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Full Length Research Paper

Mining waste-Cyanide as a source of added value by its conversion into Urea and Urea-Formaldehyde

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Served waters containing cyanide from gold mining open pits, should be treated to avoid permanent environmental pollution by the contamination of river basins, soils and sources of irrigation and drinking water. Cyanide should be always processed in covered pools, and at high pH, to prevent leaks of hydrocyanic acid. Resource management has to take in account, the *added value* of using discharged cyanide as a supply for industrial processes, like urea production. The latter, could be used as an agricultural fertilizer or for production of Urea-Formaldehyde (UF), a thermic and electric insulator with a variety of industrial applications.

Keywords: Mining waste-Cyanide, Urea, Urea-Formaldehyde

INTRODUCTION

Manufacturing industry is well aware of the economic advantage of using disposal byproducts, as the raw material for other processes. On the other hand, the mineral extraction industries sometimes are reluctant to explore the benefits of an added value to mining wastes.

Moreover, since open sky gold mining is devastating for the environment [Eisler and Wiemeyer, 2004; Korte and Coulston, 1995; Falcón, 2000; Guillermo et al, 2006], first world countries have consistently refused to let gold companies undertake mining, within their own frontiers [Korte and Coulston, 2002]. This has leaved the third world countries with the burden, of either accepting unchecked damage to their environment or the loss of revenues, which could be applied for their development [Korte and Coulston, 1995; Falcón, 2000; Guillermo et al, 2006].

Hence, the mining companies in order to obtain the right to exploit the wealth of these countries, are expected to take the compromise of eventually restore the environment as it was before. However, some companies may operate either without insurance for environmental disaster s or bank warranties, against the possibility that after the mineral have been extracted, the mining company may enter into a legal default process.

Gold mining

Gold is not soluble in water but can be dissolved by lixiviaton using cyanide.

The Elsner's reaction:

$$4\mathrm{Au} + 8\mathrm{NaCN} + \mathrm{O_2} + 2\,\mathrm{H_2O} \rightarrow 4\mathrm{Na}[\mathrm{Au(CN)_2}] + 4\mathrm{NaOH}$$

. When the low-grade gold ore is lixiviated, an oxidant effect allows cyanide to complex the gold ions in the anode zone. O_2 electrochemical attracts the gold's electrons into the cathode zone of the soluble auro-cyanide complex anion $[Au\ (CN)_2]^-$.

These complexes are very stable and the quantity of cyanide could be dosed. Depending of the type of the mineral, are needed from 0.03 to 0.05% of sodium cyanide (NaCN) to dissolve gold. However, in the practice, the quantity of used cyanide in lixiviation depends on the presence of others consumers of cyanide and the need to get an adequate level of lixiviation [Andreas et al, 2006; Mooiman and Miller, 1986].

In the conventional grinding and lixiviation by agitation, the ore is triturated in semi-autogenic mills, or in cylindrical breakers, until converted into powder. The triturated mineral is transported by ribbon to a series of lixiviation tanks. To improve the lixiviation performance the ore is agitated mechanically or by air-injection to achieve a major gold contact with cyanide and oxygen.

Water containing cyanide is extremely dangerous because its acidification at low pH, results in $CN^{-}+H^{+}$ producing free hydrocyanic acid HCN (gas). The solutions that contain cyanide in the moment of dissolution must have a pH=10.5 for cyanidation. If lime is used in the lixiviation circuit the triturated mineral should be at a pH=10 to 11. It is convenient to increase pH to 12 to avoid hydrogen cyanide toxic gas volatilization [Andreas et al, 2006]. This assures that addition of cyanide does not facilitate the surge of toxic hydrogen cyanide and that cyanide stays in the solution to dissolve the gold [Fei et al, 2010].

A deficient in the reactant O_2 in the solution could decrease the lixiviation rate, and reduce the consumption of cyanide by agents within the triturated mineral. Hence, O_2 and hydrogen peroxide (H_2O_2) to dose the paste could be used as oxidants to replace air. The resultant solution in then pumped into storage tanks before being used. The cyanide solution lixiviates the gold of the mineral, which is recollected by an impermeable membrane and pumped towards the storage installations for its posterior processing.

Gold is recuperated utilizing activated carbon. The latter absorbs the dissolve gold of the minerals forming a smaller mass of solids. Once extracted from the activated carbon, the gold in concentrated by precipitation or galvanization. Lead nitrate can improve gold leaching speed and quantity recovered, particularly in the processing of partially oxidized ores.

Then, the carbon is separated by shaking and it is summited to other treatments to recover the gold that has absorbed. The danger of wasting cyanide in adjacent lakes or rivers results in a gradual absorption of cyanide in adjoining lands and its webs [Eisler and Wiemeyer, 2004; Korte and Coulston, 1995; Falcón, 2000]. This land will lose its capacity of sustaining agriculture [Stephen et al, 2009; Friedhelm et al, 2000].

Added value project

Thus, discharged water from gold exploitation is always maintained in alkaline solution. Expended cyanide could be removed from disposal waters by chlorine (Cl_2(gas)) alkaline (1) or sodium hypochlorite (NaClO) (2), the initial reaction between chlorine and cyanide produces cyanogen chloride (CNCl) [Korte and Coulston,1998].

$$\mathrm{NaCN} + \mathrm{Cl_2} \rightarrow \mathrm{CNCl} + \mathrm{NaCl} \quad (1)$$

$$\mathrm{NaCN} + \mathrm{NaClO} \rightarrow \mathrm{CNCl} + \mathrm{NaCl} \quad (2)$$

By adding a step of sodium hydroxide addition (3) to cyanogen chloride, sodium cyanate (NaCNO) will be formed:

$$\mathrm{CNCl} + 2\,\mathrm{NaOH} \rightarrow \mathrm{NaCNO} + 2\,\mathrm{H_2O} + \mathrm{NaCl}$$
(3)

Reactions with organic compounds are very exothermic and can cause combustions, but generally exploitation of gold effluents do not contain these compounds in significant quantities.

Cyanide oxidation cycle in ammonium cyanate

The reaction from cyanide to cyanate requires 2.7 parts of Cl_2 and 1.1 NaOH (4). If the addition of NaOH is followed by ammonium hidroxyde it can be obtained ammonium cyanate (NH_4CNO) (5). At pH=11 the reaction is faster. Cyanogen chloride (CNCl) is volatil and odorous, but it is not mortal like cyanidric acid.

$$\mathrm{CNCl} + \mathrm{NH_4OH} + \mathrm{NaOH} \rightarrow \mathrm{NH_4CNO} + \mathrm{ClNa} + \mathrm{H_2O}$$
(4)

Resultant waters are odoriferous but without cyanide toxicity. It can be utilized directly to irrigation or to fill dams for biomass production with sun ligth. A clear plastic cover over this reservoirs may allow to diminish ugly smells [Korte and Coulston,1998; Harris et al,1992; Riveros, 1990].

If potassium hydroxide is used instead of sodium hydroxide, it would produce water enriched with the fertilizers potassium. The cyanate anion CNO^{-} could be also neutralized with ammonium hydroxide.

The reaction to decompose cyanate to carbon dioxide (CO_2) and nitrogen (N_2) imply 4.17 parts of Cl_2 and 3.1 NaOH.

$$2\,\mathrm{NaCNO} + 4\,\mathrm{NaOH} + 3\,\mathrm{Cl_2} \rightarrow 2\,\mathrm{CO_2} + 6\,\mathrm{NaCl} + \mathrm{N_2} + 2\,\mathrm{H_2O}$$
(5)

Oxidation of cyanate to carbon dioxide and gaseous nitrogen (5), diminish ugly smells by removing cyanate.

Alternatively, the ammonium cyanate (NH_4CNO) could be heated according to modifications of the original Friedrich Wöhler method to produce Urea (H_2NCONH_2) (6).

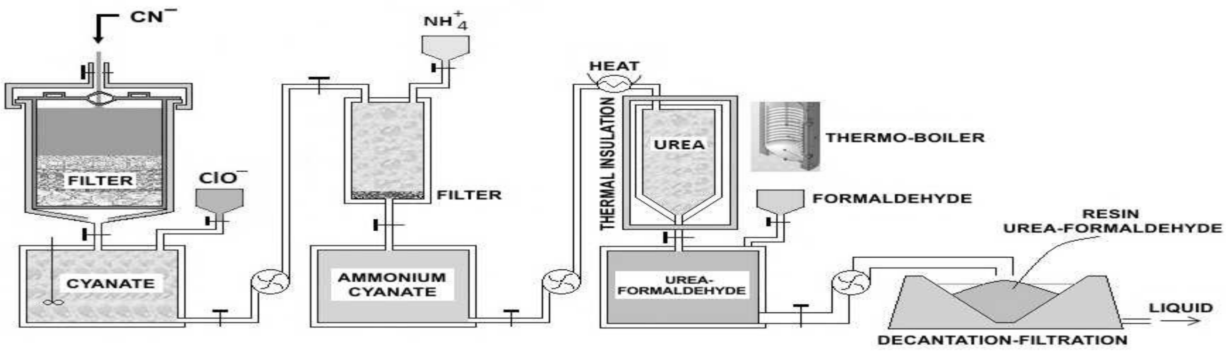
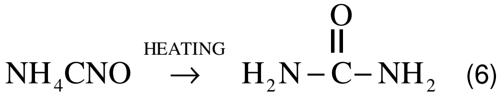


Fig 1 Scale model for re-utilization of cyanide into a urea production cycle which can be integrate to supply a reactant for Urea-formaldehyde resin production



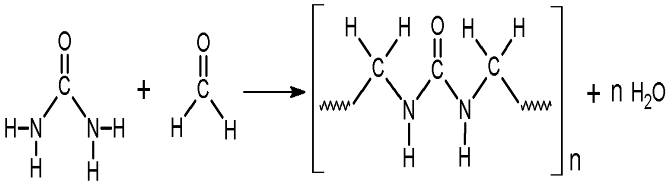
$$NH_4CNO \xrightarrow{\text{HEATING}} H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \qquad (6)$$

Local agriculture production would be benefit from availability of the fertilizer at low production cost because of the lack of significant transportation costs. Mutual benefits would tend to create links between the company and the inhabitants of the area. This may mitigate political-social restiveness, and favor the acceptance of the mining company as a partner of regional development.

As urea solutions tend to decompose in cyanate a treatment with a precipitant agent (lead sulfate) and its decants-filter to obtain solid urea. Its use in agriculture is preponderant because in its solid form is transportable and storable.

Cost evaluation of different industrial process to decrease CN^- contamination could be done at the laboratory level by coupling reactions in an assembly of chemical production vessels [Mooiman and Miller,1986; Fei et al,2010]. Urea could be integrated with other processes for example in the manufacture of many adhesives by combinations with formaldehyde, phenol, etc. [Vázquez et al 2005] which are widely used in surface coatings and construction.

The following equation describes urea polymerization with formaldehyde ($H_2C=O$) for production of Urea-formaldehyde resin (UF), a high heat resistance polymer.



UF is a thermosetting compound, colorless, but mixes well with different dyes. UF is a product more easily adapted to changes in the preference of designers and customers, than Bakelite and it is also a harder, and efficient thermic and electric insulator. It could supply industries which manufacture control units and control elements of electrical circuits, decorations, housing small appliances, etc.

DISCUSSION

The economic cost of cleaning the raw water, a waste from gold extraction with cyanide in an open sky gold minning usually is left to the care of the countries, in which the mining operations were conducted.

The introduction of ecological protective processes should be required in order to modernize industrial practices. Hence, it could be a must to obtain an added value procedure for the use of toxic cyanide as chemical precursor like urea, for which there is considerable demand as a fertilizer. Therefore, there is an incentive to develop technologies decreasing costs of decontamination.

Future costs of soil and water restitution would decrease to ecological levels, reducing sanitary costs and reparations judgments. Operational costs had projected with a mean of US$ 155 by ounce and an investment return rate of 14%, with an average gold value of US$ 325 by ounce, therefore the actual value of about US$ 1700 allows great earnings. Of these, just a small amount would be required to prevent or reverse contamination of the waters which offer this project. Urea production in the surroundings of the gold mining open pits could significantly decrease company decontamination expenses, because could be associated to the infrastructure investment required for gold mining in the area.

CONCLUSIONS

Effective treatment of the cyanide present in the waste water in open sky gold mining by added value processes, could give an incentive to mining companies to get involved in prevention or reversal of environmental pollution. If added value proposals are implemented it could be expected to add additional jobs for the area population. Added value by using the cyanide for manufacturing not only decreases contamination of the river basins, soils, etc., but also contributes to improve the economy and a more integrated development of the involved region.

Verticalized *added value* investment, by adding to the primary production other products, could open jobs for the gold mining displaced farmers. The final gold ore purification should be done in the country in were the mines are located, because the enriched gold ore contains platinum and other valuable metals.

If these ones are extracted from gold ore elsewhere, the involved mining company could be significantly decreasing their compensation to the host country, for given up non-renewal resources. Moreover, the company in its country of origin may not be able to claim tax-deductions, for supporting the development of educational and human capabilities, within the mineral rich countries.

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