



Project Summary

Destruction of Cyanide in Wastewaters: Review and Evaluation

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Twelve technologies were applied to the destruction of cyanides in wastewaters by reviewing available literature and by conducting discussions with industry and government agencies. The 12 technologies reviewed were alkaline chlorination, natural degradation, oxidation of cyanide by sulfur dioxide and air, ozonation alone and in conjunction with ultraviolet (UV) irradiation, precipitation by addition of heavy metals, ion exchange, activated carbon, reverse osmosis, electrodialysis, the Kastone[®] process, electrolytic hydrolysis, and titanium oxide/UV irradiation.

The scope of the problem of cyanide in wastewater or leachate and the effectiveness of 12 different technologies which have been applied to the destruction of cyanide were assessed by review of available literature and discussions with industry and government authorities. Brief summaries of the problem and the current technologies are contained in this report. In general, the primary concern with cyanide effluent is its propensity to form complexes which are difficult to remove and can later break down to highly toxic forms.

During the course of this study, a new approach to the destruction of cyanide and cyanide complexes was developed. This process involves the reduction of cyanide, iron cyanides,

and thiocyanates by irradiation with ultraviolet light in the presence of a catalyst, titanium oxide. The UV/TiO₂ process parameters were investigated by the Hittmann Ebasco laboratory using a series of test mixtures in distilled water, and, after the optimal conditions were established, four composite industrial waste samples were tested to examine the effects of different matrices on the process. Recommendations were made for further evaluation of the chemistry and development of the TiO₂/UV process technology for field testing.

Copper chloride was found to increase the rate of cyanide conversion in simple and complex cyanide. Temperature was found to have little significant effect, while pH in the range 9.0 to 13.0 had no effect on the conversion. The most effective wavelength for irradiation was in the range of 340-360 nm. Titanium oxide at 200 ppm and copper chloride at 300 ppm were the optimal concentrations of catalysts. Precipitates of metal hydroxides and chromates were found to inhibit the reaction as the result of what appears to be a preferential absorption of the UV radiation. Under optimal laboratory conditions a solution containing approximately 60 ppm of iron cyanide is converted to cyanate in 1 hr. Thiocyanate does not effect the conversion of iron cyanides at concentrations of 600 ppm and is itself converted to sulfate and cyanate.

This Project Summary was developed by EPA's Water Engineering

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

More than 350,000 tons of cyanide compounds are produced each year in the United States. Much of this production is used in metal electroplating, hardening of steel, paint manufacturing, photographic processing, and mining and ore dressing operations. Ferricyanides and ferrocyanides are found in waste streams from all these processes. The most common waste treatment processes are alkaline chlorination, ozonation, and electrolytic decomposition, but none of these processes are effective in destroying complex cyanides, particularly ferrocyanides and ferricyanides. Although these compounds are considered nontoxic in their natural states, sunlight irradiation of solutions containing them results in conversion to free cyanides.

This study assesses 12 different technologies that have been applied to the destruction of cyanides by reviewing available literature and by conducting discussions with industry and government agencies. The twelve cyanide destruction technologies reviewed were:

- Alkaline chlorination
- Natural degradation
- Oxidation of cyanide by sulfur dioxide and air
- Ozonation alone and in conjunction with ultraviolet (UV) irradiation
- Precipitation by addition of heavy metals
- Ion exchange
- Activated carbon
- Reverse osmosis
- Electrodialysis
- Kastone process
- Electrolytic hydrolysis
- Titanium oxide/UV irradiation

Though a wide variety of techniques have been discussed for detoxifying cyanide, the only process currently found effective and tested on a pilot scale for the treatment of complex cyanides is ozonation in conjunction with UV irradiation. Cyanide concentrations increased in laboratory studies using (1) titanium oxide as a photo catalyst in a solution containing simple cyanides and (2) irradiation with UV light. This report presents the results of a bench-scale investigation for evaluating the effectiveness of the titanium oxide/UV

process for the treatment of wastewaters containing simple cyanide, complex iron cyanides, and thiocyanate. A series of test mixtures containing ferrocyanide, ferricyanide, simple cyanide, and thiocyanate were used to determine optimum concentrations, and several industrial waste samples were then treated to examine process effectiveness on complex matrices.

Test Procedure and Results

A photochemical reactor was used for UV treatment of various surrogate cyanide solutions and industrial effluents. A 450-watt, high-pressure quartz mercury vapor lamp was used to provide UV energy. This high-pressure lamp was chosen because of its high energy output and wide spectral band. To enhance the incident radiation of the solution, the outside of the reactor vessel was covered with aluminum foil. Eleven different one-liter mixtures containing ferrocyanide, ferricyanide, thiocyanate, and potassium cyanide of analytical reagent grade were used for experimental evaluation.

Dry compressed air was sparged through the solution at 250 mL/min, and the solution was stirred for 10 min. The UV lamp was then turned on, and titanium oxide (anatase form, 80 to 100 mesh, anhydrous), copper chloride or other reagents were added, depending on the test being performed. Air sparging and stirring were continued throughout the irradiation. After treatment, the solution was decanted and filtered to remove the residue of titanium oxide, ferric oxide, and copper hydroxide. The supernatant was analyzed for the parameters of interest. All procedures used either EPA standard methods or methods described in *Standard Methods for the Evaluation of Water and Wastewater*.

The following key test results were observed:

- Cyanide conversion performance improved with air sparging.
- Concentrations of the catalysts (titanium oxide and copper chloride) were varied to determine the optimal concentrations. Optimal concentrations of 200 mg/L titanium oxide and 50 mg/L copper chloride at pH 13 destroyed 99.9 to 100 percent of the total cyanide available in 100 mg/L of the ferrocyanide and ferricyanide mixtures respectively. However, all subsequent tests used excess of copper chloride.
- Tests conducted on a mixture of 100 mg/L ferrocyanide and 100 mg/L

ferricyanide (93.6 mg/L total cyanide) with 300 mg/L copper chloride and 200 mg/L of titanium (as catalysts) for a 2-hr irradiation showed no detectable cyanide (the detection limit was 0.1 mg/L).

- Varying the pH between 9 and 13 resulted in no significant differences in the cyanide destruction at a titanium oxide concentration of 200 mg/L and copper chloride concentration of 30 mg/L.
- Off-gases from the experiments did not contain hydrogen cyanide.
- Temperature effects were tested at 19°, 26°, and 35°C. In all cases, a mixture of 100 mg/L ferrocyanide and 100 mg/L ferricyanide was reduced to no detectable cyanide after 2 hours. Higher temperatures appeared to improve cyanide conversion at high concentrations of ferricyanide and ferrocyanide.
- A test mixture at pH 13 containing 100.9 mg/L ferrocyanide (42.6 mg/L cyanide) was spiked with 1000.2 mg/L potassium thiocyanate (597.8 mg/L thiocyanate) and irradiated for 2 hours. Under optimal operating conditions, 200 mg/L titanium oxide and 50 mg/L copper chloride, 100 percent of the total cyanide and 47.3 percent thiocyanate were removed.
- Optimal conditions for the destruction of thiocyanate were investigated. Additions of copper chloride had an inhibitory effect above 50 mg/L. The optimal titanium oxide concentration and pH were 1000 mg/L and 13 respectively. Test results for optimum UV wavelength for thiocyanate destruction were inconclusive as they indicated that a wide band of energy was needed for the thiocyanate conversion.
- Wastewater samples from the following processes were tested to determine the applicability of the titanium oxide/UV process:
 - Gold processing effluent
 - Cadmium electroplating bath waste
 - Composite electroplating waste
 - Black and white photoprocessing reducer
- Encouraging results were obtained after high dilution and filtration, and after pH adjustment in the case of gold processing effluent. Similar encouraging results were obtained with high dilution for cadmium plating wastes and composite electroplating waste. The black and white photoprocessing reducer tests showed cyanide destruction after 1 hour irradiation.

Conclusions

A number of technologies are currently being used for the removal of cyanide compounds from effluents. The most widely accepted and used are alkaline chlorination, ozonation, ozonation with irradiation, electrolytic hydrolysis, hydrogen peroxide oxidation, and precipitation processes. Of these processes, alkaline chlorination is the most frequently used for removal of the free cyanides; it does not, however, remove iron cyanides. Electrolytic hydrolysis and ozonation with UV do remove iron-complex cyanides and free cyanide, but these treatment techniques have only recently been used for waste treatment at a few electroplating or photo-processing plants. These processes incur high capital and operational costs, depending on the type of waste stream treated and concentration of cyanide.

The titanium oxide/UV technique seems to have distinct advantages. Some of these include the lack of need for temperature or pH control, the ability to use nontoxic and inexpensive chemicals, and the destruction of thiocyanates, and complex and free cyanides.

Bench-scale tests showed that complex cyanides and simple-cyanide-containing effluents can be destroyed by using UV irradiation with titanium oxide and copper chloride as catalysts. The process requires only two reagents and no pH or temperature control for the conversion of iron cyanides and simple cyanides. Effluents that contain significant concentrations of thiocyanate can also be treated by this process without affecting the conversion of complex or simple cyanides.

Prior treatment of some waste streams is necessary to remove chromates and metal hydroxides. No other pretreatment appears to be required for the four industrial waste effluents tested. The rate of conversion of complex cyanide to cyanate appears to be limited by the amount of radiant energy absorbed by the system.

The full report was submitted in fulfillment of Contract Nos. 68-03-3037 and 68-03-3197 to Hittman Ebasco Associates, Inc., and PEI Associates, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

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The complete report, entitled "Destruction of Cyanide in Wastewaters: Review and Evaluation," (Order No. PB 88-213 046/AS; Cost: \$14.95, subject to change) will be available only from:

National Technical Information Service

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The EPA Project Officer can be contacted at:

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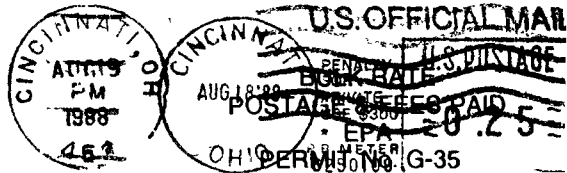
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