

THE ION-PRECIPITATE FLOTATION REMOVAL
OF
CYANIDE COMPLEXES
IN
STEEL PLANT WASTE WATERS

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Engineering (Metallurgical Engineer).

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ABSTRACT

In the work reported here, a method was developed for removing ferrocyanide from water solutions. The ferrocyanide was reacted with methyl-tricapryl-ammonium chloride, then precipitated by the addition of ferrous ion. The precipitate was removed by bubble column flotation. The stoichiometry of the reaction between the surfactant and the ferrocyanide was determined to be 3 parts organic to 1 part ferrocyanide. Dosages of ferrous iron had to be high enough to produce a concentration of 4.5×10^{-3} molar Fe^{++} in order to cause precipitation. The laboratory scale flotation column was capable of removing precipitated ferrocyanide from the system, reducing concentration by more than 86%.

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DEDICATION

This thesis is dedicated to Dr. William D. Warren, Dr. James F. Clark and Dr. Floyd A. Vanderpool in thanks for their many forms of inspiration.

INTRODUCTION

The iron and steel industry has the potential to emit many toxic substances as water pollutants. In 1974 the U. S. Environmental Protection Agency (EPA) produced a "Development Document" which set out proposed "Effluent limitations guidelines" for the steel-making industry (1). These have become regulations in essentially unchanged form (2). In the development document, the steel-making process was divided into unit operations, each of which was treated separately. While each unit operation has a unique set of contaminants, and therefore requires a different regulatory approach, some share one or more specific pollutants. Two of these operations are by-product coke-making and blast-furnace iron-making. Both contaminate water through off-gas scrubbing systems, and both produce cyanides which appear in that water.

Cyanides have been defined (3) "...as organic or inorganic compounds which contain the -CN group." The most toxic of the cyanides is hydrogen cyanide (HCN) which at room temperature is a gas that is soluble in water, with solubility increasing with pH. HCN is not common in nature, because it is highly reactive and the -CN radical readily forms many complexes.

Among the most stable of the transition metal complexes are the iron cyanides. The simple complexes of the ferrous (Fe^{++}) and ferric (Fe^{+++}) ions both contain six $-\text{CN}$ radicals, and have net valence of minus four and minus three respectively. The ferrocyanide complex, which is considered in this work, is quite stable, with an equilibrium constant of about 10^8 when formed from ferrous and cyanide ions (4). Thus the ferrocyanide complex will not decompose to release significant amounts of free cyanide ions unless exposed to ultraviolet light. In sunlight, therefore, it can break down and put toxic $-\text{CN}$ into the environment. Ferrocyanide itself is not particularly toxic, and is not subject to specific regulation.

Ferrocyanide appears in the recirculating wash water for blast furnace gas-scrubber systems. A typical system schematic is shown in Figure 1 (5). The primary purpose of these systems is to remove entrained dust from the blast furnace off-gas before it is burned in the stoves used to preheat the blast air for the furnace. The dust contains a considerable amount of fine iron oxide particles, which leads to a high concentration of ferrous ion in the scrubber water. Any HCN in the off-gas will also tend to dissolve in the scrubber water where it will, if given enough time, be

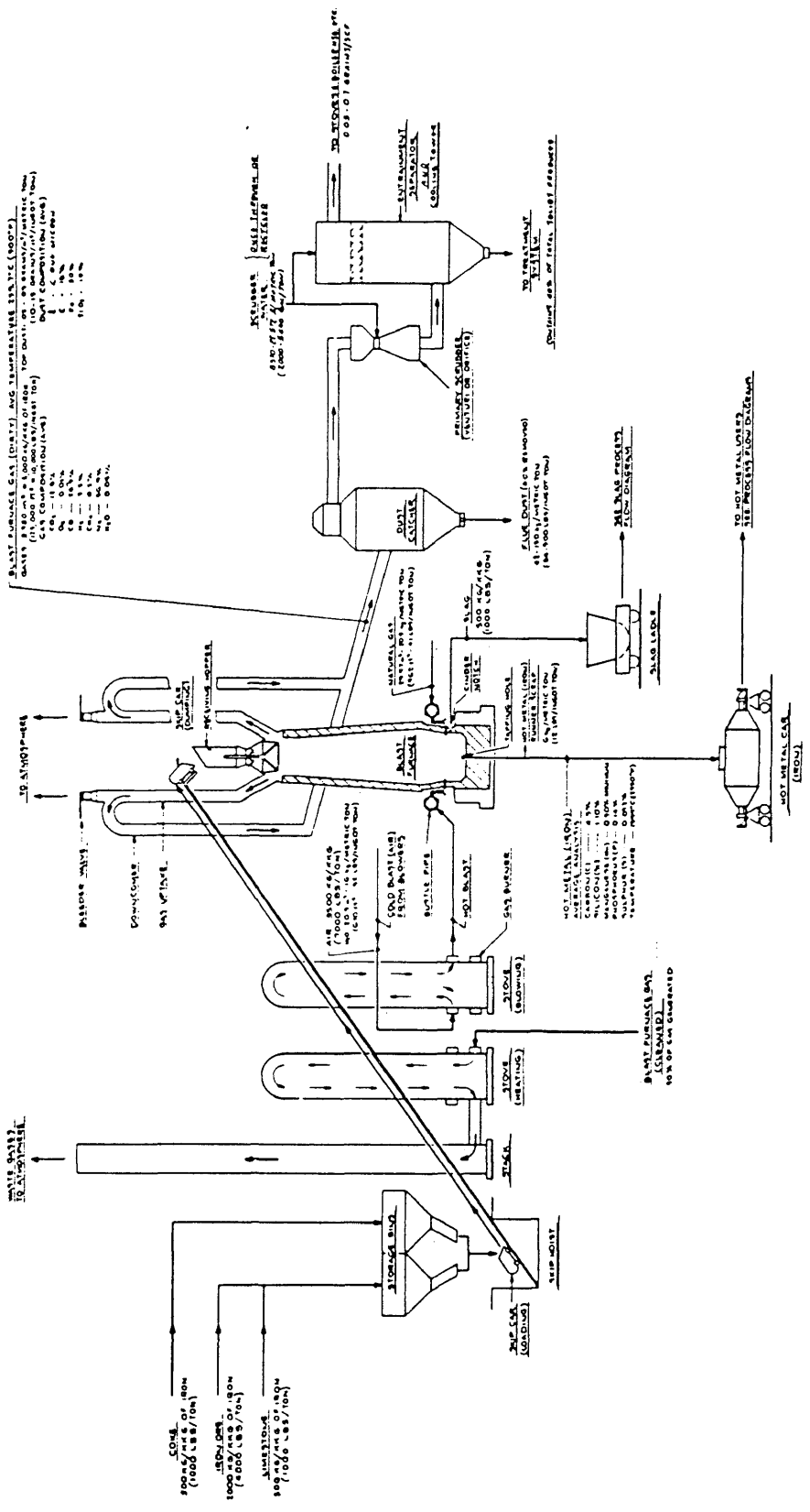


Figure 1. Schematic of a Typical Iron Blast Furnace Showing Gas Scrubber System.

complexed by the iron in the system.

Water vapor is also a constituent of the off-gas. It enters the system in the charge materials and some may be formed by reactions in the furnace. This water will condense in a wet scrubber so that there will be a build-up of water in the scrubber system. This makes total recycling of scrubber waters impossible, and a bleed stream is necessary to remove the excess. Such a stream is often called a "blow down" in industrial jargon, and it is this stream that requires treatment. Other pollutants occur in these streams, with phenol, ammonia, sulfides, and suspended solids being the most significant. Cyanide concentrations can vary from near zero to at least 24 mg/l, with the other pollutants also varying widely, see (Appendix C). Few actual data are available, since they are considered most sensitive by the companies in the industry and are therefore kept confidential.

The EPA regulations place limits on the volume of the bleed stream (6). For iron blast furnaces, the effluent is limited to a flow of 125 gallons per ton of iron product (521 liters/1000 kilograms). All pollutant levels are then specified in either pounds per thousand pounds (lbs/1000lbs) or kilograms per thousand kilograms (kg/1000kg) of product,

rather than a maximum concentration in the bleed stream. For cyanides, the method of analysis is specified as "cyanides amenable to chlorination as described in 1972 annual book of ASTM Standards, 1972, Standard D2036-2, method b, page 553" (7). The Code of Federal Regulations lists three sets of limitations for each "subcategory" of pollutant source. These are the "Best Practicable Control Technology Currently Available" (BPCTCA), the "Best Available Technology Economically Achievable" (BATEA), and the "Standards of Performance for New Sources" (NSPS). In the case of the blast furnace subcategory, the BATEA and NSPS standards are the same. In these categories, allowable cyanide levels are a maximum of 0.0004 kg/1000kg for any one day and 0.00013 kg/1000kg daily average for thirty consecutive days (see Appendix D).

The BATEA and NSPS standards are the basis for this work since they must be met by 1983, subject to Congressional or Judicial modification. If one uses the maximum water flow (521 liters/1000kg of product), and the allowable average cyanide limitation, then the calculated allowable concentration is 0.25 parts per million (by mass). This is the target concentration for the experimental work reported here.

The other unit operation in steel-making that can produce cyanide is by-product coke-making. In fact, some cyanide occurring in the iron blast furnace off-gas is carried in on coke and then is volatilized.

There are many water streams from a coke plant, as shown in Figure 2, but they are usually combined into one for treatment. Most of these streams are from multi-stage gas-scrubber systems; one primary stream, however, is the quench water from the coke quenching tower. While recirculation is practiced to as great an extent as possible, the same problem exists for the coke plant as for the blast furnace; that is, more water is continually being carried into the plant in the charge. This water is vaporized in the coke ovens and will condense in the gas-scrubbers, necessitating, as in the blast furnace off-gas scrubbers, a bleed-off or blow-down of excess water. This bleed stream contains ammonia, cyanide, oil and grease, phenol, sulfides, and suspended solids as pollutants that are to be controlled (see Appendix E). In addition, a characteristic called "biochemical oxygen demand" (BOD) is to be controlled. Of most relevance to this work, cyanide concentrations as high as 110 mg/l are encountered. It must be noted that cyanide is present primarily in its free or un-complexed form in these streams.

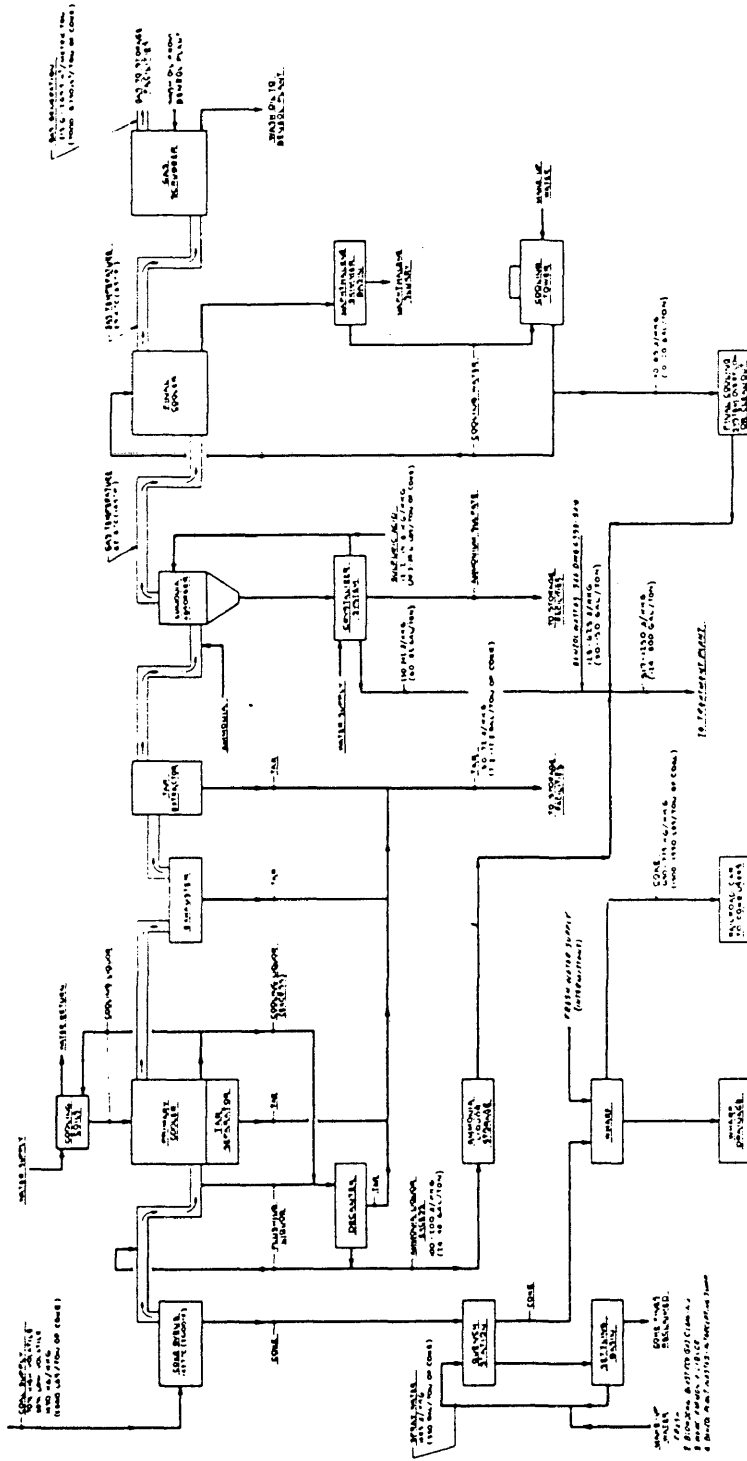


Figure 2. Schematic of a Typical By-Product Coke Plant Effluent Recovery System.

As for the iron blast furnace, the total effluent flow from a coke plant is regulated. The maximum desired flow is 417 liters/1000kg of coke produced (8). The standard for cyanide becomes 0.0001 kg/1000kg to meet a desired maximum concentration of 0.25 mg/l, the same as for the iron blast furnace. These are the BATEA standards which are the same as the NSPS for this subcategory, again similar to the blast furnace regulations. A complete listing of the standards can be found in Appendix F.

PRESENT METHODS OF TREATMENT

It is difficult to survey the literature concerning pollution control because of the secrecy surrounding much of the work on the problem. Secrecy is easy to understand, with the current anti-pollution fervor in many sectors of the country. Any company with a pollution problem is not voluntarily going to release any information about that problem which might cause the company harm in court or in public opinion. Little hard information is available on the performance of currently-used pollution control technology, particularly with respect to a well known toxic pollutant like cyanide. It is thus difficult to evaluate and compare the various existing and proposed treatment methods except

in the most general terms.

The desirable features of a treatment process for cyanide-containing effluents of a steel plant are easy to outline in broad terms. Certain characteristics of blast furnace iron- and by-product coke-making determine some of the features. The blast furnace plants visited by the EPA in preparing the 1974 development document (9) produced from 1,320 to 8,000 tons of iron per day, while some plants considered for visits produced as much as 13,700 tpd. At 521 liters/1000kg (125 gal/ton), this means that effluent flows could be as high as 1.7 million gallons per day or about 1200 gallons per minute. Remembering that it takes 0.5 ton of coke to produce 1.0 ton of iron (10), and that the desired effluent flow is 417 liters/1000 Kg of coke produced (100 gal/ton), then coke plant effluent flows could reach 685,000 gallons per day or 475 gallon per minute. This indicates the need for waste treatment processes with short retention times to minimize equipment size and hence land use, which is important at many inner-city steel plants. Another and perhaps over-riding criterion is that the overall treatment should reduce the controlled effluent characteristics to acceptable values. Finally, the process capital and operating costs should be as low as possible as these costs are added directly to the cost of the iron and

steel production.

Treatments exist that meet the above criteria for all of the pollutants in blast furnace and coke plant waters except cyanide. Cyanide presents special problems, particularly in its formation of very stable complexes. Ferrocyanide, which is the most common complex encountered in steel plants, is, as mentioned earlier, very stable, breaking down only under ultraviolet light. This causes severe difficulties for processes that attempt to remove cyanide by chemical oxidation. All current treatment systems for industrial waste water rely on chemical oxidation for cyanide removal. Many new techniques have been proposed that do not use oxidation, but no work has been reported on anything larger than laboratory scale. For this reason no valid comparisons about relative performance can be drawn until full scale or close to full scale systems have been tested.

Chlorination

Chlorination is one of the oldest of the commercial processes for treating waste waters containing cyanide. It uses hypochlorite solutions or dissolved chlorine gas to oxidize the cyanide. Hypochlorite solutions are generally

used only in very small scale applications, since chlorine gas is less expensive in large quantities. The nature of these reagents causes problems in handling and use. Both are toxic and corrosive in most systems. Chlorine gas systems must be closely monitored for leaks, and to insure that all of the gas is reacting or dissolving in the water and that none is being released into the atmosphere of the plant. Excess chlorine is needed to drive the oxidation reactions to completion, which leads to secondary pollution problems both with the reagents themselves and possibly with the formation of chlorinated hydrocarbons. Further, this technique is not able to break down the ferrocyanide complex, which is the main problem this work is attempting to address. Finally, chlorination systems have long retention times, in the range of several hours.

Ozonation

Although the first ozonation plant was built in France at about the turn of the century (11), it has only recently been widely applied in this country. Ozone is used as the oxidant in this process, and has several advantages over chlorination. There is, however, one disadvantage; ozone must be generated on-site. This increases capital cost, because of the ozone generator, but that may be offset by

the advantages of the process. Ozone is toxic, but does not present the handling problem that chlorine does. Neither will it remain in the treated water long enough to cause secondary pollution problems. The process is faster than chlorination and will require smaller facilities, which may help to offset the cost of the ozone generation plant. While this process has these advantages, it will not remove iron-cyanide complexes without assistance. A technique that combines ozonation with exposure to ultraviolet light has been demonstrated on a laboratory scale (12). The test work was carried out on ferricyanide solutions, and its applicability to steel plant wastes that contain ferrocyanide is therefore questionable. Also, as can be seen from Figure 3, the process does take considerable time. It is important to note that it takes approximately 100 minutes to produce an acceptable effluent from material that starts with a concentration at the low end of what can be expected as feed in an industrial process.

Biological Treatment

The oldest and also the newest form of waste water treatment, biological oxidation, is rapidly expanding in its application. With the ability to tailor the organisms used to the specific pollutants involved, it presents possibly

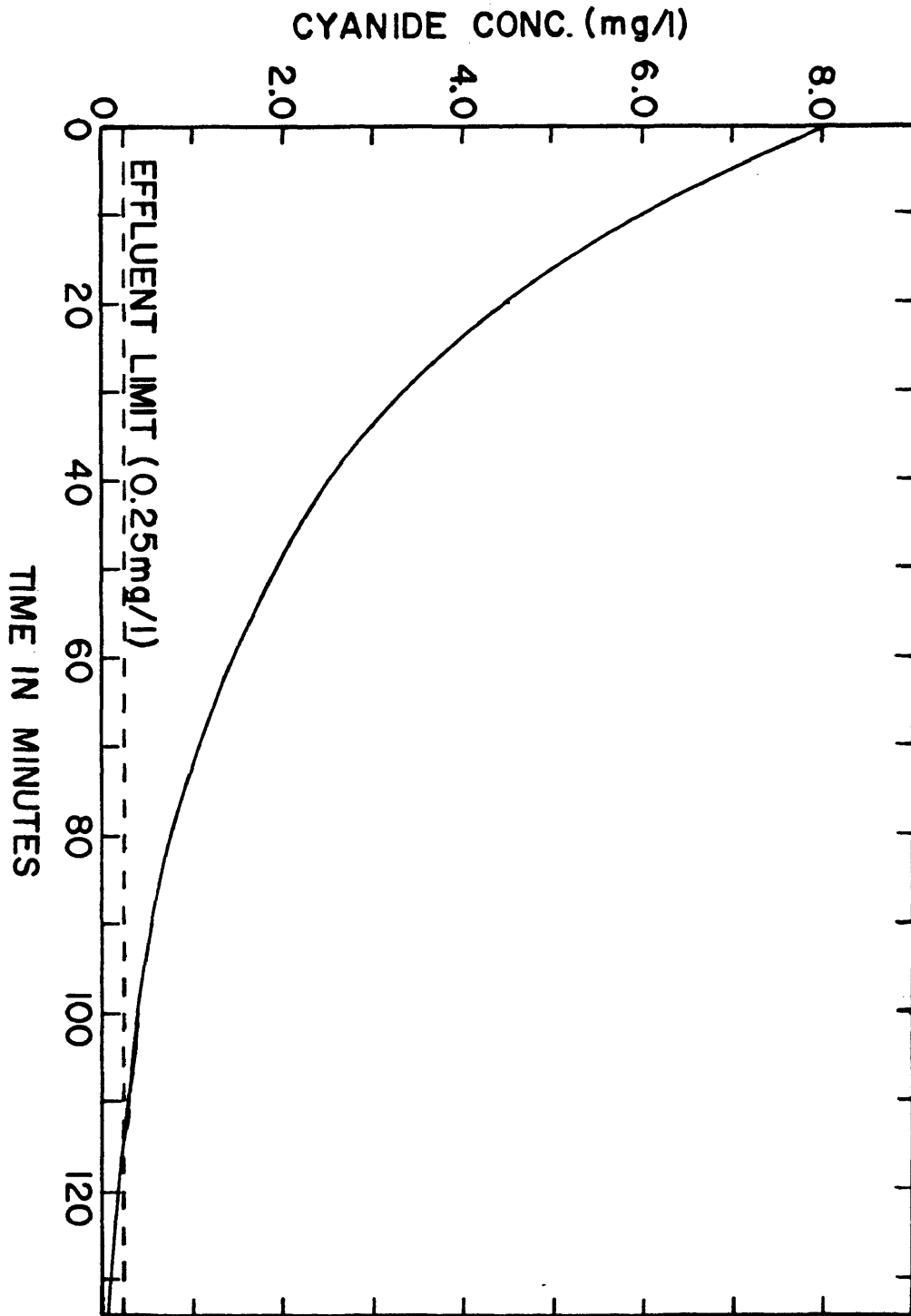


Figure 3. Removal of Ferricyanide by Ozone-Ultraviolet Treatment in a Batch Reactor.

the greatest potential for treatment of any sort of waste. The ability to tailor the micro-organisms to the system should also eliminate secondary pollution by the treatment process. Much work is being done in this area, particularly with respect to coke plant wastes (13,14). These studies concentrate on treating ammonia, with little attention paid to cyanide removal. One study (15) showed that retention times for the entire treatment can be as long as 8 hours. This is the primary problem with this approach. None of the studies mentions ferrocyanide, so the possibility for its removal remains a question.

Miscellaneous Treatments

Many other treatment methods have been suggested for wastes containing cyanide. While they look promising, few, if any, have been developed beyond a laboratory scale. These include electrolysis (16), ion exchange (17), and precipitation by inorganic reagents (18). Any reading of the annual literature survey issue of the Journal of the Water Pollution Control Federation will produce a large number of references on this subject. The work reported here is of the same nature, being preliminary laboratory development. Since the only criterion that will be used in industry to choose between treatment systems that produce

effluents that are acceptable is the overall cost of purchasing, installing, and operating said systems, detailed comparisons of laboratory scale tests will say very little about the final selection. Therefore, only general observations will be made about the comparative advantages or disadvantages of the ion-precipitate flotation system investigated here.

THE ION-PRECIPITATE FLOTATION APPROACH

The concept of Ion-precipitate flotation can be related to the leach-precipitation-flotation system of Phelps-Dodge Corporation at Morenci, Arizona. In this system for recovering oxidized copper, the oxides were leached with sulfuric acid, the copper in solution was precipitated by cementation with fine iron particles, and the resultant copper particles were recovered by conventional flotation. The only difference in concept between that system and the one proposed here is that the material to be recovered enters the system as an ion, and does not have to be leached. For the treatment of wastes containing ferrocyanide, a system consisting of precipitation of the ferrocyanide by an organic compound and removal by bubble column flotation is being proposed. Some of the advantages of such a system would be low residence time and easy

handling of the pollutant product, a solid precipitate. This system should provide a high capacity process that can treat large effluent flowrates in a small space. It may not be able to meet regulatory effluent standards by itself, but it should be able to remove the bulk of the ferrocyanide, leaving final polishing of the effluent to processes that would be overloaded with higher concentrations in the feed.

Bubble column flotation is a process of froth flotation in a "cell" that is much taller with respect to its cross section than a conventional cell. While no absolute standard was set forth in the literature, a height to diameter ratio of six to one is occasionally proposed as a minimum for a "column". Columns are especially adaptable to precipitate flotation because of their unique operating conditions. Inlets are usually near the top so that there is a counter-current contact between the air bubbles and the feed material. No mechanical agitation is provided; all mixing is due to the flow of air bubbles counter to the flow of liquid, so there is less shear than encountered in mechanically agitated systems. Lower shear forces allow for weaker bubble-particle attachment, and the attachment of smaller particles such as precipitates. The systems encountered in ion-precipitate flotation also use very small bubbles to encourage small particle attachment. Wilson (19)

uses a simple hydrodynamic model to show that bubbles in the size range of 0.2 to 0.7 millimeter are the best in typical precipitate systems.

The application of ion precipitate flotation to the removal of cyanide from aqueous solutions is not new. Grieves and Bhattacharyya (20,21,22) have been working on such an idea since 1969. In their system, cyanide at concentrations of 40 and 80 mg/l was complexed with Fe^{++} in NaCl solutions. The precipitates thus formed were removed by "foam separation" using a cationic surfactant, ethyl-hexadecyl-dimethyl-ammonium bromide. They studied many process variables and were able to remove the cyanide best when visible precipitates were formed.

Work has been done more recently on the flotation of cyanide and its complexes from simulated coke-plant waste waters (23). The system used methyl-tricapryl-ammonium chloride as the precipitant. It was found that the flotation column could very easily remove ferricyanide, but had serious difficulties with ferrocyanide, and could not remove free cyanide at all. Flotation worked well at feed concentrations greater than 5 mg/l ferricyanide.

This project was a continuation of that work. Its goal

was to discover how to make ion-precipitate flotation work for ferrocyanide in steel plant waste waters. Again, Henkel Corporation's Aliquat-336 (methyl-tricapryl-ammonium chloride) was the surfactant used. It is sold as a solvent extraction surfactant for iron, among other metals, so it would be easily available if a flotation process using it ever became a commercial reality. The testing program pursued was designed to explore the properties of the A-336/ferrocyanide system to find out why it does not respond well to flotation. Attempts were then made to modify the system to make it work better.

In concept, the proposed method would treat bleed streams from blast furnace off-gas scrubber systems directly, since ferrocyanide is the form encountered in these effluents. If any excess iron were needed, a ready source would be spent pickle liquor, which is the effluent from a process where steel is cleaned with acid to remove iron oxides from the surface of the finished item. Sulfuric or hydrochloric acid solutions are generally used, producing ferrous sulfate or ferrous chloride wastes respectively. Spent pickle liquor could also be used in treating coke plant waste waters to complex the free cyanide to ferrocyanide, which could then be treated by the flotation process. This would have the elegance of using one

troublesome effluent stream to treat another, thereby removing both sets of pollutants. The economics of actual application of that idea would be the deciding factor in its use.

EXPERIMENTAL PROCEDURE

Three separate series of experiments were run in the course of this investigation. (1) dual liquid batch extraction tests, (2) single liquid batch extraction tests, and (3) continuous column flotation tests. They were run in order, with the results of the first series used to design the second, and the second to design the third. Each series of tests is described in detail below. The variations in cyanide concentration reported in the literature led to the decision to work with ferrocyanide concentrations up to 100mg/l when expressed as CN-, meaning the total contained cyanide, as would be reported in the "total cyanide by distillation analyses" used in this work.

Reagents

Three primary reagents were used in this work. Others were used, of course, but primarily in analyses, and are discussed in Appendix A on cyanide analysis.

(a) Methyl-tricapryl-ammonium chloride, a commercial product of the Henkel Corporation, who give it the trade name Aliquat-336 (A-336). The data sheet from Henkel stated that A-336 averaged 90% activity, and this was assumed in

all dosage calculations.

(b) Ferrocyanide: Commercial reagent grade potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) was used to make all feed solutions.

(c) Ferrous Sulfate: Commercial reagent grade ferrous sulfate ($Fe(SO_4) \cdot 7H_2O$) was used for the latter two series of tests.

Dual Liquid Batch Extraction Tests

For these tests the A-336 was diluted in carbon tetrachloride to a strength convenient for whatever test was under way. Each test was run at a selected molar ratio of A-336 to ferrocyanide. The ferrocyanide was dissolved in an appropriate amount of distilled water; for the tests presented here the feed concentration was 100 mg/l as CN^- or 6.41×10^{-3} molar ferrocyanide. The two solutions were added to a vessel of appropriate size, shaken well, then allowed to separate. After they had separated, a sample of the aqueous phase was drawn off and analyzed for total cyanide by distillation (see appendix A).

Single Liquid Batch Extraction Tests

After determining the stoichiometry of the A-336/ferrocyanide reaction, a series of tests was run in which the A-336 was diluted in methanol to no greater than 100g/l so that, when it was added to the aqueous ferrocyanide solution, it would form a fine dispersion. Tests indicated that five minutes was sufficient time for the reactions to take place. After allowing five minutes agitation for the A-336 to react with the ferrocyanide, pH, chloride ion, calcium ion and ferrous ion were screened in an attempt to speed precipitation of the A-336/ferrocyanide compound. After a suitable reagent was identified, the solutions were vacuum filtered through a glass frit filter (Pyrex grade M), and the filtrate was analyzed for total cyanide by distillation. Two sets of tests were run then, the first to determine the optimum dosage of A-336, and the second to observe the effect of feed concentration on the reduction in concentration of cyanide at the optimum dosage.

Column Flotation Tests

This series of tests was performed to investigate the ability of a continuous flotation system to remove

ferrocyanide from a simulated effluent. The simulated effluent was simply ferrocyanide in tap water. A schematic drawing of the system is presented as Figure 4. A-336, diluted in methanol, was added to the first stage conditioning tank, which held a liquid volume of 290 milliliters and was agitated violently. The dosage was close to stoichiometric. The second stage conditioning tank was simply a holding tank to allow time for the A to react with the ferrocyanide. It held 2100 milliliters of solution. Ferrous sulfate solution was added in the third stage conditioning tank, which held a volume of 400 milliliters, from which the stream was fed to the flotation column. Conditioning times longer than 5 minutes after A-336 addition and 1 minute after ferrous ion addition were found to have no additional effect on the performance of the system. Therefore, the only concern was to insure that the minimum conditioning times were allowed by the tanks, and no effort was made to control conditioning time beyond that. Timed samples of the overflow and underflow were taken at various intervals during operation. The volumetric flowrates of the streams were determined from these samples, and the underflow samples were analyzed for total cyanide by distillation, with a four hour distillation time.

The levels of the operating variables were selected for

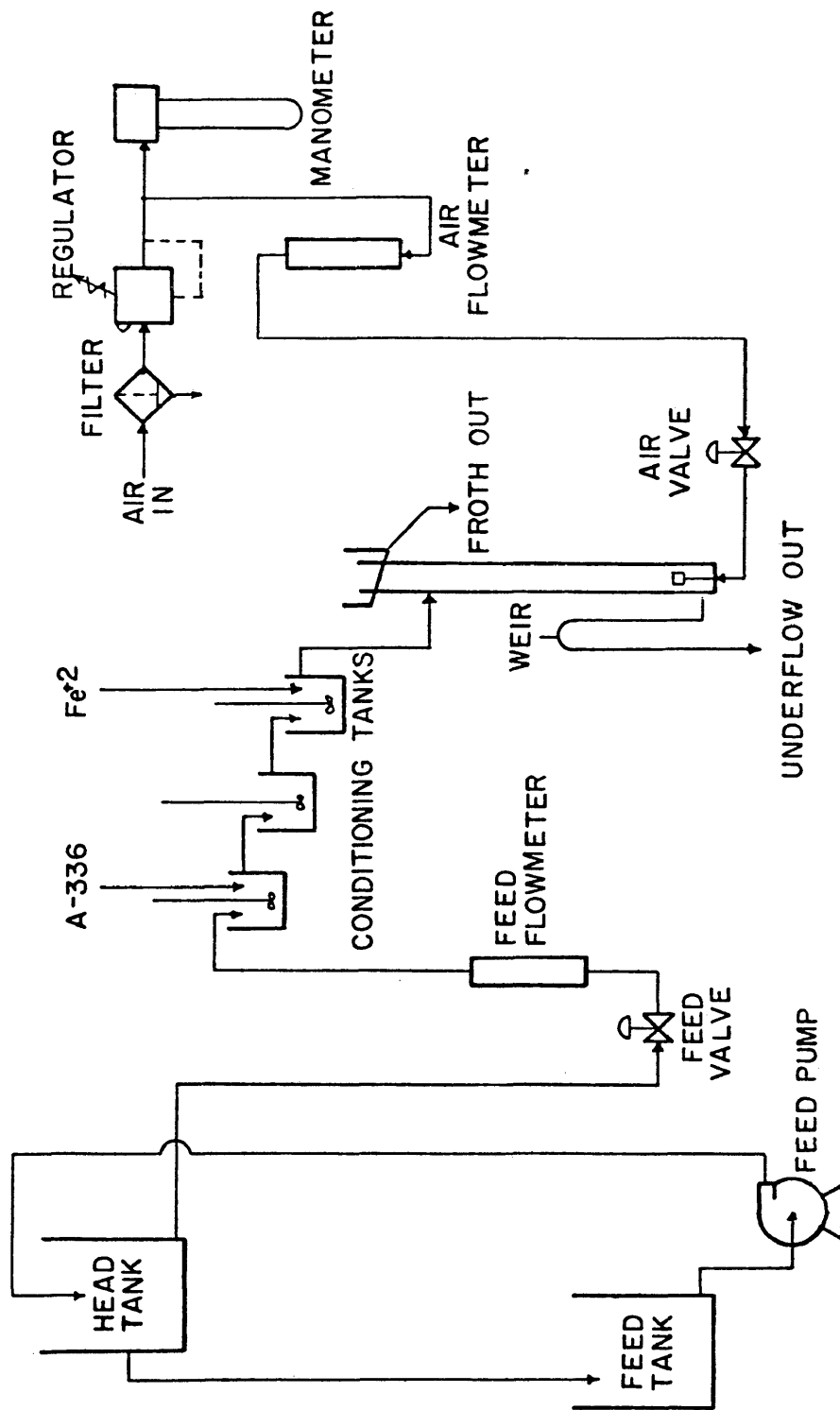


Figure 4. Schematic of Column Flotation System.

a 2^3 factorial design (24). Three operating variables were varied at two levels of each. They were column height, feed flowrate, and specific air flowrate. This required eight tests. Three more tests were run at a set of conditions at approximately the mid-point between those of the factorial design tests; these tests were replicates of each other to give an indication of experimental error. The eleven tests described above were run with a cyanide concentration of 50 mg/l in the feed. The actual levels of test feed flowrates and specific air rates used were dictated by operating experience with the column. A feed flowrate any higher than 150 ml/min would cause entrainment of the froth into the underflow. At the high specific air rates, large bubbles (of approximately half the column diameter) would occasionally be generated, and at the low air flowrates the flow meter was unstable. It was also found that adjustments of the underflow weir height were necessary for stable operation when other variables were changed.

An additional two sets of tests were run at different feed cyanide concentrations. The high cyanide concentration selected was 100 mg/l and the low cyanide concentration was 10 mg/l.

A summary of operating conditions is given in Table 1.

Table 1: Flotation Column Test Conditions

Test	Column Height inches	Feed Flowrate ml/min	Specific Air Katg sccm/cm ²	Feed Conc. mg/l CN ₄ Fe (CN) ₅	Underflow weir Height, in.	Volume of Liq. in Col. ml
1	-1,25.5 *	-1,65.5 *	-1,65*	50	12 3/4	182
2	+1,50.5	-1,69	-1,65	50	23 1/2	350
3	-1,25.5	+1,141	-1,65	50	13	187
4	+1,50.5	+1,131.5	-1,65	50	26 1/8	375
5	-1,25.5	-1,67	+1,103	50	11 1/8	154
6	+1,50.5	-1,69	+1,103	50	24	360
7	-1,25.5	+1,144	+1,103	50	13	198
8	+1,50.5	+1,139	+1,103	50	26 1/8	340
9	0,35.5	0, 94	0, 79	50	16 3/8	250
10	0,35.5	0, 92.5	0, 79	50	16 3/8	245
11	0,35.5	0, 89.5	0, 79	50	16 3/8	230
12	0,35.5	0, 73	0, 79	10	16 3/8	250
13	0,35.5	0, 84.5	0, 79	10	16 3/8	250
14	0,35.5	0, 90	0, 79	100	16 3/8	250
15	0,35.5	0, 89	0, 79	100	16 3/8	260

*The number before the comma in each of these columns, is the coded factorial design setpoint, the number following is the actual value in the units specified

The air flowmeter was operated at a constant pressure of 6 inches of mercury and was calibrated against a Hastings mass flowmeter to read in standard cubic centimeters per minute at that operating pressure. The water flowmeter was uncalibrated at the flowrates used and was used as an indicator to regulate flow only, flowrates being determined from the timed samples. The column itself was made from lengths of 1 inch diameter glass tubing with "O-ring" joints in a modular design. The inlet, overflow, and bottom, which contained the underflow port and the fitting for the air frit, were separate pieces that could be joined directly together to make a 15.5 inch column; spacing tubes could be inserted to build a column up to 85.5 inches tall.

RESULTS AND DISCUSSION

Dual Liquid Batch Extraction Tests

The most important results from these tests are shown in Figure 5. One set of results, however, should be mentioned first. In a test of reaction rate, tests were run in which the only difference between them was the time after mixing at which the aqueous sample was taken. The results indicated 97.8% reduction in ferrocyanide concentration after 10 minutes and also after 60 minutes, meaning that equilibrium was achieved rapidly, and thus the following results should represent equilibrium conditions.

A term that is convenient to use when describing the performance of these tests is the fractional decrease in concentration (CR) from the feed. This term can be defined as:

$$CR=1-u/f,$$

where u is the final aqueous cyanide concentration and f is the cyanide concentration in the feed. CR approaches a value of 1 as more of the feed cyanide is removed. Figure 5 is a plot of CR versus the molar ratio of Aliquat-336 to ferrocyanide. In the plot, the two straight lines, one from

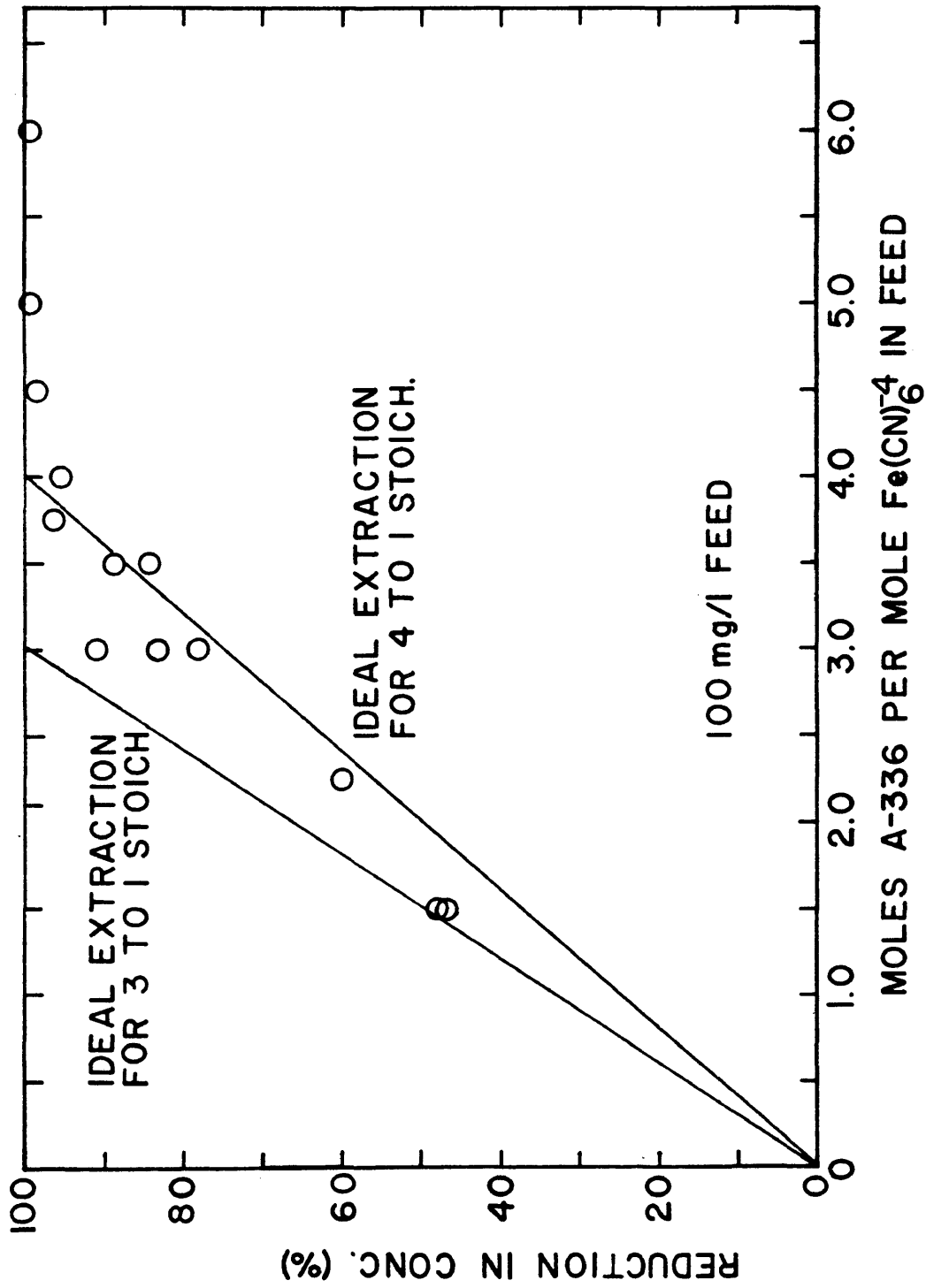


Figure 5. Removal of Ferrocyanide by A-336 in Dual Liquid Batch Extraction Tests.

the origin to a CR value of 1 at a molar ratio of 3 to 1, and the other from the origin to a CR value of 1 at a molar ratio of 4 to 1, represent ideal behavior for reaction stoichiometries of 3 moles A-336 to 1 mole of ferrocyanide and 4 moles A-336 to 1 mole of ferrocyanide respectively. Tests at dosages of less than the stoichiometric amount of A-336 would be expected to produce data points that would fall somewhat below and to the right of the ideal line for the actual stoichiometry. The displacement from the line would represent the difference between equilibrium and total extraction. All of the results from tests with less than 3 moles of A-336 permole of ferrocyanide fall between the lines in Figure 5, that is, above the ideal extraction line for a 4 to 1 stoichiometry. This indicates better than ideal extraction unless the system has a 3 to 1 stoichiometry. Remembering that ferrocyanide has a net valence of -4, and noting that A-336 should ionize by giving up the chloride it would have a valence of +1, the reaction product would have a net valence of -1, and would not precipitate unless some additional cation were present. The reductions in concentration at or above a molar ratio of 4.5 to 1 were greater than 0.97 which led to the conclusion that it was not necessary to explore higher molar ratios in subsequent testing.

Single Liquid Batch Extraction Tests

Using the above information, tests were run to find a reagent which would increase the precipitation rate of the A-336/ferrocyanide compound. Early tests of this series were run with a dosage of 1.5 times the stoichiometric amount of A-336 (molar ratio 4.5 to 1) in a 100 mg/l ferrocyanide solution, with no additional ions added. Some yellow waxy material coated the vessels and stirrers in the first five minutes after the A-336 addition in each test, and the resulting solution would be cloudy and translucent for approximately three days. After that time, in a period of a few hours the rest of the material conglomerated and floated to the solution surface. Enough of the waxy material was collected to run an X-Ray diffractometer scan, and it was found to be amorphous. A series of tests was run to see what effect pH, Cl⁻, Ca⁺⁺, and finally Fe⁺⁺ would have on the precipitation or coagulation rates of the waxy material. Ferrocyanide concentration was 100 mg/l as CN, and after adding a 1.5 stoichiometric A-336 dose, five minutes conditioning time was allowed before anything else was added. The results were strictly visual, the reagent being rejected if no visible precipitate was formed within 10 minutes after the reagent's addition. The first dosage of ferrous sulfate tested gave a concentration in excess of

5 g/l or 1.8×10^{-2} molar. A green precipitate was formed in less than one minute. Dosages resulting in concentrations of 1.8×10^{-3} , 3.6×10^{-3} , 4.5×10^{-3} , 9.0×10^{-3} , and 1.8×10^{-2} molar Fe^{++} were tested; the one yielding 4.5×10^{-3} molar Fe^{++} (1.25 g/l ferrous sulfate) was found to be the minimum dose required to rapidly produce a precipitate. Another test was run with a total dose to produce 6.3×10^{-3} molar iron being added stepwise from a 1.8×10^{-3} molar initial dose over a period of 14 minutes; no precipitate was formed.

With the minimum dosage of ferrous ion needed to cause precipitation determined, the next step was to determine the minimum dosage of A-336 needed for good extraction. Feed concentrations of 75 mg/l and 10 mg/l CN as ferrocyanide were used. The ferrous sulfate dosage was to produce an Fe^{++} concentration of 4.5×10^{-3} molar for all of the tests, and was added five minutes after the A-336. Based on the results of the dual liquid tests above, the A-336 dosage was varied from a molar ratio of 3 to 1 to 4.5 to 1, that is, stoichiometric multiples of 1 to 1.5. As shown in Figure 6, the reduction in concentration exceeded 90% at all conditions, so an A-336 stoichiometric multiple of 1 was used for all subsequent testing, this being the most economical dose.

The results of the final series of tests in this phase

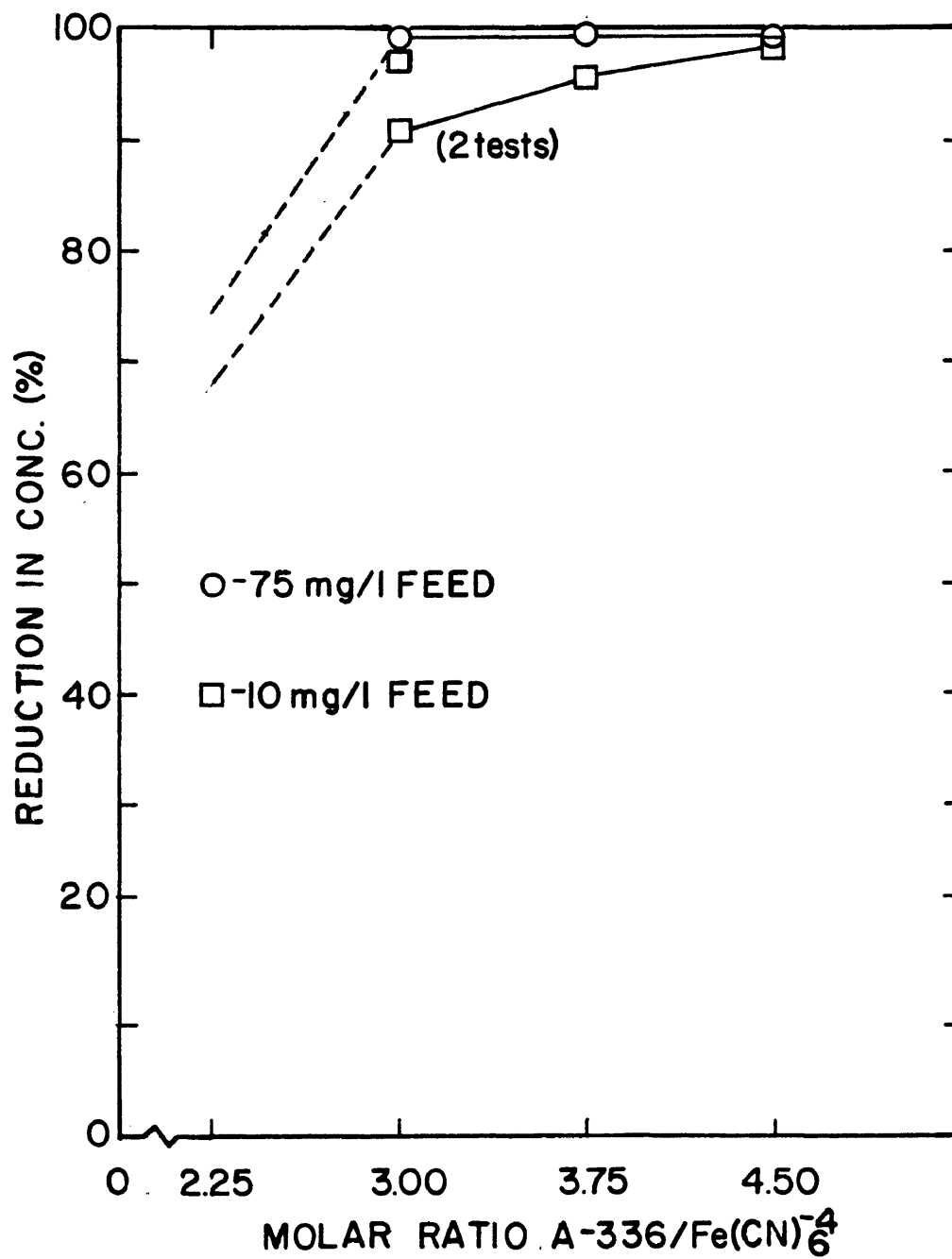


Figure 6. Effect of A-336 Dosage on Removal of Ferrocyanide in Single Liquid Batch Extraction Tests.

are presented in Figure 7. These were tests of the sensitivity of the system to feed concentration. The reductions in concentration were better than 97% for feed grades of 25 mg/l or higher, falling to 90% at 10 mg/l, 80% at 5 mg/l, and, finally, to 70% at 1 mg/l. No visible precipitates were formed in the tests with feed grades of less than 10 mg/l CN as ferrocyanide. Several explanations can be proposed for the lesser reductions from the low feed concentrations. The reaction kinetics or growth kinetics, or both, may be affected enough that the conditioning time allowed was insufficient to grow large enough precipitates for the filter to retain. It is also possible that precipitation may not occur at all in systems that are so dilute. These tests represent, at least for feed concentrations of 10 mg/l CN or greater, the ultimate removal possible by the flotation tests, because all of the organic precipitate is removed from the aqueous effluent with none (or very little) of the water going with it.

Flotation Tests

The following discussion should be prefaced by noting that the four hour distillation times used in the cyanide analyses may not have been long enough to extract all of the cyanide in the samples. There is some indication that the

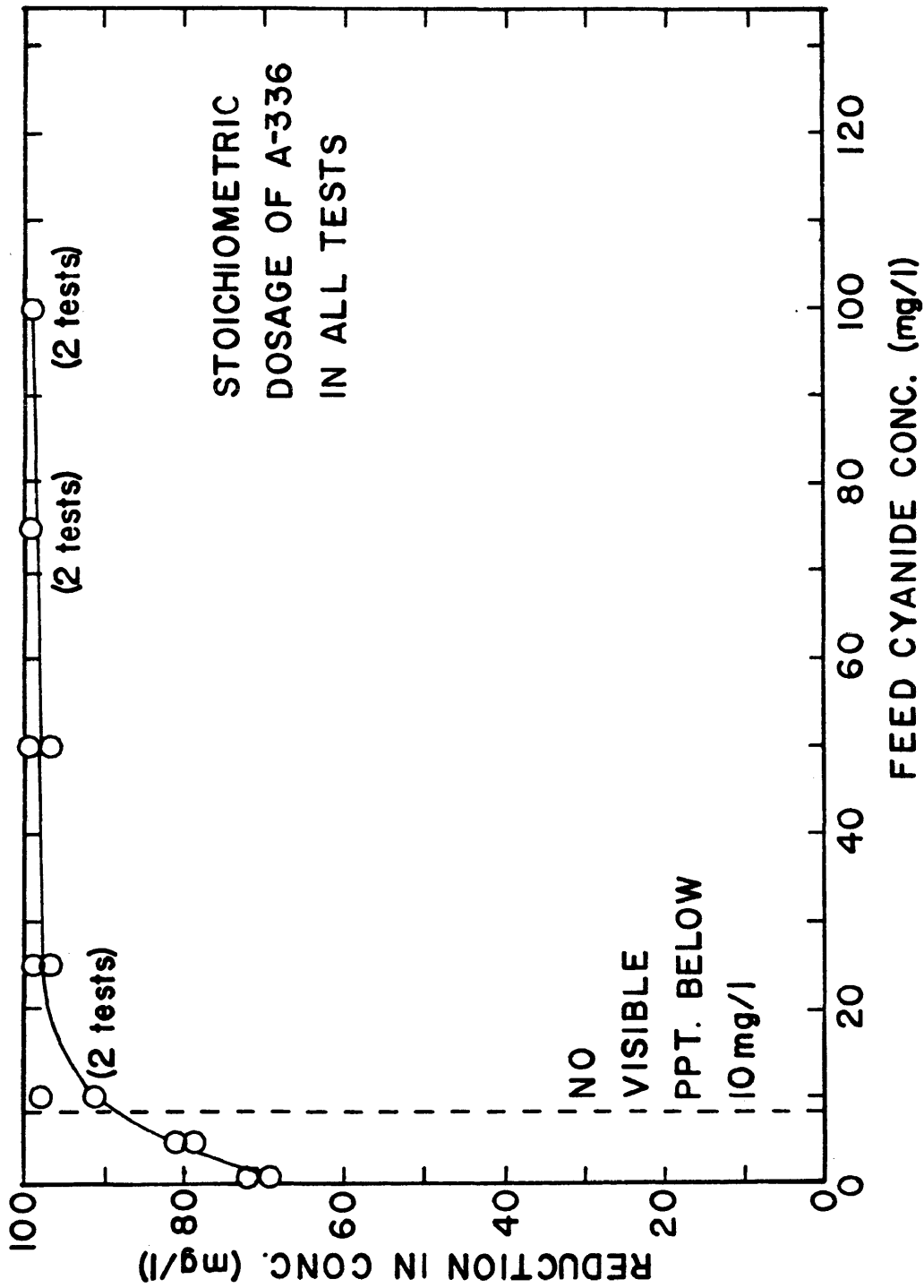


Figure 7. Effect of Feed Cyanide Concentration on Removal of Ferrocyanide in Single Liquid Batch Extraction Tests.

precipitates took a longer time to completely break down. The results reported however, are not far off the actual cyanide concentrations, and any errors should be systematic. Such errors would not invalidate the trends indicated.

In this discussion of the results of the flotation tests, the fractional reduction in concentration term defined above will be used in the same form:

$$CR=1-u/f$$

where u now is the cyanide concentration in the column underflow, and f is still the cyanide concentration in the feed. An additional quantity called "Removal" (R) is also useful. Removal is defined as:

$$R=(U/F)(1-u/f)$$

or:

$$R=(U/F)CR$$

where U is the volumetric flowrate of the underflow, and F is the volumetric flowrate of the feed.

Factorial experiments are so designed to yield an equation relating some response of the experiment to the input variables and their interactions. The results of the flotation experiments are summarized in Table 2. In a three-variable experimental design the general form of such an equation is:

Table 2: Flotation Column Test Results

Test	Column Residence Time (min)	Underflow Flowrate (ml/min)	Volume		Underflow		Fractional Reduction in Conc. %	Removal
			Feed in Underflow	Conc. mg/l	CN ⁻ in 10^{-4}	Fe(CN) ₆ ⁻⁴		
1	2.78	40.5	61.8	5.9	88.2	.545		
2	5.07	45	65.2	6.8	86.4	.563		
3	1.33	120	85.1	3.9	92.2	.785		
4	2.85	107.5	81.7	2.7	94.6	.773		
5	2.30	40	59.7	4.6	90.8	.542		
6	5.22	48.5	70.3	5.0	90.0	.633		
7	1.38	95	66.0	4.7	90.6	.598		
8	2.45	105	75.5	4.1	91.8	.693		
9	2.66	55	58.5	3.4	93.2	.545		
10	2.65	52	56.2	2.9	94.2	.529		
11	2.57	46	51.4	4.6	90.8	.467		
12	3.42	48.5	66.4	1.3	87.0	.578		
13	2.96	49	58.0	.66	93.4	.542		
14	2.78	40	44.4	10.4	89.6	.398		
15	2.92	36	36.7	12.6	87.4	.321		

$$y=A_0+A_1x_1+A_2x_2+A_3x_3+A_4x_1x_2+A_5x_1x_3+A_6x_2x_3+A_7x_1x_2x_3$$

where x_1 , x_2 , and x_3 are the normalized values of the process variables having values of either +1 or -1. In the flotation experiments x_1 represented the column height, x_2 represented the feed flow rate, and x_3 represented the specific air flowrate. Using removal R as the response, the final form of the equation, after deleting statistically insignificant terms (see Appendix B), is:

$$R=0.6415+0.0770x_2-0.0355x_2x_3$$

where $x_2=(F-103.5)/35.4$ and $x_3=(A-86)/17$, with F representing feed flowrate in ml/minute, and A representing specific air flowrate in sccm/cm. The x_2x_3 term has marginal significance. This equation would be expected to apply within the range of the variables tested. Specific air rate was expected to have a much more significant effect than was observed, but it may have been masked by the adjustment of the underflow weir that was necessary for each run.

Figure 8 is a plot of removal and reduction in concentration versus feed flowrate. In Figure 9, removal and reduction in concentration are plotted against specific air flow rate. And in Figure 10, the same two quantities are shown as functions of retention time in the column. One observation that can be made is that the reduction in concentration of cyanide from the feed to the underflow does not seem to be significantly affected by any of the process variables. In fact, the total variation of reduction in concentration, shown in Table 2, is from 87.0% to 94.6%, which is quite small when compared to the possible experimental error resulting from the problems with analysis mentioned earlier. The scatter of the removal data points makes any conclusions about them questionable, but removal does not seem to be much affected by any of the operating variables either. Even the coefficient of the feed flowrate term in the equation presented above is rather small, which is another reflection of this independence.

A strong correlation occurs between removal and feed cyanide concentration, although not between reduction in concentration and feed cyanide concentration as shown by Figure 11. This may be explained by a reference to Table 1, where it is noted that the only variable changed in tests 9 through 15 was the feed cyanide concentration. The two

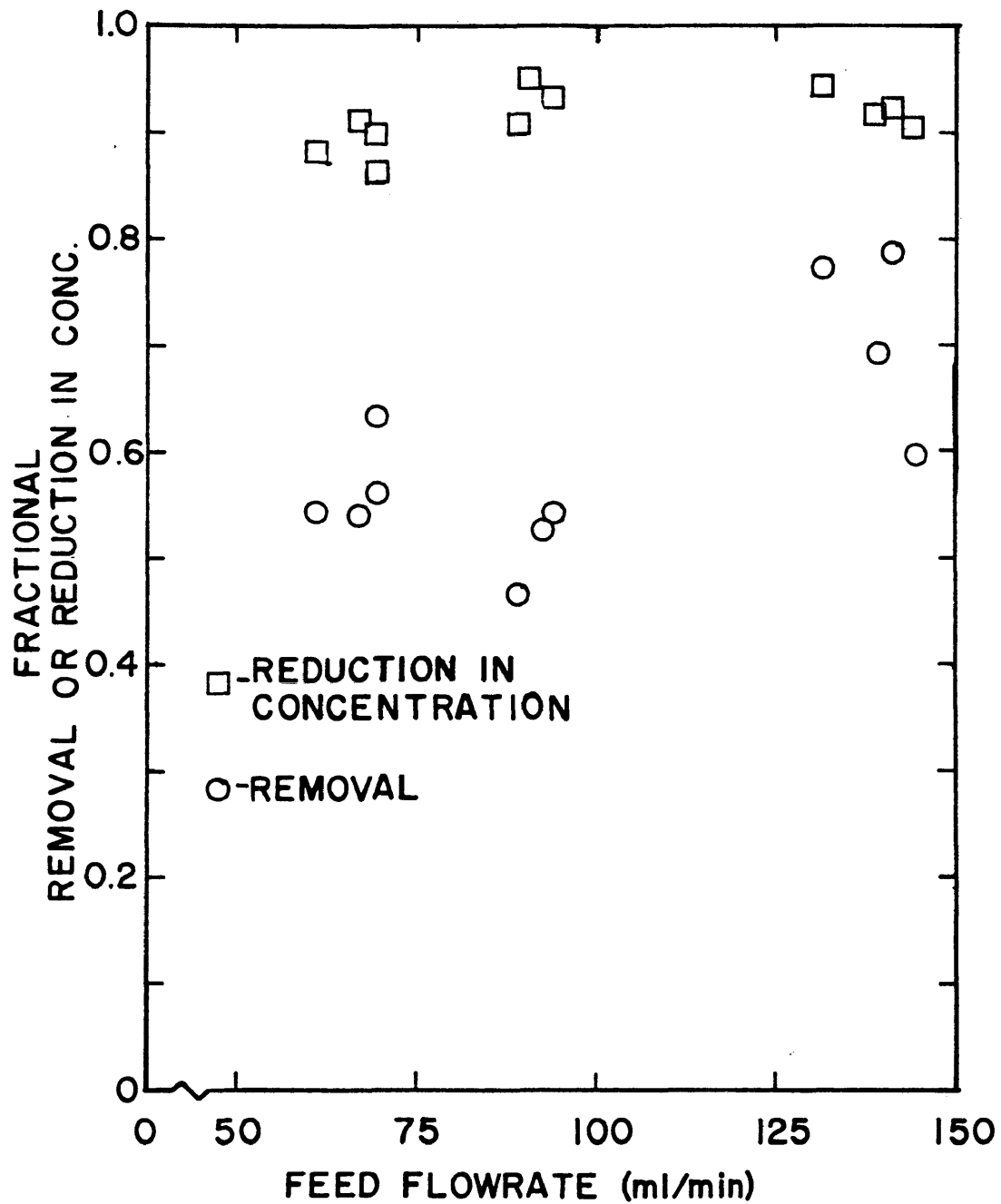


Figure 8. Performance of Flotation Column as a Function of Feed Flowrate.

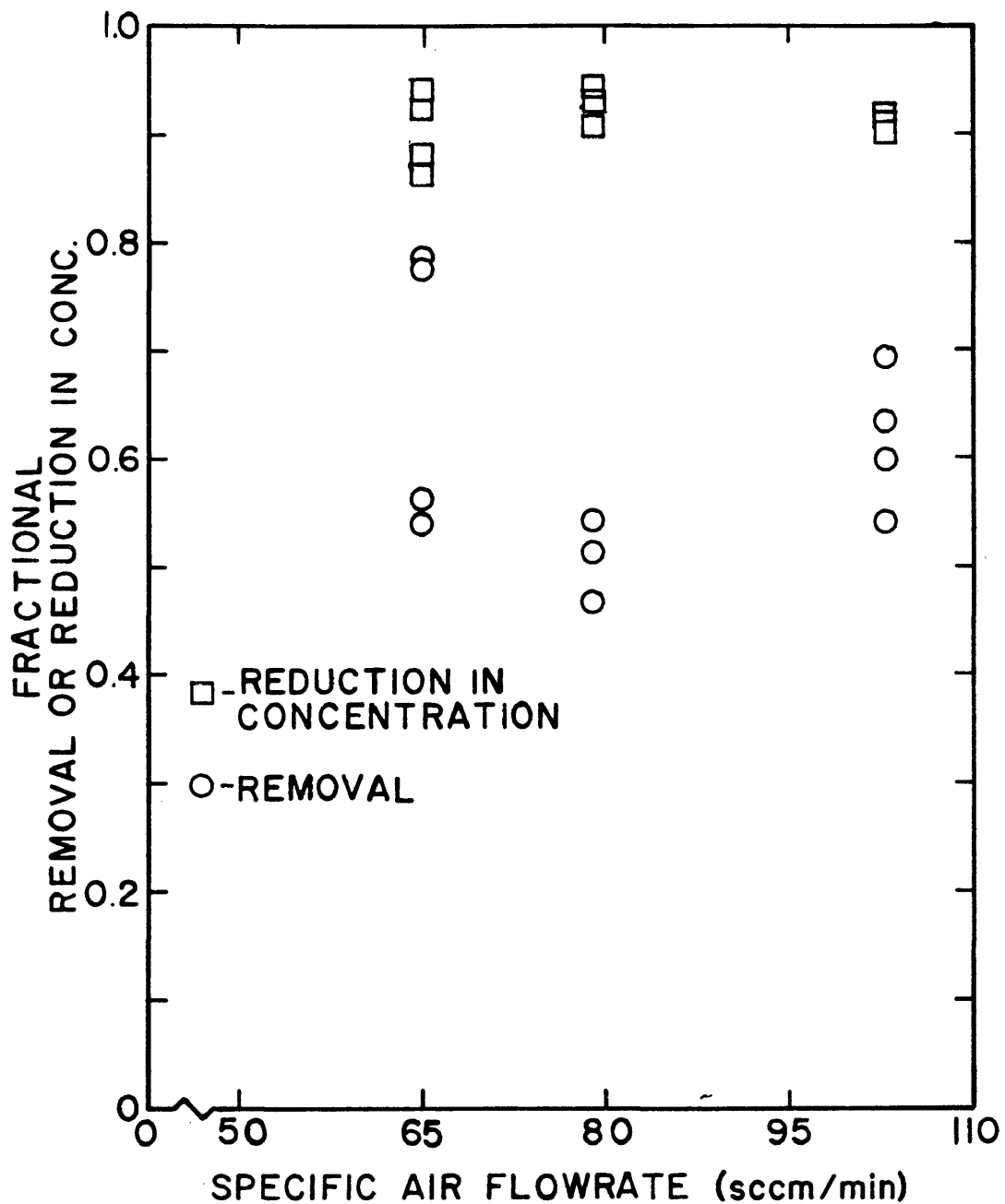


Figure 9. Performance of Flotation Column as a Function of Specific Air Flowrate.

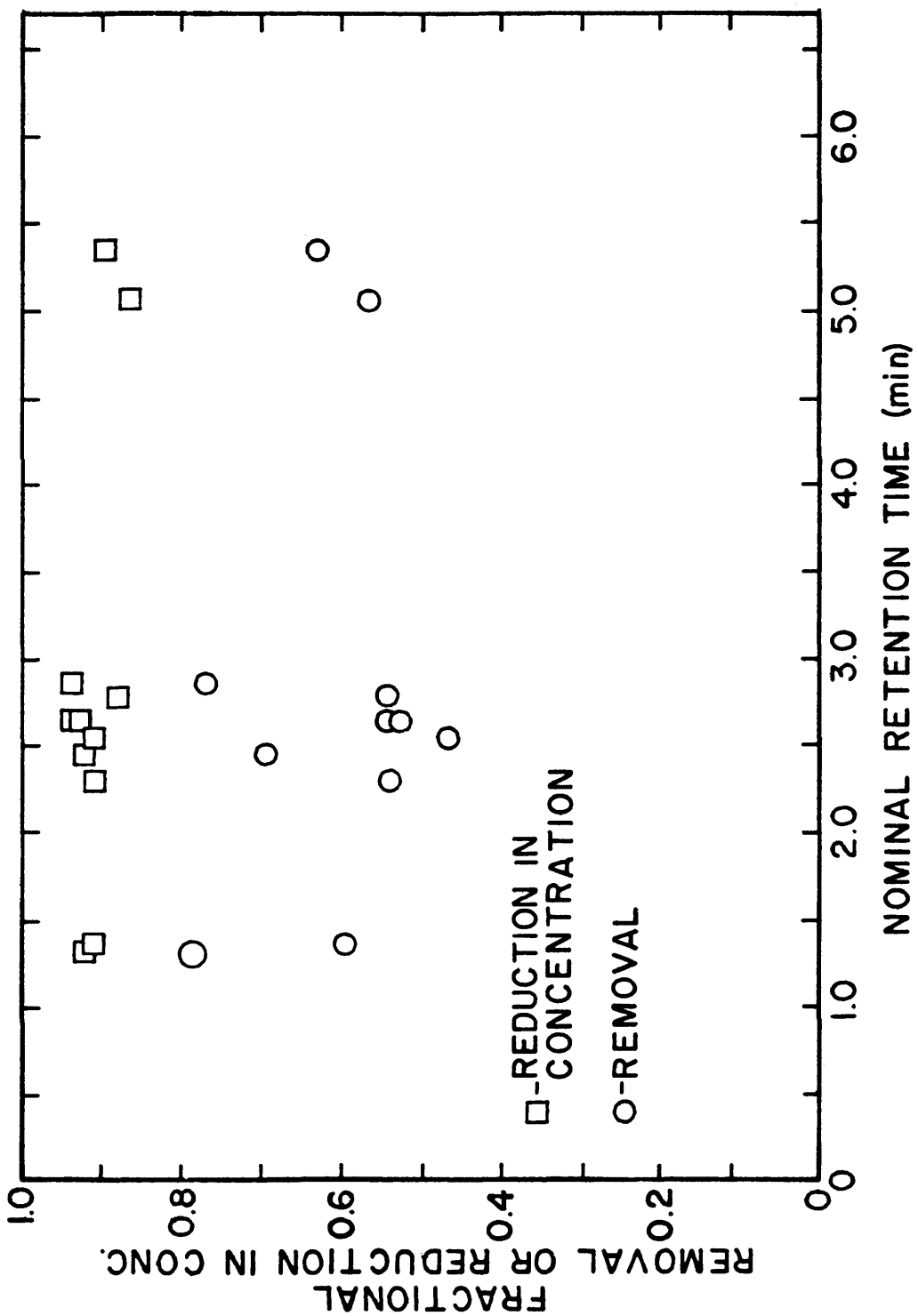


Figure 10. Performance of Flotation Column as a Function of Retention Time.

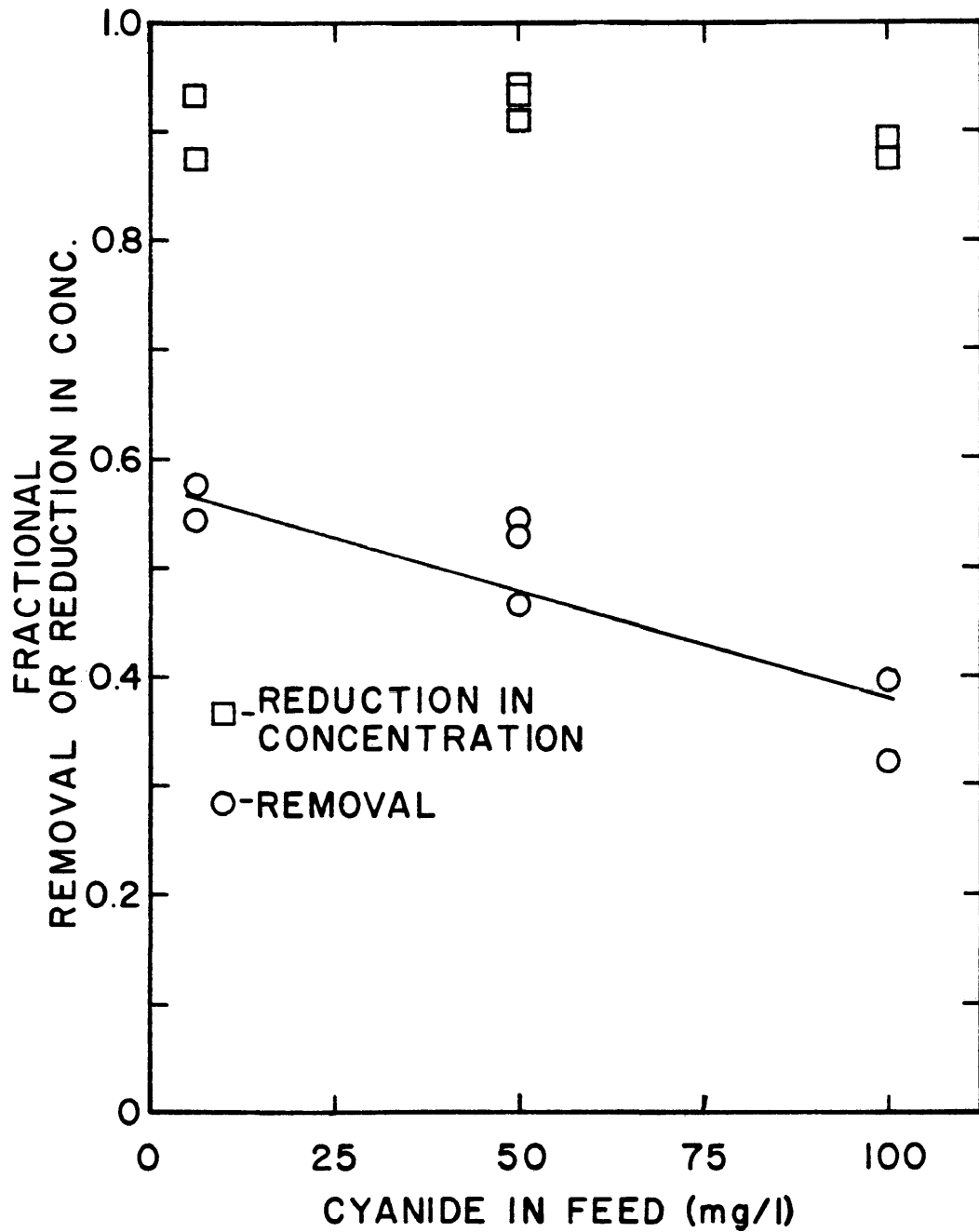


Figure 11. Performance of Flotation Column as a Function of Cyanide Concentration in the Feed.

tests at 100 mg/l produced great volumes of froth, carrying much of the water to the overflow. If the underflow weir had been adjusted to improve the water split, the removal might have been better.

As indicated in Figure 12, the flotation system never did meet the effluent guideline of 0.25 mg/l cyanide in the underflow. From Table 2, the lowest cyanide concentration in the underflow was 0.66 mg/l from a 10 mg/l feed. However, this figure also shows that lower concentrations could possibly be achieved with the use of more than one stage of flotation. For example, if a 100 mg/l feed is fed to one column, with performance as shown by Figure 13, and the underflow is fed to a second column, again with performance as shown in Figure 13, the first stage underflow would have a cyanide concentration of about 10 to 12 mg/l and the final underflow would have a concentration of around 1 mg/l. While this still is not low enough to meet effluent guidelines, it is a reduction of two orders of magnitude. It was noted earlier that this process may have to be followed by some polishing process in order to meet final effluent standards.

The above tests show that the greatest bulk of the pollutant may be removed by this process which would significantly reduce the load on the polishing system. The polishing method might be filtration through an activated charcoal bed. If the ferrocyanide that is not removed by the column has reacted with the A-336, it may be removed by charcoal, which has no effect on free cyanide or the simple

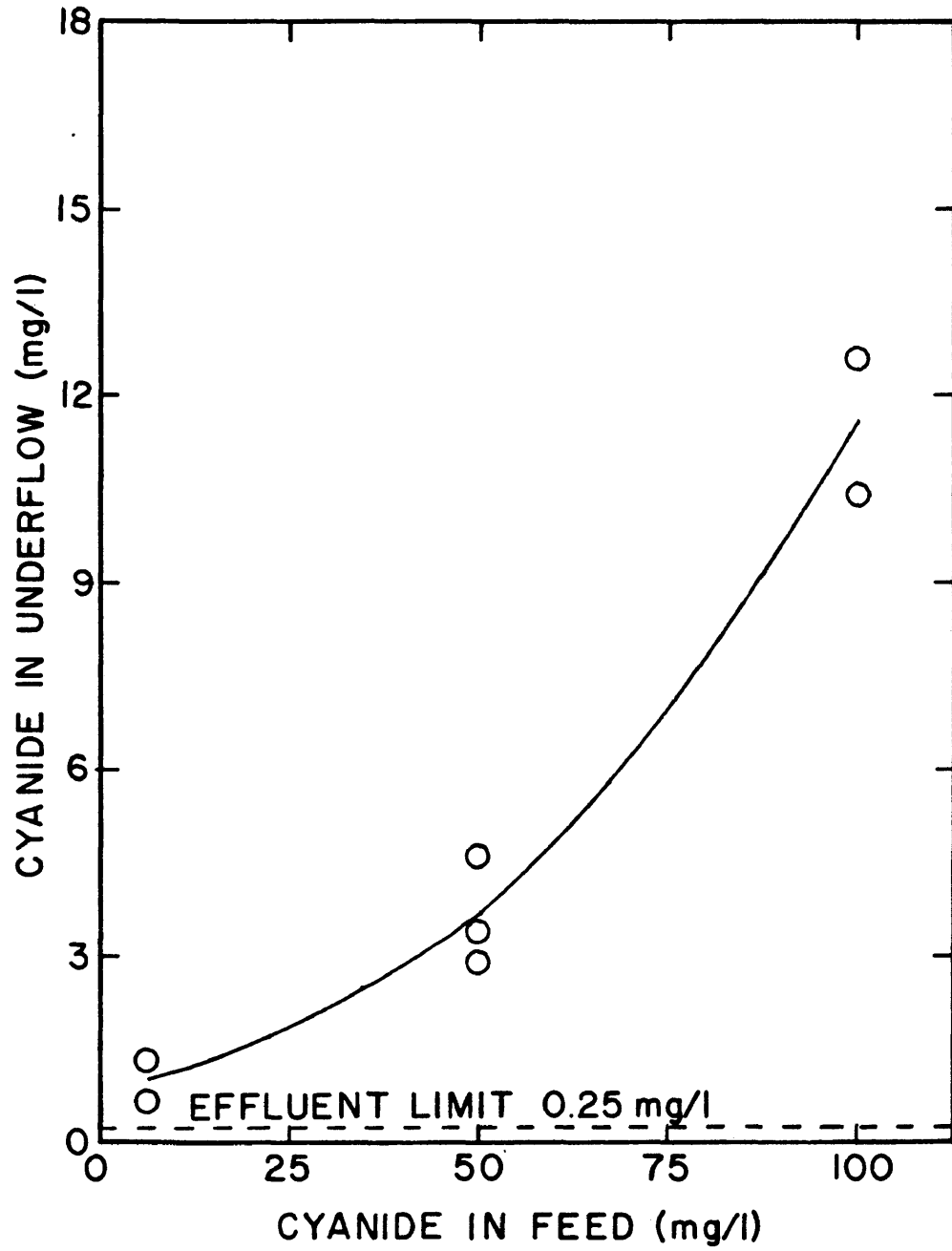


Figure 12. Effluent Cyanide Concentration Performance of Flotation Column.

complexes like ferrocyanide.

A few additional observations made during the test program should be reported here. While running the flotation system, it was necessary to clean the conditioning tanks occasionally to remove the same yellow, waxy build-up noted in the single liquid tests. If too much build-up was allowed, the solutions flowed out clear and there was little, if anything, to remove in the column. This might suggest an alternative method of treatment, wherein the wax is removed continuously by some method, perhaps by Teflon belts moving through the solution. The precipitate particles in the underflow samples settled rapidly and appeared to be fairly compact. They may be suitable for removal by some settling or centrifugation device.

While these results tell very little about the operating characteristics and capabilities of the laboratory flotation system that generated them, they do indicate that the system can remove ferrocyanide from relatively pure solutions. Operating problems associated with the very small column used here suggest that more extensive work with the same column would have little value. Future testing should take place in larger columns, closer to a size that could be used in actual industrial installations, and should

use either real or more closely simulated effluents. This work, however, has provided a starting point for that future work.

CONCLUSIONS

1. The stoichiometry of the A-336/ferrocyanide reaction is 3 parts A-336 to 1 part ferrocyanide. This leaves a charged species that will not precipitate by itself.
2. Ferrous ion addition will make the A-336/ferrocyanide compound precipitate rapidly; the addition must bring the ferrous ion concentration to at least 4.5×10^{-3} molar Fe^{++} in one step. No excess A-336 is needed to drive the reactions to completion.
3. Reductions in concentration of more than 97% were achieved in single liquid batch extraction tests, when the cyanide concentration of the feed was 25 mg/l (as ferrocyanide) or greater. The reduction was more than 90% from a 10 mg/l feed, and fell to 80% for 5 mg/l and 70% for 1 mg/l.
4. Flotation of the precipitate formed by the A-336/ferrous ion treatment is possible, resulting in reductions in concentration exceeding 87% for all tests, and removals varying from 0.321 to 0.773. The cyanide concentrations in the underflow varied from 0.66 mg/l to 12.6 mg/l, never meeting the effluent limitation of 0.25 mg/l. Some further

treatment of such streams would be required.

5. The laboratory scale test system was too small to give useable scale-up data for further testing.

6. Observations made during the course of the test work suggest other treatment methods that might be explored as alternatives to column flotation for removing the precipitates. The density and compactness of the precipitates suggest that some settling device may be used for the separation. The extreme hydrophobicity of the yellow, waxy, material formed before iron addition might be exploited in some manner to remove ferrocyanide.

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APPENDIX A: CYANIDE ANALYSES

There is no method in the literature for the direct measurement of ferrocyanide concentration. Therefore, total cyanide was measured by distillation by the technique described here. The method involves the distillation of the sample to extract all of the cyanide regardless of the form, complexed or free. A solution containing that cyanide in its uncomplexed form is produced. The cyanide concentration of that solution was measured with a specific ion electrode.

Distillation Procedure

The distillation procedure used in this project follows that of Barton et. al. (A-1), which was a modified version of the ASTM standard method (A-2). A Wheaton commercial cyanide still was used for all of the distillations. A schematic representation is presented in Figure A-1. The reagents necessary for the distillation procedure are:

- 1) 50 gram/liter sodium hydroxide (NaOH)
- 2) Saturated mercuric chloride (HgCl_2) (approximately 60 g/l)
- 3) 2.5 molar magnesium chloride (510 g/l of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)
- 4) 1:1 diluted sulfuric acid (H_2SO_4)

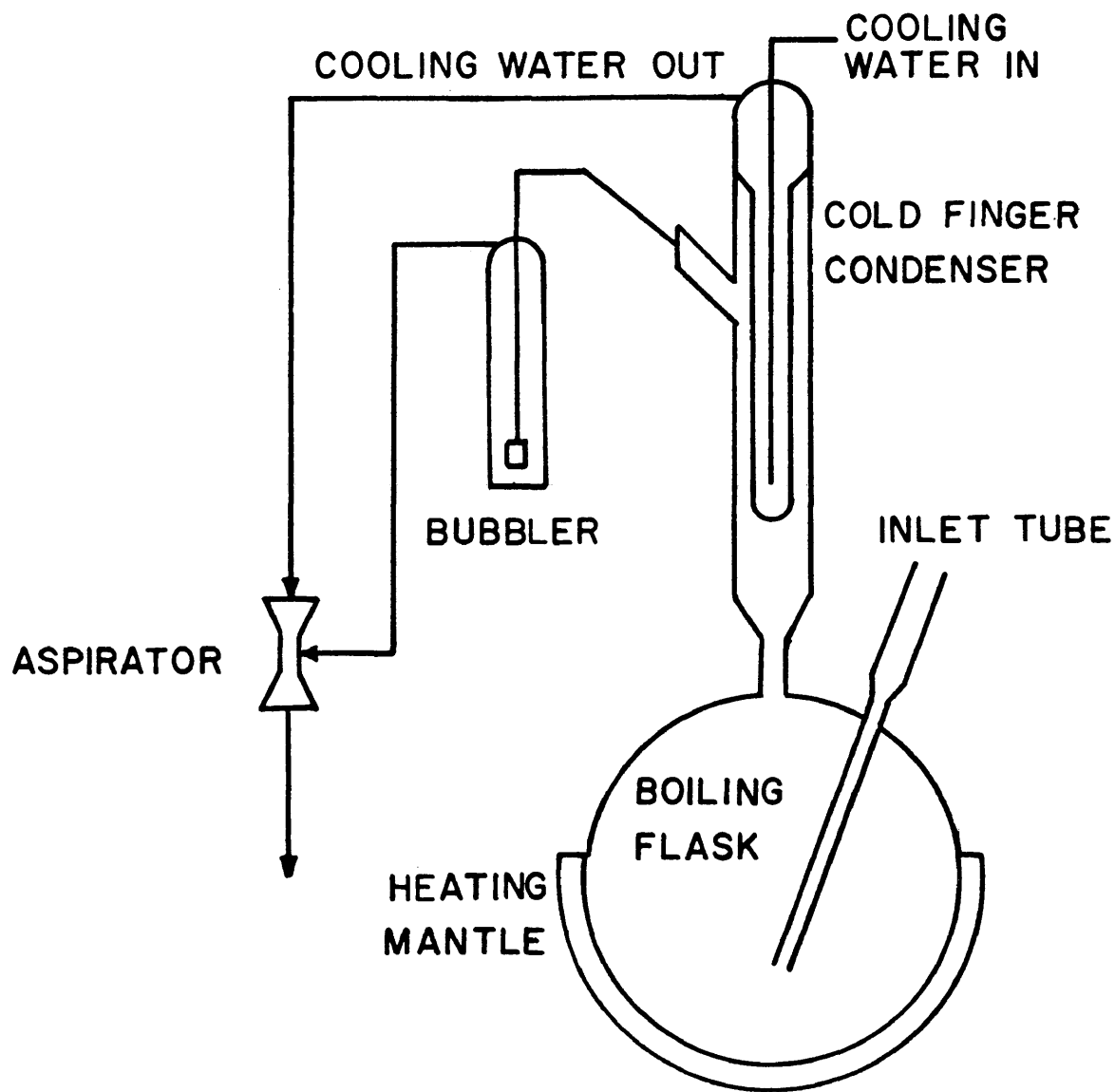


Figure A-1. Schematic of Cyanide Distillation Apparatus.

The bubbler was filled to an appropriate level with the NaOH solution in which the HCN would dissolve. The still was assembled and the sample was placed in it. Distilled water was added to bring the total volume in the still to at least 300 milliliters. The system was then sealed and the vacuum source was attached. In the system used for this work, the vacuum source was an aspirator using the cooling water to provide the vacuum. The flowrate of the cooling water was adjusted to maintain an air flowrate down the inlet tube of at least one bubble per second. The heating mantle was then turned on and adjusted to give a good boiling rate that was not violent. Reagents were added after the heat was turned on. They were added in the following amounts and order:

- 1) 10.0 ml Saturated HgCl_2 solution
- 2) 40.0 ml 2.5 molar MgCl_2 solution
- 3) 50.0 ml 1:1 diluted H_2SO_4 .

The normal distillation time was 2 hours after allowing 30 minutes for the still to heat up. The flotation underflow samples were distilled for four hours after the warm up period. The two hour distillation time was found to be adequate for all other samples. A cool-down period of 30 minutes was allowed for each sample after the heat was shut off. The distillation times quoted were considered to end when the heating mantle was turned off. The cooling water

and vacuum were left on during the cool-down time. Finally, after the cool down the bubbler solution was transferred to a volumetric flask and diluted to a convenient volume to measure the cyanide concentration.

Specific Ion Electrode Concentration Measurement

An Orion cyanide specific ion electrode was used with a single junction reference electrode (and a digital pH-millivolt meter from the same manufacturer) to measure the cyanide concentration of the bubbler solutions produced by the distillations. Two reagents were used in this portion of the analyses:

- 1) 10 molar sodium hydroxide (NaOH)
- 2) 2.50 g/l potassium cyanide (KCN) equal to 1000 mg/l CN^- .

The sodium hydroxide was added to every solution at a rate of 1 milliliter to every 100 milliliters of final solution volume. It served two purposes: one, to raise the pH to above 12 to keep the CN^- ionized, and two, to raise the background ionic strength of the solution to facilitate operation of the electrode. The cyanide solution was used to make standards for calibration of the millivolt readings from the electrode measurement. All cyanide solutions were mixed fresh at least once a week. The electrode would have

been damaged by much use in solutions with cyanide concentrations higher than 100 mg/l, so all solutions were diluted to less than that level. Problems were encountered with the stability of readings in solutions higher than 10 mg/l, so most samples were diluted to below that level also. Calibration solutions were usually made down to 0.10 mg/l, so samples with variations of as much as 2 orders of magnitude in cyanide concentration could be measured in one series of tests.

The general procedure followed for measuring the cyanide concentration of a diluted distillation product was to make up standards that bracketed the expected concentrations of the group of samples, obtain a series of calibration readings, measure the electrode potential in the samples, then repeat the calibration standards. All solutions were stirred with a magnetic stirrer while the potential measurements were made. If there were no large changes in the electrode potentials in the standards between readings, a calibration curve was constructed and the sample concentrations were obtained from that. If there were significant changes in the potential measured in any of the standards, the series was repeated.

Care was taken to rinse and dry both electrodes between each measurement. If the electrodes had not been used for a

long time, the reference electrode was disassembled and cleaned. When the stability of the readings deteriorated or the difference in potentials between the standards became larger than normal, the membrane of the cyanide electrode was polished with the strips provided by the manufacturer. These procedures made the use of the specific ion electrode technique usually easy and rapid. Failure to follow these procedures caused many hours of unnecessary trouble.

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APPENDIX B: ANALYSIS OF FLOTATION RESULTS

This analysis follows Bull and Mular, Mineral Processes: Their Analysis, Optimization and Control, Chapter 4, Colorado School of Mines, 1969.

The equation to be determined has the general form:

$$R = A_0 + A_1x_1 + A_2x_2 + A_3x_3 + A_4x_1x_2 + A_5x_1x_3 + A_6x_2x_3 + A_7x_1x_2x_3$$

Each of the coefficients can be calculated by the following:

$$A_0 = (R_1 + R_2 + R_3 + R_4 + R_5 + R_6 + R_7 + R_8) / 8$$

$$A_1 = (-R_1 + R_2 - R_3 + R_4 - R_5 + R_6 - R_7 + R_8) / 8$$

$$A_2 = (-R_1 - R_2 + R_3 + R_4 - R_5 - R_6 + R_7 + R_8) / 8$$

$$A_3 = (-R_1 - R_2 - R_3 - R_4 + R_5 + R_6 + R_7 + R_8) / 8$$

$$A_4 = (R_1 - R_2 - R_3 + R_4 + R_5 - R_6 - R_7 + R_8) / 8$$

$$A_5 = (R_1 - R_2 + R_3 - R_4 - R_5 + R_6 - R_7 + R_8) / 8$$

$$A_6 = (R_1 + R_2 - R_3 - R_4 - R_5 - R_6 + R_7 + R_8) / 8$$

$$A_7 = (-R_1 + R_2 + R_3 - R_4 + R_5 - R_6 - R_7 + R_8) / 8$$

where R_n is the result of test n. The quantity used to determine the significance of the coefficient is the sum of the squares which can be calculated as:

$$SS_n = (A_n)^2 \times 8$$

for each coefficient. These values are compared with an estimate of error variance by an "F" test. The estimate of error variance used in the analysis of the data from the

tests run here was obtained from the results of tests 9 through 11 using the equation:

$$S_e^2 = \left(\sum_{i=1}^k (y_i - \bar{y})^2 \right) / k$$

where S_e^2 is the estimate of error variance, y_i is the measured response from the i th repeat, \bar{y} is the mean response from the repeated runs, and k is the number of repeated runs.

The "F" test is simply a comparison of the value of the sum of squares for each coefficient with the product of S and the appropriate value of the F function at the appropriate degrees of freedom and desired confidence limits.

The value of S_e^2 calculated from the R values of tests 9-11 was 1.70×10^{-3} and from a standard table the appropriate values of F are as follows:

Confidence		
Limit	F	FxS
90%	8.526	1.45×10
95%	18.513	3.15×10
99%	98.503	1.67×10

The coefficients and the SS_n values calculated from the R

values of tests 1-8 are as follows:

Coefficient	Value	SS _n
A ₀	0.6415	--
A ₁	0.0240	4.61x10 ⁻³
A ₂	0.0770	4.74x10 ⁻²
A ₃	-0.0250	5.00x10 ⁻³
A ₄	-0.0033	8.45x10 ⁻⁵
A ₅	0.0225	4.05x10 ⁻³
A ₆	-0.0355	1.01x10 ⁻²
A ₇	0.0043	1.45x10 ⁻⁶

From a comparison of the above two sets of results the following equation was developed for a 90% confidence limit. Note that A₀ is always significant, A₆ is marginally significant at 90% confidence, and that nothing but A₀ is significant at higher confidence levels. Therefore, the equation that is the result of the experiments reported here is:

$$\text{Removal} = 0.6415 + 0.0770x_2 - 0.0355x_2x_3$$

where $x_2 = (F - 103.5) / 35.4$ and $x_3 = (A - 86) / 17$, if F is feed flowrate in milliliters/minute and A is specific air flowrate in sccm/cm².

APPENDIX C: CHARACTERISTICS OF WASTE WATERS FROM IRON AND
FERROMANGANESE BLAST FURNACE GAS SCRUBBER SYSTEMS

(After: Development Document EPA-440/1-74-024-a)

Characteristic	Units	Plants		
		L	N	Q
Flow	liters/1000kg	22500	14000	32200
Ammonia.....	mg/l	1.41	9.75	114
Cyanide.....	mg/l	1.44	---	23.6
Phenol.....	mg/l	0.578	0.530	0.130
Suspended Solids.....	mg/l	1720	307	5000
Fluoride.....	mg/l	0.454	2.16	---
Sulfide.....	mg/l	4.34	0.448	---
Manganese.....	mg/l	---	---	833

Plant L had the highest cyanide concentration of the iron blast furnaces listed, and plant N had the lowest. Plant Q was a ferromanganese blast furnace.

APPENDIX D: BATEA STANDARDS FOR IRON BLAST FURNACE WASTE
WATERS

(After: Code of Federal Regulations; Title 40, Chapter 1,
Part 420, Subpart D)

Effluent limitations

Effluent Characteristic	Maximum for any 1 day	Average of daily value for 30 consecutive days shall not exceed
	kg/1000kg of product	
Suspended Solids.....	0.0390	0.0130
Cyanide A*.....	0.0004	0.00013
Phenol.....	0.0008	0.00026
Ammonia.....	0.0156	0.0052
Sulfide.....	0.0005	0.00016
Fluoride.....	0.0312	0.0104
pH.....	Within the range 6.0 to 9.0	

* "The term 'Cyanide A' shall mean those cyanides amenable to chlorination as described in 1972 Annual Book of ASTM Standards, 1972, standard D2036-72, Method B, page 553."

APPENDIX E: CHARACTERISTICS OF WASTE WATERS FROM BY-PRODUCT
COKE PLANTS

(After: Development Document EPA 440/1-74-024-a)

Characteristics	Units	Plants		
		A	B	C
Flow.....	liters/1000kg	580	530	171
Ammonia.....	mg/l	1900	1380	7330
BOD*.....	mg/l	1550	1280	1120
Cyanide.....	mg/l	102	110	91
Oil and Grease.....	mg/l	--	240	101
Phenol.....	mg/l	450	350	910
Sulfide.....	mg/l	--	629	197
Suspended Solids.....	mg/l	--	36	421

* Biochemical Oxygen Demand

APPENDIX F: BATEA STANDARDS FOR COKE-PLANT WASTE WATERS
 (After: Code of Federal Regulations; Title 40, Chapter 1,
 Part 420, Subpart A)

Effluent Limitations

Effluent Characteristic	Maximum for any 1 day	Average of daily value for 30 consecutive days shall not exceed
	kg/1000kg of product	
Cyanide A*.....	0.0003	0.0001
Phenol.....	0.0006	0.0002
Ammonia.....	0.0126	0.0042
Sulfide.....	0.0003	0.0001
Oil and Grease.....	0.0126	0.0042
Suspended Solids.....	0.0312	0.0104
pH.....	Within the range 6.0 to 9.0	

* "The term 'cyanide A' shall mean those cyanides amenable to chlorination as described in 1972 Annual Book of ASTM Standards, 1972, standard D2036-72, Method B, page 553."