



Project Summary

Cyanide Removal from Coke Making and Blast Furnace Waste Waters

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The objective of this research program, supported jointly by the American Iron and Steel Institute and the U.S. Environmental Protection Agency (EPA), was determining the feasibility of removing cyanide from coke making and blast furnace waste waters by ion flotation or column precipitate flotation of iron ferrocyanides. Ion flotation was reasonably effective on ferricyanide, but not on cyanide or ferrocyanide; therefore, efforts were concentrated on the formation and flotation of iron ferrocyanide precipitates. (Note: A readily available source of ferrous iron is waste pickle liquors.)

An experimental program was designed for precipitate flotation to evaluate the effect of operational variables (iron addition, reaction time to form the iron cyanide complex, precipitation time to form the iron precipitate, collector type and dosage, conditioning time, flotation time, and air flow rates). Synthetic ferrocyanide solutions, free cyanide solutions, and two coke plant waste waters [crude ammonia liquor (CAL) and intercepting sump water (ISW)] were tested, both in batch and continuous column flotation tests. Wet oxidation tests were conducted on the froth product

Results of the tests showed that 95-99% cyanide could be recovered from the synthetic solutions containing 100 mg/l cyanide, and 91% from ISW. The most effective flotation reagent was a primary amine (dodecylamine acetate), and the most important variable in the process was the pH of flotation. A set of operating conditions (iron addition, collector addition, pH, reaction time, conditioning time, and flotation time)

were developed for both the synthetic solutions and a coke plant ISW. Preliminary wet oxidation tests indicated that the froth product could be converted to ammonia and ferric oxide by wet oxidation and the solid product would meet EPA/Office of Solid Waste extraction procedure (EP) toxicity standards. Results showed that precipitate flotation could be used as a primary process to remove most of the cyanide and could meet effluent limitations under certain conditions depending on feed concentration and volume.

Ion exchange tests on synthetic solutions produced effluents which met discharge standards. This may be one possible secondary method of treatment. However, no work was done on flotation effluents or plant liquors.

It was also noted in this test program that the iron-iron cyanide precipitate settled quite rapidly once it was formed. Although no work was done in this area, most of the cyanide could possibly be removed by precipitation and thickening, followed by wet oxidation of the thickener underflow.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, 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 and Summary

Fifty years ago, coke production from by-product ovens surpassed coke production from beehive ovens. The advantages of by-product processing were that it reduced the air pollution problems

associated with coking, and recovered marketable by-product chemicals. However, the gas processing introduced a significant water pollution problem. The problem was formally defined by the U.S. EPA, following passage of the Federal Water Pollution Control Act Amendment in 1972 (P.L. 92-500). In May 1982, the EPA issued final regulations defining iron and steel manufacturing point source category effluent limitations guidelines (Federal Register Vol. 47, No. 103, pp. 23135-23404). For by-product coke making, these regulations set a 30-day average limitation of 0.00351 kg of cyanide per tonne of coke produced by application of the best technology economically achievable (BAT).

The level of cyanide in coke plant waste water streams varies from 20 to 400 mg/l. In addition to the cyanide, the plant liquors contain fixed and free ammonia, free and emulsified oils, phenols, and various suspended solids. These contaminants are the by-product of pyrolysis reactions during the carbonization of coal. The process waters are contaminated during the processing of the coke oven gas for the recovery of coal chemicals. The plant contains three major process streams: crude ammonia liquors (CAL), barometric condenser liquors (BCL), and intercepting sump water (ISW). The CAL (also referred to as waste ammonia liquors) are the condensed water vapors separated from tar in the tar plants. The BCL result from the direct contact of cooling water with vapors released in the crystallizing and concentrating of ammonia sulfate by vacuum evaporation. The ISW is a combination of the water from the oil/water separators and the various plant drains.

Cyanide concentrations in the combined effluent flow vary from plant to plant, depending on the total effluent volume. In one plant, producing 5442 tonnes (6000 short tons) of coke per day, the total effluent volume is 1452 l/tonne of coke, and the effluent cyanide concentration is 50.3 mg/l. BAT limitations would require reducing the effluent cyanide concentrations to no more than 2.42 mg/l. In a second plant, process improvements drastically reduced the total effluent volume, primarily by altering the ammonium sulfate condenser system: in this plant, producing 2721 tonnes (3000 short tons) of coke per day, the total effluent volume is 681 l/tonne of coke, and the cyanide concentration is 56.8 mg/l. Therefore the BAT effluent cyanide limitation would be no greater than 5.16 mg/l.

The primary objective of this study was to determine the feasibility of removing the cyanide from these waste waters by either ion flotation or by precipitate flotation of an iron-iron cyanide precipitate. Secondary studies were conducted on ion exchange removal of ferrocyanide.

The objective of the ion flotation studies was to complex the various cyanide species with a quaternary amine and then remove the resulting hydrophobic complex by flotation. The precipitate flotation phase involved complexing the cyanide with ferrous iron, precipitating the ferrocyanide complex as an iron ferrocyanide, and removing the precipitate (and thus the cyanide) by microparticulate flotation. (Note: Previous investigators have shown that (1) when ferrous iron is added, the cyanide level is at minimum at about pH 8 as a result of complex formation and precipitation of $\text{Fe}_2\text{Fe}(\text{CN})_6$; (2) the rate of complex formation is greatest above pH 7.5; and (3) precipitated iron cyanide can be floated with a cationic collector at pH 6. Consequently, current efforts were directed toward determining the conditions necessary for the formation of ferrocyanide complexes, precipitation of the complexes, and flotation of the precipitate.

Experimental

Continuous ion flotation and batch precipitate flotation tests were carried out in a 4.7 cm diameter by 70.0 cm tall column equipped with a froth overflow launder. Continuous precipitate flotation tests were run in a 25 mm (1 in.) column shown schematically in Figure 1.

Ion flotation tests were run on synthetic solutions of $\text{K}_4\text{Fe}(\text{CN})_6$ containing 36.8 mg/l $\text{Fe}(\text{CN})_6^{3-}$ by dispersing the amine in a small volume of the feed solution prior to its addition to the bulk of the feed solution. Following a conditioning period (10-12 minutes), the feed was pumped through the flotation column counter-current to the air flow, and the froth product was removed.

Batch precipitate flotation tests were run on 1l samples of synthetic solutions of $\text{K}_4\text{Fe}(\text{CN})_6$ and KCN as well as on coke plant effluents. The solutions were reacted in a conditioning vessel with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the pH adjusted, the collector added immediately, and the slurry conditioned. The slurry was then pumped into the column and floated at an air flow rate of 0.4 volumes air per volume of solution. The synthetic solutions contained 100 mg/l total cyanide, and some solutions also contained 5000 mg/l NaCl.

Continuous precipitate flotation tests were run on synthetic $\text{K}_4\text{Fe}(\text{CN})_6$ solutions by first adding the amine, A-336, to complex the ferrocyanide, and then adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to form the precipitate.

Ion exchange tests on synthetic $\text{K}_4\text{Fe}(\text{CN})_6$ solutions containing 25 mg/l total cyanide plus 5000 mg/l NaCl were run in a 40 cm diameter column containing 200 ml of wet settled resin (Rohm and Haas, IRA-958). All cyanide assays were performed using the standard ASTM method for cyanide in water.

Ion Flotation

Distribution tests using a chloroform solution containing 1% by volume of a quaternary amine, Aliquat-336 (General Mills, A-336), demonstrated that the amine would complex cyanide, ferrocyanide, and ferricyanide. Ferricyanide had the highest distribution coefficient. Consequently, ion flotation tests were run on synthetic ferricyanide solutions. Flotation results as a function of the system variables were as follows:

Amine Concentration

In chloride-free solutions, cyanide recoveries reached at maximum of about 83% at an amine/ferricyanide mole ratio of 3.75/1. In high chloride solutions, recoveries continually increased but were lower than in chloride-free solutions except at very high concentrations of amine.

Flotation Variables

Increased conditioning times increased recovery until a steady state was reached at about 13 minutes. Variation of the flotation time from 1.07 to 2.3 minutes increased recoveries from 75 to 83%, whereas changes in the air flow rate from 0.08 to 0.22 l/min/cm² had only a minor effect.

Feed Concentration

Nearly constant recoveries of about 82% were obtained over a feed concentration range of 30-70 mg/l ferricyanide. Recoveries decreased below this range to about 65% at 5.0 mg/l ferricyanide. The pH of the solution had little effect over a pH range of 4-7.

Limited work on ion flotation of cyanide and ferrocyanide was discontinued because cyanide did not float well and ferrocyanide required very long conditioning times. Consequently efforts were directed toward precipitate flotation of iron ferrocyanides.

Precipitate Flotation

Batch precipitate flotation was studied initially on synthetic solutions of ferrocyanide, followed by studies on free cyanide solutions and on plant liquors.

Ferrocyanide Solutions

Initial tests were run on ferrocyanide solutions to study the effect of iron addition, collector addition, and pH. The collector used was a quaternary amine, Aliquat-336 (General Mills, A-336). Conditioning time was 15 minutes, and flotation time was 5 minutes. Two levels of iron, 7 molar (90 mg/l) and 70 molar (144 mg/l) percent excess (based on formation of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$) were used at collector levels of 283 and 567 mg/l A-336 and pH values of 3.0 and 7.0. Results showed that pH was the most important variable. Flotation, using 144 mg/l iron and 283 mg/l A-336 over a pH range of 3-8, gave essentially constant recoveries of 90-95% from pH 3 to 6. Above pH 6, recovery decreased rapidly.

Addition of collector above 100 mg/l A-336 gave relatively constant recoveries of over 90% at pH 4 using 144 mg/l Fe and 5 minutes conditioning time. Below 100 mg/l A-336, recovery dropped off rapidly.

In solutions containing NaCl, higher collector additions were required. Moreover, recovery increased steadily from 85% to 95% as the collector or concentration was varied from 50 to 800 mg/l.

Free Cyanide Solutions

For free cyanide solutions, a complexing reaction must take place prior to the precipitation reaction. Reaction times of 5 and 10 minutes, after addition of iron but before collector addition, were studied at two iron levels — 144 and 215 mg/l using 283 mg/l A-336 at pH 4. Both the conditioning and flotation times were 5 minutes. At the lower iron level, recoveries increased with increased reaction time; however, at the higher iron level, increased reaction time had little effect. Similar results were obtained on chloride-containing solutions, although overall recoveries were slightly lower.

Collector Type

A second cationic collector, dodecylamine acetate (12-D), and an anionic collector, sodium lauryl sulfate (NLS), were investigated as a function of pH at an iron level of 215 mg/l. Collector levels were 31 mg/l for 12-D and 45 mg/l for NLS. The effectiveness of the NLS fell off sharply above pH 6, indicating that above this pH the particles are negatively

charged. In contrast, the positively charged 12-D was effective up to pH 9 with recoveries as high as 98%. This primary amine was more effective than the quaternary amine A-336, particularly above pH 7. In addition, much lower levels of the primary amine were required: recoveries of over 97% were obtained with additions of only 24 mg/l of 12-D. The froth volume and stability was good over all pH ranges with 12-D; whereas, little froth was obtained above pH 7 with A-336.

The addition of a frother, 20 mg/l of 2-methyl-4 pentanol (MIBC), gave 97% recovery with only 12 mg/l of 12-D.

Plant Liquors

A drum of intercepting sump water (ISW) and a drum of crude ammonia liquor (CAL) were used for the tests. The CAL was dark colored and had a strong odor due to high concentrations of ammonia and phenol. The total cyanide content was 10 mg/l. The ISW was a dirty brown color and contained 89 mg/l total cyanide.

ISW Liquors - Effect of pH

Since the work on synthetic solutions showed that pH was the most important variable, a series of tests were run on the ISW at various pH levels. Test conditions were 24 mg/l of collector 12-D, 200 mg/l of iron, and reaction, adsorption, and flotation times of 15, 10, and 5 minutes, respectively. Recoveries increased with increasing pH to a maximum of 91% at about pH 7. Variations in reaction time over the range of 5-30 minutes yield nearly constant recoveries of about 91%. Recoveries decreased with reaction times longer than 30 minutes.

CAL Liquor

The CAL liquor was floated at pH 7 with 24 mg/l of 12-D and 200 mg/l iron. Reaction, adsorption, and flotation times of 15, 5, and 5 minutes, respectively, were used. Cyanide recovery was about 40%. Additional coagulation resulted when amine was added; these solids were also reported in the froth product. Flotation under the same conditions, except without amine, resulted in a 60% recovery. This indicates that the oils present in the liquor may be acting as collectors.

The above results indicate that a batch flotation process:

- (1) Will remove over 98% of the cyanide from synthetic solutions containing 100 mg/l cyanide.

- (2) Will remove over 90% of the cyanide from plant liquors containing approximately 90 mg/l cyanide. If the same percentage removal can be achieved at feed concentrations of the order of 50 mg/l, the higher of the two effluent standards can be met.

- (3) Has the potential of a primary process for bulk removal of cyanide and possibly a process for meeting effluent standards if additional flotation stages are added. In addition the underflow is relatively clean, indicating the possible removal of other contaminants.

Continuous Precipitate Flotation

Continuous precipitate flotation tests were run on synthetic $\text{K}_4\text{Fe}(\text{CN})_6$ solutions using reverse addition of amine and iron; i.e., the amine, A-336, was added as a complexing agent followed by the addition of iron as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Initial two-phase batch extraction tests using CCl_4 as the amine solvent indicated an average 3.5/1 amine/ferrocyanide stoichiometry. Dispersion of the amine in ferrocyanide solution produced a finely dispersed wax. Subsequent addition of iron produced a floatable amine-iron-cyanide precipitate. Minimum iron addition was found to be 250 mg/l. Results of batch tests on solutions containing 10 and 75 mg/l cyanide showed recovery was not materially affected by amine additions greater than a 3/1 mole ratio of amine/ferrocyanide. Using an amine/ferrocyanide ratio of 3/1 plus 250 mg/l iron, very high cyanide recoveries (95-98%) were obtained in batch tests on feed solutions containing cyanide.

Using the above system of reverse amine-iron addition, continuous tests were run in the system shown in Figure 1. Column performance (1 in. column) was not affected significantly by changes in feed flow rate, specific air rate, or retention time.

The effect of feed concentration on cyanide effluent concentration is shown in Figure 2. The effluent limitations of 2.4 and 5.1 mg/l for the operation described earlier are shown by the dotted lines. These results indicate that:

- (1) Substantial removal of ferrocyanide can be achieved.

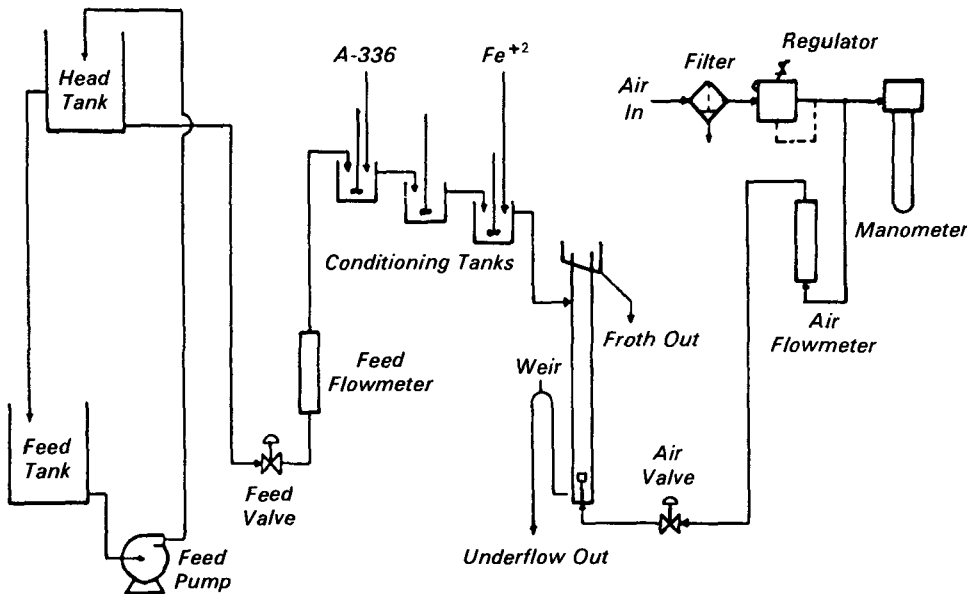


Figure 1. Continuous column flotation system.

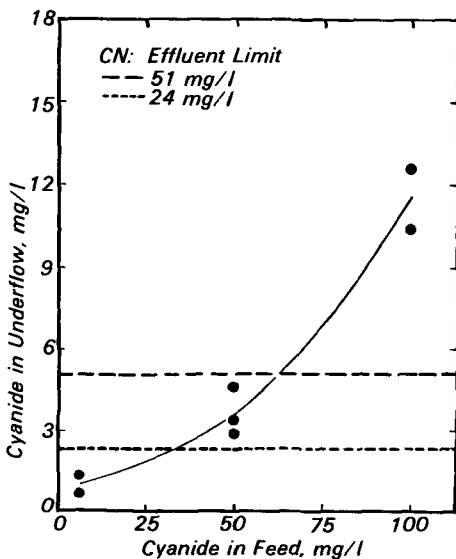


Figure 2. Effluent cyanide performance of flotation column.

- (2) For feed cyanide concentrations less than 62 mg/l, the effluent limitation of 5.1 mg/l can be met, and for feed cyanide concentrations less than 35 mg/l the lower limitation of 2.4 mg/l can be achieved.

Disposal of Flotation Concentrate

Wet oxidation of the flotation concentrate using the Wetox® Process appears to be a technically feasible process for

and blast furnace waste waters by flotation of iron cyanide precipitates would be of value, particularly if it involved semi-pilot scale tests on a multistage continuous basis on plant liquors. In addition to column flotation, other flotation processes (e.g., submerged air flotation) bear investigating. Further studies on wet oxidation of the flotation concentrate would help determine optimum operating conditions.

Conclusions

The results of experimental studies on the removal of cyanide from coke making and simulated blast furnace waste waters by amine flotation of iron ferrocyanide precipitates indicate that most of the cyanide can be removed by this process. In certain cases, depending on the feed cyanide concentration and feed volume, effluent limitations can be met.

Cyanide recoveries of 95-99% were obtained from both ferrocyanide solutions and non-complexed cyanide solutions containing 100 mg/l cyanide plus high NaCl concentrations. Cyanide recoveries of as high as 91% were obtained from a plant liquor (intercepting sump water) containing 89 mg/l cyanide.

The most important variable in the process was pH, and the most efficient collector was a primary amine (dodecylamine acetate) at pH 8. A quaternary amine (Aliquat-336) was effective up to pH 6, but recoveries dropped sharply at higher pH values.

The cyanide in the froth product can be effectively destroyed by wet oxidation.

Ion exchange using a strong base resin was capable of producing an acceptable effluent (less than 0.25 mg/l cyanide) from synthetic solutions containing 25 mg/l cyanide as ferrocyanide plus 5000 mg/l chloride; however, the effectiveness of this process as a secondary stage following flotation was not determined.

detoxifying the concentrate. In this process, cyanide is converted to NH_3 and iron to iron oxide. Preliminary tests on a concentrate containing 2000 mg cyanide produced a liquor containing less than 1.0 mg/l of cyanide and an off-gas containing less than 0.5 mg cyanide. Further work in this area could optimize the process.

The levels of all metallic contaminants (D004 to D011) in the solid residue were less than the maximum allowable concentrations as determined by EP Toxicity Test Procedure (Federal Register, Vol. 45, No. 98, May 19, 1980).

Ion Exchange

A limited series of tests were run on ferrocyanide solutions containing 25 mg/l cyanide using IRA-958. The breakthrough point was arbitrarily set at an effluent concentration of 0.25 mg/l cyanide. Successive cycles were run with elution after each cycle using 15% NaCl solution at pH 12. Excellent adsorption was obtained at flow rates of 19.4 and 16.0 bed volumes per hour. Volume throughputs to breakthrough were about 380 at 19.4 bed volumes per hour and 500 at 16.0 bed volumes per hour. Very little decrease in throughput was noted over three cycles. No tests were run on plant liquors; therefore, the effect of other anions present in these liquors is unknown.

Recommendations

Further investigation of this process for the removal of cyanide from coke making

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The complete report, entitled "Cyanide Removal from Coke Making and Blast Furnace Waste Waters," (Order No. PB 83-259 671; Cost: \$10.00, 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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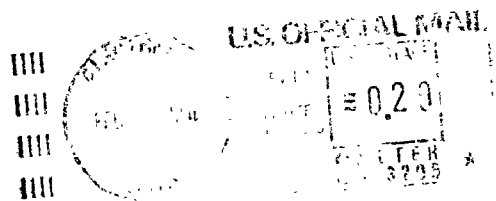
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