Adapted from WCPH, primary treatment consisted of a rotary drum screen followed by disk screens, secondary treatment was water hyacinths (Tchobanoglous et al. 2003)

2 WTP of the city of Thessaloniki, northern Greece operating in the activated sludge mode Wastewater sampling was conducted in two one-week campaigns during November and December 2001 (Karvelas et al. 2003).

3 WTP from San Luis Potosí México. Operating dual treatment, Average metallic ion concentrations in wastewater treatment plant for 3 months of monitoring February - April 2014 (CEASLP 2014).

**Table 5.** Average metallic ion concentrations registered in effluents from a wastewater treatment plant in Mexico. The data was produced after three months of monitoring.

Parameter	Average Secondary effluent $\mu\text{g/L}$	Range	Standard deviation
Cu	12.5	10-20	7.07
Cr	13	10-30	2.823
Ni	6	0-6	ND
Fe	350	290-410	55.67
Pb	14	0-14	ND
Zn	15	0-15	19.63

Average metallic ion concentrations registered from February to April 2014 (CEASLP 2014).

**Table 6.** Average anion concentrations registered in effluents from a wastewater treatment plant in Mexico. The data was produced after three months of monitoring.

Parameter	Average Secondary effluent mg/L	Range mg/L	Standard deviation
NO <sub>3</sub> <sup>-</sup>	1.92	1.4-2.4	0.22
PO <sub>4</sub> <sup>3-</sup>	0.973	0.255-1.71	0.73
CO <sub>3</sub> <sup>2-</sup>	376.5625	344-409	31.95

Average anion concentrations registered from February to April 2014 (CEASLP 2014)

Figure 1

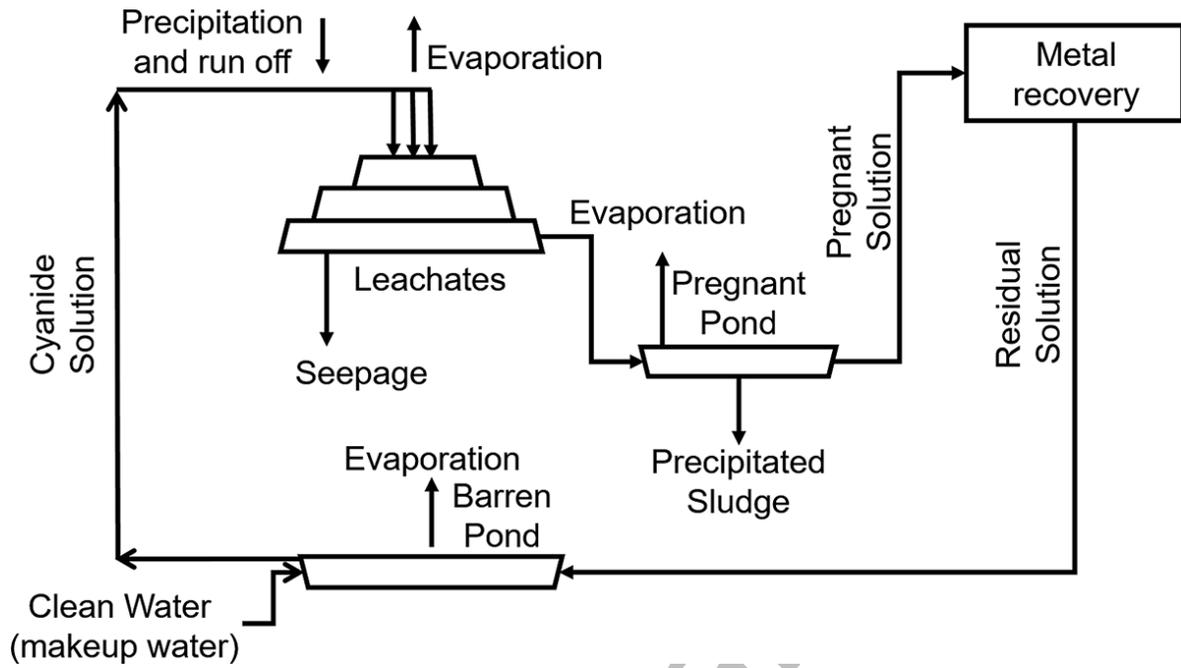


Figure 2

