REMOVAL OF SILVER AND MERCURY FROM COD WASTE SOLUTIONS

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(ABSTRACT)

Ion exchange and precipitation technologies were examined for the selective separation and recovery of silver and mercury from COD waste solutions. Batch equilibrium studies were conducted to determine ion exchange selectivity of several commercial and regenerated resins. Resin capacity and metal ion recovery efficiency were evaluated in continuous-flow column studies. Solubility studies were included to determine if metal ions could be selectively separated and included in a treatment regime for removal and recovery of silver and mercury from the waste solution. Reduction of waste volume was also an important consideration for precipitation of metal ions.

The results indicated that ionic strength considerations dictate overall treatment and recovery efficiency. Silver and mercury ions were removed by ion exchange while iron and chromium uptake did not occur. Highest removal efficiencies were observed for a mercury-specific resin and an anionic resin compared to cationic or mixed resins. Column capacity was severely impacted by the acidic, high strength, waste solution. Additional studies showed that the solution ionic strength and dissolved solids concentration were more important than solution pH in determining ion exchange preference and column capacity. Reuse of column regenerant solutions in the COD

test procedure indicated the strength of sulfuric acid was critical in obtaining complete oxidation of a synthetic waste solution.

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TABLE OF CONTENTS

Page

ABSTRACT

ACKNOWLEDGEMENTS iv

LIST OF TABLES vii

LIST OF FIGURES. ix

Chapter

I INTRODUCTION 1

II LITERATURE REVIEW. 3

Hazardous Waste Regulations. 3
Treatment of COD Waste Solutions 8
Alternate Testing Methods. 8
Use of Alternate Metal Salts 9
Modifications to the *Standard Methods* Procedure. . 10
COD Waste Solution Treatment Methods 14
Solution Chemistry 19
Ion Exchange Theory. 25
History and Development of Ion Exchange Resins . . 25
Ion Exchange Equilibrium and Selectivity 26
Ion Exchange Isotherms 33

III METHODS AND MATERIALS. 36

Analytical Methods 37
Batch Equilibrium Ion Exchange Studies 39
Amberlite IR-120 Plus. 41
Duolite C-20 41
Duolite ES-465 42
Laboratory Resins. 43
Continuous-Flow Column Studies 44
Solubility Studies 46
Solubility-Ion Exchange Studies. 47
Solids Analyses. 48
Total Solids 48
Total Dissolved Solids 48
Total Suspended Solids 48
COD Determination Using Recovered Silver Solutions . 49

TABLE OF CONTENTS (Continued)

Chapter Page

IV RESULTS. 52

Solubility Studies 52
Ion Exchange Studies 56
  Batch Equilibrium Studies. 56
  Continuous-Flow Column Studies 75
Solids Analyses. 93
COD Determination Using Recovered Silver Solutions . 94

V DISCUSSION 101

VI SUMMARY AND CONCLUSIONS. 107

VII LITERATURE CITED 110

APPENDIX A 113

APPENDIX B 115

VITA 122

LIST OF TABLES

Table		Page
1	Comparison of Silver and Mercury Uptake in Equilibrium Experiments Using Commercial Resins. . . .	67
2	Silver and Mercury Uptake in Equilibrium Experiments Using Laboratory Resins and COD Waste Solutions. . . .	73
3	Continuous-Flow Column Operation Data.	76
4	Removal and Recovery Efficiency of Metal Ions From Continuous-Flow Ion Exchange Columns	81
5	Reduction in COD Waste Metal Ion Concentrations Following pH Adjustment.	90
6	Characterization of Sludge Resulting From Precipitation Treatment of COD Waste Solutions at pH 7.6.	95
7	Comparison of COD of a Synthetic Waste Using Standard Catalyst Solutions and Recovered Silver Catalyst Solutions From Ion Exchange Columns.	97
8	Comparison of COD of a Synthetic Waste Using Varying Strengths of Sulfuric Acid Catalyst Solutions.	99
B-1	Metal Ion Removal From COD Waste Solutions by Batch Ion Exchange Treatment as a Function of Contact Time (Resin Corning-Y).	116
B-2	Effluent Metal Ion Concentrations From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions With Resin Corning-Y (Service Cycle #1)	117
B-3	Effluent Metal Ion Concentrations From 50% H_2SO_4 Regeneration of Resin Corning-Y Ion Exchange Column (Regeneration Cycle #1).	118
B-4	Effluent Metal Ion Concentrations From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions With Resin Corning-Y (Service Cycle #2)	119
B-5	Effluent Metal Ion Concentrations From 50% H_2SO_4 Regeneration of Resin Corning-Y Ion Exchange Column (Regeneration Cycle #2).	120

LIST OF TABLES (Continued)

Table Page

B-6 Effluent Metal Ion Concentrations and pH From Continuous-Flow Ion Exchange Treatment of Treated (pH 4.7) COD Waste Solutions (Resin Corning-BR). . . . 121

LIST OF FIGURES

Figure Page

1 Activity Coefficients of Aqueous Ions Based on the Extended DeBye-Hückel Equation and the Güntelberg Approximation. 20

2 Theoretical Concentration of Supernatant Silver Ion as a Function of pH in 0 and 0.5 M Ionic Strength Solutions. 23

3 Theoretical Concentration of Supernatant Mercury Ion as a Function of pH in 0 and 0.5 M Ionic Strength Solutions. 24

4 Soluble Metal Ion Concentrations in COD Waste Solutions as a Function of pH. 55

5 Metals Removal by Batch Ion Exchange From a Synthetic Waste Solution With Resin Duolite C-20 57

6 Metals Removal by Batch Ion Exchange for Resin Amberlite IR-120 Plus. 59

7 Comparisons of Metal Ion Residual Concentrations From Ion Exchange Batch Studies Using Resin Duolite C-20 for Treatment of COD Waste and Synthetic Waste Solutions. 60

8 Comparisons of Metal Ion Residual Concentrations From Ion Exchange Batch Studies Using Resin Duolite ES-465 for Treatment of COD Waste and Synthetic Waste Solutions. 62

9 Freundlich Isotherms for Silver and Mercury Ion Exchange From Synthetic Waste and COD Waste Solutions With Commercial Resins 65

10 Metals Removal by Batch Ion Exchange for Resin Corning-BL 69

11 Metals Removal by Batch Ion Exchange for Resin Corning-Y. 70

12 Metals Removal by Batch Ion Exchange for Resin Corning-BR 71

LIST OF FIGURES (Continued)

Figure Page

13 Freundlich Isotherms for Silver and Mercury Ion Exchange From COD Waste Solutions With Laboratory Resins 72

14 Breakthrough Curves for Silver and Mercury Ions From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions With Resin Corning-Y 80

15 Breakthrough Curves for Silver and Mercury Ions From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions With Resin Corning-BR. 83

16 Breakthrough Curves for Silver and Iron From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions Followed by an Iron Synthetic Waste Solution (Resin Corning-BR) 87

17 Breakthrough Curves for Silver From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions Followed by a Silver Synthetic Waste Solution (Resin Corning-BR). 88

18 Breakthrough Curves for Silver and Hydrogen Ions From Continuous-Flow Ion Exchange Treatment of Treated (pH 4.7) COD Waste Solutions (Resin Corning-BR). . . . 92

I. INTRODUCTION

The Chemical Oxygen Demand (COD) test is performed routinely in most environmental laboratories and is used to measure the oxygen equivalent of organic matter present which can be oxidized by hexavalent chromium (1). The dichromate reflux method is the method typically used and approved for determination of COD in water and wastewater. The test procedure generates a highly acidic waste solution which contains high concentrations of chromium, hydrogen, iron, mercury, silver, and sulfate ions.

There has been an increased interest in recovery of metals from COD waste solutions in recent years. Due to both the toxic effects of chromium, mercury, and silver, and the highly acidic nature of these wastes, they are regulated according to the Resource Conservation and Recovery Act of 1976 (RCRA) (2). Therefore, COD waste solutions must be disposed of as hazardous wastes. The expense of using large quantities of silver sulfate to perform COD analyses also provides an incentive for on-site recovery of silver from COD waste solutions.

Previous studies have dealt primarily with precipitation methods to recover silver and mercury and have established the practicality of these methods and noted the limitations which exist. Little published research has been conducted examining the possibility of using ion exchange methods for the removal and recovery of metal ions from COD waste solutions. It was proposed that metal removal could be performed successfully from COD solutions using ion exchange. Regeneration of ion exchange resins would permit recovery and reuse of metals in the COD experimental procedure. It was also proposed that further treatment of ion exchange column effluent could produce a nonhazardous solution suitable for discharge to a sanitary sewer and a metal-containing sludge which would require disposal as a hazardous waste.

One objective of this research was to determine an effective and economically feasible method for the recovery and reuse of silver and mercury from COD waste solutions. Another objective was to develop a treatment method which would reduce the large volume of hazardous waste which requires handling and disposal according to RCRA regulations.

Precipitation and ion exchange treatment processes have not routinely been attempted for recovery of metals from solutions of extreme ionic strength, such as COD waste solutions. Solution ionic strength affects the reactivity of species and may alter the typical removal characteristics that have been noted for heavy metals. Therefore, an additional objective of this study was to investigate the impact of solution ionic strength on removal and recovery characteristics.

II. LITERATURE REVIEW

The following literature review has been included to provide a summary of the regulations and basic terminology associated with a hazardous waste such as COD waste solution, previous research conducted concerning treatment of COD waste solutions, solution chemistry, and ion exchange theory. Because there is extensive literature available pertaining to all of the above topics, only the aspects dealing with COD waste solutions will be discussed.

Hazardous Waste Regulations

The Resource Conservation and Recovery Act of 1976 (RCRA) (2) was written to close the loop of pollution control. Significant legislation had been enacted dealing with the problems of both water and air pollution; no longer could the burden of pollution be buried underground. RCRA required that wastes, expecially hazardous wastes, be followed from "the cradle to the grave" with full documentation. In 1980, the Environmental Protection Agency (EPA) estimated that approximately 57 million metric tons of hazardous wastes were produced annually in the United States, of which only 10% were handled in an environmentally acceptable way (3). Although RCRA was enacted to improve practices in solid waste disposal and establish regulatory control of hazardous wastes from generation through disposal, there were several important areas of interpretation which where left to be debated within EPA. EPA has made important decisions with respect to the RCRA hazardous waste program and will continue for some time to issue additional regulations.

On May 19, 1980, under the authority of RCRA, EPA promulgated the first phase of regulations, implementing the hazardous waste management system established by RCRA (4). These regulations became effective on November 19, 1980 and covered the identification, generation, storage, treatment, transportation, and disposal of hazardous wastes.

According to RCRA regulations, a "solid waste" is any garbage, refuse, sludge, or any other waste material which is not excluded in Section 261.4 of the regulations. "Any other waste material", according to RCRA definitions, includes any solid, liquid, semi-solid, or contained gaseous material which is discarded or is being accumulated, stored or physically, chemically, or biologically treated prior to being discarded (4).

RCRA regulations have defined solid wastes as "hazardous" if: (1) they meet the Subpart C Characteristics of Ignitability, Corrosivity, Reactivity, or Extraction Procedure (EP) Toxicity, or (2) they are listed under Subpart D and are contained in Section 261.31. 261.32, or 261.33 of the regulations (4).

COD waste solutions are considered a hazardous waste according to Section 261.22 of the regulations, Characteristic of Corrosivity (4). COD waste solutions are corrosive due to the highly acidic nature of these wastes. This section requires that aqueous waste materials with a pH less than or equal to 2 or greater than or equal to 12.5 be classified as hazardous wastes. COD waste solutions also contain concentrations of chromium, mercury, and silver which exceed the allowable limits according to Extraction Procedure (EP) of EP Toxicity Criteria (4).

RCRA regulations define the term "generator" of a hazardous waste as any person, by site, whose act or process produces hazardous waste identified or listed in Part 261 of the regulations (4). Under the regulatory definition, any person can be deemed a hazardous waste "generator" regardless of whether that person owns or operates a particular plant site.

EPA originally excluded from regulation hazardous waste generators who produced a quantity of waste less than 1000 kg/month. However, the exclusion did qualify that these small quantity generators ensure their waste be disposed of in State-approved facilities designed to handle municipal or industrial wastes. It is the intent of EPA to phase down the coverage of small quantity generators to an exclusion level of 100 kg/month. According to recent RCRA revisions (5), laboratories which generate less than 1000 kg/month hazardous waste will no longer be exempt from the regulations unless a 90% reduction in the volume of hazardous wastes generated is accomplished. Small labs, such as those which generate small quantities of COD waste solution, will ultimately be required to follow the regulatory guidelines established for hazardous waste generators and transporters if the new exclusion level is exceeded.

This will inevitably incur additional expenses to these facilities, including transportation and disposal costs. For example, at an average rate of $165.00/50 gallons, Virginia Polytechnic Institute and State University spends approximately $20,000 annually on transportation and disposal of hazardous wastes. Implementation of the new exclusion level will drastically affect many small facilities and increase the need for recovery and reclamation techniques for these facilities.

A wastewater generator is required to designate a permitted treatment, storage, disposal (T/S/D) facility, along with one alternate permitted T/S/D facility, to receive its hazardous waste. In addition, the generator is responsible for maintaining records which identify the quantity, constituents, and disposition of the hazardous waste. Proper use and labeling of appropriate containers for storage, transport, or disposal of the hazardous waste and submission of reports to EPA that identify the disposition and quantity of hazardous waste are also required (4).

A hazardous waste generator can store hazardous wastes on-site for a period of up to 90 days without obtaining a permit as a storage facility (4). This provision applies regardless of whether the wastes are treated on-site or taken to an off-site T/S/D facility. If a hazardous waste is stored on-site for a period exceeding 90 days, the generator is considered an owner or operator of a storage facility and is subject to the permit requirements.

The most complex set of regulations are those imposed on owners and operators of T/S/D facilities. A facility is regulated as a "treatment facility" if the operator of the facility uses any method, technique, or process, including neutralization, designed to change the physical, chemical, or biological character or composition of the hazardous waste so as to neutralize the waste, recover energy or material resources from the waste, or render the waste nonhazardous (4). The operator of the treatment facility is then subject to full regulation according to the T/S/D facility regulations. However, "reclamation" is not defined in the regulations. This distinction is an important one because "reclamation" of hazardous wastes is temporarily exempt from regulation. Therefore, the ability to recycle metals from hazardous wastes, such as COD waste solutions, can potentially allow the generator to avoid the permitting process and regulatory problems associated with T/S/D facilities.

Hazardous waste regulations, enforced by EPA, place an increased burden on both large and small businesses and industries. The cost of compliance is only one of the consequences of RCRA. The intent of RCRA was to enforce proper management of hazardous wastes and to encourage resource conservation and recovery; the ultimate goal is protection of human health and the environment. Only by applying scientific principles and sound engineering judgment to new methods of resource recovery can the full benefit of the hazardous waste program be realized.

Treatment of COD Waste Solutions

The COD test is used extensively by commercial, industrial, university, and municipal wastewater treatment authority laboratories. The dichromate reflux method is the most commonly used method and is preferred because it insures 95% to 100% oxidation of organic matter and it can be used on a wide variety of samples (1). This method is reproducible, relatively simple, and does not require sophisticated and expensive equipment which warrants costly maintenance or repair. However, there are several disadvantages to the dichromate reflux method for COD determination. Recently, there has developed much concern due to high levels of mercury and silver salts present in COD waste solutions which could potentially be released to the environment. The high cost of silver sulfate, used as a catalyst in the determination, has also encouraged additional research concerning COD waste solutions. Alternatives which would reduce or eliminate the risk of toxic metals released into the environment or reduce the cost of COD analyses are considered in the following sections.

Alternate Testing Methods. Three alternate methods have been suggested to replace the COD determination (6, 7). These methods include biochemical oxygen demand (BOD), total organic carbon (TOC), and the permanganate "oxygen consumed" test. Both BOD and TOC are used for determining the concentration of organic matter present in water and wastewater (1). However, there are disadvantages related to both BOD and TOC determinations. BOD and COD analyses do not quantify the same parameter. BOD measures the biochemical degradation of organic compounds, while COD measures the chemical oxidation by dichromate. The BOD determination is quite lengthy, making it unsuitable as an operational parameter. BOD samples must be analyzed immediately to avoid degradation which results in a low estimation of the true BOD. Also, the BOD method is often not reproducible and is difficult to standardize (6).

TOC may be a more acceptable alternative to COD testing. TOC analyses can be adjusted, by dilution or increased sample size, to obtain accurate results throughout a wide range of organic carbon concentrations. Also, TOC analyses are reproducible and relatively accurate. A disadvantage to this method is the high cost of equipment (8).

The permanganate "oxygen consumed" test utilizes a permanganate oxidizing system in place of dichromate. This method results in values well below the theoretical oxygen demand for many compounds. The degree of oxidation varies from one compound to another, making this method unreliable (6).

Use of Alternate Metal Salts. Moore (9) has suggested several alternatives to the silver catalyst used in COD analyses. He investigated a series of catalysts and only two (manganese sulfate and cobalt sulfate) appeared to have limited success. Moore (9) used an additional 58% (millimoles/milliliter sample) manganese and cobalt, which resulted in only 54% and 50% oxidation of sodium acetate, respectively. Only by increasing the amount of manganese sulfate in the procedure to 2 grams/20 milliliter (g/mL) sample could 90% oxidation of acetate be obtained. The silver sulfate requirement for 90% oxidation of acetate is 0.06 g/20 mL sample (9).

Clark and McKinney (8) conducted similar experiments with the following alternate catalysts: copper, nickel, cobalt, iron, magnesium, zinc, and manganese. Results from the experiments indicated that cobalt sulfate or manganese sulfate may be suitable alternate catalysts. COD analyses were performed on wastewater treatment plant samples and food processing wastes, using manganese sulfate or cobalt sulfate as the alternate catalyst. They found the two catalysts to be effective in some cases, while suppressing oxidation in other cases. However, they suggested that both manganese and cobalt could produce results acceptable for operational control, especially where cost is an important factor.

Modifications to the Standard Methods Procedure. Several modifications to the dichromate reflux procedure have been suggested in an attempt to reduce both the cost of COD analyses and the potential environmental impact of the toxic metals. Moore (9) investigated the elimination of silver sulfate from the COD analysis. He found that COD values were reduced by approximately 10% for municipal wastewater when silver sulfate was omitted from the test procedure. Many compounds, such as acetic acid and other short chain organic acids, require silver sulfate for complete oxidation (6, 8).

Reducing the amount of silver catalyst from 22 grams/4 kilogram (g/kg) bottle to 7.5 g/bottle can be used to lower the cost of COD analyses without significantly decreasing the accuracy of results (9). Test results indicated that 95% oxidation of acetate could be obtained by using the reduced quantity of silver sulfate (9).

Another alternative suggested to reduce the cost of COD analyses was the use of technical grade silver sulfate rather than the more expensive reagent grade chemical (6). Analyses performed on municipal wastewater and fresh sludge resulted in an average error of 1.31% and maximum error of 3.79% when technical grade silver sulfate was compared to reagent grade silver sulfate (6).

Ryding and Forsberg (10) suggested a mercury-free method for determining COD. This method, called the RR-method (RR being a Swedish abbreviation for the words "wastewater treatment plant" and "receiving body of water" (10)), used 0.075 Normal (N) or 0.025 N potassium dichromate ($K_2Cr_2O_7$) and 0.0075 N or 0.01 N ferrous ammonium sulfate (FAS). Wastewater samples with an average oxygen demand of 10-300 milligrams per liter (mg/L) were treated with 0.075 N $K_2Cr_2O_7$ and 0.0075 N FAS. Fresh water samples with an average oxygen demand of 10-100 mg/L were treated with 0.025 N $K_2Cr_2O_7$ and 0.01 N FAS. The Standard Methods (1) determination required 0.250 N $K_2Cr_2O_7$ and 0.25 N FAS solutions. The concentration of silver sulfate used in the RR-method (10) was identical to that required for the Standard Methods (1) procedure. The RR-method (10) did not require mercuric sulfate nor a substitute for it.

Lake water samples were mixed with the dichromate/sulfuric acid reagent and autoclaved for one hour in a closed flask. Titration with ferroin indicator and FAS resulted in no significant difference between actual and theoretical COD values for lake water samples which contained less than 1.0 gram per liter (g/L) chloride. However, when lake water samples which contained 5.0 g/L chloride were analyzed by the RR-method (10), a significant increase in COD values resulted.

Further studies indicated 10% lower COD values for lake and river water samples analyzed using the RR-method (10) compared to Standard Methods (1). Wastewater treatment plant samples resulted in similar COD values for both the RR-method (10) and Standard Methods (1) determinations.

There appeared to be several advantages to the RR-method (10). A large number of samples could be performed by one technician per day. The RR-method (10) was more cost-effective because it required smaller reagent volumes than those used in the Standard Methods (1) procedure. Mercuric sulfate addition was found to be unnecessary for water and wastewater samples containing low chloride concentrations.

The limitations of the RR-method (10) were also noted. Water samples containing high chloride concentrations required mercuric sulfate addition. Addition of silver sulfate was also necessary in all cases. The method could be used for monitoring programs for wastewater treatment plants, but was not suggested for sophisticated scientific work, due to the resulting lower yield.

The cost of the Standard Methods (1) procedure can be lowered by using smaller sample volumes, thus reducing the quantity of silver and mercuric sulfates required. However, this practice is limited to wastewater samples which do not contain high concentrations of suspended solids.

Semi- or fully automated techniques are designed to be performed with reduced sample and reagent volumes (EPA Method 410.4) (11). This method requires a sample volume of 2.5 mL and only 35 mg silver sulfate and 50 mg mercuric sulfate per sample. Wastewater samples are digested in a culture tube containing a digestion solution of potassium dichromate, concentrated sulfuric acid, and mercuric sulfate, and a catalyst solution of silver sulfate and concentrated sulfuric acid. Digestion is carried out in an oven at 150°C. After two hours, the appearance of chromium (III) is measured spectrophotometrically. The semi-automated method (11) adequately compares with respect to precision and accuracy to the Standard Methods (1) procedure. In addition, the semi-automated method (11) is easier to perform, because titration of the digested solution is not required. The procedure requires a spectrophotometer and an oven; both are typically available in analytical laboratories. The procedure also significantly reduces the quantity of high strength waste produced.

COD Waste Solution Treatment Methods. Several treatment methods have been developed in an attempt to recover and reuse silver and mercury from COD waste solutions. Smith (12) cited a method recommended by Her Majesty's Stationery Office (HMSO) (13) which removed both silver and mercury. Following hydrochloric acid addition to COD waste solutions, the supernatant liquid was treated with ferrous sulfide. This procedure produced silver chloride and mercuric sulfide precipitates.

The procedure appeared to be relatively simple to perform and did not require large quantities of chemicals. However, there are several disadvantages to the method. Because chlorides cause significant interferences, the silver chloride produced would require further treatment prior to reuse in the COD test method. The procedure must be performed under a ventilation unit due to hydrogen sulfide evolution. Also, all supernatant solutions would require regulated disposal or additional treatment and pH-adjustment prior to discharge.

Aslam and Walker (14) developed a method similar to the method cited by Smith (12) for removal of silver and mercury from COD waste solutions. Sodium chloride was added to COD waste solutions to produce silver chloride precipitation. The solution was filtered and the filtrate treated with powdered ferrous sulfide. Mercury was removed from the waste solution as a mercuric sulfide precipitate.

A rather rigorous sequence of chemical additions was necessary to prepare the silver and mercury for reuse in the COD test procedure.

Silver chloride was mixed with granular zinc metal and sulfuric acid, resulting in metallic silver. After repeating this treatment scheme several times, 99.9% pure silver was obtained. The metallic silver was then added to sulfuric acid. The resultant silver sulfate could then be used in the COD test procedure.

The collected mercuric sulfide was heated with hydrochloric acid, filtered, washed, and treated with aqua regia. Mercuric chloride was produced and dissolved in distilled water, filtered, and the solution cooled to reproduce mercuric chloride crystals. This solution was refiltered in order to collect the mercuric chloride crystals, which were then redissolved in water, ethyl alcohol, and sodium hydroxide. Mercuric oxide was formed and treated with sulfuric acid to produce mercuric dioxysulfate. The mercuric dioxysulfate precipitate was then filtered, washed, and available for reuse in the COD test method.

This method removed 99.9% of the silver present in COD waste solutions and obtained 99.9% pure silver. The percentage of silver lost in each recycling process was determined to be approximately 0.5%. The method proposed by Aslam and Walker (14) removed 98.0% of the mercury found in COD waste solutions. Concentrations of mercury present in discharged solutions ranged from 45-74 mg/L (14).

A comparison was made between COD values obtained using the recovered metals and values obtained using standard chemicals according to the <u>Standard Methods</u> (1) procedure. Statistical analyses indicated there were no significant differences in resultant

COD values and that the method proposed by Aslam and Walker (14) was reliable. Both silver and mercury were quantitatively removed, separated, and recycled using this method. However, the process involved a number of steps and required large amounts of chemicals.

Dean et al. (15) suggested a method of treatment which resulted in mercuric sulfide precipitation. COD waste solutions were combined with other acidic wastes and diluted to twice their volume. The solution was adjusted to pH 7 by sodium hydroxide addition. Kjeldahl nitrogen and Nessler ammonia determination waste solutions were added, resulting in a solution pH of 10 or higher. Sodium thiosulfate was added to the solution to produce a mercuric sulfide precipitate.

This process did not produce silver or mercury in a form which could be reused in the COD test procedure. In addition, the waste precipitate generated would require additional treatment to separate the metal sludges. An alternative to sludge treatment required shipment of the mercury-containing wastes to a commercial reprocessor for mercury recovery. This procedure increased the volume of waste solution to be treated by using dilution techniques and required large quantities of chemical solutions. Also, additional test procedures would be required to determine if the supernatant solution could be discharged, as suggested by Dean et al. (15).

Electrochemical methods have been suggested for recovery of silver and mercury from COD waste solutions. Gould et al. (16) suggested the use of cementation, the process by which a metal in solution is displaced by another metal higher in the electromotive series. The reduced metal is then removed from solution by typical solids-liquid separation techniques. The process is often used in the refining industry to recover such metals as copper and gold, and in the photoprocessing industry to recover silver. Rickard and Brookman (17) used zinc reduction and complex formation to remove mercury from a chemical wastewater by reduction to elemental mercury.

Gould _et al_. (16) treated COD waste solutions with metallic iron (iron wire) and achieved 96% to 99% removal of the silver and mercury present in the waste solution. It was suggested that the resulting silver and mercury amalgams could be recycled directly into the COD test procedure or processed further for recovery of both metals.

One advantage of the cementation process was that metals of high purity were not required for reduction of silver and mercury, and the method appeared relatively inexpensive and simple to perform. Additional studies were required in which recovered metals were recycled in the _Standard Methods_ (1) procedure to determine the effectiveness of the cementation process.

Hendrickson _et al_. (18) combined precipitation and metal reduction techniques to accomplish removal and recovery of silver and mercury from COD waste solutions. Silver was precipitated as silver chloride by the addition of sodium chloride. The amount of chloride required for treatment was determined based on the significant chloro-complexes present at the optimum chloride concentration required for silver precipitation, the amount needed to form the solid, silver chloride, and the free chloride concentration. Following an aging period, the COD waste/sodium chloride solution was filtered and the filtrate treated with steel wool for mercury removal. Mercury was removed from solution by precipitation of mercurous chloride and elemental mercury.

Silver chloride precipitates were then treated for recovery of silver. Concentrated ammonium hydroxide was added, followed by reduction of the silver by addition of metallic copper. The solution was filtered and the silver metal dissolved in sulfuric acid for reuse in the COD test procedure. The method suggested by Aslam and Walker (14) could also be used to recover silver from the silver chloride precipitate. It was suggested that the mercurous chloride and mercury mixture be treated with aqua regia to form mercuric chloride followed by the Aslam and Walker (14) method of mercury recovery. The remaining solution required neutralization, nearly 20,000 volumes of tap water per volume of waste, prior to disposal.

The method suggested by Hendrickson et al. (18) appeared to be an easy, effective, and inexpensive wasy to recover silver and mercury from COD waste solutions. However, additional treatment of silver chloride and mercuric chloride precipitates was required prior to recycle in the Standard Methods (1) procedure in order to convert the chloride salts to the sulfate form. The method suggested by Aslam and Walker (14) was recommended. Successful recycle of silver and mercuric chloride would be limited without additional treatment because the presence of chlorides causes interferences in the

Standard Methods (1) procedure. Another limitation of the method suggested by Hendrickson et al. (18) was the large quantities of dilution water required prior to waste disposal.

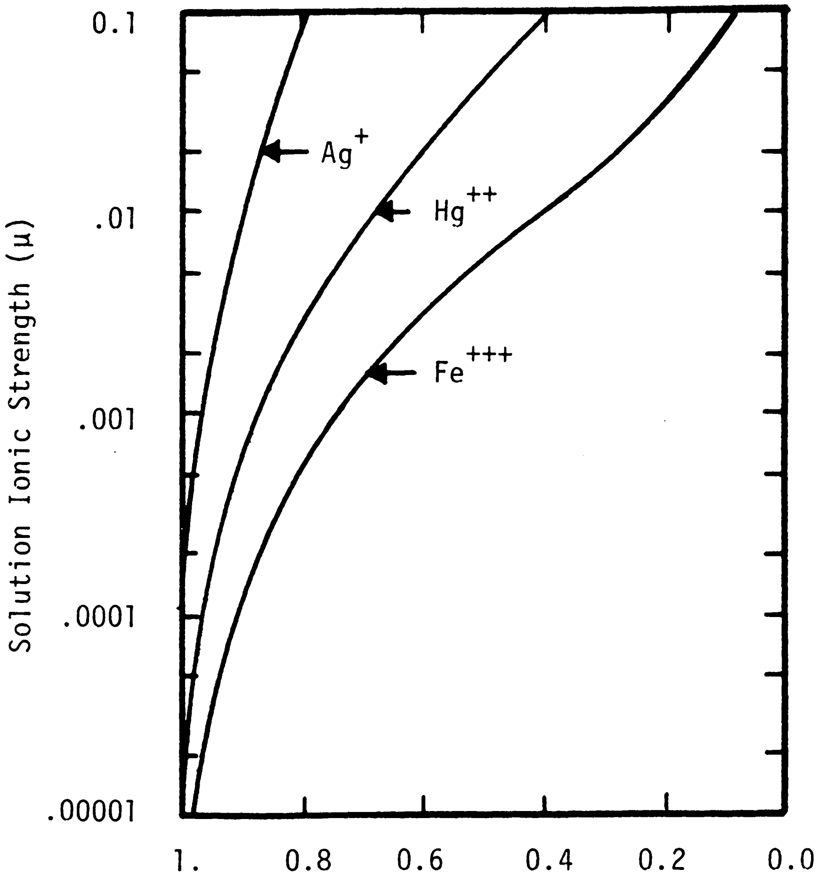
Solution Chemistry

The metal ions present in COD waste solutions include silver, mercury, iron, and chromium. In addition, COD waste solutions contain high concentrations of hydrogen and sulfate ions. The presence of these ions results in a complex waste solution of high ionic strength in which electrostatic interactions between the ions affect equilibrium conditions. Therefore, the activity of ions present in COD waste solutions must be considered in all chemical reactions.

The ionic strength of a solution can be determined based on the quantity, μ, devised by Lewis and Randall, to describe the intensity of the electric field in a solution (19):

$$\mu = \tfrac{1}{2} \sum_{i} (c_i z_i^2) \qquad [1]$$

where μ is the ionic strength of the solution, c_i is the molar concentration of ionic species "i", and z_i is the charge of species "i". Figure 1 shows the effect of ionic strength on the activity coefficients of certain aqueous metal ions (19). These curves are calculated based on the extended DeBye-Hückel equation and the



Ion Activity Coefficient

Figure 1. Activity Coeffieients of Aqueous Ions Based on the Extended DeBye-Hückel Equation and the Güntelberg Approximation. After (Snoeynik and Jenkins), reference (19).

Güntleberg approximation of the DeBye-Hückel equation (19). The extended DeBye-Hückel equation is given as (19):

$$-\log\gamma_i = \frac{Az_i^2\,\mu^{\frac{1}{2}}}{1 + Ba_i\,\mu^{\frac{1}{2}}} \qquad [2]$$

where γ_i is the activity coefficient of species "i", A and B are constants relating to the solvent, and a_i is a constant relating to the diameter of the hydrated ion. The Güntleberg approximation of the DeBye-Hückel equation follows as (19):

$$-\log\gamma_i = \frac{0.5\ z_i^2\,\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} \qquad [3]$$

These equations are valid for solutions of ionic strength less than approximately 0.1 M (19). The Davies equation (20) can be used to determine the activity coefficients in solutions of ionic strength less than 0.5 M. The Davies equation is given as (20):

$$-\log\gamma_i = Az_i^2\left[\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.3\,\mu\right] \qquad [4]$$

Although there is no theory which provides an adequate estimate of activity coefficients for ionic strengths greater than 0.5 M, Figure 1 indicates that the activity of trivalent and divalent cations decreases more rapidly than that of monovalent cations as the solution ionic strength increases. This is an important consideration for high ionic strength solutions such as COD waste solutions where the ions in solution will behave in a nonideal manner due to electrostatic interactions between the ions.

The ionic strength of a solution affects the solubility of metal hydroxide species. This effect is shown for silver hydroxide and mercuric oxide, in Figures 2 and 3, as a reduction in the region whereby precipitation occurs. An additional impact of solution ionic strength on the solubility of metal hydroxides and oxides is an increase in the soluble molar concentration required to reach saturation of the metal ion species.

Figures 2 and 3 show that silver and mercury ions can potentially be effectively removed from solution by hydroxide precipitation. The solubility of each of the metal ions present in COD waste solutions is important in the treatment of the waste solutions. Determining specific pH ranges where metal ions can be selectively separated from solution can be incorporated in a treatment process for the removal of metals from COD waste solutions. Selective precipitation studies were shown by Knocke to be an effective treatment method for mixed metal systems (21). For example, nickel and copper were both recovered in relatively pure (>98% separation) hydroxide suspensions in a two-stage, pH-adjustment treatment system.

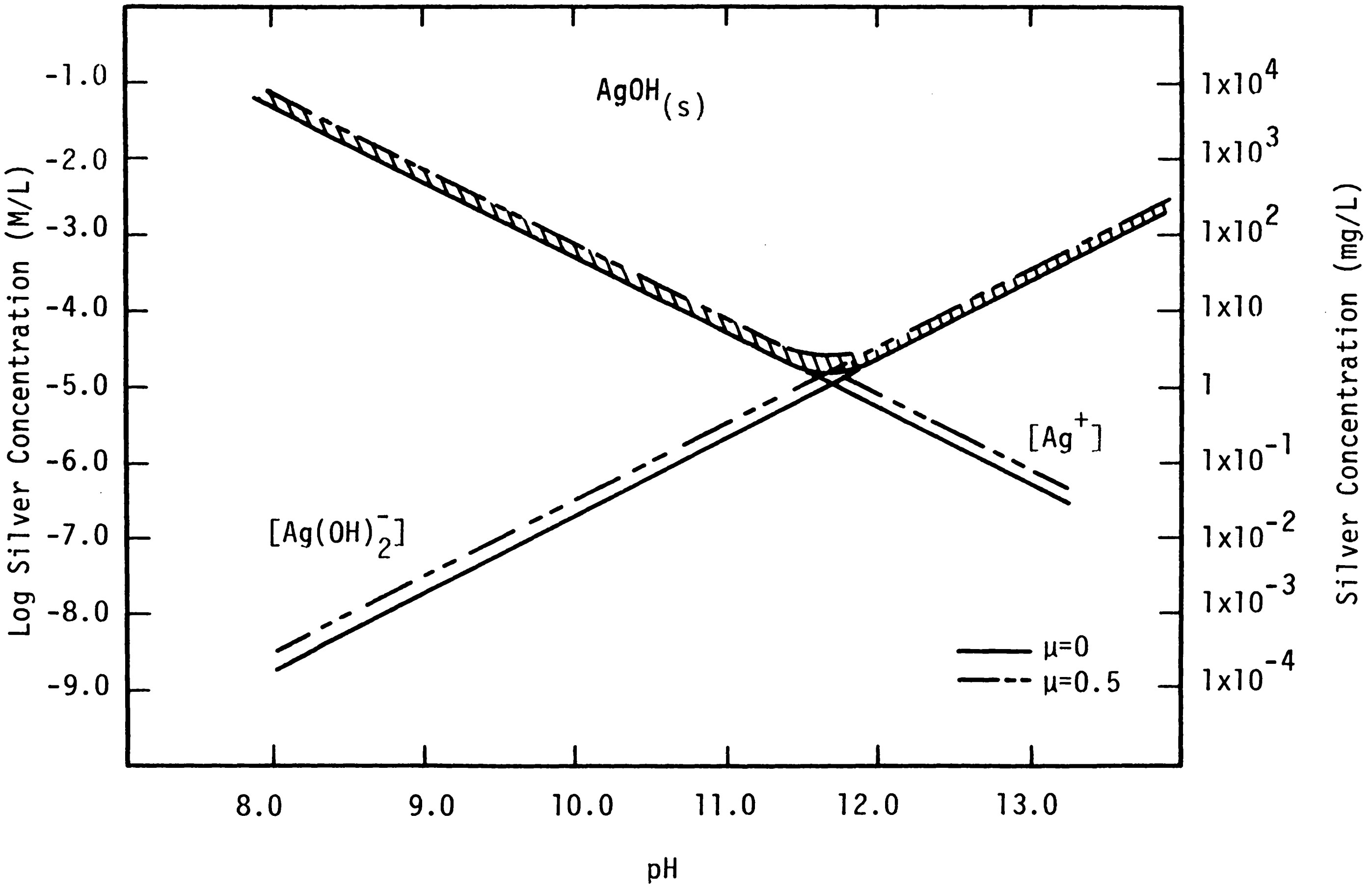


Figure 2. Theoretical Concentration of Supernatant Silver Ion as a Function of pH in 0 and 0.5 M Ionic Strength Solutions.

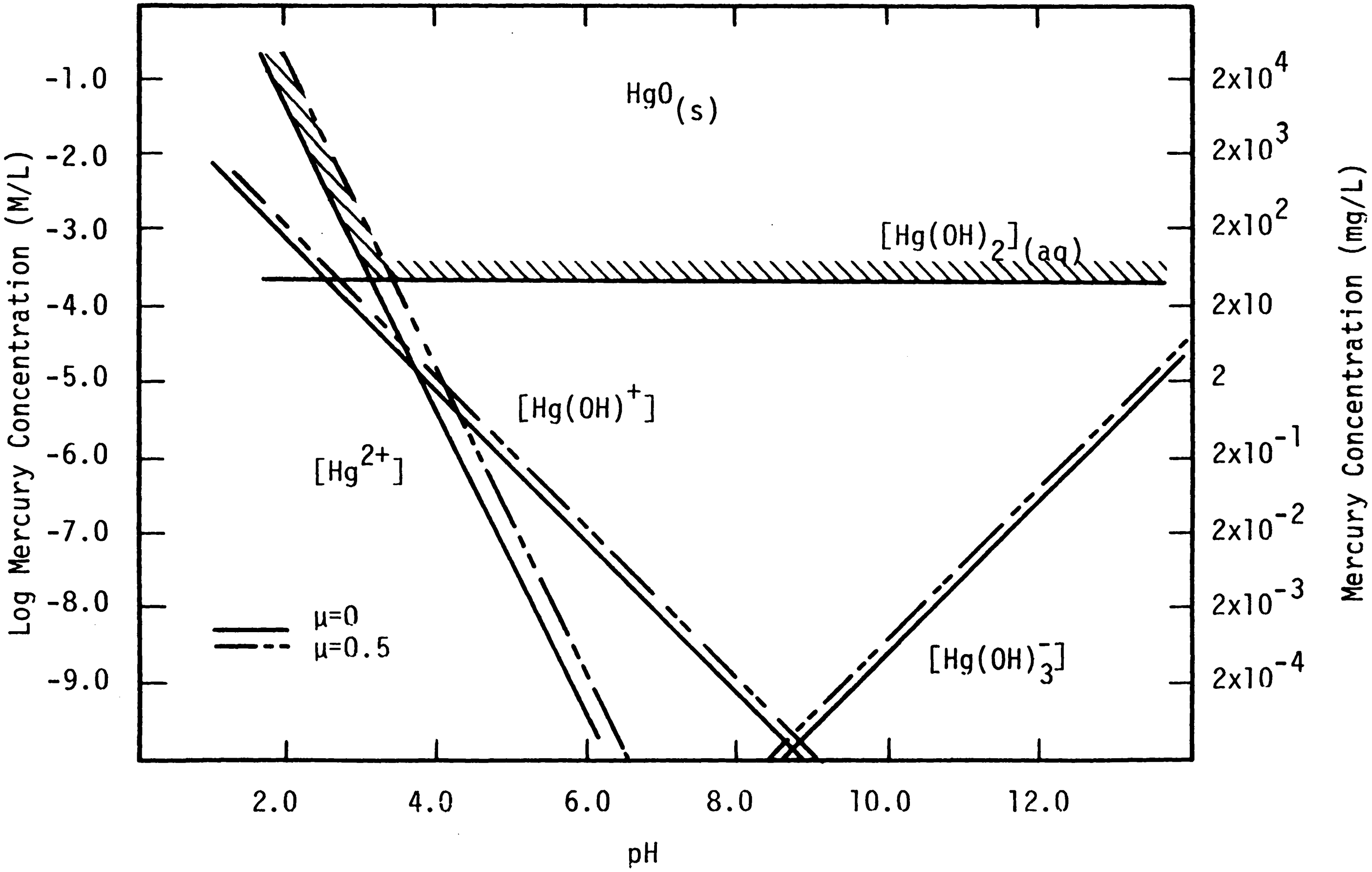


Figure 3. Theoretical Concentration of Supernatant Mercury Ion as a Function of pH in 0 and 0.5 M Ionic Strength Solutions.

Ion Exchange Theory

History and Development of Ion Exchange Resins. Ion exchange is a diffusion process which involves the exchange of ions in solution with the counter ions of insoluble polymers containing fixed anionic or cationic groups. The process was discovered in 1850 by Spence, Thompson, and Way (22), and involved removal of cations. It was applied in 1905 when Gans initially attempted to remove gold from seawater with manganese zeolite. Instead, he showed that the process could be used for water treatment by successfully removing iron and manganese (22).

The early use of ion exchange for pollution control in the field of metal ion removal and recovery was limited initially by the availability of only cation exchangers that were only stable in neutral solutions. Then, in 1942, D'Alelio (23) invented a sulfonated, cross-linked, polystyrene resin, and McBurney (23), in 1949, invented the corresponding polystyrene anion exchange resin. Later, the carboxylic resin was developed (23). After the development of sulfonated coal products and sulfonate-containing synthetic polymers, ion exchange could be used for removal of such metals as gold, silver, radium, nickel, copper, mercury, and chromium (22).

Since the development of synthetic resins, the majority of ion exchange resins used for industrial application are polystyrene-based materials. The strongly acidic cation exchangers commonly used are produced by the sulfonation of a copolymer of styrene and divinyl benzene (DVB). Chloromethylation, followed by amination of the styrene-DVB copolymer, produces the strongly basic quaternary ammonium type anion exchange resins (24). Ion exchange resins are also available in weak acid cation, weak base anion, amphoteric and ion specific forms (25).

Ion Exchange Equilibrium and Selectivity. The physical structure of the polymeric exchange resins is composed of microporous, insoluble electrolytes. The polymer network contains 50-60% water by volume (24). The framework of ion exchange resins carries a fixed positive or negative electrical charge. All ionic species with the same sign as the exchange framework are denoted co-ions. This electric charge is electrically counteracted by ions of opposite sign, called counter ions (25). Counter ions are free to move within the framework and can be replaced by other ions with the same sign.

Electroneutrality is maintained within the network of a resin. This electroneutrality must be preserved even as counter ions are exchanged during the diffusion process. Because electroneutrality is preserved, ion exchange is a stoichiometric process. Every ion which is removed from the solution is replaced by an equivalent amount of another ionic species (25).

Two common theories have been developed to quantify ion exchange equilibrium. Mass action laws can be used to describe the distribution of ions in solution and resin phases or the Donnan equilibrium model for membranes can be used (26). The Donnan theory gives a thermodynamic interpretation of ion exchange equilibrium and therefore, is more sophisticated and mathematically rigorous.

Considering ion exchange as a simple stoichiometric reaction, a general reaction equation can be developed as follows (27):

$$\underset{\text{(solution)}}{A^{n+}} + \underset{\text{(resin)}}{n(R^-)B^+} \rightleftharpoons \underset{\text{(solution)}}{nB^+} + \underset{\text{(resin)}}{(R^-)_nA^{n+}} \qquad [5]$$

According to the law of mass action, the equilibrium expression for this reaction can be written as (27):

$$K_B^A = \frac{(a_B)^n(a_{R_nA})}{(a_A)\ (a_{RB})^n} \qquad [6]$$

where a_B and a_A are the activities of the ions B and A, respectively, in solution and a_{RB} and a_{R_nA} are the corresponding activities of the ions in the resin. The term K_B^A, the selectivity coefficient, is not actually constant, but depends on experimental conditions.

For dilute solutions, the activity coefficients for ions in solution are near unity and a_B and a_A may be replaced by their respective molar concentration $[B^+]$ and $[A^{n+}]$. However, for high strength waste solutions (such as COD waste solutions) the replacement of ion activities with molar concentrations would not be appropriate. The resin phase cannot be treated as a dilute aqueous solution because the internal ion concentration of ordinary resins is typically 5-6 molal (27). Therefore, activity coefficients are essential. The resulting equilibrium expression for dilute aqueous solutions is as follows (27):

$$K_B^A = \frac{[B^+]^n(\overline{X}_{R_nA})(\overline{\gamma}_{R_nA})}{[A^+]^n(\overline{X}_{RB})^n(\overline{\gamma}_{RB})^n} \qquad [7]$$

where $\overline{\gamma}$ is the activity coefficient, $\overline{X}_A$ is equal to $[A^{n+}]$ / C, and C is the total ionic concentration of the solution.

Another useful parameter for expressing ion exchange equilibrium is the separation factor or selectivity quotient, which is defined as the following (27):

$$Q_s = \frac{K_d^A}{K_d^B} = \frac{(\text{moles } A^{n+} \text{ / g resin})(\text{moles } B^+ \text{ / mL solution})}{(\text{moles } B^+ \text{ / g resin})(\text{moles } A^{n+} \text{ / mL solution})} \qquad [8]$$

$$Q_s = \frac{[R_nA][B^+]}{[RB][A^{n+}]} = \frac{(X_{R_nA})[B^+]}{(X_{RB})[A^{n+}]} \qquad [9]$$

where $[R_nA]$ / $[RB]$ is the molar ratio of the ions A^{n+} and B^+ in the ion exchange resin in equilibrium with the molar concentrations $[A^{n+}]$ and $[B^+]$ in the solution. The selectivity quotient is an indication of the ionic preference of the particular resin for multivalent-monovalent systems. A value of $Q_s = 1$ indicates the resin has no preference for either ion. For $Q_s > 1$ the resin has preference for A^{n+} and for $Q_s < 1$ the ion B^+ is favored (27).

Important factors which determine the selectivity of an ion exchange resin include the following:

1. Electrostatic interactions between the charged framework and the counter ions which are a function of size and valence of the counter ions.
2. Interactions between the ions and their environment.
3. Steric exclusion of large counter ions from the narrow pores of the ion exchanger.
4. Swelling of the ion exchange resin.

The Donnan theory gives a thermodynamic interpretation of ion exchange equilibrium and can be used to explain the selectivity of an ion exchanger due to electrostatic interactions. The Donnan potential is an electric potential difference which occurs between ion exchangers and electrolytic solutions (25). There are considerable concentration differences between a cation exchanger placed in a dilute solution of a strong electrolyte. The cation concentration is larger in the ion exchanger, and the mobile anion concentration is larger in the solution. Migration of cations into the solution and anions into the ion exchanger results in an accumulation of positive charges in the solution and negative charges in the ion exchanger. The first few ions which diffuse build up an electric potential difference between the two phases. This "Donnan potential" pulls cations back into the negatively charged ion exchanger and anions back into the positively charged solution (27). The electric potential between ion exchangers and dilute solutions can attain very high values, and is largest when the concentration difference between the ion exchanger and the solution is large. Therefore, the efficiency of the Donnan potential and electrolyte exclusion increases with decreasing solution concentration (27).

The valences of the counter ions also have a strong effect on ion exchange equilibrium. The force with which the Donnan potential acts on an ion is proportional to the ionic charge. The counter ion of higher charge is more strongly attracted, and hence preferred by the ion exchanger, as the absolute value of the Donnan potential increases with dilution of the solution. Therefore, the electroselectivity of an ion exchanger for ions present in a dilute solution is in order of decreasing valence.

At very high solution concentrations, usually in excess of 3 moles/liter, the differences in exchange potentials of ions of different charge diminish (27). In some cases, exchange resins may have a greater affinity for ions of lower charge, but of higher exchange potential. Solutions which contain high concentrations of ions (such as COD waste solutions) do not exhibit a high Donnan potential. The initial electric potential difference which exists between an ion exchanger and an electrolytic solution is not as strong in concentrated ionic solutions as that exhibited in dilute solutions. Therefore, the tendency for higher valence ion electroselectivity decreases for solutions of high ionic concentration or high ionic strength (25).

The behavior of ion exchange resins is further complicated by the interactions between the ions and their environment. The presence of complex species in solution and the interactions of both complexed and uncomplexed species with the fixed ionic groups or the resin matrix affect ion exchange equilibria (25).

Anionic species such as chloride ions (typically excluded by cation exchangers) can enter the ion exchanger in the form of cationic complexes (25). Likewise, metals, which in cationic form are excluded by anion exchangers, can avoid the Donnan barrier by entering the exchanger in the form of anionic complexes (25).

The selectivity of cation exhangers is affected when solutions contain metal cations and complexing anions. Since cation exchangers prefer ions of higher positive charge and exclude ions of higher negative charge more efficiently, the selectivity for the competing, lower valence cation species is high when strong complexes are formed with higher valence cations. Metal ion uptake by anionic exchangers is, however, enhanced by the formation of complex species. Anionic complexes are not excluded by the Donnan effect and can be taken up by an anion exchanger (25).

Strong specific interactions may also occur between the co-ions and the fixed ionic groups or the resin matrix. These interactions provide a "driving force" which attracts co-ions to the ion exchanger and counteracts electrolyte exclusion. Cupric, silver, zinc, and mercuric salts are strongly sorbed by weak-base anion exchangers with amino groups which form amine complexes with the metal co-ion (25).

Swelling of ion exchange resins also affects ion exchange equilibrium (27). Ion exchange resins swell in water and polar solvents as the coiled and packed chains of the resin matrix unfold and make room for solvent molecules. The chains do not completely separate or dissolve due to cross linkages. Equilibrium is attained when the elastic forces of the matrix balance the dissolution tendency.

The effect of the counter ion on swelling is complex and several factors must be considered. In moderately and highly crosslinked resins, most of the solvent is present in the form of solvation shells; therefore, the size and solvation tendency of the counter ion are important factors. The resin expands when a counter ion is replaced by another ion which occupies more room. Weakly crosslinked resins contain large amounts of "free" solvent and the valence of the counter ions becomes the most important factor. The tendency to take up free solvent depends on the number of counter ions in the resin. When bivalent ions replace monovalent ions, the number of counter ions is reduced by half; this, in turn, reduces the osmotic pressure difference. Therefore, weakly crosslinked resins swell less when the valence of the counter ion is high (27).

Resins in equilibrium with electrolyte solutions swell more strongly when the solution concentration is low. High solution concentration also reduces the osmotic pressure difference in the interior of the resin, causing a reduction in the "driving force" for solvent uptake (25).

In general, the following statements can be made about ion exchange equilibrium (25):

1. The ion exchanger prefers counter ions of higher valence.
2. The preference for counter ions of highest charge increases with the dilution of the external electrolyte and is strongest with exchangers of high internal molarity.
3. The ion exchanger prefers the counter ion which interacts more strongly with the fixed ionic groups or with the resin matrix.
4. The ion exchanger prefers the counter ion which participates least in complex formation with the co-ion.
5. Swelling of ion exchange resins is favored by low valence of the counter ion.
6. Swelling of ion exchange resins is favored by low concentration of the external solution.

Ion Exchange Isotherms. Positive adsorption in a solid-liquid system results in the removal of solutes from solution onto the solid surface until dynamic equilibrium is obtained between the solute in solution and the solute on the solid surface (27). Chemical and electrical potentials control the exchange of mobile ions between the solid and solute in ion exchange processes (26). The equilibrium distribution between the solid and liquid phase can be expressed, for ion exchange systems, by sorption isotherms. Langmuir and Freundlich isotherms are widely used functional expressions for the variation of adsorption with the concentration of adsorbate in solution at constant temperature (27).

The Langmuir adsorption model is valid for single-layer adsorption and can be derived from either kinetic or thermodynamic considerations of adsorption. Its important underlying assumptions include (27):

1. The maximum adsorption corresponds to a complete monolayer.
2. The energy of adsorption is constant at each surface site.
3. The energy of an adsorbed particle is independent of the presence or absence of adjacent adsorbed particles.

The Langmuir equation can be written as follows (27):

$$q_e = X/M = Q^o bC_{eq}/(1 + bC_{eq}) \qquad [10]$$

where q_e is the amount of solute adsorbed (X) per unit weight of adsorbent (M), and C_{eq} is the corresponding solution phase concentration. The constant "b" in the Langmuir equation is related to the energy of adsorption, $e^{-\Delta H/RT}$, and "Q^o" is the maximum amount of adsorbate required to form a complete monolayer. The equation may also be expressed in the following linear form (27):

$$1/q_e = M/X = 1/Q^o + 1/Q^o bC_{eq} \qquad [11]$$

If the Langmuir isotherm applies, an arithmetic plot of $1/q_e$ versus $1/C_{eq}$ will result in a straight line with an intercept of $1/Q^0$ and a slope of $1/Q^0b$.

The Freundlich equation for isothermal adsorption was empirical at the time of its proposal but can also be derived kinetically and thermodynamically. The Freundlich equation is used for heterogeneous surface energies in which K, the energy constant, varies due to variations in the heat of adsorption (27). The Freundlich equation is written as:

$$q_e = X/M = KC_{eq}{}^{1/n} \qquad [12]$$

where n and K are constant. Data are usually plotted logarithmically to fit the equation:

$$\log q_e = \log K + 1/n \log C_{eq} \qquad [13]$$

The resulting straight line gives a slope of 1/n, which is an approximation of sorption intensity, and an intercept of log K (at $C_{eq} = 1$) which approximates sorption capacity (27).

The Freundlich equation generally agrees with the Langmuir equation for moderate concentration ranges. However, the Freundlich equation does not reduce to linear adsorption at very low or very high concentrations.

III. METHODS AND MATERIALS

The following section describes the methods and materials used for determining the effectiveness of ion exchange and precipitation methods for metal removal and recovery from COD waste solutions. Analytical procedures used included determination of pH, metal concentrations, and total, dissolved, and suspended solids concentrations. Metals analyses required were silver (Ag), mercury (Hg), iron (Fe), and chromium (Cr). Laboratory experiments which were performed included batch ion exchange studies, continuous-flow column studies, precipitation experiments, and combined precipitation and column studies. Finally, COD determinations were performed on samples using recovered silver solutions from ion exchange columns. These results were compared to COD results obtained using standard reagents according to the EPA Manual Colorimetric Method for Determining Chemical Oxygen Demand (EPA Method 410.4) (11).

COD waste solutions used throughout the study were generated in the Environmental Engineering Water Quality Laboratory, Department of Civil Engineering, Virginia Polytechnic Institute and State University. The waste solutions were generated from routine COD tests conducted on municipal wastewater and industrial wastewaters, according to Section 508 of Standard Methods (1). Only bottles which contained clear, blue contents and no visible sediments were chosen as test solutions. A uniform solution was obtained for experimental procedures by combining COD waste solutions in a five gallon Pyrex carboy to a volume of ten liters. The solution was routinely analyzed for silver, mercury, iron, and chromium concentrations and pH.

Analytical Methods

Several methods were examined in an attempt to determine the most suitable method for mercury analysis. Mercury forms a stable complex with ethylenediaminetetraacetic acid (EDTA) (28). A substitution titration was evaluated in which the solution containing mercury was mixed with magnesium-EDTA (Mg-EDTA). The Hg-EDTA complex is much more stable than the Mg-EDTA complex, allowing the magnesium ions to be released into solution. The liberated magnesium ions are then titrated, at a pH of 10, with EDTA and Eriochrome Black-T indicator.

A 1:10 dilution of COD waste was made using tap water. A two hundred milliliter (mL) volume of the diluted COD waste was mixed with 10.0 mL of 0.1 Molar (M) Mg-EDTA and the solution was adjusted to pH 10.0 with 5.0 Normal (N) or 0.5 N sodium hydroxide (NaOH). Four mL of pH-10 buffer were added, in addition to Eriochrome Black T indicator solution, and the solution was titrated with 0.01 M EDTA. A color change of red to blue indicated the endpoint. Repeated titrations performed on COD waste solutions, using the above detailed substitution method, did not produce the expected color change.

To determine the deficiencies of the EDTA substitution titration used on COD waste solutuions, several synthetic solutions with known metal concentrations were tested. First, a synthetic waste solution containing 200 milligrams per liter (mg/L) Hg (II) was tested using the EDTA substitution titration. In addition, a synthetic waste solution containing 200 mg/L Hg (II), 100 mg/L Ag (I), and 25 mg/L Cr (III) was also tested. Titration of both synthetic test solutions resulted in mercury values significantly less than the actual mercury concentration.

Titration of COD waste solutions using the EDTA substitution method did not produce the expected color change. The iron which was present in COD waste solutions, but not included in either of the synthetic solutions, most likely interferred with the indicator, blocking its action. Therefore, it was concluded that the EDTA titration would not be a suitable method for determining mercury concentrations throughout the study.

Polarographic methods are often used to determine mercury concentrations (28). Analysis of COD waste solutions using the dropping mercury electrode technique was attempted. However, the presence of silver and ferric ions caused interferences which eliminated the possibility of using this method for mercury analysis.

Analysis for mercury concentrations in COD waste solutions was performed successfully using the manual cold vapor atomic absorption (AA) method (EPA Method 245.1 for Hg Determination) (11). A Perkin-Elmer Model 703 Atomic Absorption Spectrometer (Norwalk, CT) and

Perkin-Elmer Mercury Analysis System (Norwalk, CT; System No. 303-0832) were used.

Analysis for silver, iron, and chromium concentrations were performed on an atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT; Model 703) by direct (flame) aspiration. Hydrogen ion concentrations were measured using a Fisher Accumet (Pittsburgh, PA; Model 610A) pH meter.

Batch Equilibrium Ion Exchange Studies

Batch equilibrium experiments were performed to examine the capacity of ion exchange resins for specific metals found in COD waste solutions (Ag, Hg, Fe, and Cr). These studies were first conducted on COD waste solutions using the following three virgin resins purchased commercially: Amberlite IR-120 Plus (Rohm & Haas, Philadelphia, PA), Duolite C-20 (Duolite International, Inc., Cleveland, OH), and Duolite ES-465 (Duolite International, Inc., Cleveland, OH).

Amberlite IR-120 Plus is a high quality, gel-type, high capacity, cation exchange resin. The resin matrix is a synthetic, sulfonated, polystyrene type (29). Duolite C-20 is also a high capacity, bead form, cation exchange resin. The resin matrix of Duolite C-20 is a crosslinked polystyrene with aryl sulfonate functional groups (30). Duolite ES-465 is an ion exchange resin designed specifically for mercury fixation. The polystyrene matrix is crosslinked with DVB and contains thiol groups which form stable compounds with mercury called mercaptides (31). Manufacturers' information indicates that Amberlite IR-120 Plus and Duolite C-20 can be operated over a pH range of 0-14 and Duolite ES-465 over a pH range of 1-13.

A series of batch reactor studies was also performed on spent, ion exchange resins. The source of resins was the Virginia Tech Civil Engineering Water Quality Laboratory demineralization apparatus (Corning Mega-Pure System, Corning, NY; High Capacity Cartridge, 3508-B). The cartridges consist of three distinct resins, which will be designated in this report as Corning-BL, Corning-Y, and Corning-BR. Information supplied by the manufacturer indicated each resin type as follows: Corning-BL--strong acid cationic; Corning-Y--weak base anionic; Corning-BR--mixed, cationic/anionic (32). The Mega-Pure Cartridge has a total capacity of 155,500 milligrams (mg) hardness (2400 grains) (33).

Batch experiments were conducted using 600 mL Pyrex glass beakers and a Phipps & Bird, six paddle stirrer (Richmond, VA; Model No. 300). Samples of COD waste solutions were initially adjusted to a pH of approximately 1.0, using 50% NaOH, for all batch reactor studies. Due to the hydrophilic nature of the Rohm & Haas resin, weight measurements were used to quantify Amberlite IR-120 Plus. This problem was not evident with the resins manufactured by Duolite International, Inc. Therefore, volumetric measurements were used to quantify Duolite C-20 and Duolite ES-465. Samples for residual metal analyses were collected using 5.0 mL or 10.0 mL volumetric glass pipets. All samples were analyzed for Ag, Fe, and Cr concentration. Analyses for residual Hg concentration were performed on selected samples due to the length of time involved in performing the Hg determination.

Amberlite IR-120 Plus. Two hundred mL volumes of COD waste solution were mixed with 5.0, 10.0, and 15.0 g of Amberlite IR-120 Plus and stirred for 24 hours at a paddle speed of 90 rpm. Ten mL samples were collected after 1 hour and 24 hours of mixing and analyzed for residual metal concentrations.

An evaluation of the rate of metal removal from COD waste solutions was also conducted. Five grams of Amberlite IR-120 Plus were combined with a 200 mL volume of COD waste solution and stirred at 90 rpm for 1 hour. Six samples were collected during a 1-hour interval.

Duolite C-20. The exchange capacity of Duolite C-20 was evaluated by combining 2.0, 8.0, 14.0, and 20.0 mL of resin and 100 mL of COD waste solution in batch reactors. Ten mL samples were collected after 1 hour and 24 hours of mixing at a paddle speed of 90 rpm.

Two hundred mL of COD waste solution were mixed with 16.0 mL of Duolite C-20 in order to evaluate the removal rate of metal ions. The mixture was stirred at 90 rpm and six samples were collected during a 1-hour interval.

An additional batch equilibrium experiment was conducted using a synthetic waste solution and Duolite C-20. First, a synthetic waste solution was prepared by dissolving silver nitrate ($AgNO_3$), mercuric sulfate ($HgSO_4$), ferric sulfate ($Fe_2(SO_4)_3$), and chromium nitrate ($Cr(NO_3)_3$) in tap water and adjusting the pH to 1.3. The metal concentrations of the solution were 760 mg/L Ag (I), 1630 mg/L Hg (II), 1500 mg/L Fe (III), and 320 mg/L Cr (III).

Batch reactor studies were performed in a similar manner using 1.0, 10.0, 15.0, and 25.0 mL of Duolite C-20 per 200 mL of synthetic waste solution. Ten mL samples were collected from the reactors at 1 hour and 24 hours.

Removal rates were evaluated by mixing 15.0 mL of Duolite C-20 with 200 mL of synthetic waste solution at 90 rpm. Six samples were collected during a 1-hour interval.

Duolite ES-465. Batch equilibrium studies conducted using Duolite ES-465 were similar to those done using Amberlite IR-120 Plus and Duolite C-20. The quantities of resin used were 0.5, 10.0, and 50.0 mL of resin per 200 mL of COD waste solution. The resin-COD waste mixtures were stirred at a paddle speed of 90 rpm for 1 hour and 24 hours, and 10.0 mL samples were analyzed for metal concentrations.

Removal rate experiments were performed by combining 5.0 mL of resin with 300 mL of COD waste solution. The mixture was stirred at 90 rpm and 8 samples were collected during a 1-hour period.

Another series of batch reactor studies was conducted using Duolite ES-465 and a synthetic waste solution. Silver nitrate ($AgNO_3$), mercuric sulfate ($HgSO_4$), ferric sulfate ($Fe_2(SO_4)_3$), and chromium nitrate ($Cr(NO_3)_3$) were dissolved in tap water to produce the following metal concentrations: 800 mg/L Ag (I), 2100 mg/L Hg (II), 1480 mg/L Fe (III), and 290 mg/L Cr (III). The pH of the synthetic waste solution was adjusted to 1.1 using 10% H_2SO_4.

A volume of 200 mL of synthetic waste solution was combined with 0.5, 10.0, and 50.0 mL of Duolite ES-465 and mixed at 90 rpm for 24 hours. Ten mL samples were collected from each batch reactor after 1 hour and 24 hours of mixing.

Removal rate experiments were conducted using 5.0 mL of Duolite ES-465 and 300 mL of synthetic solution. Six samples were collected during a 1-hour interval.

Laboratory Resins. Batch reactor studies were then performed on regenerated lab resins from the Mega-Pure Cartridges (Corning-BL, Corning-Y, and Corning-BR). The resins were removed from the exhausted deionization column, regenerated with 10% H_2SO_4, rinsed with deionized water and allowed to dry at ambient temperature. The batch studies were conducted with 1.0, 10.0, 15.0, and 25.0 g of resin per 200 mL of COD waste solution. Samples were collected following 1-hour and 24-hours stirring times for each of the three resins. Removal rate studies were conducted using 15.0 g of resin per 200 mL of COD waste solution and 8 samples were collected during a 1-hour interval. Duplicate studies were performed for each resin in a manner similar to the studies described above in order to verify the results of the first batch reactor studies.

Continuous-Flow Column Studies

Based on silver uptake efficiency, Corning-Y and Corning-BR were selected for use in continuous-flow, column experiments. The resins were regenerated with 10% H_2SO_4 and prepared in the manner described above for batch equilibrium experiments. The glass columns selected for these experiments were Pierce ChromatoFlo series B (Rockford, IL) ion exchange columns with an inner diameter of 9 mm and outer diameter of 17 mm. Each column measured approximately 25 cm in length. Two identical columns were used and connected in series. Approximately 25-30 g of resin material were used for each column experiment and glass wool was packed at each column end to prevent the resin material from escaping the column in the effluent. A Masterflex pump (Cole-Parmer Instrument Co., Chicago, IL; Model 7016-20) was used for pumping solutions through the columns. COD waste solutions were routinely pumped in an upflow direction through the packed columns, while acid regeneration cycles were pumped in a downflow manner. Throughout all continuous-flow column experiments, flow rates were continuously monitored, effluent samples were periodically collected, and all samples were analyzed for Ag, Fe, and Cr concentrations. Due to the length of time required to perform Hg analyses, residual Hg concentration analyses were conducted on selected samples. Continuous monitoring of effluent Ag concentration was used to determine when to terminate column operation. All acid regeneration cycles were conducted using 50% H_2SO_4.

Additional column experiments were conducted using Corning-BR resin. Due to the cation exchange preference observed throughout the batch reactor and column studies, an alternate regeneration technique was evaluated. Two glass columns were packed with 24.5 g of Corning-BR resin and COD waste was pumped through the column. This procedure was followed by treatment of the resin column with a solution of ferric sulfate ($Fe_2(SO_4)_3$). The solution was prepared by dissolving $Fe_2(SO_4)_3$ in deionized water and adjusting the pH to 1.4 with 10% H_2SO_4. The iron concentration of the solution was 4120 mg/L. The $Fe_2(SO_4)_3$ solution was pumped through the column in a downflow manner and effluent samples were collected and analyzed. This procedure was followed by a typical sulfuric acid regeneration cycle.

The final continuous-flow column experiment was conducted using Corning-BR resin. The study described below was conducted to further evaluate the exchange capacity of Corning-BR resin. Two glass columns were packed with 24.0 g of Corning-BR resin and a COD waste solution was pumped through the column as previously described. Following exhaustion of the column with respect to silver ion removal, a synthetically-prepared solution of silver sulfate (Ag_2SO_4) was applied to the ion exchange column in a downflow direction. The solution was prepared by dissolving Ag_2SO_4 in deionized water and adjusting the solution pH to 1.6 with 10% H_2SO_4. The silver concentration of the synthetic solution was 2160 mg/L. Effluent samples were collected and analyzed for metal concentrations. Column operation was terminated following breakthrough of soluble silver ions. Due to equipment malfunction, regeneration of the columns was not performed.

Solubility Studies

Precipitation studies were conducted in order to determine the solubility of each of the metal ions. Initial studies were conducted using a 1:10 dilution of COD waste solution with tap water.

Two hundred mL volumes of diluted COD waste were titrated with 5.0 N or 1.0 N NaOH to the following pH values: 2.0, 2.5, 3.0, 4.0, 5.0, 8.0, 8.5, 9.0, 10.0, 10.5, 11.0, 11.5. Following a 24-hour period, the pH of each solution was checked and readjusted. Each solution was then filtered through 12.5 cm diameter, quantitative filter paper (Fisher Brand, Pittsburgh, PA; 9-790-4E) and the filtrate collected. The filtrate samples were analyzed for Ag, Hg, and Cr concentrations. At the time the initial precipitation study was conducted, the importance of Fe ions present in solution was overlooked and analyses for Fe concentrations were not performed.

Following the initial precipitation study, a similar study was conducted using undiluted COD waste solution. The study was designed to determine the feasibility of selectively removing metal ions from COD waste solutions by precipitation methods. The pH values selected for sample collection were determined based on the results from the initial precipitation study. One liter of COD waste was titrated with 50% NaOH or 5.0 N NaOH to a final pH of 7.5. Ten mL samples were volumetrically collected during titration, at the following pH values: 0.6, 1.8, 2.7, 3.4, 5.0, and 7.4. Continuous mixing of the COD solution was used during sample collection. After a period of 48 hours, the clear supernatant solution samples were analyzed for Ag, Hg, Fe, and Cr concentrations.

Solubility-Ion Exchange Studies

A combined solubility-ion exchange study was performed using undiluted COD waste. This study was included to determine if ion exchange and precipitation treatment of COD waste solutions could be combined to selectively remove and recover metals for reuse in the COD test procedure and produce a reduced volume of hazardous waste material which would require disposal. One liter of COD waste solution was first adjusted to an approximate pH of 4.7 using 50% NaOH or 5.0 N NaOH. The pH-adjusted solution was centrifuged at 5000 rpm for 15 minutes (Beckman, Palo Alto, CA; Model J-21C Centrifuge). The pH of the solution was checked following centrifugation.

Two glass columns were packed with a total of 27.0 g of Corning-BR resin and connected in series. The centrifuged, supernatant solution was then pumped in an upflow direction through the ion exchange columns and 10.0 mL effluent samples were collected and analyzed for metal concentrations. In addition, the pH of each of the effluent samples was recorded. The column was then rinsed in a downflow manner with deionized water, followed by a sulfuric acid regeneration cycle.

Solids Analyses

Total Solids. Five hundred mL of undiluted COD waste solution were titrated to a final pH of 7.6 using 50% NaOH or 5.0 N NaOH. The solution was thoroughly mixed and the procedure for determining Total Solids (Method 209A) was followed according to Standard Methods (1). The total solids concentrations were calculated.

Total Dissolved Solids. Section 209B of Standard Methods (1) describes the procedure used for determining total dissolved solids. Five mL sample volumes of the above described pH-adjusted COD waste solution were used. In addition, pH-adjusted (pH 7.6) COD waste solutions were centrifuged at 5000 rpm for 15 minutes and 10.0 mL sample volumes were collected from the centrifuged supernatant. Samples were dried at 103^{o}C for 2 hours and total dissolved solids concentrations were determined.

Total Suspended Solids. The procedure used to determine total suspended solids is outlined in Section 209C of Standard Methods (1).

Ten mL sample volumes of pH-adjusted (pH 7.6) COD waste were used for this procedure and the total suspended solids were calculated.

COD Determination Using Recovered Silver Solutions

The objective of the following study was to determine if recovered silver from acid regeneration of ion exchange columns could be used in the COD test procedure. COD determination of a synthetic waste solution was conducted using a modification of the EPA Manual Colorimetric Method (Method 410.4) (11). The Standard Methods (1) determination was not used due to the large quantities of silver sulfate/sulfuric acid reagent required. The Standard Methods (1) test required 30 mL of sulfuric acid reagent containing a silver concentration of approximately 6000 mg/L, to determine the COD of a 20 mL wastewater sample. These quantities of regenerated silver/ sulfuric acid solution were not available from the column studies conducted. The EPA-Micro Method (11) required only 3.5 mL of silver sulfate/sulfuric acid reagent for the COD determination of a 2.5 mL wastewater solution.

The EPA Method (11) used identical concentrations of potassium dichromate, silver sulfate, and mercuric sulfate as the dichromate reflux method (1). Wastewater samples are combined with a digestion solution containing potassium dichromate, mercuric sulfate, and sulfuric acid, and a catalyst solution containing silver sulfate and concentrated sulfuric acid, and refluxed in an oven at 150°C. The appearance of chromium (III), produced by oxidation of the organic matter present, is measured spectrophotometrically at 600 nm. The modification of the EPA Method (11) measured the concentration of chromium (VI) remaining following oxidation of organics. The modified method was used due to interferences caused by the presence of Cr (III) in the silver/ sulfuric acid solutions obtained by regeneration of exhausted Corning-BR ion exchange columns.

Potassium acid phthalate solutions with equivalent COD concentrations of 25 mg/L to 1000 mg/L were analyzed in order to develop a standard COD concentration / % Transmission curve. Following reflux of the standard solutions, a 1:3 dilution (1 reflux mixture : 3 water) of each standard was prepared and spectrophotometric measurements were recorded using a wavelength of 440 nm. At 440 nm, Beer's Law is more closely followed when diluted reflux mixtures are used (34).

Three catalyst solutions were used in the COD determination of a synthetic waste solution. First, exhausted Corning-BR resin columns were regenerated with 50% sulfuric acid and the acid effluent containing silver ions was collected. Effluent solutions from several continuous-flow column studies were combined and used as a catalyst solution in the modified EPA Method (11) for determining COD. Concentrations of metal ions in the regenerant catalyst solution were 1100 mg/L Ag, 650 mg/L Hg, 50 mg/L Fe, and 40 mg/L Cr. A second quantity of column regenerant was collected and spiked with silver sulfate to equal the concentration required by the EPA Method

(11). The spiked catalyst solution contained 5000 mg/L Ag, 240 mg/L Hg, 30 mg/L Fe, and 20 mg/L Cr. The third catalyst solution was prepared with fresh silver sulfate and concentrated sulfuric acid in accordance with the EPA Method requirements (11). A synthetic waste solution of approximately 800 mg/L COD was prepared with Bactopeptone and COD analyses were performed using the three catalyst solutions. Spectrophotometric readings were recorded as percent transmission at a wavelength of 440 nm using a 1:3 dilution of the refluxed mixture. COD values of each synthetic waste solution were obtained from the COD concentration / % Transmission standard curve.

The effect on COD values of the concentration of sulfuric acid used for the catalyst solution was also evaluated. Synthetic waste solutions of approximately 600 mg/L COD and 1000 mg/L COD were prepared with Bactopeptone. Catalyst solutions were prepared with concentrated sulfuric acid, 50%, and 25% sulfuric acid. Fresh silver sulfate was added to each acid solution to produce the following silver concentrations: concentrated sulfuric acid solution, 7400 mg/L Ag; 50% sulfuric acid, 4000 mg/L Ag; 25% sulfuric acid, 4100 mg/L Ag. The synthetic waste solutions were refluxed according to EPA Method 410.4 (11) and percent transmission values were recorded at a wavelength of 600 nm. The COD values of each waste solution were obtained from an available COD concentration / % Transmission standard curve.

IV. RESULTS

Data collected throughout this study were intended to evaluate the feasibility of using ion exchange and precipitation methods for treatment of COD waste solutions. Of primary interest were ion exchange methods for removal and recovery of silver and mercury. Solubility studies were conducted to determine if precipitation could be included in the treatment scheme for additional removal of metal ions from COD waste solutions.

Solubility Studies

The chemical concentration of COD waste solution can be calculated from the quantity of metal salts used in the dichromate reflux procedure and the concentration of dichromate and ferrous ammonium sulfate (FAS) solutions required. The sample size, quantities of reagents, and normalities of standard solutions are selected for use in the procedure based on the estimated COD of the wastewater being tested. Calculations of theoretical metal ion concentrations in COD waste solutions were based on a 20 mL sample size, 10 mL $K_2Cr_2O_7$ (0.25 N), 30 mL sulfuric acid reagent, 0.5 g $HgSO_4$, 0.10 N FAS, and a final volume of 200 mL after titration. The theoretical metal ion concentrations were calculated as 920 mg/L Ag, 1700 mg/L Hg, 500 mg/L Fe, and 220 mg/L Cr. Analysis of COD test solutions for metal ion concentrations varied, but typically were within 20% of the calculated values, with the exception of iron concentrations. Iron concentrations present in COD test solutions were usually on the order of 800-1000 mg/L. The calculated values of metal ions present in COD waste solutions were used as a basis for the preparation of synthetic solutions used throughout the study.

Due to the presence of concentrated sulfuric acid used in preparing reagents for the dichromate reflux precedure, COD waste solutions contain high concentrations of hydrogen and sulfate ions in addition to metal ions. It was thought that the extremely high ionic strength of the solution would affect both the precipitation and ion exchange equilibrium reactions. The typical ionic strength of COD waste solutions was calculated as 8.1 M using Equation 1 (formulated by Lewis and Randall (19)).

The original intent for calculating ionic strength conditions in the COD waste solutions was to allow for the modification of solubility product constants to account for ionic strength effects on species' reactivity. Unfortunately, the literature does not provide an acceptable mathematical expression for making such modifications under the high ionic strength conditions of this study. Instead, the Davies equation (20) is considered the acceptable equation for modifying constants under high ionic strength conditions; however, its stated maximum is an ionic strength of 0.5, well below the ionic strength of the COD solutions. Thus, it was not considered appropriate to quantitatively modify the equilibrium constants using invalid expressions for the extreme ionic strength of COD waste solutions. Therefore, the solubility product constants for silver hydroxide and mercuric oxide, given in Appendix A, were adjusted according to the maximum ionic strength conditions stated by the Davies equation (20) in order to establish the general trend of ionic strength effects on species' solubility.

Solubility diagrams for silver hydroxide and mercuric oxide, shown in Figures 2 and 3, respectively, were constructed first, with solubility product constants assuming activity coefficients equal to unity and second, with constants modified for an ionic strength of 0.5 M, according to the Davies equation (Equation 4) (20) for activity coefficients. These calculations show that as the ionic strength of a solution increases the concentration of metal ion required to reach saturation also increases and the region for precipitation of the metal hydroxide decreases.

A precipitation study was conducted by titrating an undiluted COD waste solution with NaOH. Soluble metal ion concentrations (mg/L), plotted in Figure 4 as a function of solution pH, show that mercury, iron, and chromium ion concentrations could be significantly reduced by metal hydroxide precipitation at pH 5.0. Approximately 50% of the silver ions present in solution were also insolubilized at pH 5.0. Treatment of the COD waste solution by pH adjustment to 7.5 further reduced the soluble mercury, iron, and chromium concentrations.

Results from this study provided useful information for a potential two-stage treatment process for COD waste solutions. Selective precipitation by pH adjustment to approximately pH 5.0

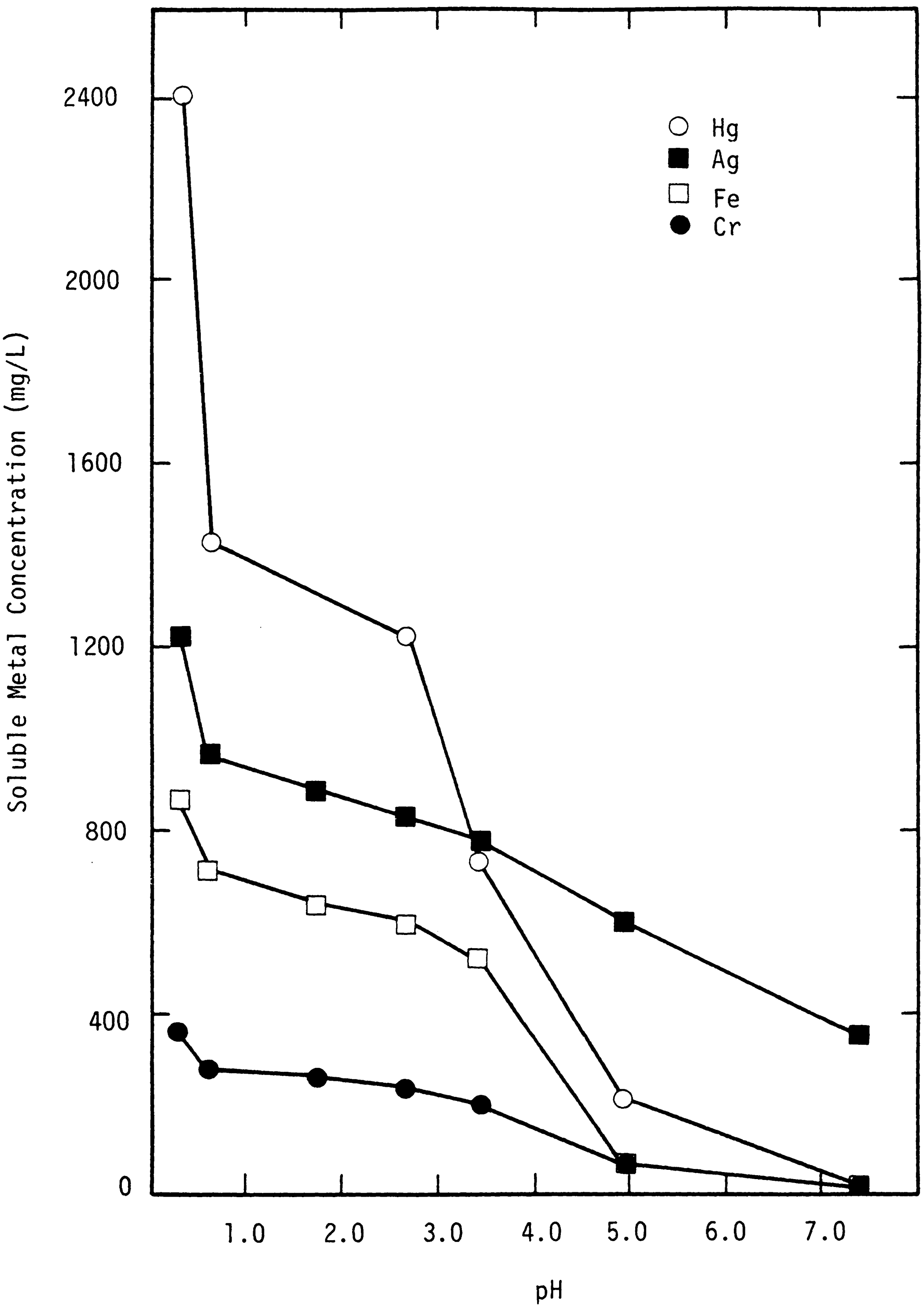


Figure 4. Soluble Metal Ion Concentrations in COD Waste Solutions as a Function of pH.

removes significant amounts of mercury, iron, and chromium from the waste solution while silver remains soluble. Following pH adjustment the remaining solution can be treated further by ion exchange methods for removal and recovery of silver ions.

Ion Exchange Studies

Batch Equilibrium Studies. Ion exchange batch equilibrium studies were conducted using three virgin resins purchased commercially: Amberlite IR-120 Plus, Duolite C-20, and Duolite ES-465. The initial batch studies were performed to determine if metal cations could be removed from COD waste solutions by ion exchange treatment; in addition, the effects of COD waste solution ionic strength on ion exchange equilibrium reactions were also investigated.

Samples were withdrawn from the batch reactors at various intervals during a 1-hour contact time and again after 24 hours to determine how rapidly equilibrium was reached in these systems. In general, there was no significant difference noted in the residual soluble metal concentrations when comparing 1-hour and 24-hour contact times. Representative data presented in Figure 5 show that equilibrium was typically reached within five minutes, which was the first sampling time chosen for these studies. Thus, it may be concluded that the ion exchange reactions are rapid and equilibrium is reached in these systems in a very short period of time. Since this was found true in each instance, the following

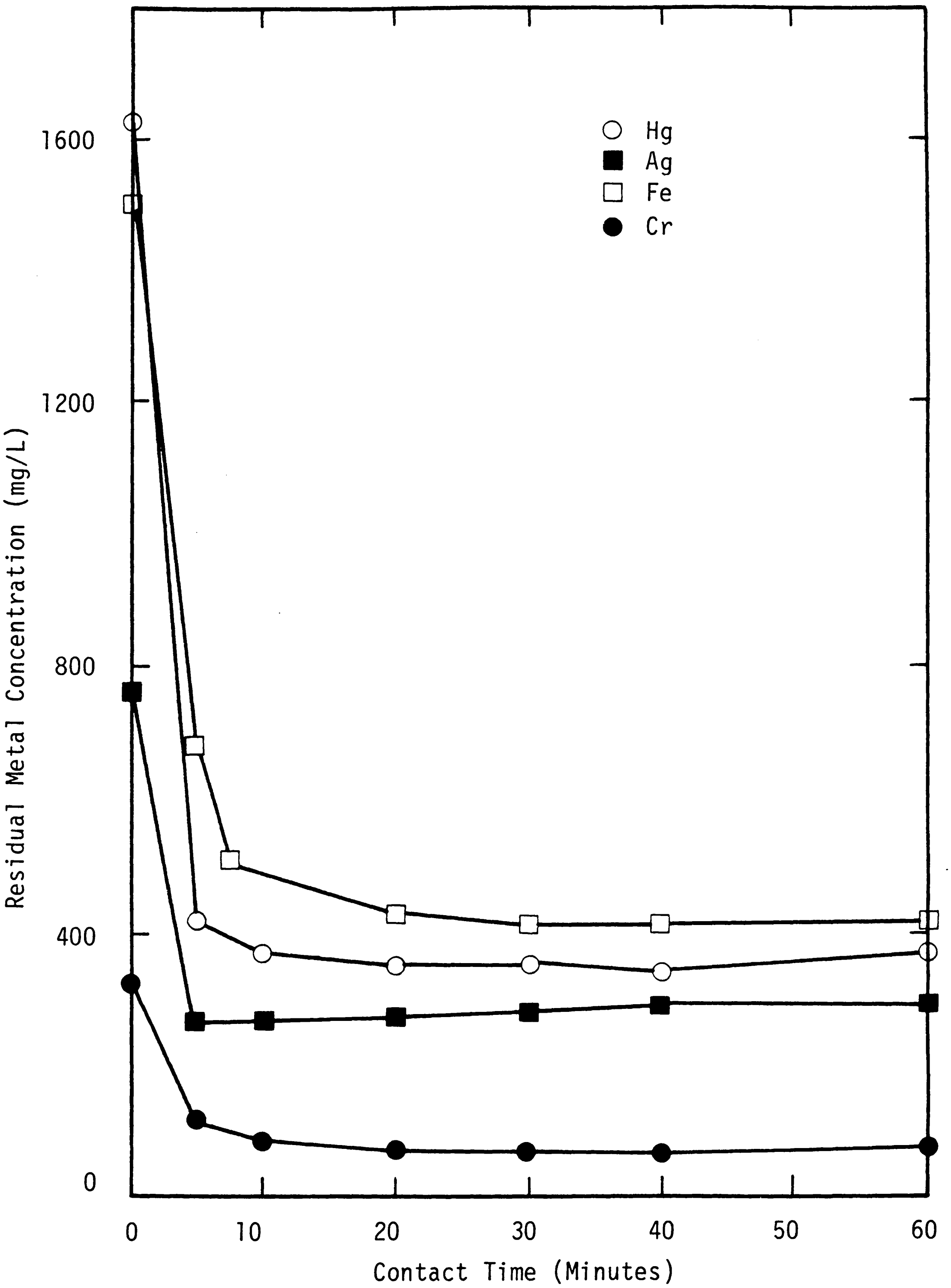


Figure 5. Metals Removal by Batch Ion Exchange From a Synthetic Waste Solution With Resin Duolite C-20.

discussion of batch equilibrium results will present only the residual metal concentrations after 24-hour contact times.

Amberlite IR-120 Plus is a cation exchange resin designed for general industrial water softening. Results from the initial batch reactor study (presented in Figure 6) indicated that Amberlite IR-120 Plus was effective in removing both silver and mercury ions from COD waste solutions. Removal of silver and mercury ions increased with increased resin quantity. Figure 6 shows that Amberlite IR-120 Plus was less effective in removing iron and ineffective for removing chromium ions from solution.

Batch equilibrium studies were conducted with Duolite C-20 using a COD waste solution and a synthetic heavy metal waste solution in order to compare the effect of solution ionic strength on ion exchange equilibrium reactions. The synthetic waste solution was prepared with similar initial metal ion concentrations as those found in COD waste solutions and was adjusted to pH 1.3. The ionic strength of the synthetic waste solution was calculated as approximately 0.19 M, compared to a typical COD waste solution ionic strength of 8.1 M.

The results of the batch equilibrium studies (Figure 7) indicate the effect that high solution ionic strength has on ion exchange reactions. Duolite C-20 was effective in removing significant amounts of all metal cations of concern from the synthetic waste solution as resin volume was increased while removing only small amounts of silver and mercury from the COD waste solution. No

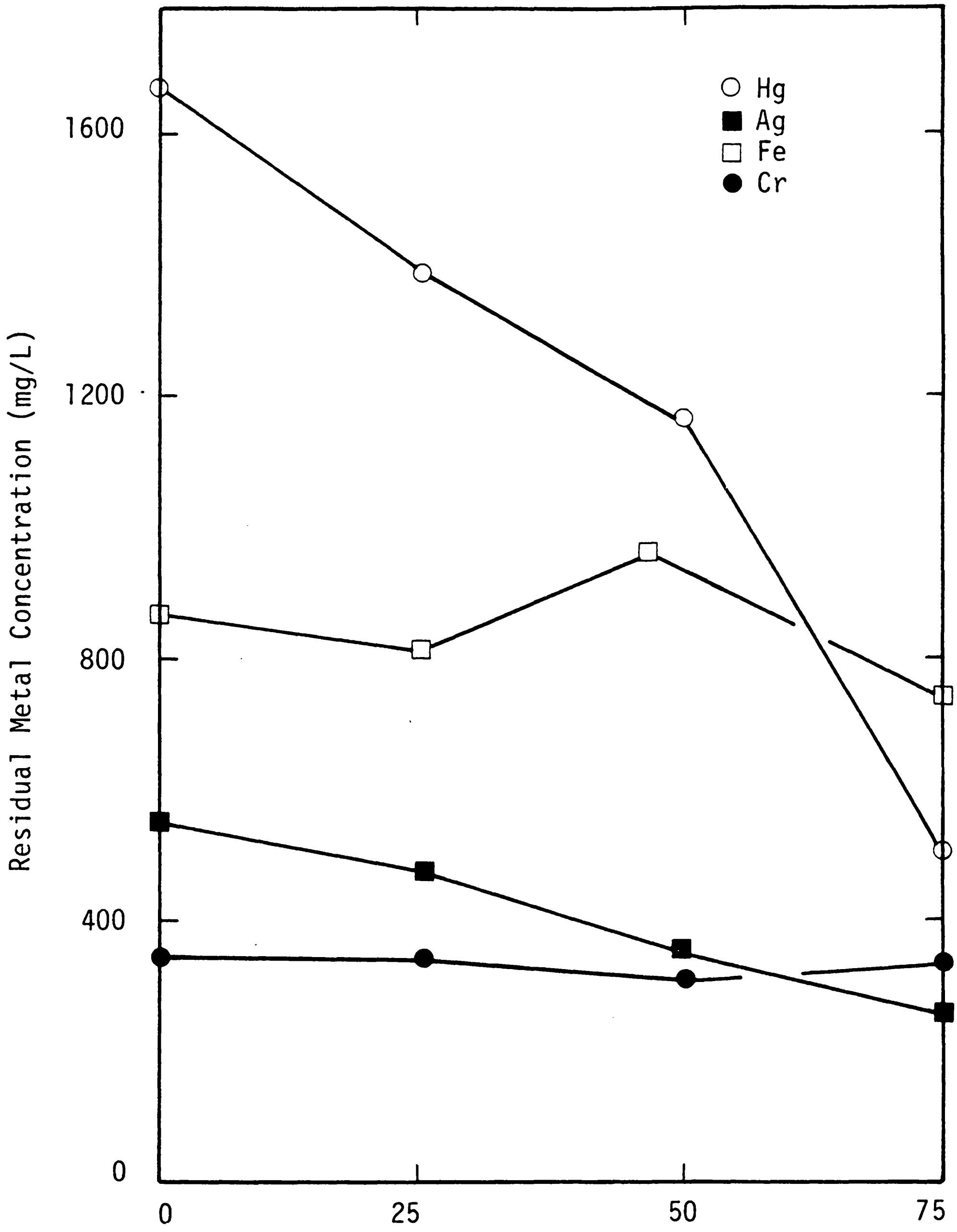


Figure 6. Metals Removal by Batch Ion Exchange for Resin Amberlite IR-120 Plus.

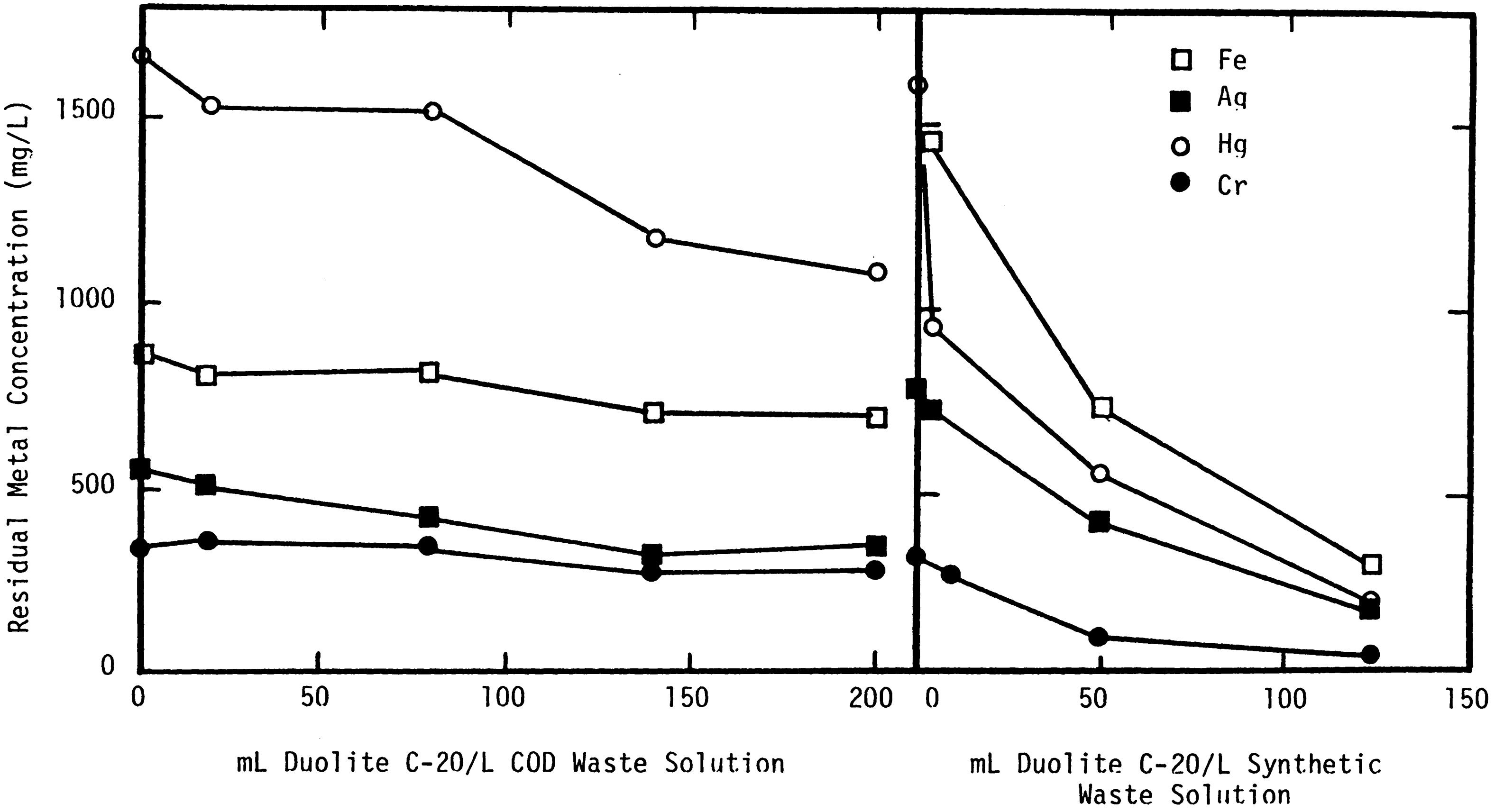


Figure 7. Comparisons of Metal Ion Residual Concentrations From Ion Exchange Batch Studies Using Resin Duolite C-20 for Treatment of COD Waste and Synthetic Waste Solutions.

significant reduction in iron or chromium ions occurred from COD waste solutions with increased resin volume. Mixing time did not appear to have a significant effect on metal ion uptake by Duolite C-20 from the synthetic waste solution and the COD waste solution when 1-hour and 24-hour data were compared.

The third resin evaluated was Duolite ES-465, a special ion exchange resin designed for mercury fixation applications. Batch equilibrium studies were conducted with both the COD waste solution and a synthetic heavy metal waste solution and Duolite ES-465. As indicated in Figure 8, significant mercury and silver ion removal occurred for each resin quantity used with the COD waste solution. Results similar to those obtained for COD waste solution batch equilibrium studies were observed for all metals of interest for the synthetic waste solution studies. The extreme differences in solution ionic strengths did not appear to affect metal ion removal or exchange preference with Duolite ES-465, a cation specific resin (Figure 8). However, the difference in COD waste solution ionic strength and synthetic waste solution ionic strength resulted in significant differences in the observed ion exchange reactions for Duolite C-20 (Figure 7).

After obtaining the equilibrium data, an attempt was made to review possible methods for analyzing and interpreting the exchange results from these mixed-metal wastewaters. Also, it was hoped that the potential impacts of ionic strength on exchange capacity could be examined through the method of data presentation. A review of

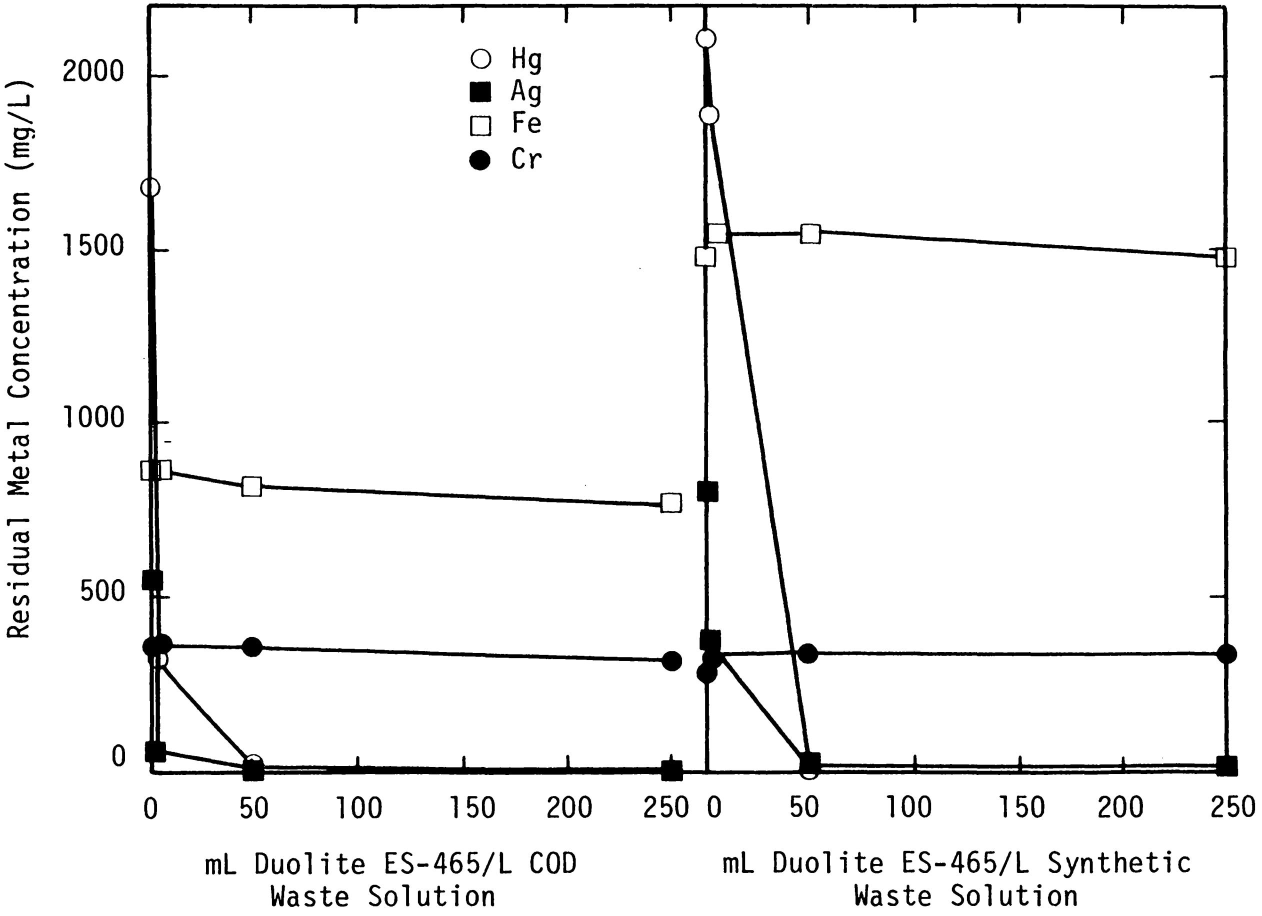


Figure 8. Comparisons of Metal Ion Residual Concentrations From Ion Exchange Batch Studies Using Resin Duolite ES-465 for Treatment of COD Waste and Synthetic Waste Solutions.

the literature showed various methods for analyzing ion exchange data. Often, when considering differences in selectivity in mixed metal systems, researchers will calculate a selectivity quotient which relates the relative ions being exchanged with respect to their solution and resin concentrations. Unfortunately, with the wastes examined, this calculation was not deemed possible. The selectivity quotient is normally calculated in comparison to the exchanged ion released to solution, in this case the hydrogen ion. Although pH was monitored during the exchange reaction, the difference in pH noted was not significant enough to make such calculations. On an equivalence basis, the number of hydrogen ions released during the ion exchange reaction was not significant in comparison to the background hydrogen ion concentration present in the waste itself.

Weber (20) expressed the viewpoint that, due to similarities between the adsorption and ion exchange processes, it is possible to analyze ion exchange data by using the Freundlich and/or Langmuir isotherm models. After evaluating the equilibrium data with respect to both isotherm equations, it was determined that the data best fit the more empirical Freundlich model.

Data obtained from the 24-hour batch equilibrium studies were used to develop Freundlich isotherms for silver and mercury ions. Isothermal adsorption plots were not developed for iron or chromium due to the limited uptake of both metals noted during the equilibrium studies. Adsorption of silver and mercury ions from COD waste solutions did not follow the Freundlich equation for Amberlite IR-120

Plus and Duolite C-20. Figure 9 represents isotherms for those experimental studies which followed the Freundlich equation.

The Freundlich isotherms for Duolite C-20 indicate that a greater amount of mercury uptake occurred compared to silver uptake from the synthetic waste solution. The steeper slope of the mercury isotherm also shows that uptake remained relatively constant as resin quantity was increased.

The Donnan theory of electroselectivity accounts for the preference of a cation exchanger for higher valence counter ions (25). In this case, the Donnan potential exhibited in the low ionic strength synthetic waste solution was large enough that exchange of mercury ions occurred in preference to silver ion excahnge. Under high ionic strength conditions the difference in exchange potential diminishes, often accounting for resin affinity for ions of lower charge (27). Unfortunately, the experimental data obtained from studies conducted with Duolite C-20 and a COD waste solution did not follow the Freundlich equation; therefore, a comparison of isotherms could not be made.

Uptake of silver and mercury by Duolite ES-465 is shown for both the COD waste solution and a synthetic waste solution in Figure 9. For both solutions, silver exchange was preferred to mercury exchange at equilibrium concentrations greater than 0.1 meq/L, as indicated by the slope of the isotherm. At concentrations less than approximately 0.1 meq/L, mercury is the preferred ion adsorbed. The slighter slope of the mercury isotherm is accounted for by the nature

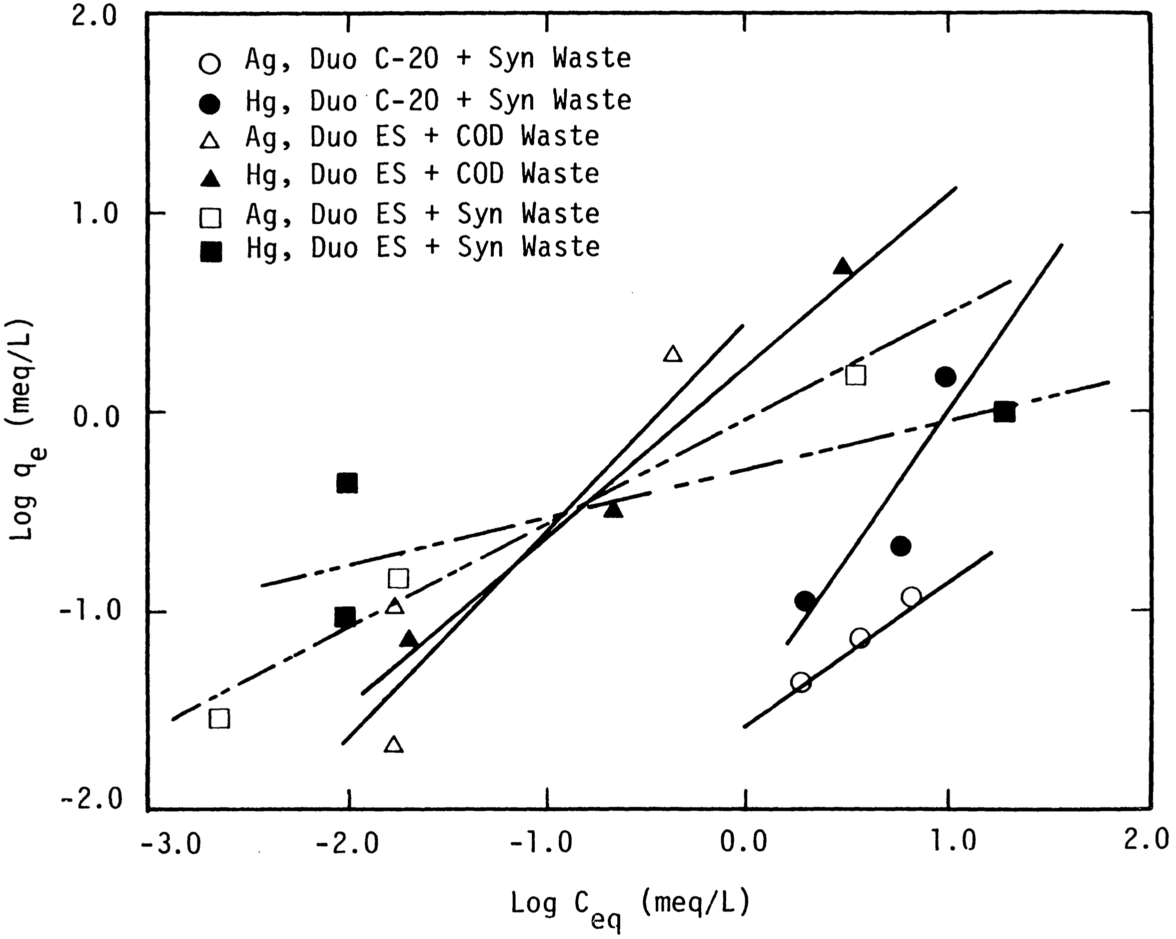


Figure 9. Freundlich Isotherms for Silver and Mercury Ion Exchange From Synthetic Waste and COD Waste Solutions With Commercial Resins.

of the resin itself; Duolite ES-465 is a specially designed resin for mercury fixation over a wide range of concentrations (31).

The effect of high solution ionic strength on Duolite ES-465 adsorption appeared to result in higher metal ion uptake from the COD waste solution. Table 1 quantifies the results of the batch equilibrium studies as values of q_e (meq ion/mL resin) for each equilibrium metal ion concentration (C_{eq} as meq/L). Values of q_e were on the order of a magnitude higher for both silver and mercury from the COD waste solution compared to the synthetic waste solutions.

Ion exchange batch equilibrium studies were also conducted using acid regenerated resins from the Virginia Tech Civil Engineering Water Quality Laboratory demineralization apparatus; these resins will be referred to throughout this study as Corning-BL, Corning-Y, and Corning-BR. The resin types were characterized as follows (32): Corning-BL--strong acid cationic; Corning-Y--weak base anionic; Corning-BR--polishing resin consisting of a mixture of cationic and anionic resins. These studies were performed in a manner similar to those described previously for the commercial resins. Samples were withdrawn from batch reactors at varous time intervals during a 1-hour contact time and again after 24 hours. As noted with the commercial resins, equilibrium was rapid, typically obtained within 10 minutes; therefore, the discussion will follow with data presented for 24-hour contact time residual metal concentrations.

Each resin exhibited similar exchange preferences for metal ion removal from COD waste solutions. The results of the batch equilibrium

Table 1. Comparison of Silver and Mercury Uptake in Equilibrium Experiments Using Commercial Resins.

Isotherm	Silver		Mercury	
	C_{eq} (meq/L)	q_e (meq Ag/mL resin)	C_{eq} (meq/L)	q_e (meq Hg/mL resin)
Duolite C-20 + Synthetic Waste	7.2	0.11	16.3	1.92
Duolite ES-465 + COD Waste Solution	5.1	13.61	16.7	18.74
Duolite ES-465 + Synthetic Waste	7.4	2.50	21.0	0.96

studies are shown in Figures 10-12. No removal of iron or chromium occurred with Corning-BL (Figure 10), Corning-Y (Figure 11), or Corning-BR (Figure 12) as resin quantity was increased in each experiment. Removal of silver and mercury occurred with each of the three resins as resin quantity was increased, although removal occurred to varying degrees for each resin tested. Corning-Y resin (Figure 11) showed the highest removal efficiency with respect to silver and mercury ions; Corning-BL resin (Figure 10) was least efficient at metal ion uptake from the COD waste solution.

These results were further quantified after analyzing adsorption isotherms for the three resins evaluated. Isothermal plots were not developed for iron or chromium due to the limited uptake of both metals observed during the equilibrium studies. Langmuir and Freundlich adsorption plots were constructed for silver and mercury ions. Adsorption of silver ions was best described by the Freundlich equation for each of the three resins. Mercury ion uptake did not reduce to a linear form according to either the Freundlich or the Langmuir equation for resins Corning-BL and Corning-BR.

Freundlich isotherms are plotted in Figure 13 for each of the resins for which the equation fit. The isotherms show that Corning-Y, an anionic resin, was the most effective resin in removing silver ions from COD waste solutions. Residual silver ion concentrations were reduced to 10^{-2} meq/L in batch reactor experiments conducted with Corning-Y. These results are also quantified in Table 2 where

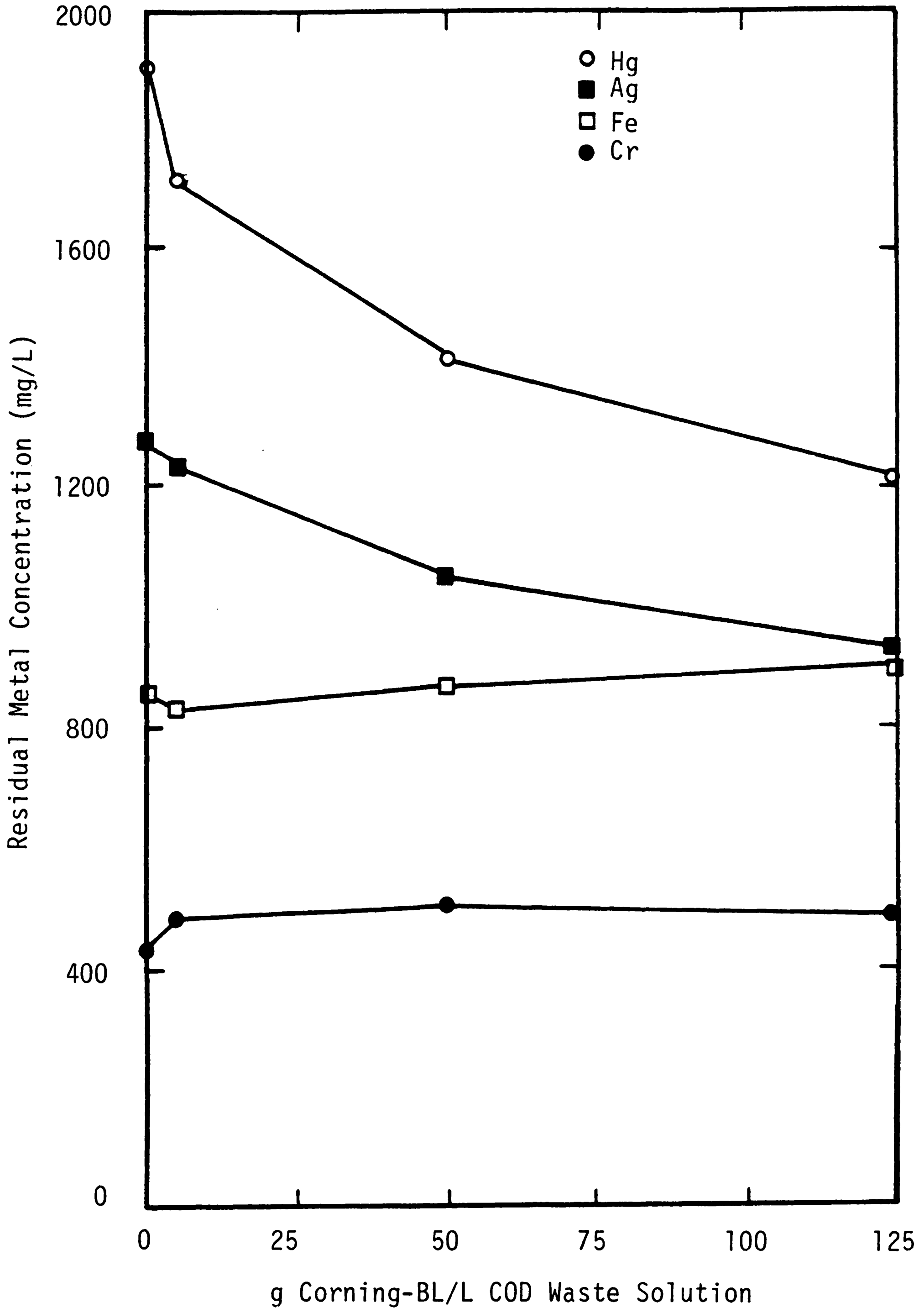


Figure 10. Metals Removal by Batch Ion Exchange for Resin Corning-BL.

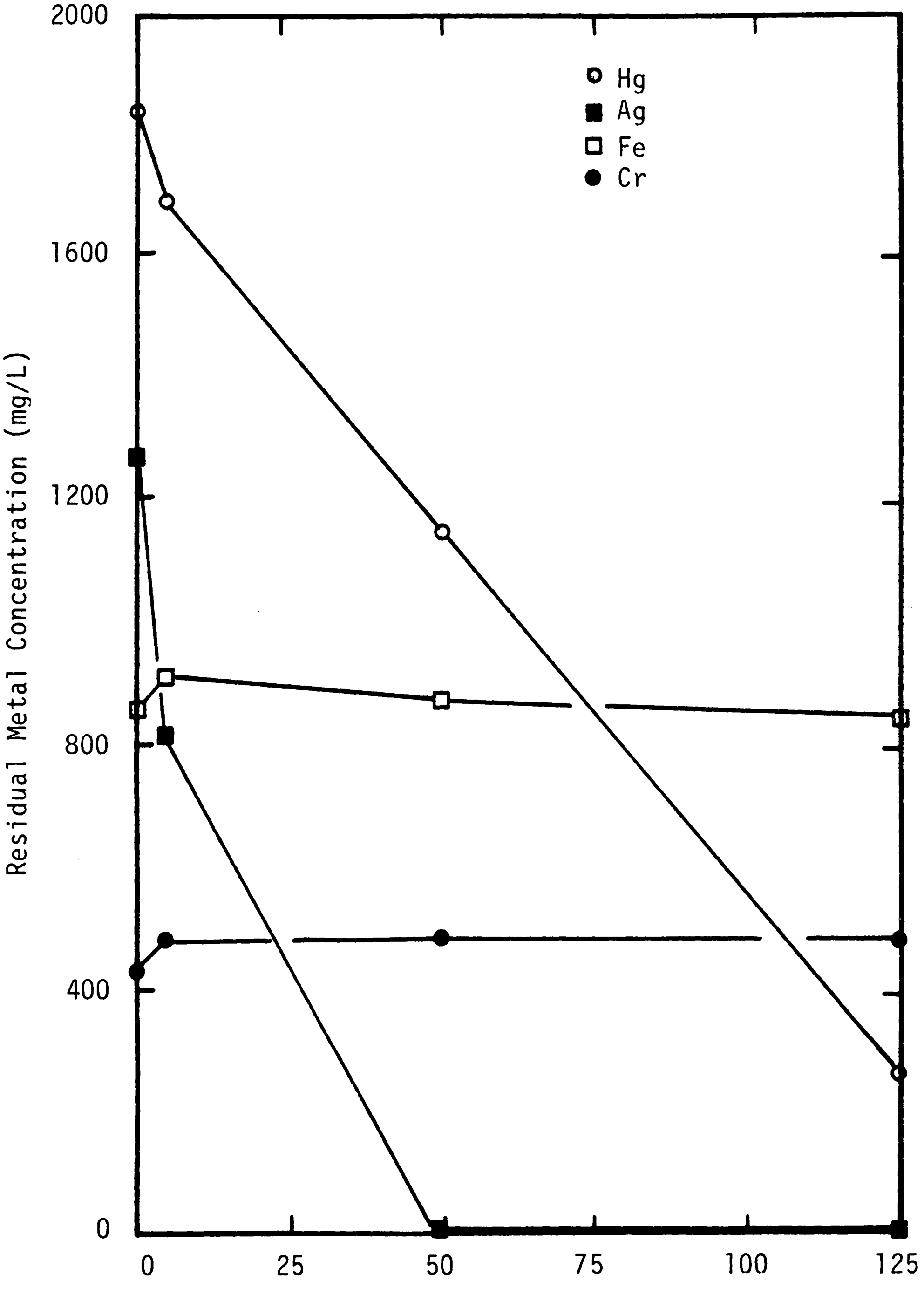


Figure 11. Metals Removal by Batch Ion Exchange for Resin Corning-Y.

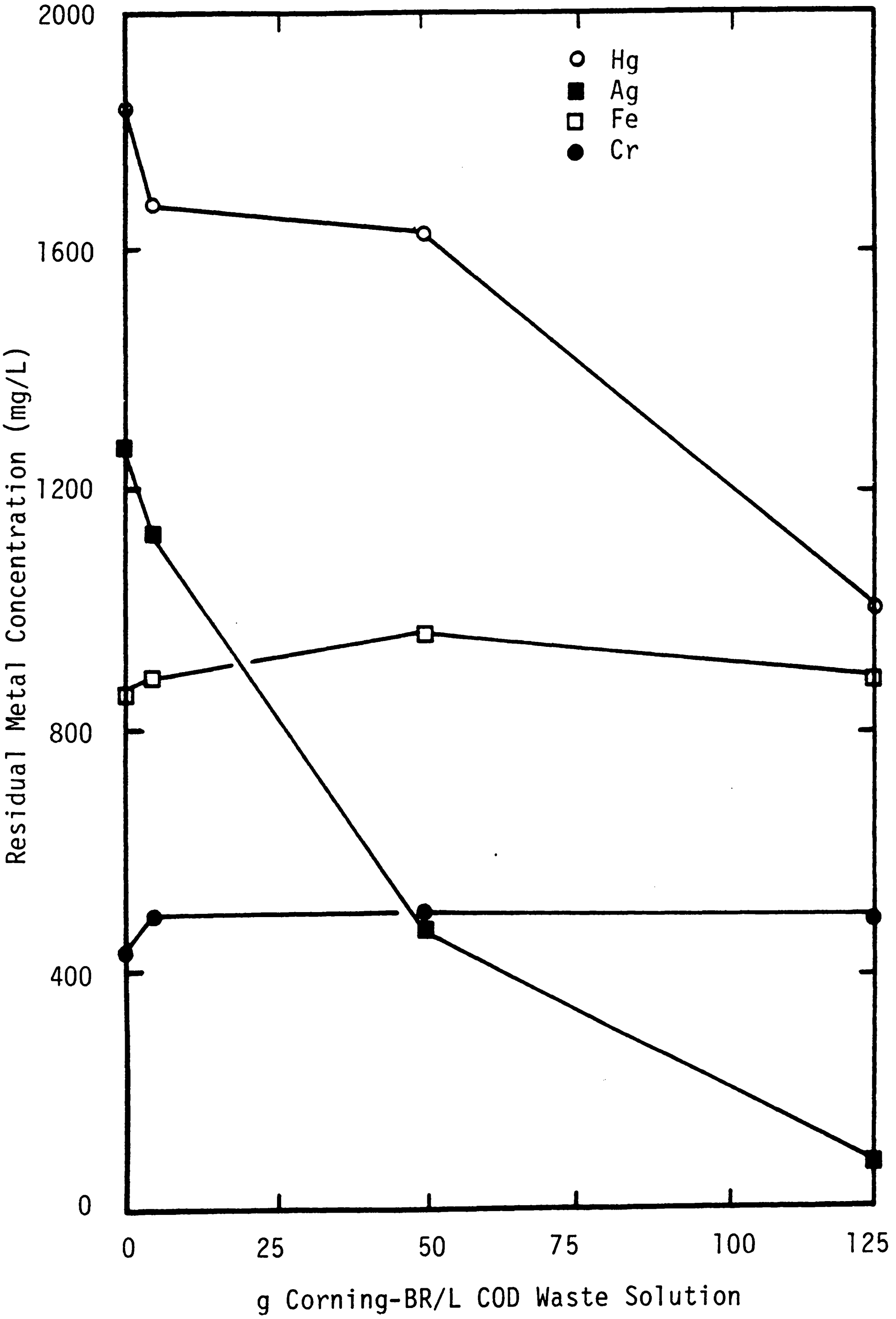


Figure 12. Metals Removal by Batch Ion Exchange for Resin Corning-BR.

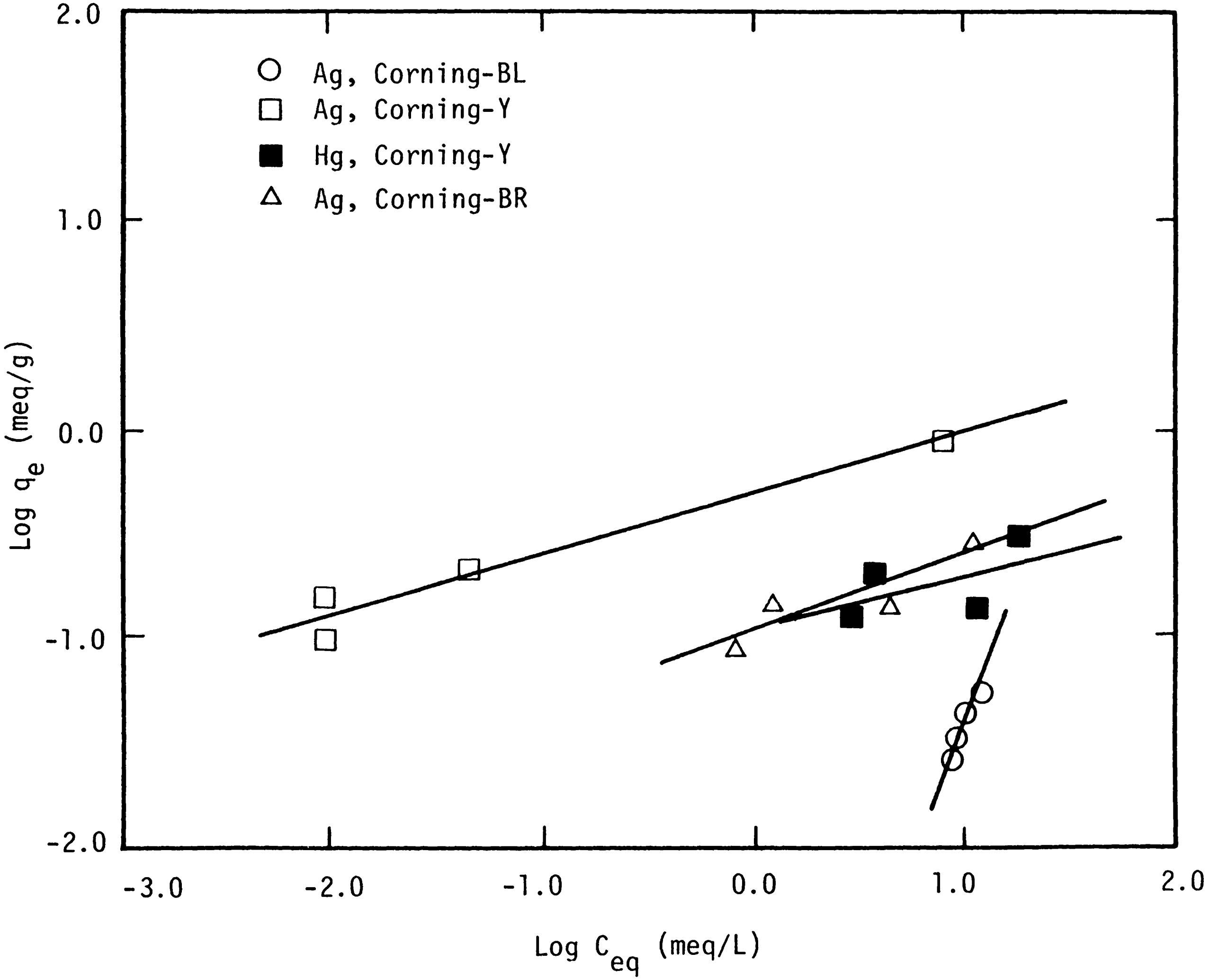


Figure 13. Freundlich Isotherms for Silver and Mercury Ion Exchange From COD Waste Solutions With Laboratory Resins.

Table 2. Silver and Mercury Uptake in Equilibrium Experiments Using Laboratory Resins and COD Waste Solutions.

Isotherm	Silver		Mercury	
	C_{eq} (meq/L)	q_e (meq Ag/g resin)	C_{eq} (meq/L)	q_e (meq Hg/g resin)
Corning Resin-BL	11.8	0.06	-	-
Corning Resin-Y	11.8	1.00	18.4	0.23
Corning Resin-BR	11.8	0.25	-	-

resin capacities (q_e) are given at equilibrium metal ion concentrations (C_{eq}).

Corning-Y was less effective for removal of mercury ions than silver ions as was Corning-BR for removal of silver ions. The preference of Corning-Y resin for silver and mercury ion uptake by an anionic resin may be attributed to the formation of negatively charged metal-sulfato complexes (25). In addition, weak base anion exchangers with amino groups have a strong affinity for silver and mercuric salts due to the formation of amine complexes with the metal co-ions, thus resulting in efficient removal of metal cations by anion exchange resins (25).

Removal of silver and mercury from COD waste solutions with Corning-BR can be attributed to both anion and cation exchange. A similar mechanism as that discussed above for Corning-Y would result in anion exchange of negatively charged silver and mercury complexes. In addition, the high ionic strength of the COD waste solution causes a more rapid decrease in the activity of the trivalent iron and chromium cations and divalent mercury ions (Figure 1). This decrease in ion activity, in addition to the decrease in the Donnan potential caused by high solution concentration, can result in an exchange preference for ions of lower charge (27). This exchange preference was observed for each resin; silver removal was most efficient, while limited mercury uptake occurred. No exchange of the trivalent iron or chromium ions occurred.

The cationic resin, Corning-BL, was the least effective in silver ion uptake; at an equilibrium silver concentration of 11.8 meq/L (1270 mg/L), q_e was calculated as 0.06 meq Ag/g resin (Table 2). The steep slope of the silver isotherm for Corning-BL shows that uptake remained relatively low as resin quantities were increased (Figure 13).

Continuous-Flow Column Studies. Experiments using ion exchange columns operated in a continuous flow, fixed-bed mode were conducted with resins Corning-Y and Corning-BR. These resins were selected for use in the column studies based on the exchange capacity determined from the batch equilibrium studies. Due to the low exchange capacity for silver and mercury ions, the cationic resin, Corning-BL, was not evaluated in column experiments. The objective of the column studies was to evaluate resin operating capacity and regeneration potential.

Table 3 lists the operation data for each service and regeneration cycle used in the column studies. Service cycles were conducted in order to maintain a resin exchange contact time of approximately 10 minutes except for the first service cycle conducted with Corning-Y, which was operated at a contact time of 6.8 minutes. Columns were operated in the service cycle until effluent silver concentrations equaled influent concentrations, which generally required a minimum of 300 mL of COD waste solution. Regeneration cycles were conducted with 50% H_2SO_4 until silver ion concentrations reached approximately 100-150 mg/L in the regenerant solution.

Effluent samples were collected during column operation at

Table 3. Continuous-Flow Column Operation Data.

Operation Cycle	Volume Resin Used (mL)	Average Flow Rate (mL/min)	Empty Bed Contact Time (minutes)	Total Volume Waste Treated (mL)	Total Volume 50% H_2SO_4 Regenerant Used (mL)
Corning-Y + COD Waste Solution					
Service #1	37.1	5.5	6.8	500	-
Regeneration #1	37.1	2.0	-	-	130
Service #2	37.1	3.9	9.5	600	-
Regeneration #2	37.1	2.5	-	-	60
Corning-BR + COD Waste Solution					
Service #1	32.4	3.1	10.5	300	-
Regeneration #1	32.4	2.2	-	-	100
Service #2	32.4	2.7	11.9	300	-
Regeneration #2	32.4	1.3	-	-	50
Corning-BR + pH 4.7 Treated COD Waste Solution					
Service #1	32.4	3.2	10.2	350	-
Regeneration #1	32.4	1.2	-	-	60

Table 3. Continuous-Flow Column Operation Data (Continued).

Operation Cycle	Volume Resin Used (mL)	Average Flow Rate (mL/min)	Empty Bed Contact Time (minutes)	Total Volume Waste Treated (mL)	Total Volume 50% H_2SO_4 Regenerant Used (mL)
Corning-BR					
COD Waste Solution Service Cycle	29.4	3.4	8.6	300	-
$Fe_2(SO_4)_3$ Service Cycle	29.4	1.6	18.4	490	-
Regeneration	29.4	1.9	-	-	140
Corning-BR					
COD Waste Solution Service Cycle	28.8	2.7	10.8	320	-
Ag_2SO_4 Service Cycle	28.8	0.55	52.4	1070	-

regular intervals and analyzed for silver, mercury, iron, and chromium concentrations. In all cases except where a synthetic waste solution containing ferric sulfate was treated in a Corning-BR resin column, effluent iron and chromium concentrations remained equal to influent concentrations. Therefore, the following presentation of results and discussion will concentrate on removal and regeneration efficiencies of silver and mercury ions. Effluent iron and chromium concentrations are provided in Appendix B.

The resin operating capacity of each service cycle was calculated by first plotting effluent (C_e) silver and mercury concentrations versus the volume of waste treated (ion exchange breakthrough curves). The area between the influent metal ion concentration (C_0) and effluent concentration (C_e) was calculated as the total mass of metal ions removed. The columns were operated to complete exhaustion with respect to silver and mercury uptake; therefore, the area calculated as metal ion uptake per gram of resin represents the resin operating capacity.

Resin regeneration efficiencies were determined in a similar fashion. Effluent metal ion concentrations were plotted against the volume of regenerant solution used. The area under the regeneration curve was then integrated as the mass of metal ions recovered. The area which was calculated per gram of resin represents regeneration efficiency.

A Corning-Y resin column was treated with a COD waste solution during two service cycles and regenerated with 50% H_2SO_4 following each service cycle. Figure 14 represents the silver and mercury breakthrough curves for the first service cycle; raw data for the second service cycle and each regeneration cycle are presented in Appendix B. A summary of the silver and mercury removal and regeneration efficiencies indicates that only 4.1% of the total Corning-Y column removal capacity (2.0 eq/L resin) was used after column exhaustion during the first service cycle (Table 4). The percent of the total capacity of the resin utilized decreased to 1.6% following failure of the column after the second service cycle conducted with a COD waste solution. The exchange capacity of Corning-Y during the initial service cycle was lower with respect to mercury than silver ions. Mercury breakthrough was also much more rapid than silver breakthrough during column operation. Results from the second service cycle indicated the exchange capacity of both silver and mercury decreased when compared to the first service cycle. Recovery of silver and mercury ions, during the regeneration cycles, was less than 10% in all cases for Corning-Y (Table 4). Regeneration efficiency also decreased with respect to mercury ions, when comparing cycle #1 to cycle #2.

Continuous-flow column study results for silver and mercury removal from a COD waste solution using Corning-BR are presented in Figure 15. As observed with the Corning-Y resin column, breakthrough of mercury ions occurred prior to breakthrough of silver ions during operation of the Corning-BR resin column. Mercury concentrations in the column effluent increased to levels higher than

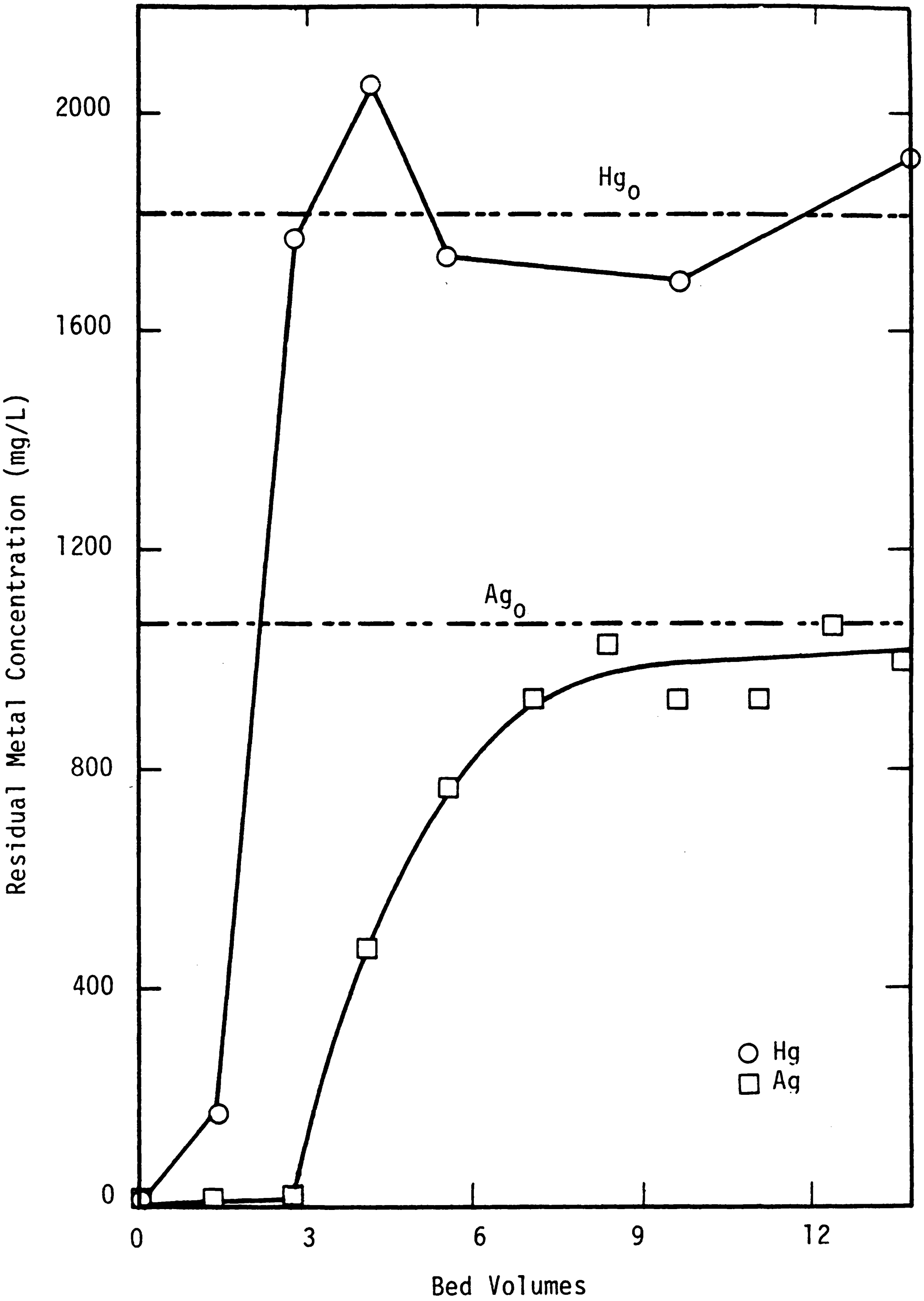


Figure 14. Breakthrough Curves for Silver and Mercury Ions From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions With Resin Corning-Y.

Table 4. Removal and Recovery Efficiency of Metal Ions From Continuous-Flow Ion Exchange Columns.

Resin	Silver		Mercury		
	meq/g Removed from Waste Solution	% Recovered in Regeneration	meq/g Removed from Waste Solution	% Recovered in Regeneration	% of Total Capacity
Corning-Y					
Cycle #1	0.060	3.1	0.044	9.8	4.1
Cycle #2	0.017	2.9	0.025	1.7	1.6
Corning-BR					
Cycle #1	0.048	26	0.014	44	2.6
Cycle #2	0.017	47	0.053	13	2.9
Corning-BR					
pH 4.7 Treated COD Waste Solution	0.042	12	0.011	25	2.2
Corning-BR					
Service #1	0.10	-	-	-	-
Service With Ag_2SO_4	0.77	-	-	-	36

Table 4. Removal and Recovery Efficiency of Metal Ions From Continuous-Flow Ion Exchange Columns (Continued).

	Silver		Iron		
Resin	meq/g Removed from Waste Solution	% Recovered in Regeneration	meq/g Removed from Waste Solution	% Recovered in Regeneration	% of Total Capacity
Corning-BR					
Service #1	0.083	-	-	-	-
Service With $Fe_2(SO_4)_3$	-	22	2.7	-	-
Regeneration #1	-	13	-	120	120

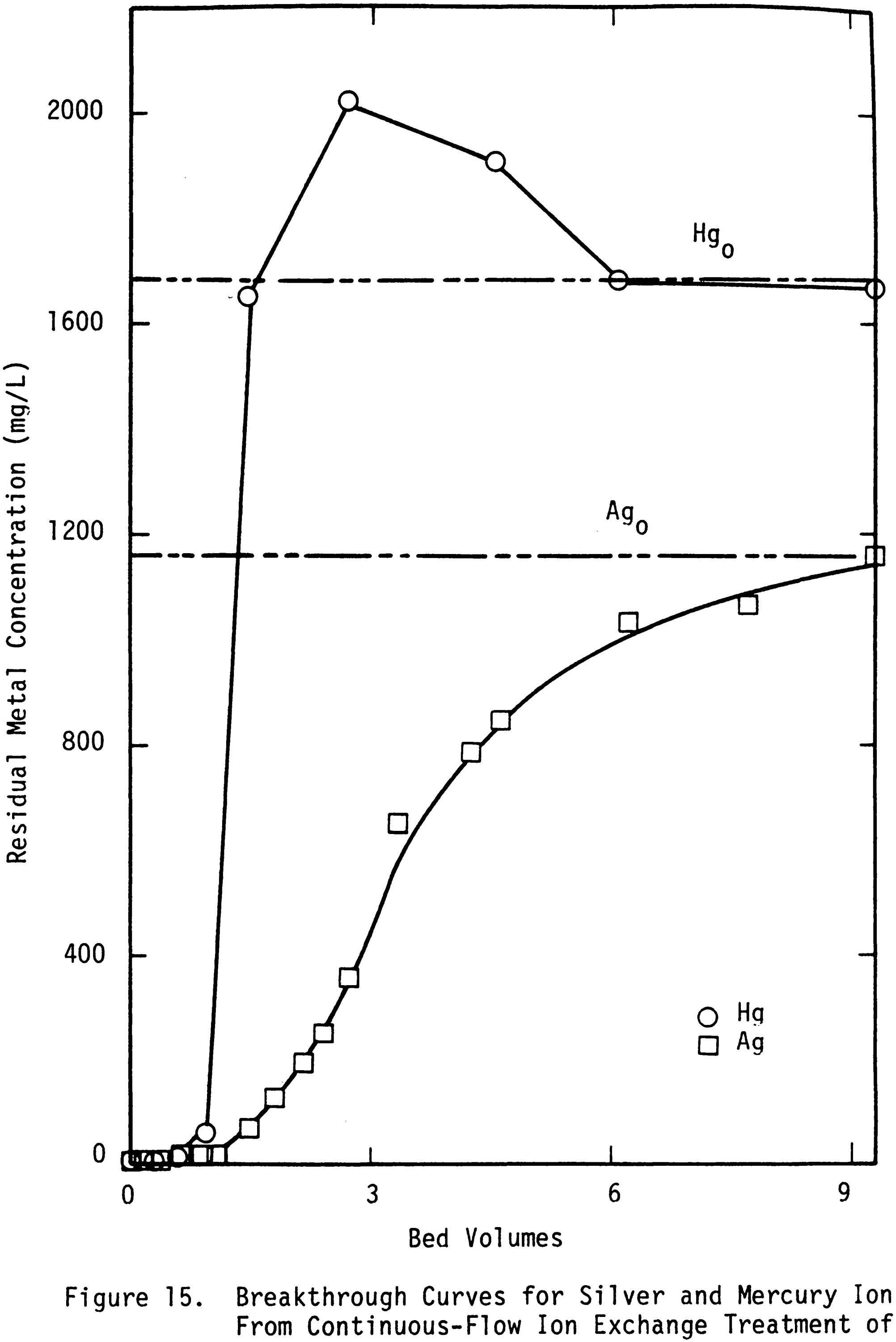


Figure 15. Breakthrough Curves for Silver and Mercury Ions From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions With Resin Corning-BR.

those initially present in the COD waste solution, during portions of the first service cycle. The apparent release of mercury ions from the ion exchange resin was also observed for service cycle #2. The total silver and mercury ions removed from the COD waste solution prior to failure of the column was low compared to the total column capacity; less than 3% of the available exchange capacity reported for the resin was used in each service cycle. Silver ion exchange capacity was 0.048 meq Ag/g resin, while 0.014 meq Hg/g resin were exchanged during the first service cycle. Exchange of silver decreased to 0.017 meq Ag/g resin during the second cycle while mercury ion exchange increased to 0.053 meq Hg/g resin. These results, along with regeneration efficiencies, are summarized in Table 4.

Comparison of the two resins, Corning-Y and Corning-BR, showed that Corning-Y had a higher initial capacity for both silver and mercury ions (on a milliequivalent per gram of resin basis) than Corning-BR (Table 4). However, regeneration of the Corning-BR column with 50% H_2SO_4 resulted in a higher percentage of recovered silver (26%) and mercury (44%) than was recovered by acid regeneration of Corning-Y. Recovery of silver for Corning-Y was only 3.1% and mercury was 9.8% for the first regeneration cycle.

The low percent of available exchange sites actually used upon column failure was attributed to the extreme ionic strength of the COD waste solution. Several factors can produce low ion exchange column capacities when resins are used to treat high ionic strength solutions including a reduction in the amount that a resin swells and a reduction in the osmotic pressure difference in the interior of a resin, causing a decrease in the driving force for solvent uptake (25).

The low regeneration efficiency of the resins was partially attributed to the nature of the resins; Corning-Y is an anion exchange resin and Corning-BR is a mixture of both cation and anion exchange sites. Anion resins are typically regenerated with a basic pH solution or a salt solution. Therefore, higher regeneration efficiencies could be anticipated if solutions such as NaOH or NH_4OH were used. This procedure was not implemented because acid regenerant solutions containing recovered silver and mercury ions could be recycled in the COD test procedure, whereas basic solutions would not be desirable. The presence of cation exchange sites which would be amenable to acid regeneration probably accounted for the higher regeneration efficiency which was observed for Corning-BR.

Due to the extreme reduction in resin column capacity observed during COD waste solution treatment, two additional column studies were conducted with Corning-BR to evaluate the effect of high ionic strength on total resin capacity.

A solution containing 4120 mg/L ferric sulfate ($Fe_2(SO_4)_3$) was adjusted to pH 1.4 and pumped through the resin column following failure of the column treated with a COD waste solution. The ionic strength of the $Fe_2(SO_4)_3$ solution was calculated as 0.57 M. The column was then regenerated with 50% H_2SO_4. The silver ion breakthrough curve from COD waste solution treatment and the iron breakthrough and silver recovery curves generated from treatment of the synthetic waste solution are presented in Figure 16 and summarized in Table 4.

The breakthrough curve for silver ions shows a resin capacity of 0.083 meq Ag/g resin. Subsequent treatment of the same resin column with $Fe_2(SO_4)_3$ resulted in recovery of 22% (0.019 meq Ag/g resin) of the silver from the resin and uptake of an additional 2.7 meq Fe/g resin from the $Fe_2(SO_4)_3$ solution (Figure 16). This resulted in greater than 100% utilization of the stated capacity of the Corning-BR resin column (Table 4). Regeneration of the column with 50% H_2SO_4 recovered 0.011 meq Ag/g resin and 3.2 meq Fe/g resin, accounting for 100% recovery of exchangeable iron ions and 13% recovery of the silver ions exchanged on the Corning-BR resin.

Another column containing Corning-BR was treated with COD waste solution until the effluent silver concentration was equal to the influent silver concentration. A synthetic waste solution containing a soluble silver concentration of 2160 mg/L was then prepared with silver sulfate (Ag_2SO_4) and adjusted to pH 1.6. The ionic strength of the solution was calculated as 0.043 M. Following treatment of a COD waste solution, the synthetic waste solution was treated in the same Corning-BR ion exchange column. The silver breakthrough curves for both the COD waste solution and the synthetic waste solution are shown in Figure 17. The capacity of the resin for silver ion uptake from the COD waste solution was determined as 0.10 meq Ag/g resin

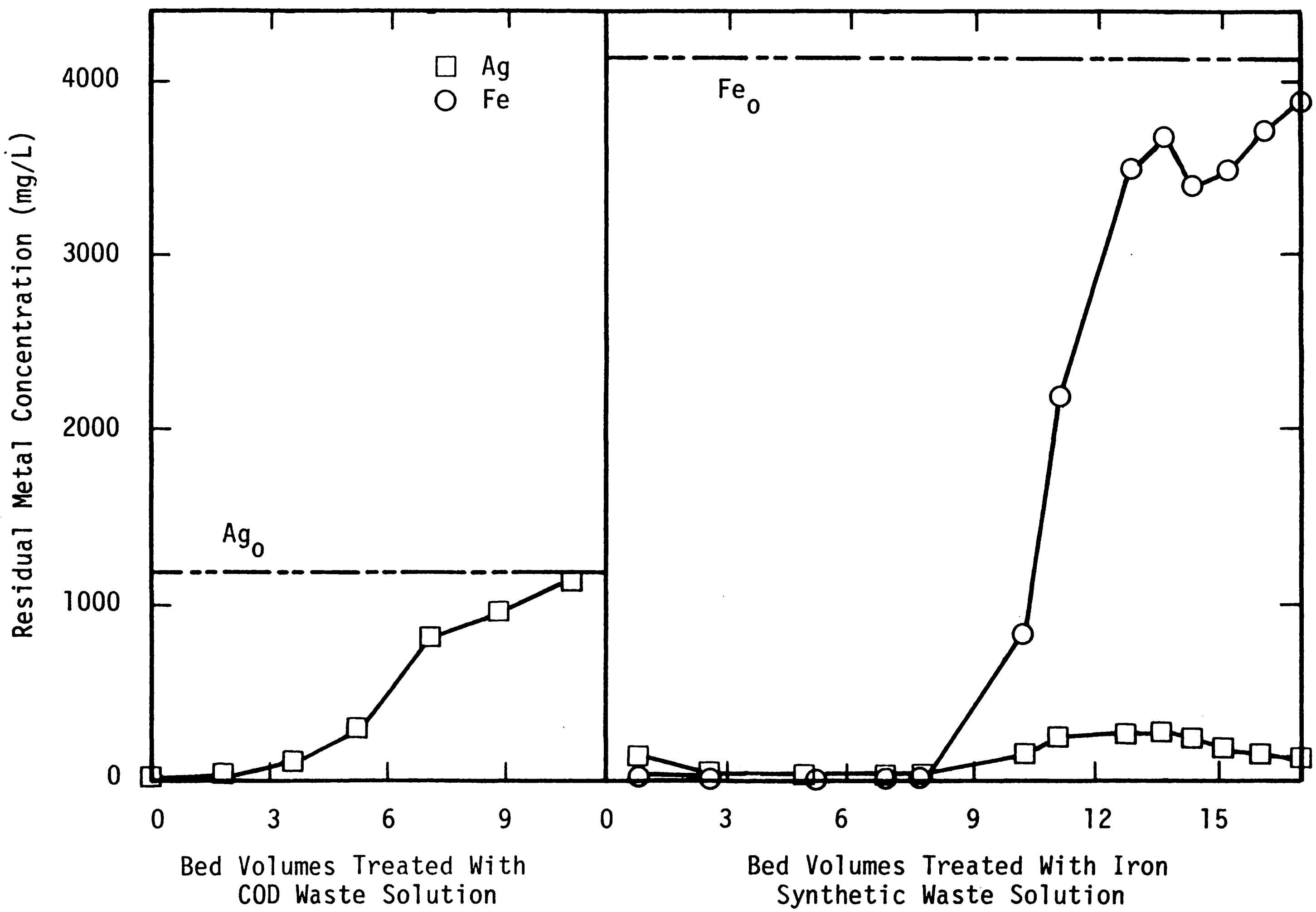


Figure 16. Breakthrough Curves for Silver and Iron From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions Followed by an Iron Synthetic Waste Solution (Resin Corning-BR).

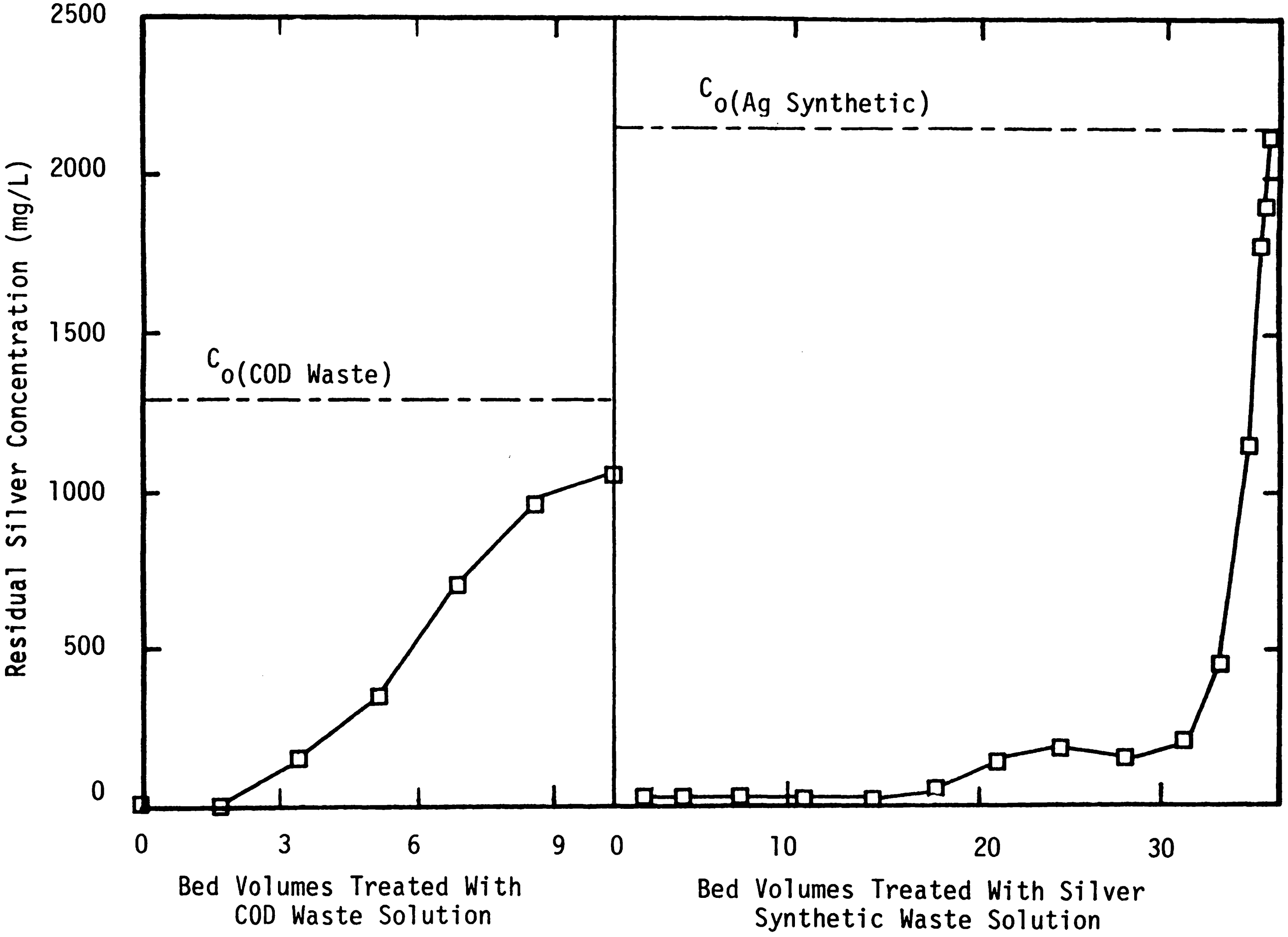


Figure 17. Breakthrough Curves for Silver From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions Followed by a Silver Synthetic Waste Solution (Resin Corning-BR).

and an additional capacity of 0.77 meq Ag/g resin was available for silver ion removal from the silver synthetic waste solution. Treatment of the two waste solutions resulted in utilization of 36% of the total resin capacity (Table 4). Acid regeneration of the column was not performed due to operational problems which occurred.

Results from the two column studies conducted with synthetic waste solutions of low ionic strength demonstrated the effects of solution ionic strength on resin capacity and ion selectivity. The high ionic strength of the COD waste solutions resulted in significant reductions in the column exchange capacity utilized. In addition, a higher percent of the total column capacity was utilized by the higher valence iron cations compared to the monovalent silver ions, when separate low ionic strength waste solutions were treated.

The final column experiments involved combining ion exchange and precipitation studies in order to determine if the two treatment processes could be used together to selectively remove and recover silver ions for reuse. Results from a precipitation study previously presented in Figure 4 showed that mercury, iron, and chromium ion concentrations could be significantly reduced by adjusting the pH of a COD waste solution to approximately 5.0, while leaving 50% of the silver ion concentration in solution. Therefore, a COD waste solution was adjusted to pH 4.7 by NaOH addition. Initial waste and treated (pH 4.7) waste soluble metal ion concentrations are given in Table 5. Mercury, iron, and chromium ions were efficiently removed; soluble

Table 5. Reduction in COD Waste Metal Ion Concentrations Following pH Adjustment.

Metal Ion	Initial Concentration (mg/L)	Concentration at pH 4.7 (mg/L)
Silver	1220	610
Mercury	2410	130
Iron	870	30
Chromium	360	20

silver ion concentrations were reduced from 1220 mg/L to 610 mg/L, as a result of the pH adjustment. The solid precipitate was separated and the supernatant solution used in a continuous-flow column containing Corning-BR resin. The silver ion breakthrough curve is shown in Figure 18, in addition to column effluent hydrogen ion concentrations. Iron and chromium ion concentrations remained equal to influent concentrations during the column operation. Mercury ion concentrations were reduced to approximately 130 mg/L in the pH-adjusted COD waste solution prior to ion exchange treatment. Mercury ion breakthrough was not as rapid as that observed for previous Corning-BR column studies conducted with untreated COD waste solution; the raw data are given in Appendix B.

Resin capacity was not significantly affected by the increased pH of the influent solution. The amount of silver exchanged by the resin was 0.042 meq Ag/g resin; mercury uptake was 0.011 meq Hg/g resin (Table 4). These results were similar to those determined during previous column studies conducted using Corning-BR and COD waste solutions; only 2.2% of the total reported exchange capacity was used when pH-adjusted waste was treated until the column failed. Column effluent hydrogen ion results are also shown in Figure 18. The resin, operated in the hydrogen cycle, released 0.045 meq H^+/g resin during column operation, showing a close agreement with the total amount of silver exchanged onto the resin. Silver and mercury regeneration efficiencies decreased to 12% and 25% respectively for the column treated with pH-adjusted COD waste solution; regeneration

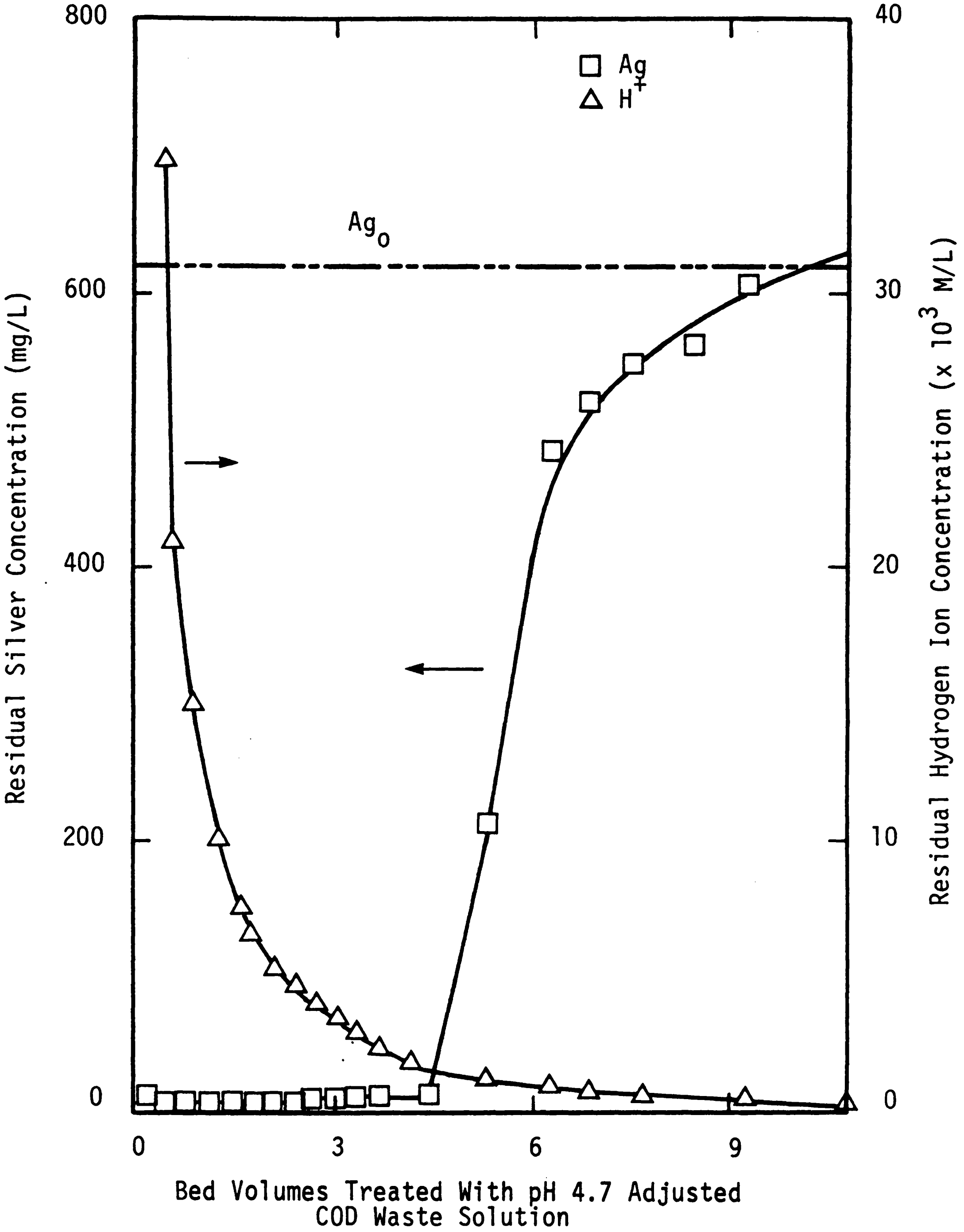


Figure 18. Breakthrough Curves for Silver and Hydrogen Ions From Continuous-Flow Ion Exchange Treatment of Treated (pH 4.7) COD Waste Solutions (Resin Corning-BR).

of a Corning-BR column treated with COD waste solution was approximately 26% for silver ions and 44% for mercury ions (Table 4).

Results from this study indicate that the extreme low pH of the COD waste solution (pH < 1.0) did not adversely affect the ion exchange reaction to the extent that solution ionic strength did. COD waste solutions and treated (pH 4.7) COD waste solutions are both solutions of extremely high ionic strength; total utilization of resin capacity was less than 3% for each waste solution. These results also show that silver and mercury regeneration efficiency decreased when Corning-BR was used to treat a pH-adjusted waste solution.

Solids Analyses

Solids analyses were conducted on COD waste solutions to determine the extent to which pH adjustment of the waste solution would reduce the volume of waste which requires handling. Although precipitation of metals does not easily result in a recoverable product, costs can be significantly affected by reductions in the volume of hazardous waste which requires transport, disposal, or treatment. Careful selection of the proper solution pH, combined with ion exchange treatment, can provide a treatment regime for both removal and recovery of selected metal ions and reduced volumes of hazardous wastes which would require treatment or disposal.

Total solids, total dissolved solids, and total suspended solids concentrations of a COD waste solution were determined. The solution was adjusted to pH 7.6 with NaOH. The results are summarized in Table 6 and show that the total solids concentration of the solution was 374 g/L. The total suspended solids concentration was 17 g/L and total dissolved solids concentration was 371 g/L. The results shown represent average values of triplicate determinations.

COD Determination Using Recovered Silver Solutions

Acid regenerant solutions were collected from the continuous-flow column studies and used in the COD test procedure in order to determine if recovered silver could be effectively reused. The solutions were collected from acid regeneration of exhausted Corning-BR resin columns. The volume of regenerant collected was small, due to the low regeneration efficiency of the resin; therefore, an alternate method to the dichromate reflux method for determining COD was required. The EPA Micro-Method (11) was used; this method requires only 3.5 mL of sulfuric acid catalyst solution compared to the *Standard Methods* (1) requirement of 30 mL of sulfuric acid reagent. The concentration of silver used in each method is identical (6000 mg/L Ag).

Three catalyst solutions were used in the COD determination of a synthetic waste solution of Bactopeptone. One catalyst solution was prepared according to the EPA Method requirements (11). Effluent

Table 6. Characterization of Sludge Resulting From Precipitation Treatment of COD Waste Solutions at pH 7.6.

	Concentration g/L
Total Solids	374
Total Dissolved Solids	371
Total Suspended Solids	17

regenerant solutions were used as the remaining two test solutions; one solution was used, as collected, from the column and the second solution was collected and spiked with silver sulfate. The chemical composition of each solution is listed in Table 7.

The EPA Method (11) is designed to detect trivalent chromium (Cr^{+3}) at a wavelength of 600 nm. However, the regenerant solutions from the ion exchange columns contained concentrations of 30-50 mg/L Cr^{+3} (Table 7) which caused erroneous results in the COD test procedure due to the detection of additional Cr^{+3} other than that present from the oxidation-reduction reaction. The EPA Method (11) was modified according to Molof and Zaleiko (34) to detect Cr^{+6} at a wavelength of 440 nm. Analyses of standard potassium hydrogen phthalate (KHP) solutions and Bactopeptone samples of varying concentrations indicated that the standard concentration versus % Transmission curve would be accurate only for COD values between approximately 250 and 1000 mg/L. The test procedure was also modified to use 1:3 (1 part reflux mixture : 3 water) dilutions of each standard and test solution for spectrophotometric measurements. According to Molof and Zaleiko (34), Beer's law is more closely followed at 440 nm when diluted reflux mixtures are used. Interferences due to ferric ions (Fe^{+3}) were not of concern according to Jirka and Carter (35) who investigated and found no interferences at concentrations below 5 g/L Fe^{+3}.

Results from the test procedure show a COD of the synthetic waste solution (Bactopeptone) of 890 mg/L when standard reagents and

Table 7. Comparison of COD of a Synthetic Waste Using Standard Catalyst Solutions and Recovered Silver Catalyst Solutions From Ion Exchange Columns.

	Chemical Composition of Catalyst Solution					
Reagent	H_2SO_4 Strength* (%)	Silver (mg/L)	Mercury (mg/L)	Iron (mg/L)	Chromium (mg/L)	COD (mg/L)
Standard Catalyst Solution	100	6000	-	-	-	890
Effluent From Acid Regeneration of Corning-BR Ion Exchange Column + Ag Spike with Ag_2SO_4	50	5000	240	30	20	630
Effluent From Acid Regeneration of Corning-BR Ion Exchange Column	50	1100	650	50	40	700

*100% denotes concentrated H_2SO_4 (36 N) required by the COD test procedure (11).

catalyst solutions were used (Table 7). Effluent taken from the ion exchange columns and used in the COD test procedure resulted in COD values of 630 mg/L for the catalyst solution spiked with silver sulfate and 700 mg/L COD for the unspiked catalyst solutions. Both regenerant solutions contained 50% H_2SO_4 compared to 100% H_2SO_4 used in the standard catalyst solution. The spiked catalyst solution contained 5000 mg/L Ag and the unspiked catalyst solution contained 1100 mg/L Ag (Table 7). These results indicated that the decrease in observed COD values was attributed to the reduced concentration of H_2SO_4 used, rather than the reduced silver ion concentration. This theory was further evaluated by conducting another series of COD tests.

Synthetic waste solutions of approximately 600 mg/L COD and 1000 mg/L COD were prepared with Bactopeptone. Catalyst solutions which contained 100% H_2SO_4, 50% H_2SO_4, and 25% H_2SO_4 were used in the EPA Method (11). The silver concentration of each catalyst solution was determined as 7400 mg/L, 4000 mg/L, and 4100 mg/L respectively. COD values of the synthetic waste solution were determined according to the EPA Method (11) using a wavelength of 600 nm.

Results from the test procedure given in Table 8 show a COD of 980 mg/L when standard catalyst reagents (100% H_2SO_4, 7400 mg/L Ag) were used. A COD of 720 mg/L was determined for an identical waste solution when a 50% H_2SO_4 catalyst solution containing 4000 mg/L Ag was used. The 25% H_2SO_4 catalyst solution produced a COD value of 510 mg/L (Table 8). A similar trend was observed for a lower strength waste solution of 570 mg/L COD. COD values of 320 mg/L and

Table 8. Comparison of COD of a Synthetic Waste Using Varying Strengths of Sulfuric Acid Catalyst Solutions.

		COD (mg/L)	
H_2SO_4 Strength* (%)	Silver (mg/L)	860 mg/L Bactopeptone	500 mg/L Bactopeptone
100	7400	980	570
50	4000	720	320
25	4100	510	330

*100% denotes concentrated H_2SO_4 (36 N) required by the COD test procedure (11).

330 mg/L were recorded respectively, for the 50% and 25% H_2SO_4 catalyst solutions used in the test procedure.

The results from this study were not conclusive but indicated that the strength of sulfuric acid used in the COD test procedure may be a more critical parameter than the concentration of silver. Moore (9) determined that reducing the amount of silver catalyst used in the Standard Methods (1) procedure to 7.5 g Ag_2SO_4/2.5 L H_2SO_4 (to produce a silver concentration of 2075 mg/L) did not significantly decrease the accuracy of COD test results. Another factor important in the COD test procedure is the chemical nature of the organic compounds; refractory organics may require both 100% H_2SO_4 and maximum silver concentrations in order to accomplish complete oxidation in either the Standard Methods (1) or EPA Method (11) for COD determination.

V. DISCUSSION

The waste generated from the dichromate reflux method for determining Chemical Oxygen Demand (1) is highly acidic and contains high concentrations of silver, mercury, iron, and chromium ions. One objective of this study was to investigate the impact of solution ionic strength on removal and recovery characteristics of metal ions from COD waste solutions. Results obtained from the studies indicate that the high ionic strength of COD waste solutions and high metal ion concentrations dictate both ion exchange and precipitation reactions.

Increases in solution concentration cause a reduction in the electric potential difference (Donnan potential) between the ion exchanger and electrolytic solution. The reduction in selectivity for higher charged species, in addition to the reduction in activity of trivalent cations in high ionic strength solutions, affected the removal of metal ions from COD waste solutions. Iron and chromium ions remained in solution while silver and mercury ions were exchanged by the cationic resins evaluated. Removal of silver and mercury ions also occurred with anionic resins due to chemical interactions between the resin matrix and the metal ions in solution.

The effect of high ion concentrations and high ionic strength solutions on ion exchange equilibrium reactions is an important consideration for the selection of resins. Ion exchange processes are often selected for removal of divalent and trivalent metal ions from aqueous solutions. Removal of these metal ions from high strength waste solutions, such as COD waste solutions, may not occur. However, the use of cation exchange or anion exchange resins may be practical in certain applications for removal of monovalent and divalent metal ions which would not typically be considered for removal by ion exchange processes in mixed metal wastewaters.

Another factor for consideration when evaluating the potential of ion exchange for treatment of waste solutions such as COD waste is the specificity of the resin. The ion exchange preference of ion-specific resins, such as the mercury-specific resin evaluated (Duolite ES-465), was not affected by the ionic strength of the COD waste solution. Neither iron nor chromium ions were removed from COD waste solutions or a low ionic strength synthetic waste treated with this resin. This exchange preference can be attributed to the specificity of the resin. Duolite ES-465 contains thiol groups which form highly stable compounds with mercury called mercaptides (31). Therefore, the nature of the resin itself is important in selecting the proper resin for ion exchange treatment.

Although Duolite ES-465 was more efficient than either of the commercial cation resins evaluated (Duolite C-20 and Amberlite IR-120 Plus) for removal of silver and mercury ions, use of this resin for recovery of metal ions may be limited. A concentrated solution of hydrochloric acid (37% HCl) is required for total regeneration of a Duolite ES-465 resin column (31). This regeneration technique would not be suitable for reuse of silver and mercury in the COD test procedure due to the high concentration of chloride ions which cause interferences in the Standard Methods (1) procedure. An alternate regenerant such as sulfuric acid, which would provide a desirable solution for reuse in the COD test procedure, may not efficiently regenerate the resin column due to the specific nature of the resin. Therefore, although removal of metal ions such as silver and mercury may be efficient with a particular resin, regeneration with the desired acid solution may not be effective.

Additional objectives of this study were to determine if ion exchange and precipitation could provide an economically feasible method for recovery and reuse of silver and mercury, in addition to a reduction in the volume of hazardous waste which would require ultimate disposal. Removal of silver and mercury ions from COD waste solutions was accomplished by ion exchange, although silver removal efficiencies were low for each resin evaluated. Mercury removal was less efficient than silver removal from the waste solution. The ionic strength of the COD waste solution affected column capacity; less than 5% of the total column exchange capacity was utilized for resins Corning-Y and Corning-BR. Results from the study also indicated that recovery of metal ions from acid regeneration of the columns was low and ranged from 3 to 50%. Therefore, the resins evaluated in continuous-flow column studies did not provide a feasible method for removal and recovery of silver and mercury from COD waste solutions.

Successful use of ion exchange treatment of COD waste solution and acid regeneration for recovery and reuse of silver and mercury in the COD test procedure was further minimized by the use of 50% sulfuric acid regenerant solutions. Sulfuric acid regeneration of exhausted resins provides an advantage because the metal ions can be recovered in the sulfate form. However, test results indicated that the concentration of sulfuric acid solution used was an important factor in providing for complete oxidation of organic matter. The concentration of silver sulfate used in the catalyst solution did not appear to be the critical parameter in COD determination of Bactopeptone. Therefore, reuse of the regenerant solution in the COD test procedure may be prohibitive due to the concentration of regenerant used.

Additional research should be conducted to determine if alternate resins are available which would provide higher removal and recovery efficiencies of silver and mercury ions. In addition, the effect of sulfuric acid and silver catalyst concentrations on complete oxidation of organics should be evaluated with various wastewaters.

Reductions in the volume of waste which require disposal could be accomplished by precipitation of metal hydroxides. Suspended solids concentrations of 17 g/L would result in a significant reduction in the volume of waste material which requires disposal. The remaining supernatant solution contained dissolved solids concentrations of approximately 371 g/L. However, the concentration of metal ions in the supernatant solution was low and the solution could possibly be disposed of as a nonhazardous waste, thereby reducing the cost of regulated handling.

Combined ion exchange and precipitation processes offer the potential for removal of silver and possibly mercury and selective precipitation of the remaining metal ions. Better removal and recovery efficiencies of silver and mercury may have been obtained during this study if dilutions of the original COD waste solution had been made prior to application to the ion exchange resin. This would have resulted in a reduction in waste ionic strength and corresponding increase in ion activity. Too great a dilution should be avoided, though, since a significant decrease in solution ionic strength might begin to enhance the removal of trivalent ions such as iron and chromium, as was observed with synthetic waste solutions. These ions were excluded during high ionic strength operations, resulting in the production of a regenerant stream that contained principally silver and some mercury.

There are certain practical advantages to the use of a recovery system such as the one described herein. First, it can potentially allow for the recovery and reuse of a chemical species like silver which is an expensive reagent to purchase. Second, because COD waste solutions are classified as hazardous wastes according to RCRA (2, 4), the cost associated with transportation and the ultimate disposal of hazardous materials can be reduced if the volume of waste which requires handling is reduced by treatment and recovery techniques.

In addition, recent RCRA revisions (5) have redefined the allowable quantity of waste exempt from full regulation. Small commercial and research facilities which generate more than 100 kg/month of hazardous waste will soon be required to comply with more stringent hazardous waste regulations than before. Ion exchange and precipitation treatment of COD waste solutions can not only reduce the volume of hazardous waste but potentially allow for recovery and reuse of expensive chemical reagents such as silver sulfate. By incorporating a recovery step into the overall treatment of COD waste solutions, the user of this technology retains the status of generator only, and is not required to comply with additional complex regulations required for hazardous waste treatment facilities. If treatment is provided with no attempt at materials recovery, then RCRA criteria designate such facilities as being both generators and treators of hazardous materials. This results in a significant increase in regulatory criteria applicable to that industry and generates much more paperwork which must be dealt with. By incorporating recovery, the facility may avoid designation as a treator of hazardous materials, even though treatment is being provided. A well designed treatment approach may result in significant reductions in overall waste quantities which must be safely disposed of, reducing overall treatment costs and possibly environmental hazards as well.

VI. SUMMARY AND CONCLUSIONS

The primary objective of this investigation was to determine if ion exchange could be used as an effective and economically feasible method for the recovery and reuse of silver and mercury from COD waste solutions. Another objective was to develop a treatment approach which would reduce the large volume of hazardous waste which requires handling and disposal. In addition, the effect of solution ionic strength on ion exchange removal and recovery characteristics was evaluated.

Results from ion exchange batch equilibrium and column studies indicated that ion exchange treatment and recovery efficiency was a strong function of solution ionic strength. Silver and mercury ions were removed through ion exchange treatment and recovered by acid regeneration, although removal and recovery efficiencies were low for both ions. The use of pH adjustment was shown to effectively reduce mercury, iron, and chromium concentrations in the treated wastewater and produce a reduced volume of hazardous material which would require handling and disposal. Regenerant solutions of 50% sulfuric acid containing principally silver ions did not provide complete oxidation of Bactopeptone in the COD test procedure.

The following conclusions were made based on the results obtained during this investigation.

1. Ion exchange selectivity was reduced due to high solution ionic strength; silver and mercury ions were exchanged with each of

the resins evaluated, while iron and chromium removal from COD waste solutions did not occur. The selectivity of the resins was attributed to a reduction in the Donnon potential and the higher relative activity of mono- and divalent cations in the high ionic strength solution.

2. Ion exchange selectivity increased in low ionic strength solutions; exchange of iron and chromium occurred, in addition to silver and mercury, from a synthetic waste solution treated with a cationic resin (Duolite C-20). Due to the low ionic strength of the synthetic waste, iron and chromium activity increased and the electroselectivity for ions of higher valence increased with the Donnan potential, accounting for exchange of the trivalent cations.
3. Solution ionic strength reduced resin capacity; significant additional capacity was available for exchange of both silver and iron cations following treatment of the resins with COD waste solutions. Increases in ion activity and additional swelling of the resin, which occurred when the resin was treated with a low ionic strength solution, were responsible for the additional resin capacity.
4. Ion exchange treatment of COD waste solutions resulted in low removal and recovery efficiencies of both silver and mercury ions due to the impact of solution ionic strength on the exchange reactions. Therefore, ion exchange methods require further evaluation before an economically feasible

method is available for recovery and reuse of metal ions from COD waste solutions.

5. Precipitation treatment can be used to selectively remove metal ions from COD waste solutions. This process will reduce the volume of waste which requires regulated handling, thereby reducing disposal costs.

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APPENDIX A

Metal Ion Hydrolysis Reactions

Metal Ion Hydrolysis Reactions (36)

AgOH

$AgOH_{(s)} \rightleftharpoons Ag^+ + OH^-$	$\log K_{so} = -8.17$
$Ag^+ + OH^- \rightleftharpoons AgOH_{(s)}$	$\log K_1 = 3.02$
$Ag^+ + 2OH^- \rightleftharpoons Ag(OH)_2^-$	$\log \beta_2 = 4.69$

HgO

$HgO_{(s)} + 2H^+ \rightleftharpoons Hg^{+2} + H_2O$	$\log {}^*K_{so} = 2.56$
$Hg^{+2} + H_2O \rightleftharpoons HgOH^+ + H^+$	$\log {}^*K_1 = -3.68$
$Hg^{+2} + 2H_2O \rightleftharpoons Hg(OH)_{2(aq)} + 2H+$	$\log {}^*\beta_2 = -6.29$
$Hg^{+2} + 3H_2O \rightleftharpoons Hg(OH)_3^- + 3H^+$	$\log {}^*\beta_3 = -21.1$
$HgOH^+ + H_2O \rightleftharpoons Hg(OH)_{2(aq)} + H^+$	$\log {}^*K_2 = -2.57$

APPENDIX B

Raw Data From Batch and Continuous-Flow Column Studies

Table B-1. Metal Ion Removal From COD Waste Solutions by Batch Ion Exchange Treatment as a Function of Contact Time (Resin Corning-Y*).

	Concentration (mg/L)			
Contact Time (Minutes)	Ag	Hg	Fe	Cr
0	1270	1840	850	430
1	330	-	870	490
5	1	1190	910	470
15	1	880	880	520
30	1	610	860	480
60	1	330	900	470

\- Data not collected

* 75g resin Corning-Y/L COD Waste Solution

Table B-2. Effluent Metal Ion Concentrations From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions With Resin Corning-Y (Service Cycle #1).

Volume Waste Treated (mL)	Concentration (mg/L)			
	Ag	Hg	Fe	Cr
Initial Conc.	1070	1810	910	430
50	2.3	170	880	410
100	6.4	1770	960	430
150	480	2050	910	410
200	770	1740	920	430
250	910	-	-	-
300	1030	-	940	410
350	910	1700	-	-
400	900	-	920	390
450	1060	-	-	-
500	1000	1920	1020	420

- Data not collected

Table B-3. Effluent Metal Ion Concentrations From 50% H_2SO_4 Regeneration of Resin Corning-Y Ion Exchange Column (Regeneration Cycle #1).

Volume 50% H_2SO_4 Regenerant (mL)	Concentration (mg/L)			
	Ag	Hg	Fe	Cr
10	80	100	<15	<5
20	70	-	<15	<5
30	80	110	20	10
40	140	450	-	-
45	60	290	<15	5
55	60	270	-	-
65	40	110	<15	<5
75	30	60	-	-
85	30	-	<15	<5
95	30	-	-	-
100	30	50	-	-
110	20	-	-	-
120	30	-	-	-
130	30	-	-	-

\- Data not collected

Table B-4. Effluent Metal Ion Concentrations From Continuous-Flow Ion Exchange Treatment of COD Waste Solutions With Resin Corning-Y (Service Cycle #2).

Volume Waste Treated (mL)	Concentration (mg/L)			
	Ag	Hg	Fe	Cr
Initial Conc.	1070	1810	910	430
10	20	57	-	-
20	380	830	670	320
30	720	-	800	360
40	920	1490	-	-
50	1210	-	840	390
60	1070	1250	-	-
70	1160	-	850	410
80	1150	1770	-	-
90	1150	-	850	390
100	1290	1580	-	-
150	1410	-	900	420
200	1400	-	-	-
250	1210	1690	850	410
300	1400	-	-	-
350	1370	-	840	390
400	1200	-	-	-
450	1380	-	810	400
500	1330	-	-	-
550	1030	-	920	430
600	1110	1790	-	-

\- Data not collected

Table B-5. Effluent Metal Ion Concentrations From 50% H_2SO_4 Regeneration of Resin Corning-Y Ion Exchange Column (Regeneration Cycle #2).

Volume 50% H_2SO_4 Regenerant (mL)	Concentration (mg/L)			
	Ag	Hg	Fe	Cr
10	40	50	15	<5
20	30	-	-	-
30	20	30	15	<5
40	20	-	-	-
50	20	20	15	<5
55	20	-	-	-

\- Data not collected

Table B-6. Effluent Metal Ion Concentrations and pH From Continuous-Flow Ion Exchange Treatment of Treated (pH 4.7) COD Waste Solutions (Resin Corning-BR).

Volume of pH Adjusted Waste Treated (mL)	Effluent pH	Concentration (mg/L)			
		Ag	Hg	Fe	Cr
Initial Conc.	4.7	610	130	30	20
10	1.5	10	<1.0	-	-
20	1.7	6.0	-	-	-
30	1.8	2.7	-	-	-
40	2.0	3.8	-	-	-
50	2.1	2.7	<1.0	40	20
60	2.2	1.4	-	-	-
70	2.3	1.5	-	-	-
80	2.3	1.4	-	-	-
90	2.4	1.7	-	-	-
100	2.5	4.0	2.0	40	20
110	2.6	1.2	-	-	-
120	2.6	3.0	-	-	-
150	2.7	9.2	-	40	20
175	2.9	210	-	-	-
210	3.0	480	80	30	20
225	3.1	520	-	-	-
250	3.2	540	70	30	20
300	3.3	610	-	-	-
350	3.4	688	80	-	-

\- Data not collected

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