

Removal Of Cyanides By Hydrogen Peroxide From Exhausted Silver Plating Baths

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Abstract

The main objective for the work was to determine the dosage and effectiveness of hydrogen peroxide in removing cyanide from waste silver plating baths. The effects of catalyst concentration (Cu) and hydrogen peroxide concentrations, retention time and rate of free cyanide destruction were investigated. Experiments were conducted on silver plating baths using the variable-dose of hydrogen peroxide and catalyst concentration. The rate of removal of cyanide was observed to increase, with increasing peroxide doses for either absence or presence of Cu catalyst. Catalyst addition proved to be effective by enhancing the cyanide removal rate. Varying retention times were given to samples and cyanide destruction was observed to rise with increasing retention times. Silver was also precipitated out at the end of reaction time (8-10 hours). Ammonia was formed during this destruction process and the reaction continued for 4-5 hours. The dosage requirement was derived to be 9-10g H₂O₂/g CN⁻ removed.

Keywords: Cyanide, removal, hydrogen peroxide

Introduction

Cyanide (CN⁻) is a toxic species that is found in industrial effluents generated by metal finishing, metal plating plants, other chemical and metallurgical industries. Cyanide is a singly-charged anion containing equimolar amounts of carbon and nitrogen atoms triply bonded together: C≡N⁻ or CN⁻. It is a strong ligand which is capable of complexing at low concentrations with virtually any heavy metal.

The application of old methods like alkaline chlorination process has become limited due to toxic nature of

intermediate and by-products, and unique methods, such as biological, the iron cyanide precipitation, SO₂/Air, acidification/volatilization and re-neutralization, ion exchange and hydrogen peroxide processes have mainly developed.

Oxidation is one of the techniques, which is well known for cyanide wastewater treatment. Common oxidants used for the removal of weakly bound cyanides include chlorine, peroxide and chlorine dioxide.

Research shows that in the oxidation process, cyanide oxidizes and is

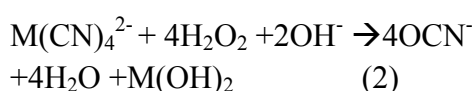
converted to cyanate ion which is 1000 times less environmentally hazardous than cyanide. The maximum allowable cyanide concentration in electroplating wastewater is 0.2 ppm according to CPCB standards.

A common method for the oxidation of cyanide wastewater is chlorination at high pH to form CNO^- , CO_2 , N_2 and NH_4^+ .

However, there are several disadvantages with this type of treatment:

1. It is expensive especially in the case of concentrated solutions;
2. It is not so effective for cyanide complex wastes;
- and
3. It produces a large quantity of sludge, which contains heavy metal after chemical decomposition and subsequent precipitation processes.

In this paper, focus has been laid on copper catalyzed hydrogen peroxide which removes free and complex cyanides including the stable iron complexes cyanides through oxidation. Using hydrogen peroxide systems depends on the reaction time, temperature, pH, the desired products cyanate, CO_2 and NH_3 , the types of cyanides being treated and the system economics. The oxidation reaction with hydrogen peroxide takes place by following reaction:



With any hydrogen peroxide system, a pH of 9-10 should be maintained if

cyanide is present to avoid release of hydrogen cyanide HCN gas. Reaction rate can be increased in several ways : raising temperature, increasing catalyst dosage and/or using excess H_2O_2 .

Overall, the advantages of the hydrogen peroxide process can be summarized as follows: capital costs are comparable (or less) to other chemical treatments; the process is relatively simple in design and operation; all forms of cyanide can be removed; heavy metals are significantly reduced through precipitation; close pH control is not required; the process is adaptable for batch and continuous flow operations; no production of high quantities of waste sludge and dissolved solids; and the process has been shown effective in bench-, pilot- and full-scale operations.

On the other hand, the disadvantages are as follows: the process may not be generally suitable for treatment of tailings slurries; chemical costs may be relatively high; high concentrations of cyanate can be produced, potentially increasing the ammonia concentration in the solution.

The aim of this work was to investigate the effectiveness and optimum dosages of hydrogen peroxide required for cyanide removal.

Materials and Methods

Samples :

The samples for the treatment were obtained from exhausted cyanide baths of silver plating. These baths of silver were considered as waste because they did not contain the silver content as required for plating (minimum 1g). The treatment of cyanide at source was important to prevent the shock loading

at the effluent treatment plants by discharge of the exhausted baths, which contained a very high concentration of cyanide.

Experiments:

All the experiments were carried out with glass beakers of 100ml size. Initially the 2 sample bottles were prepared by diluting the cyanide bath sample with ultrapure water. The initial cyanide concentration in both bottles prepared, was 1.732g/L and 1.62g/L respectively.

Different samples prepared from both the bottles were taken for various experiments. First experiment was carried out for determining the change in rate of cyanide removal. Two samples were prepared by taking each of 30ml from the bottle-1 (with 1.73g/L CN concentration) in 2 different beakers. These 2 beakers were named as A, and B. 5ml H_2O_2 (6%w/v) was added to both the beakers. In beaker A catalyst was not added, while in beaker B, copper sulphate (5% of initial cyanide concentration) was added. Both the beakers were investigated for the rate of cyanide removal at regular intervals. Both A and B were given a retention time for 4-5 hours.

Second experiment was carried out to know the optimum dosage for catalyst and was carried out for samples prepared from the bottle-2 (containing 1.62g/L cyanide concentration). Five samples were prepared with varying amount of catalyst 5%,10%,15%,20%(of cyanide initial concentration) and a blank without catalyst. These all beakers contained constant amount of hydrogen

peroxide (8mL of 6%w/v). These beakers were kept for a retention time of 4-5 hours. The final cyanide concentration was measured for all the beakers.

Analytical methods:

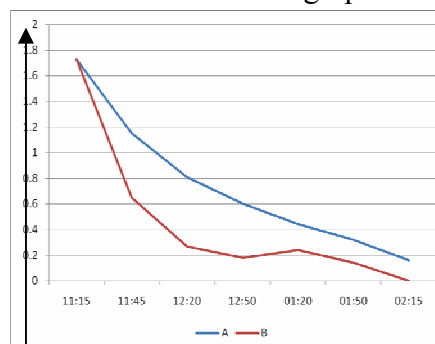
Cyanide concentration was measured as free cyanide, KCN and NaCN but as silver cyanide baths contain majorly cyanide as KCN so for experimental purposes, KCN concentration was considered.

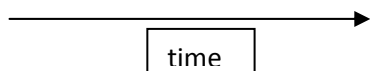
Cyanide measurement was done by argentometric titration with $AgNO_3$. This analysis was carried out by auto titrator. Heavy metal concentrations were measured using atomic absorption spectrometer based on Standard Methods. A 6% w/v hydrogen peroxide aqueous solution was used as the stock solution for all experiments. Copper sulfate ($CuSO_4 \cdot 5H_2O$) (Merck) was used as the copper catalyst. All chemicals used were laboratory reagent grade. Distilled and ultrapure water was used for stock solution preparations and dilutions.

Results

The results of first experiment were as obtained as under:

With time the variations in cyanide removal were as shown in graph:





The above graph shows the increase in cyanide removal with time for both the beakers (A as well as B). It can be observed from the graph that the cyanide removal rate in beaker B i.e with catalyst was more than the one in beaker A i.e without catalyst.

It was found that ammonia formation started after 3-5 minutes of reaction initiation. Ammonia was confirmed by its smell and by HCl too.

For second experiment it was observed that the cyanide removal with all varying amount of catalysts and without a catalyst came as below detectable limit. But it can be said from the results that by adding 5% catalyst, the rate of removal is slower. Also it was observed that ammonia formation in beakers of higher amount of catalyst (15, 20%) was faster than in lesser amount of catalyst (5%).

After 4-5 hours it was observed that the silver started to precipitate at the bottom of the beaker, along with cupric precipitates. These silver precipitates were observed to increase with time. Silver content was confirmed after filtration of the sample and dissolving the samples in nitric acid, and analysing the final silver content of all the beakers.

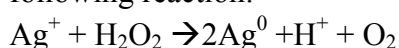
Also, mass balance was performed for those samples and initial and final silver content.

Initial silver content in bottle : 0.57g/L

Beaker no	Final silver (g/L)
1(without catalyst)	0.196

2(5% CuSO ₄)	0.253
3(10% CuSO ₄)	0.235
4(15% CuSO ₄)	0.270
5(20% CuSO ₄)	0.243

This separation was according to the following reaction:



The concentration of copper was measured in initial and final sample and was found that copper sulphate is precipitated out again along with silver precipitates.

Beaker No	Cu initial g	Cu final g
1	0	0
2	0.00206	0.002
3	0.0051	0.0049
4	0.0076	0.0086
5	0.0102	0.01

Conclusions

Both the rate as well as the extent of cyanide destruction increased with increasing peroxide doses for either absence or presence of Cu catalyst. Catalyst addition was very effective for enhancing the cyanide destruction rate and also in decreasing the peroxide doses. However, increasing the copper concentration dosage may also increase downstream problems related to metals separation and treatment. Reaction times necessary to achieve Cyanide concentrations below detectable limit were found about 2-4 h for the optimum peroxide and copper concentration.

However, a peroxide dose of 9g/g of cyanide removal was sufficient for the target cyanide concentration after 3-4 h

of reaction time with the 5-15% catalyst. Also, though the reaction started within short time but continues for 3-4hours for complete removal of cyanide. During the experiment Ag got precipitated out which is one of the advantages of this process. This Ag depends on the stoichiometry and reaction times.

It can be inferred from this study that hydrogen peroxide as a green chemical is potentially a suitable reagent for the treatment of waste silver plating baths allowing the recovery of silver as well as the removal of cyanide and possibly other constituents present.

References

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