MINERALS COUNCIL OF AUSTRALIA

> FACT SHEET - CYANIDE DESTRUCTION PROCESSES

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Cyanides (CN-) are used to solubilize metal ions in basic solution. Consequently, cyanide compounds are found in wastewater streams from processes such as gold and silver ore refining and blast furnace stack gas scrubbing.

Cyanide is an extremely strong chelating agent, reacting readily with transition metal ions, forming very stable complexes, which are extremely resistant to oxidation. Therefore, cyanide compounds can be classified as oxidizable and non-oxidizable cyanides.

A range of different techniques are available for the treatment of cyanides in wastewater. Some of these techniques are outlined in further detail below. In addition, bacterial cyanide destruction circuits are increasingly being considered for application in Australian mining operations.

Natural degradation involves the removal of cyanide in gold mill wastewaters by natural means whilst the wastewaters are detained for prolonged periods in tailings storage facilities or holding ponds. The degradation of cyanide results from a combination of physical, chemical and biological processes, including volatisation; photodecomposition; hydrolysis and adsorption on solids. Of these mechanisms volatilization is considered to be the most important.

The speed and extent of natural degradation is influenced by a number of variables including: cyanide species and their concentrations in solution; pH; temperature; bacteria present; sunlight; aeration; and pond conditions (area, depth, turbidity, turbulence etc).

Chemical treatments

The choice of treatment option depends on the nature of the cyanide compound as only oxidizable cyanides can be treated by chlorine dioxide or other oxidants.

Hydrogen peroxide is the most common oxidant, but requires high pH (through caustic addition). The reaction between cyanide and hydrogen peroxide produces cyanate (CNO-) and water. Cyanate is regarded as being at least 1,000 times less toxic than cyanide. The cyanate will hydrolyse over time depending on the pH to give carbon dioxide and an ammonium salt or carbonate and ammonia.

The reaction between cyanide and hydrogen peroxide takes time but can be catalysed by the presence of copper. Copper is often present in effluents originating from the treatment of ores but in some cases, it may be necessary to add small amounts of copper sulfate to accelerate the reaction.

INCO process (oxidation by SO2) The principle behind the INCO process is the oxidation of cyanide and thiocyanate anions into cyanate. Metal cyanide complexes are also broken down resulting in precipitation of both the metal hydroxides (e.g. those of Cu, Zn, Ni) and retro cyanide solid precipitates (e.g. Cu2Fe(CN)6))

S02 can be introduced in the gaseous/liquid form or as sodium metabisulphite. The reaction is catalysed by the presence of copper, which may have to be added (as copper sulphate). Air is also required, as is lime to maintain the pH at optimum levels (8-10) as the reaction proceeds. The entire INCO process can take place within simple stirred tank reactor circuits and is quite simple to operate and monitor its performance.

SART: Sulphidisation, Acidification, Recycling and Thickening. Sulphidisation refers to controlled addition of stoichiometric additions of soluble sulphide salts (e.g. sodium hydrosulphide) to the waste cyanide solution. Acidification results in the dissociation of metal cyanide complexes (e.g. Cu, Zn) and the formation of HCN. The free metal cations created combine with the sulphide ions and precipitate out as insoluble metal sulphides. These precipitates are thickened and separated for separate processing. After removal of solids, the liquors can be neutralised with Sodium hydroxide or lime and then recycled back to the leaching process, thereby recovering and recycling the cyanide.The technology is particularly appropriate when high levels of copper are present in solution allowing the processing, by intensive cyanidation, of copper rich gold concentrates.

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Chlorine dioxide is unique in its ability to be used at moderately basic pH's. All other oxidants require pH's greater than 12. In the case of chlorine this is necessary to hydrolyze toxic cyanogen chloride (CNCl) gas formed during treatment. Cyanogen chloride is not formed during chlorine dioxide treatment of cyanides. Chlorine dioxide oxidizes simple cyanide to cyanate (a less toxic substance) and/or carbon dioxide and nitrogen. The end products depend on reaction conditions. With free cyanide the reaction with chlorine dioxide is reported to be instantaneous.

Cyanide complexes containing Ag+, Cu+, Zn2+, Ni2+, Pb2+, and Cd2+ dissociate fairly easily and are destroyed by chlorine dioxide. However Cyanide is most commonly encountered in its complexed form, often with iron (and cobalt), which is not oxidizable by chlorine dioxide

Alkaline chlorination is effective for oxidation of all cyanides except iron complexes, noble metal, and cobalt complexes. Chlorine has the lowest chemical costs, but requires high pH to avoid cyanogen chloride formation. The presence of ammonia will also create a high demand for chlorine.

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