A Look at Chemical Degradation vs. Biodegradation of Cyanide and Metal-Complexed Cyanides Found in Industrial Wastewater Generated by the Mining Industry

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Abstract

The mining industry has been using cyanide in their metal recovery processes for over 100 years. During this time, the mining industry has found several ways to destroy and recover the cyanide from their processes. However, due to cyanide's toxicity and potentially devastating environmental effects, it is still a major environmental concern. This paper examines both the chemical and biological treatment processes currently used by the mining industry to treat their cyanide wastes. Further, some discussion is made about the added water quality benefits of using a biological treatment process instead of a chemical process. The paper finishes by discussing the economic and environmental viability of a biological treatment process, as well as future applications of microorganisms, and even plants, in the biodegradation of cyanide.

Keywords

Biodegradation, Biofilm, Cyanidation, Denitrification, Nitrification, Rotating Biological Contactor (RBC), Suspended Sludge System

Introduction

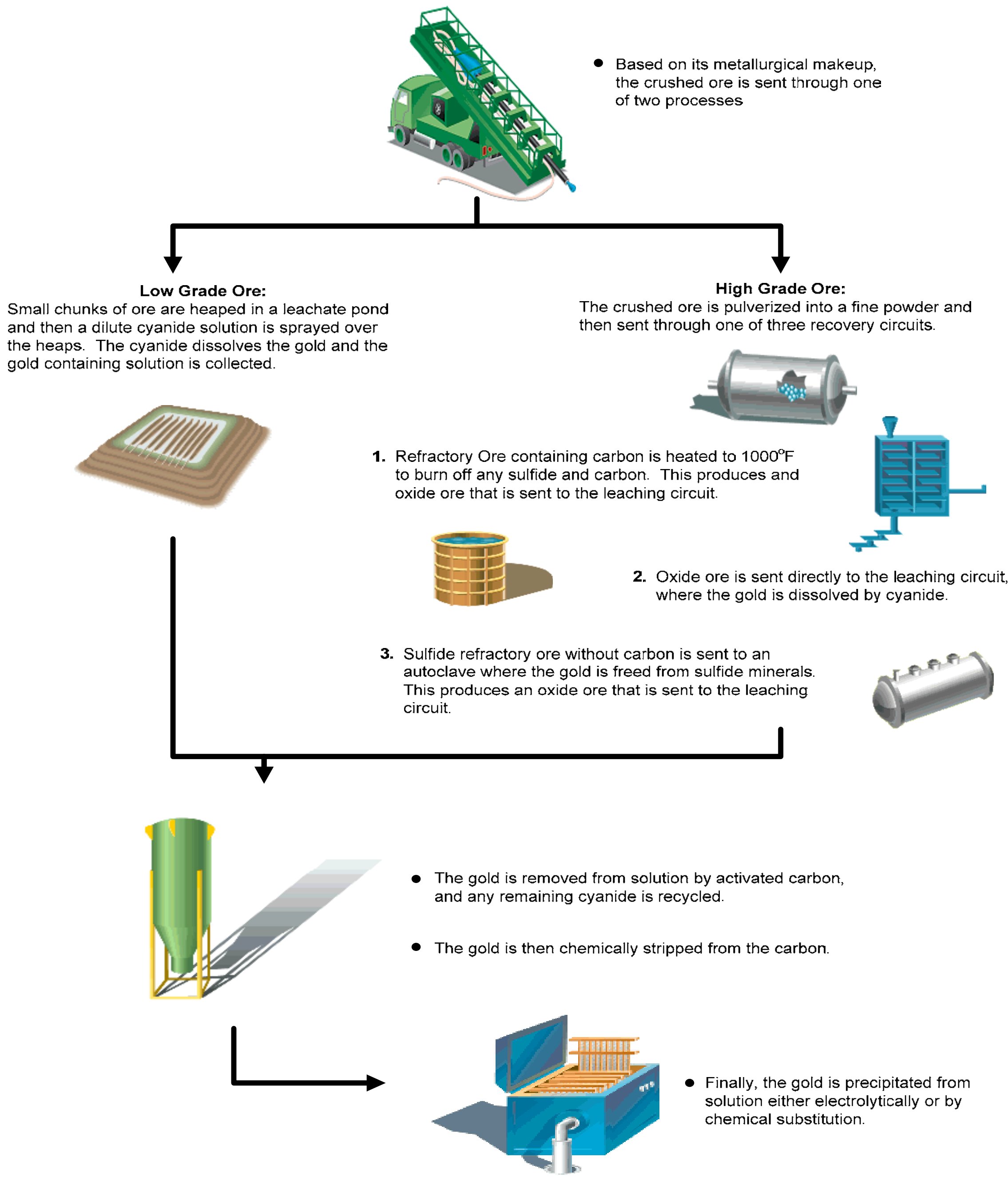
Since ancient times humankind has placed a high value on precious metals, such as gold and silver. It is no wonder than, that man, to this day, invests considerable effort and resources into the mining and extraction of these metals. Unlike humankind's unwavering lust for gold and silver, the method by which these metals are mined has changed over the years. Over the last 100 years or so, the most popular process for mining precious metals has been cyanidation.

The cyanidation process used in today's mining industry was developed by John Seward MacArthur in 1887. MacArthur's process involved finely grinding the mined ore and then mixing it with a dilute solution of sodium cyanide in the presence of atmospheric oxygen. Under these conditions the cyanide anions will dissolve and combine with the gold and silver cations in the ore to form a metal complex. This metal complex can then be removed from solution, and the gold and silver can be recovered through another process. An overview of the process can be viewed in Fig. 1 below.

What is of most concern in this paper is how the cyanide waste from the mining process is dealt with. Cyanide and cyanide complexes, in high concentration, can be toxic to many living organisms. For example, in the late 1980's large amounts of acid mine drainage and contaminants, including high concentrations of cyanide, were released into the Alamosa River from the Summitville mine leach pond. By the early 1990's, large fish kills were being documented in the Alamosa River up to 20 miles down stream from the contamination site (Colorado Riparian). Disasters like this one are rare, but further illustrate just how important it is to effectively neutralize the cyanide waste products generated by the mining industry.

Currently there are several methods, chemical, physical, and biological, that can be utilized to effectively degrade cyanide. The chemical and physical methods tend to be complex and costly. Biological treatment, however, is becoming less costly with advances in biotechnology and can be just as effective. This paper will examine both the chemical and biological destruction processes that transform cyanide into less toxic compounds, and discuss the feasibility of implementing biological treatment as an alternative to the current standard.

Fig. 1 The Cyanidation Process Used by the Mining Industry
(Adapted from http://www.responsiblegold.org/goldproduction.asp)



Chemical and Physical Treatment Alternatives

The use of large quantities of cyanide by the mining industry has led to the development and subsequent implementation of several physical and chemical processes to remediate the waste products of mining by cyanidation (Baxter and Cummings 2006). Determining which process is the most appropriate method of cyanide removal for a particular mining operation should be based on the chemical characteristics of the waste, the volume of waste that is expected to be treated, the environmental settings of the treatment site, and any regulations that manage discharges from the site (Akcil 2003). With this in mind, it is important to understand that although chemical destruction processes for cyanide may differ greatly from one method to the next, most operate by converting cyanide into less toxic compounds through oxidation reactions. Some of the most commercially accepted processes that are proven to reduce levels of cyanide in treated effluent are sulfur dioxide/air (INCO), hydrogen peroxide, and alkaline breakpoint chlorination. Each of these processes is described below.

Sulfur dioxide/air (INCO):

The sulfur dioxide/air process, also known as INCO, combines sulfur dioxide (SO_2) and air with a copper catalyst to oxidize cyanide (CN^-) to cyanate (OCN^-), a less toxic compound.

$$SO_2 + O_2 + H_2 0 + CN^- \xrightarrow{Cu^{2+} catalyst} OCN^- + SO_4^{2-} + 2H^+ \quad (1)$$

The INCO process was developed primarily for the treatment of tailing slurries. The reaction produces a low pH in the slurry, which is countered by the addition of lime. Not only does the lime raise the pH to acceptable level, but it also leads to the production of metal hydroxide sludge (Baxter and Cummings 2006).

Hydrogen peroxide:

The hydrogen peroxide process works much like the sulfur dioxide/air process. It uses the same copper catalyst, but instead of sulfur dioxide and air it uses hydrogen peroxide, a much more potent oxidant than the oxygen in air.

$$H_2O_2 + CN^- \xrightarrow{Cu^{2+} catalyst} OCN^- + H_2 0 \quad (2)$$

The hydrogen peroxide process, unlike the sulfur dioxide/air process, is primarily used in the treatment of effluent, because of the high consumption of hydrogen peroxide in the treatment of slurries (Akcil 2003). The hydrogen peroxide process is widely used in North American mining operations because it is cheap, it operates over a wide rang of pH's, and it produces effluent with acceptable cyanide levels without increasing total dissolved solids.

Alkaline breakpoint chlorination:

Alkaline breakpoint chlorination is amongst the earliest methods developed and used in the chemical oxidation of cyanide (Baxter and Cummings 2006). It is a two-step process. The first step involves converting cyanide to cyanogen chloride (CNCl). The second step involves the hydrolysis of cyanogen chloride into cyanate (OCN^-).

$$Cl_2 + CN^- \rightarrow CNCl + Cl^- \quad (3)$$

$$CNCl + H_2 0 \rightarrow OCN^- + Cl^- + 2H^+ \quad (4)$$

In today's mining operations the alkaline breakpoint chlorination method has been almost entirely replaced by other treatment methods. This is primarily due to the high cost of reagents to control the pH generated by the reactions and the reactions high consumption of chlorine.

Biological Treatment Alternatives

The ability to degrade simple and inorganic cyanides has been demonstrated by both eukaryotes and prokaryotes from a diverse range of taxa across a wide range of metabolic pathways (Baxter and Cummings 2006). Some of the pathways that have been observed in laboratory experiments include hydrolytic, oxidative, reductive, substitution, and transfer reactions (Baxter and Cummings 2006). However, in today's mining industry, the most accepted and most feasible form of biological treatment of cyanide is through the use of bacteria. Some of the more notable bacteria utilized are *Pseudomonas, Achromobacter, Flavobacterium, Nocardia, Bdellovibrio, Mycobacterium*, and the tried and true nitrifiers, *Nitrosomonas* and *Nitrobacter*.

In the biological treatment process, bacteria are used to naturally biodegrade both free and metal-complexed cyanides to bicarbonate and ammonia (Akcil 2003). The metals that are freed in the process are either absorbed by the biofilm or are precipitated out of solution (Akcil 2003). It is important to note that the rate at which these metal-cyanide complexes (Zn, Cu, Ni, and Fe) degrade is directly related to their chemical stability.

The use of microorganisms in the destruction of cyanide in tailing solutions and other mining related wastewaters is a proven alternative to the traditional chemical and physical processes in use today (Akcil 2003). Additionally, the ability of a biological system to be adapted/engineered to handle large flows and high cyanide levels makes biological treatment even more valuable to industrial mining companies.

Homestake Mining Co. – Biological treatment processes:

The successfully biodegradation of metal-cyanide complexes has been shown in aerobic and anaerobic conditions in both bench scale and pilot studies (Baxter and Cummings 2006). One of the most successful industrial applications is an aerobic biological treatment process employed at a Homestake Mining Co. operation in South Dakota. First, the wastewater is dosed with phosphoric acid, which the bacteria use as a nutrient source. Then, the wastewater is fed into a set of rotating biological contactors (RBCs) populated with a strain of *P. paucimobilis* that was acclimated specifically to this mine's waste (Baxter and Cummings 2006). In the first set of RBCs, cyanide and thiocyanate are degraded by oxidative reactions to ammonia, carbonate, and sulfate. In the second set of RBCs, ammonia is converted to nitrate. Flow charts of both the process and the mechanisms of Homestake aerobic biological treatment process are shown in Fig. 2 and Fig. 3 respectively.

Fig. 2 Aerobic Biological Treatment Process in Homestake's South Dakota Mine (Akcil 2003)

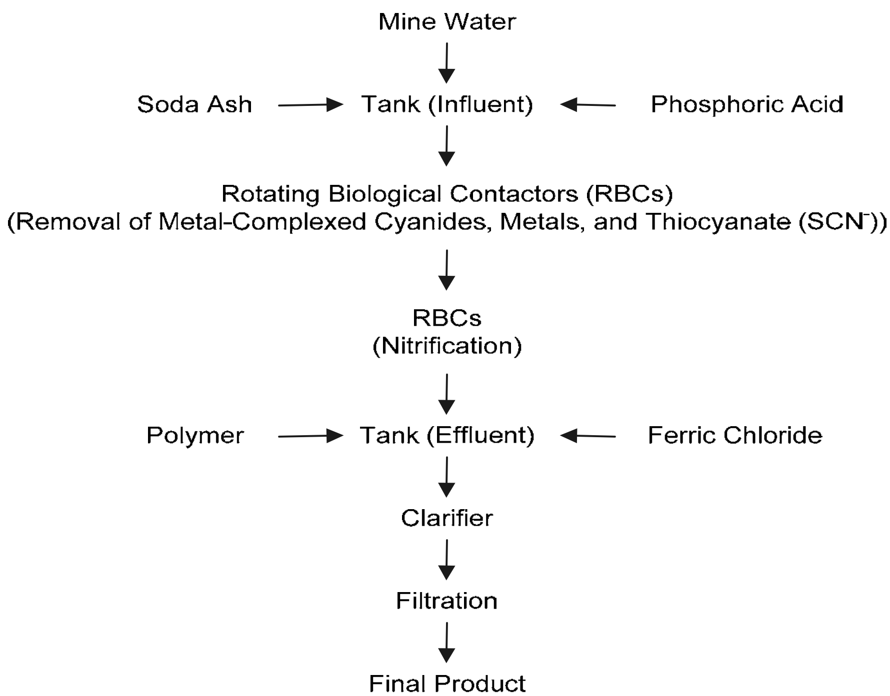
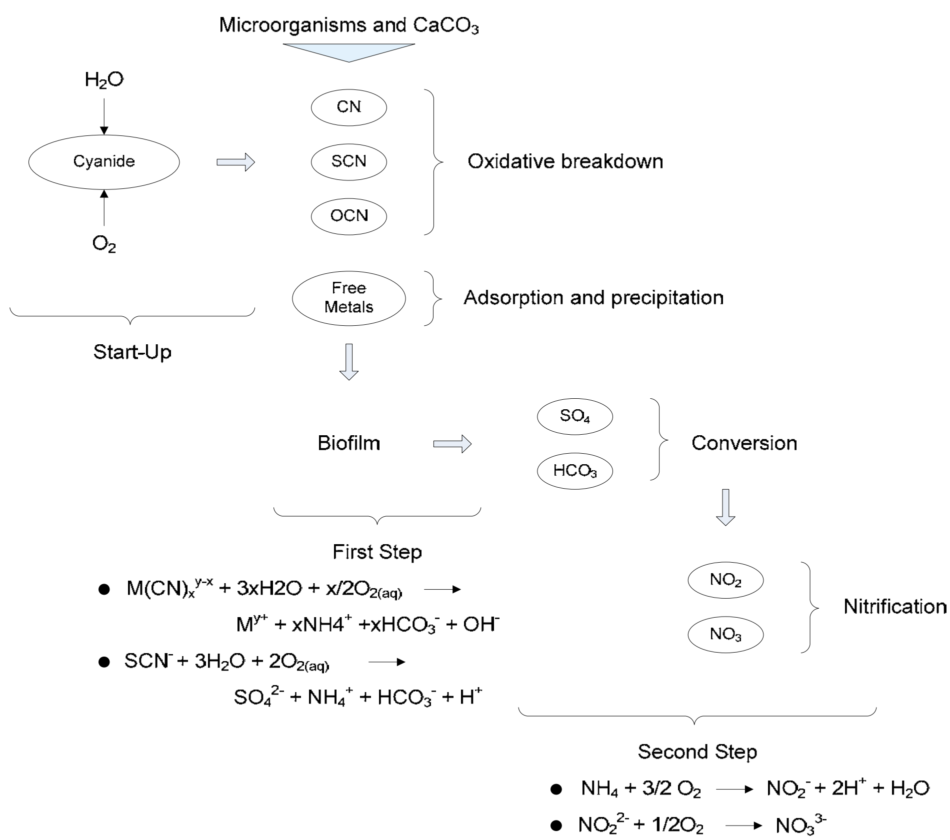


Fig. 3 Mechanisms of Homestake's Aerobic Biological Treatment Process (Akcil 2003)



At the end of the process nearly all of the cyanide is removed from the wastewater resulting in an effluent that is safe enough to be discharged into a receiving stream. The removal rates of cyanide from the wastewater, depending on plant operations, vary from 91 – 99.5% of the total cyanide (Baxter and Cummings 2006).

After the success of their first biological treatment process in South Dakota, the Homestake Mining Co. designed and implemented a passive biological treatment process in their Nickel Plate mine in Canada. Unlike their first process, this one was design to treat seepage from tailings impoundments. The passive biological treatment process works on the same principles as a suspended sludge system and it incorporates both aerobic and anaerobic treatment (Baxter and Cummings 2006). In addition to removing cyanide, thiocyanate, cyanate, and metals, this process also removes ammonia nitrogen.

By adding an anaerobic chamber to the process, the Nickel Plate treatment plant is able to sustain nitrifying bacteria in addition to the cyanide biodegrading bacteria. The presence of nitrifying bacteria in the treatment process allows the system to perform nitrification and denitrification. Nitrification is the process by which ammonia is converted to nitrate, and denitrification is the process by which nitrate is converted to nitrogen gas. By removing the ammonia and nitrates, the treatment plant is able to produce a higher quality effluent. Flow charts of the Nickel Plate treatment process and nitrification/denitrification cycle are shown in Fig. 4 and Fig 5 respectively.

Fig. 4 Biological Treatment Process at Homestake's Nickel Plate Mine in Canada (Akcil 2003)

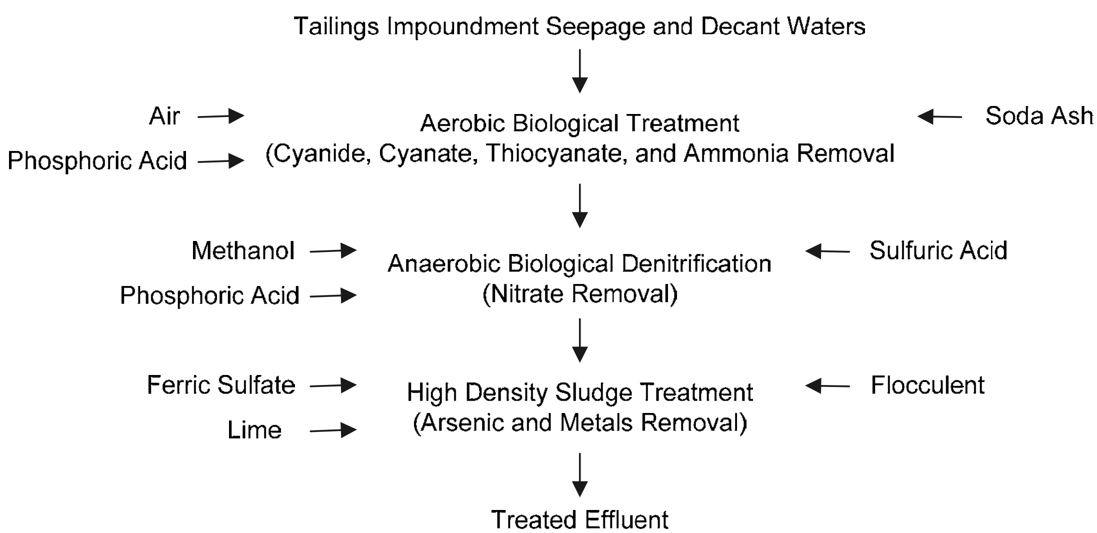
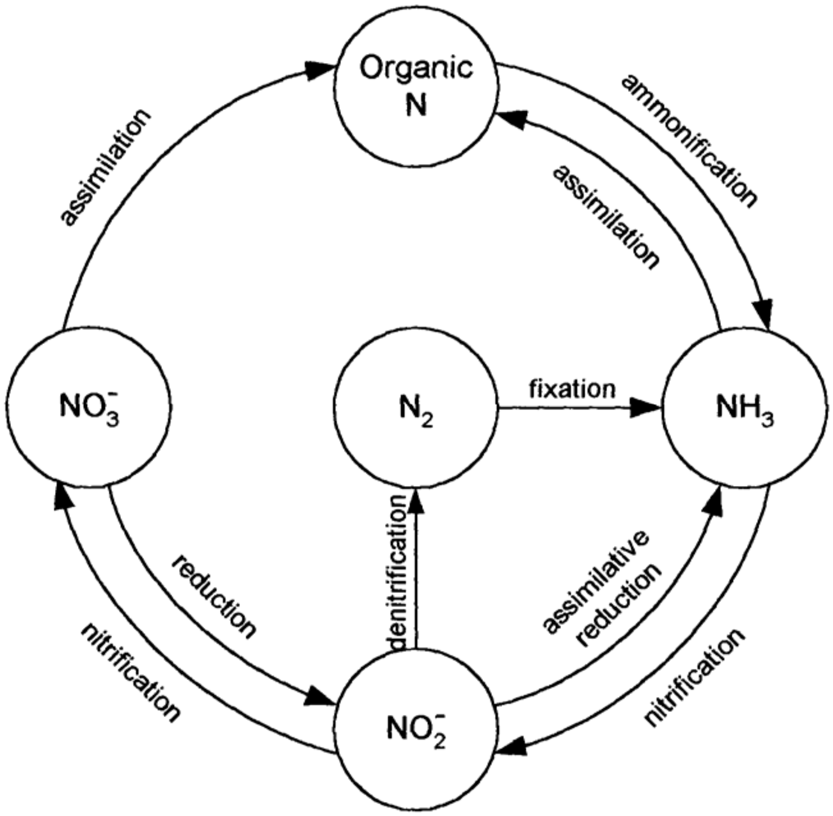


Fig. 5 The Nitrogen Cycle, Including Nitrification and Denitrification



Basic Setup:

Biological treatment in today's mining industry is still fairly uncommon, however, many metallurgical plant, especially those involved in the extraction of gold and silver, are beginning to retrofit their facilities with a biological/chemical hybrid system (Akcil 2003). Most of the necessary modifications are minor and result in cost savings for the plant. A full scale hybrid biological/chemical treatment system in operation today follows three reaction stages identified by Akcil (2003):

1. Combined activated sludge treatment:
    a. Conversion of thiocyanate (SCN^-) to ammonia (NH_3)
    b. Oxidation of ammonia to nitrate (NO_3^-)

2. Denitrification
    a. Reduce nitrite (NO_2) to nitrogen gas (N_2)

3. High density sludge (HDS) ferric sulfate treatment
    a. Precipitate arsenic and other metals as sulfate (SO_4^-)

The Economics of Chemical/Physical vs. Biological Treatment

When performing a cost benefit analysis on any cyanide treatment process, one must consider all of the economic, environmental, and legislative requirements involved (Baxter and Cummings 2006). Compared to chemical treatment processes, biological treatment processes normally have a much higher initial investment cost. However, in the long run, biological treatment has a much lower operating cost (Akcil 2003). Another advantage to biological treatment is it allows both the removal of cyanide and the denitrification of the ammonia produced as a result of the cyanide removal. This in turn results in a much more environmentally friendly effluent.
Keep in mind, though, that biological treatment does have some economic disadvantages. One of the major disadvantages to biological treatment is its susceptibility to climatic conditions. The microorganisms that drive the process, as a rule of thumb, require an operating temperature of at least 50^{o}F. Cold conditions during the winter would impose an additional thermal requirement on the plant to maintain an acceptable temperature for biological activity. In addition, aerobic treatment of wastes is sensitive to high organic carbon loading. High organic loading could reduce the effectiveness of the treatment process (Baxter and Cummings 2006).

Under current environmental requirements of mining wastewater effluent, it can be difficult, sometimes, to justify using biological treatment over chemical. Should the government decide to make the environment regulations of mining wastewater effluent more stringent, it would definitely benefit the push for biological treatment. This is because biological treatment can produce much cleaner effluents at a lower cost than conventional chemical treatment processes.

Are There Future Applications of Biological Treatment?

As long as man continues to use cyanide in industrial processes, such as mining, there will continue to be a need for more effective and economic bioremediation technologies. Many industrial wastewaters impose harsh environmental conditions on microorganisms. Some of these conditions include extreme pH and other toxic pollutants in addition to cyanide. Due to these ever-changing conditions, researchers are constantly testing to identify new microorganisms that utilize and degrade cyanide and cyanide compounds.

In a recent study performed by Luque-Almagro *et al.* (2005), *P. pseudoalcaligenes* CECT5344 was identified as being able to degrade cyanide and metal-complexed cyanides (Baxter and Cummings 2006). What is remarkable about this microorganism is that it is able to degrade cyanide in wastewaters with as much as 30 mM free cyanide at pH 11.5. Even more remarkable is that Luque-Almagro *et al.* (2005) observed *P. pseudoalcaligenes* CECT5344 growing in jewellery industry wastewater that contained heavy metals (Baxter and Cummings 2006).

Another recent development in the field of cyanide biodegradation is the possible use of plants (Baxter and Cummings 2006). Trapp *et al.* (2003) conducted a study on the ability of a grass, *Sorghum bicolour*, to biodegrade cyanide and cyanide complexes in irrigation water. The study showed that the grass could successfully degrade cyanide concentrations of up to 125 mg/L. In addition to the possibility of using the grass as a successful mechanism to treat gold mining effluent, Trapp *et al.* (2003) suggested that the bioaccumulation of gold by the grasses could enhance gold recovery by the mine (Baxter and Cummings 2006).

Conclusion

As long as mining and other metallurgical industries continue to produce a variety of cyanide containing wastes, there will always be demands for economic and environmentally friendly methods to treat those wastes. In recent years, the tried and true chemical remediation methods have been challenged by new and innovative biological treatment methods. Several of these biological treatment methods have been proven to be successful both in the lab and in large-scale operations, such as the Homestake Mining Co. mines in South Dakota and Canada.

Although biological treatment processes usually require a high initial investment, their operations costs can be substantially lower than those of a chemical process. In those situations where the economic benefits of a biological treatment do not quite meet the benefits of a chemical process, future changes to environmental requirements should be considered. Chemical treatment methods can only treat the cyanide portion of the waste and leave behind ammonia, another potentially toxic compound at high concentrations. Biological treatment systems can treat not only cyanide, thiocyanide, and cyanate, but also ammonia and nitrate through a biologically run nitrification and denitrification process run in conjunction with the cyanide biodegradation process.

Current and ongoing research continues to discover new microorganisms and methods to make biological treatment even more economically beneficial, and it has already surpassed the competition (chemical treatment) in producing more environmentally friendly effluent. Thus, biological treatment of cyanide and cyanide complexes is definitely an up-and-coming contender in the world of industrial cyanide-waste treatment.

References

Akcil, A. (2003) Destruction of Cyanide in Gold Mill Effluents: Biological versus Chemical Treatments. Biotechnology Advances, 21: 501-511.

Akcil, A. (2002) First Application of Cyanidation Process in Turkish Gold Mining and its Environmental Impacts. Minerals Engineering, 15: 695-699.

Akcil,A., Karahan A.G., Ciftci H. and Sagdic O. (2003) Biological Treatment of Cyanide by Natural Isolated Bacteria (*Pseudomonas sp*.). Minerals Engineering, 16: 643-649.

Barclay, M., Hart, A., Knowles, C.J., Meeussen, J.C.L., and Tett, V.A. (1998) Biodegradation of Metal Cyanide by Mixed and Pure Cultures of Fungi. Enzyme and Microbial Technology, 22: 223-231.

Barclay, M., Tett, V.A., and Knowles, C.J. (1998) Metabolism and Enzymology of Cyanide/Metallocyanide Biodegradation by *Fusarium solani* Under Neutral and Acidic Conditions. Enzyme and Microbial Technology, 23: 321-330.

Baxter, J. and Cummings, S.P. (2006) The Current and Future Applications of Microorganism in the Bioremediation of Cyanide Contamination. Antonie van Leeuwenhoek, 90: 1-17.

Buckingham, A. (2003) Summitville Mine Superfund Site. The Newsletter of the Colorado Riparian Association, 14, 3. http://coloradoriparian.org/GreenLine/V14-3/Summitville.php. October 15, 2003.

Dhillion, J.K. and Shivaraman, N. (1999) Biodegradation of Cyanide Compounds by a *Pseudomonas* species (S1). Canadian Journal of Microbiology, 45: 201-208.

Dictor, M.C., Battaglia-Brunet, F., Morin, D., Bories, A., and Clarens, M. (1997) Biological Treatment of Gold Ore Cyanidation Wastewater in Fixed Bed Reactors. Environmental Pollution, 97, 3: 287-294.

Ritcey, G.M. (2005) Tailings Management in Gold Plants. Hydrometallurgy, 78: 3-20.

Warhurst, A. and Mitchell, P. (2000) Corporate Social Responsibility and the Case of Summitville Mine. Resources Policy, 26: 91-102.