

# CYANIDE DESTRUCTION

## CYANIDE DETOXIFICATION

Most gold plants around the world are required by law to destroy cyanide and metal cyanide complexes in their tailings prior to discharge from the metallurgical site into the natural environment. Many plants destroy the cyanide in a contained area within the metallurgical site, so as to minimize the exposure of wildlife, particularly birds, to these toxic solutions.

## WHAT INFLUENCES PROCESS SELECTION?

There are a number of technologies available for destroying cyanide and its metal complexes, and the choice of the best method for a particular application is not simple. Complexity arises because:

- environmental regulations vary with respect to allowable concentration limits in the treated tailings
- the various detoxification techniques vary widely in their ability to eliminate certain species
- the chemical composition of the tailings from each plant is unique
- reagent consumption and cost varies from one country and location to the next

## COST EFFECTIVENESS IS CRITICAL

The cost of treating cyanide tailings can be a significant percentage of total operating costs, and unlike other operating costs, yields no economic "return". It is therefore very important, for both regulatory and economic reasons, to select the correct process, and then optimize the operating conditions to minimize reagent dosages. This requires a good knowledge of local regulations as well as skillful laboratory test work and piloting.

SGS has extensive experience with the methods that are most commonly used or promoted, and can determine the advantages and disadvantages of each for different applications.

- Chlorination
- Hydrogen Peroxide
- SO<sub>2</sub>/Air
- Ferrous Sulphate Complexation
- Ozonation
- Caro's Acid

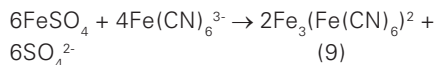
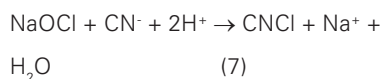
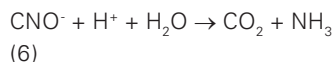
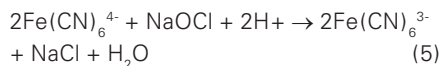
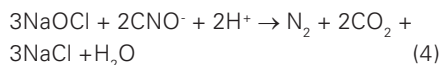
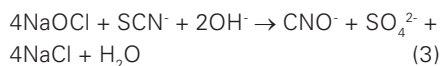
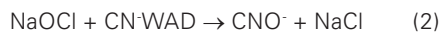
## COMPARISON OF COMMON DETOXIFICATION METHODS

### ALKALINE CHLORINATION

#### Reagents



#### Reactions



### Advantages

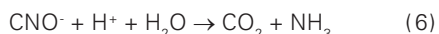
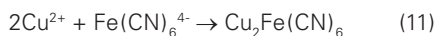
- Relatively simple to operate
- Strong oxidant
- Can oxidize thiocyanate (reaction 3)
- Can oxidize cyanate to N<sub>2</sub> and CO<sub>2</sub> (reaction 4 in a second stage), avoiding the hydrolysis of cyanate to undesirable ammonia (reaction 6)
- No copper catalyst required
- Fast kinetics
- Can oxidize CN-WAD efficiently (hence CN-WAD is also called "CN amenable to chlorination") leaving low toxic iron cyanide in solution

### Disadvantages

- Non-selective, leading to high reagent consumption
- Requires high pH (pH 11) to ensure rapid and complete hydrolysis of highly toxic cyanogen chloride gas (reaction 8)
- As for other methods, ferrocyanide is not destroyed, but only partially oxidized to ferricyanide (reaction 5). Requires an additional stage and reagent to remove iron cyanide (if required) as a base metal iron cyanide precipitate (such as in reaction 9)
- May leave residual chlorine in solution, thereby requiring a polishing pond or aeration stage for removal

**HYDROGEN PEROXIDE****Reagents**

$\text{H}_2\text{O}_2$ ,  $\text{Cu}^{2+}$  catalyst

**Reactions****Advantages:**

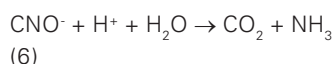
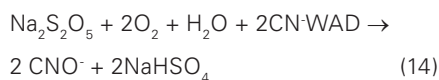
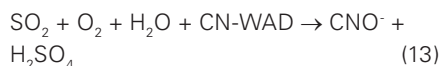
- Relatively simple to operate
- No production of toxic gases
- More selective toward CN-WAD than chlorination (cyanate is not oxidized and only a small portion of thiocyanate is oxidized)
- Ferrocyanide is precipitated as a base metal ferrocyanide complex (reaction 11). It may be necessary to add more base metal than the copper needed to catalyze the oxidation reaction. Ferrous sulphate will be cheapest.
- Can oxidize CN-WAD efficiently

**Disadvantages:**

- Require copper in solution as a catalyst (20 mg/L or higher)
- Tends to leave some residual copper in solution
- Can react with sulphides in the solid phase, which results in high reagent consumption
- High unit cost for the reagent
- Cyanate hydrolyzes to undesirable ammonia (reaction 6)
- Ferrocyanide is not destroyed, but precipitates as a base metal ferrocyanide complex. The precipitate can redissolve at basic pH (pH>9) and release ferrocyanide back to solution
- Copper may redissolve in a high chloride environment

**SO<sub>2</sub>/AIR****Reagents**

$\text{SO}_2 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_5$ ,  $\text{Cu}^{2+}$   
catalyst (12)

**Reactions****Advantages**

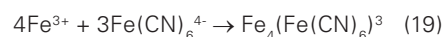
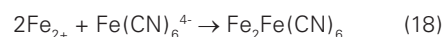
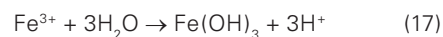
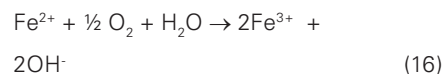
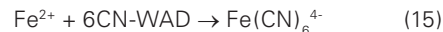
- Low reagent cost
- More selective than chlorination and hydrogen peroxide toward CN-WAD (cyanate is not oxidized and a only small portion of thiocyanate is oxidized)
- Sulphite salts such as sodium metabisulphite or sodium sulphite can be used (reaction 14)
- Ferrocyanide is precipitated as a base metal ferrocyanide complex (reaction 11). It may be necessary to add more base metal than the copper needed to catalyze the oxidation reaction. Zinc sulphate is preferred.
- Can oxidize CN-WAD efficiently

**Disadvantages:**

- Quite difficult to operate
- Requires copper in solution as a catalyst (>30 mg/L Cu)
- Tends to leave some residual copper in solution
- Requires longer retention time than alkaline chlorination and hydrogen peroxide
- Requires very good dispersion of air and  $\text{SO}_2$  gas (vigorous mixing)
- Cyanate hydrolyzes to undesirable ammonia (reaction 6)
- Ferrocyanide is not destroyed, but precipitates as a base metal ferrocyanide complex. The precipitate can redissolve at basic pH (pH>9) and release ferrocyanide back into solution
- Copper may redissolve in high chloride environment

**FERROUS SULPHATE COMPLEXATION****Reagent**

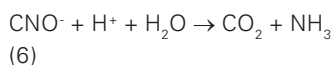
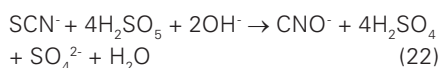
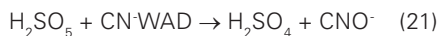
$\text{FeSO}_4$

**Reactions****Advantages**

- Low reagent cost
- Relatively simple to operate
- CN-WAD is converted to ferrocyanide, which is precipitated as green ferro ferrocyanide at neutral pH (reaction 18) and/or prussian blue, ferri ferrocyanide at lower pH (reaction 19)
- Can sequester CN-WAD efficiently
- Does not oxidize cyanide to cyanate and, therefore, does not produce ammonia

**Disadvantages:**

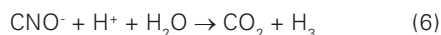
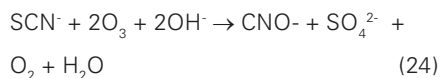
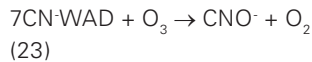
- Difficult to achieve <5 mg/L CNT because of residual, soluble ferrocyanide
- Requires longer retention time than chemical oxidation methods
- May require aeration to convert  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$
- Does not oxidize thiocyanate
- Cyanide is not destroyed, but precipitates as mixed iron ferrocyanides. The precipitates can redissolve at basic pH (pH>9), releasing ferrocyanide back to solution

**CARO'S ACID****Reagents****Reactions****Advantages**

- Strong oxidant, fast kinetics
- Does not require copper catalyst
- No production of toxic gas
- Can oxidize part of the thiocyanate
- Can remove ferrocyanide as a base metal iron cyanide precipitate
- Can oxidize CN-WAD efficiently

**Disadvantages:**

- Less selective than the alternative processes. Reacts more readily (than hydrogen peroxide and  $\text{SO}_2/\text{air}$ ) with sulphides in solids, leading to high reagent requirement
- High reagent cost
- More difficult to handle than peroxide because of fairly large amount of heat generated during mixing peroxide with concentrated sulphuric acid
- May need to add copper, iron or zinc salts to precipitate iron cyanide
- Tends to leave some residual copper in solution
- Copper and/or zinc may redissolve in high chloride environment
- Cyanate hydrolyzes to undesirable ammonia (reaction 6)
- Ferrocyanide is not destroyed, but may precipitate as a base metal iron cyanide complex. The precipitate can redissolve at basic pH ( $\text{pH} > 9$ ) and release ferrocyanide back into solution

**OZONATION****Reagent****Reactions****Advantages:**

- Strong oxidant, fast kinetics
- Does not require copper catalyst
- Can oxidize thiocyanate
- Can oxidize CN-WAD efficiently

**Disadvantages:**

- Non selective. Reacts more readily (than hydrogen peroxide or  $\text{SO}_2/\text{air}$ ) with sulphides in solids, leading to high reagent requirement
- May react with the solid phase and release undesirable species such as arsenic into solution
- High reagent cost
- Can release toxic  $\text{O}_3$  gas, requiring scrubbing
- Requires  $\text{O}_3$  resistant equipment
- May need to add copper, iron or zinc salts to precipitate iron cyanide
- Tends to leave some residual copper in solution
- Cyanate hydrolyzes to undesirable ammonia (reaction 6).
- Ferrocyanide is not destroyed, but may precipitate as a base metal iron cyanide complex. The precipitate can redissolve at basic pH ( $\text{pH} > 9$ ) and release ferrocyanide back into solution.

**CONTACT INFORMATION**

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