

PHYSICAL-CHEMICAL TREATMENT OF ACID MINE WATER FROM A SUPERFUND SITE

MARCIA H. BATES

JOHN N. VEENSTRA

Associate Professors

JOHN BARBER

RAJU BERNARD

JULIE KARLESKINT

PARWEIZ KHAN

RAGHUPATHI PAKANTI

MICHAEL TATE

Research Assistants

*Oklahoma State University
Stillwater, Oklahoma*

ABSTRACT

Various physical-chemical treatment methodologies were evaluated for treating over 76,000 acre feet of acid mine water at the Tar Creek Superfund site in Northeastern Oklahoma. Chemical precipitation, chemical precipitation with polymer addition, activated carbon, and ion exchange were used to reduce levels of iron, zinc, cadmium, and lead to acceptable levels. All treatment techniques used were successful, but cost considerations eliminated ion exchange and activated carbon as viable options.

With the discovery of lead and zinc near Lincolnton, Oklahoma around 1901, mining activities in the three state area of Oklahoma, Kansas, and Missouri were initiated. The most active area was the Picher Field which is located in Ottawa

County, Oklahoma and Cherokee County, Kansas. Mining work in this area required continuous pumping to remove water. Iron sulfides, which were then subsequently exposed in drift ceilings, were oxidized by exposure to atmospheric oxygen. When mining activities declined and pumping ceased, the water level steadily climbed. The previously oxidized sulfides dissolved in the presence of the water forming acid mine water which resulted in the solubilization of zinc, cadmium, and lead. It is estimated that there are over 76,000 acre-feet of acid mine water in the abandoned mines of the Picher field.

Since 1979, the acid mine water has been discharging into the Tar Creek watershed in northeastern Oklahoma. The waters of Tar Creek feed the Neosho River which is one of the two major rivers in the area. The impact of the acid mine drainage on Tar Creek has been severe. The majority of the biota of the creek have disappeared and red stains from ferric hydroxide precipitates are found on banks and bridge abutments. The impact of Tar Creek on the Neosho River has been less severe. Red stains are apparent but except for zinc, no water quality standards have been violated [1].

The Tar Creek area was identified as one of the major hazardous waste sites in the United States, and, as such, was eligible to receive Superfund money. Treatment of the mine drainage using physical-chemical techniques such as precipitation, carbon adsorption, or ion exchange is one of the available options for management of the problem. Chemical precipitation is a viable and useful alternative for the removal of metals from waste streams. Sulfide precipitation of chromium, cadmium, zinc, copper, and nickel has been investigated by Whang et al. [2], and Brantner and Chichon [3] have studied carbonate, hydroxide, and sulfide precipitation of copper, lead, cadmium, and zinc. Jurkiewicz [4] and Gould et al. [5] have also studied cadmium precipitation from several wastewaters. Grosse et al. [6], DuPont [7], and Nishimura and Tozawa [8] have reported on the use of lime precipitation for treatment of metal wastes. The use of magnesium hydroxide as compared to lime to precipitate metals has been described by Teringo [9].

The potential for the use of activated carbon for the removal of metals has long been recognized, and numerous individuals have investigated the sorption of various metals onto carbon [10-14]. Corapcioglu and Huang [15] found that the most important factors affecting the sorption of metals onto carbon are carbon type, pH, and surface loading. Koshima and Onishi [16] investigated the adsorption of twenty metals onto activated carbon as a function of pH. Ku and Peters [17] have suggested the use of activated carbon as a polishing step to be used following chemical precipitation for metal removal.

Ion exchange has also been successfully used to remove metals from waste streams and may also serve as a polishing step after chemical precipitation [18]. Waitz evaluated several Rohm and Haas Amberlite resins for heavy metal removal using zinc, cadmium, nickel, manganese, magnesium, sodium, and chromium, and found that ion exchange was effective in removing the metals

from waste streams [19]. Shcheglov and Sedova studied the potential for using cation exchange for the removal of copper from wastewaters [20], and Mathur et al. investigated the use of cationic resins for the removal of heavy metals from industrial wastes [21]. The removal of lead and calcium by the ion exchange process has been studied by Loizidou using two different natural zeolites [22].

The purpose of the study reported in this article was to specifically evaluate chemical precipitation using lime and polymers for treating the Tar Creek acid mine drainage. Initial studies were also performed using activated carbon and ion exchange for treatment to obtain data necessary for cost considerations. However, due to the time constraints, detailed evaluations of the use of the carbon and ion exchange resin were not obtained.

METHODS

Twenty-six sampling sites were established by the Oklahoma Water Resources Board to monitor stream water quality and mine discharge into the Tar Creek watershed [1]. The major sites of acid mine drainage into Tar Creek were identified as 4s and 14. Water quality at both sites was monitored frequently with site 4s being the highest in zinc, cadmium, and lead, whereas site 14 had the highest iron concentration.

Acid mine drainage was collected once from site 14 and three times from site 4s by representatives of the Oklahoma Water Resources Board. Samples were collected in nitric acid washed glass bottles which had been purged with nitrogen and capped. The caps were further sealed with parafilm. Upon obtaining the samples without introduction of oxygen, the bottles were again capped and sealed with parafilm prior to transport to the Civil Engineering Laboratories at Oklahoma State University. Once at the labs, bottles were only opened as needed, and when opened, were purged with nitrogen to maintain a reducing environment. This sampling, collection, and maintenance method proved to be very effective for preservation of the samples in an anaerobic environment.

The primary alternative investigated in this study was chemical precipitation of the metals followed by settling. Preliminary data were also gathered on the applicability of activated carbon adsorption and ion exchange. The experimental procedures for each of these processes are discussed individually on the following pages.

CHEMICAL PRECIPITATION

Reduction of the heavy metal concentrations was achieved by chemical precipitation using a 10 percent by weight slurry of lime as calcium hydroxide. Analyses were also conducted to determine if settling could be improved through

the addition of polyelectrolytes. The polymers utilized in this study were Betz 1100 and Cyanamide 1839A. Both were added in 1 mg/L doses.

Betz 1100 is an anionic, low charge density, high molecular weight polymer, which can be used either as a flocculant or as a sludge conditioning aid to provide enhanced solids-liquid separation. This polymer has been tested and found to be effective for the settling of iron oxide suspensions, the settling of precipitated hydrous metals, and the settling of mixed chromium-cyanide wastes. Cyanamide 1839A is a liquid, high molecular weight, slightly anionic flocculant. This polymer has been found to be effective over a wide pH range and can be used to improve settling and filtration rates. Use of this polymer has been recommended for mechanical dewatering systems, gravity settling, and for water clarification.

ACTIVATED CARBON

The granular activated carbon utilized in this study for both batch and continuous flow investigation was obtained from Westvaco (Nuchar WV-G 12 X 40). One hundred mL samples from sites 4s and 14 were each treated with various carbon doses during batch studies (1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 grams). The samples and the carbon were placed in nitric acid washed Erlenmeyer flasks, were sealed with parafilm, and were placed on a mechanical shaker for a previously determined twenty-four-hour equilibration period. After this equilibration period, the samples were filtered through a Whatman glass fiber filter, and the filtrates were analyzed for Fe, Zn, Cd, and Pb. Activated carbon column studies were run at the native water pH using a flow rate of 5.3 mL/min and loading rate of one gallon per minute per square foot (gpm/ft²). One-half inch diameter glass columns with a fritted disc and containing two feet of carbon were used as carbon columns. Three carbon columns arranged in series and operating in a downflow mode were used to collect data during the continuous flow studies.

ION EXCHANGE

The effectiveness of ion exchange in removing heavy metals from the acid mine drainage was studied using Amberlite IRC-718, which was obtained from the Rohm and Haas Company. Fifty mL burettes with a diameter of one-half inch were used as exchange columns. The resin was added to the columns in a distilled deionized water slurry to achieve a bed depth of eighteen inches. Two columns were established, and one each was fed with drainage from 4s and 14 at a flow rate of 1.53 mL/min and a loading rate of 0.3 gpm/ft². The mine drainage was aerated approximately two hours and filtered to remove precipitated iron

prior to addition to the ion exchange columns. Fifty milliliter volumes of effluent were collected at periodic intervals and the samples were analyzed for Fe, Zn, Cd, and Pb.

ANALYTICAL TECHNIQUES

All metals were analyzed using a Perkin Elmer 5000 Atomic Absorption Spectrophotometer equipped with a HGA 400 graphite furnace. Depending on the concentrations, the metals were determined using either flame or flameless atomic absorption techniques.

TDS and TSS determinations were also carried out in accordance with the methods described in *Standard Methods* [23]. Whatman 934-AH glass fiber filters were used to remove solids from samples. pH determinations were made using either a Beckman or an Orion pH meter. Alkalinity, sulfate, and chloride were measured using Hach Chemical Company procedures [24].

RESULTS AND DISCUSSION

Water Quality Standards

In the treatment of the mine wastes and the characterization of the effluent, water quality standards were necessary for ascertaining treatment feasibility and efficiency. The values represented in Table 1 were utilized. Those values for Zn, TDS, pH, Pb, and Cd represent the maximum allowable in Oklahoma for discharge of wastewaters into intermittent streams or storm sewers [25]. The value of 0.3 mg/L for iron is a drinking water standard [26]. Table 2 shows the results of the water quality analyses of samples from sites 4s and 14. From observing the values for lead shown in Table 2 for sites 4s and 14, it can be seen that, with respect to lead, the raw water quality is within the limits utilized. The raw water cadmium concentration for site 14 is also within the discharge limits set for this study.

Chemical Precipitation Studies

Chemical precipitation studies were initiated to determine what fraction of the four metals could be removed by this process. The data obtained for sites 4s and 14 are shown in Figures 1 and 2, respectively. For these and all subsequent figures, values below the detection limits for the Perkin Elmer 5000 Atomic Absorption were plotted at the detection limit. In addition, the broad range in concentration necessitated plotting on semi-log paper.

Table 1. Water Quality Standards Used in Judging Effluent Quality

<i>Parameter</i>	<i>Standard</i>
Fe	0.3 mg/L
Zn	1.0 mg/L
Pb	0.1 mg/L
Cd	0.03 mg/L
pH	6-9 SU
TDS	1500 mg/L
TSS	45 mg/L

Table 2. Water Quality Analyses of Samples from Sites 4s and 14

<i>Parameter</i>	<i>Site 4s</i>	<i>Site 14</i>
Fe	341 mg/L	526 mg/L
Cd	0.13 mg/L	0.02 mg/L
Zn	232 mg/L	141 mg/L
Pb	0.06 mg/L	0.02 mg/L
Alkalinity	200 mg/L	320 mg/L
pH	5.2 SU	5.8 SU
TDS	5346 mg/L	5060 mg/L
Sulfate	2750 mg/L	2250 mg/L
Chloride	10 mg/L	3 mg/L
Ca as Ca	590 mg/L	648 mg/L
Mg as Mg	330 mg/L	195 mg/L

From Figure 1, it can be seen that maximum removal of iron and zinc from the drainage from site 4s occurred at a pH of 10 or higher. The pH values necessary to reach the water quality standards presented in Table 1 were approximately 9.75 for iron and 9.5 for zinc. Maximum removal of cadmium and lead from samples from site 4s occurred at a pH of 9.6 for cadmium and 10.4 for lead.

From Figure 2, it can be observed that the maximum removal of iron from samples from site 14 was obtained at a pH of 10.0, whereas maximum zinc removal occurred at pH values greater than 9.25. The pH values necessary to reach the 0.3 mg/L iron standard and the 1.0 mg/L zinc standard were 9.25 and

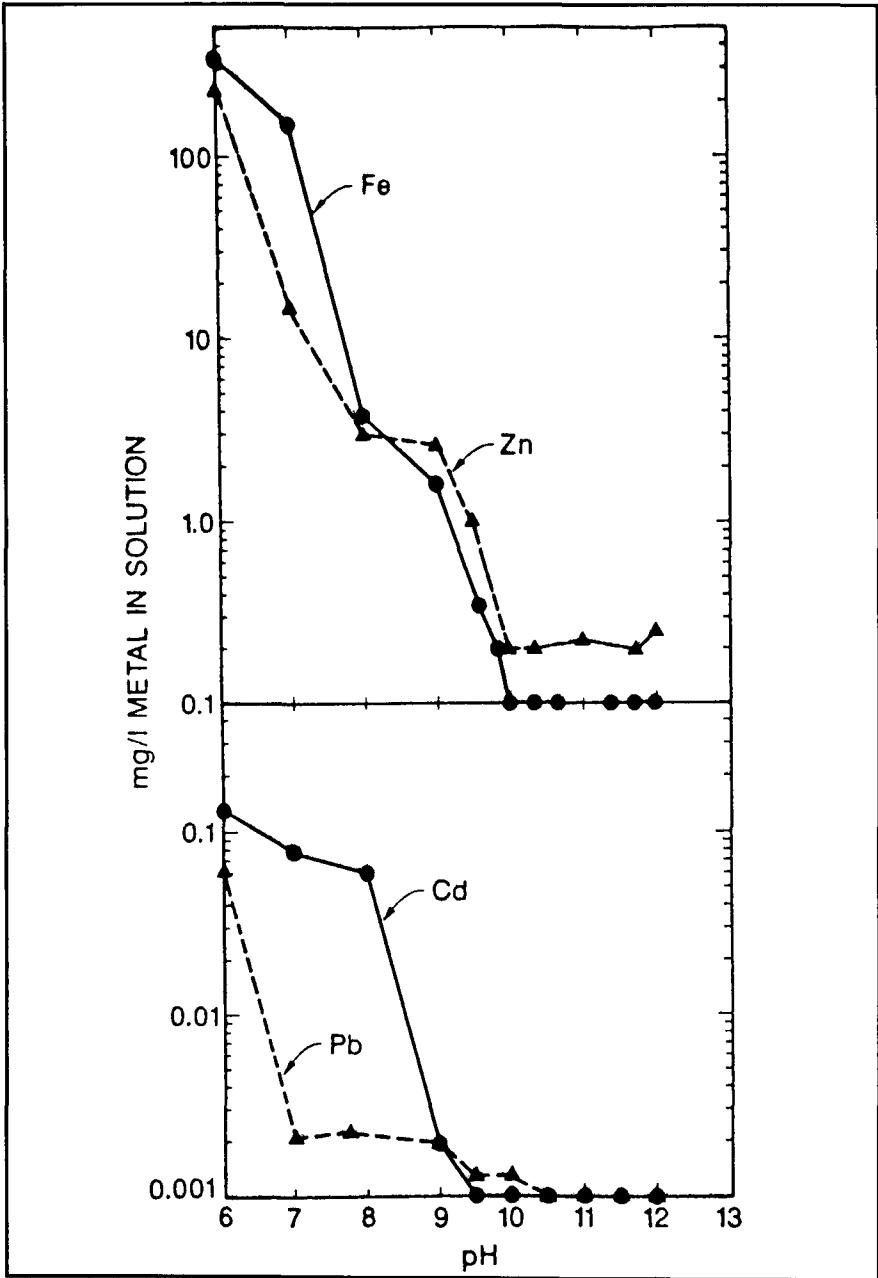


Figure 1. Results from chemical precipitation studies using lime: mg/L metal in solution versus pH—Site 4s.

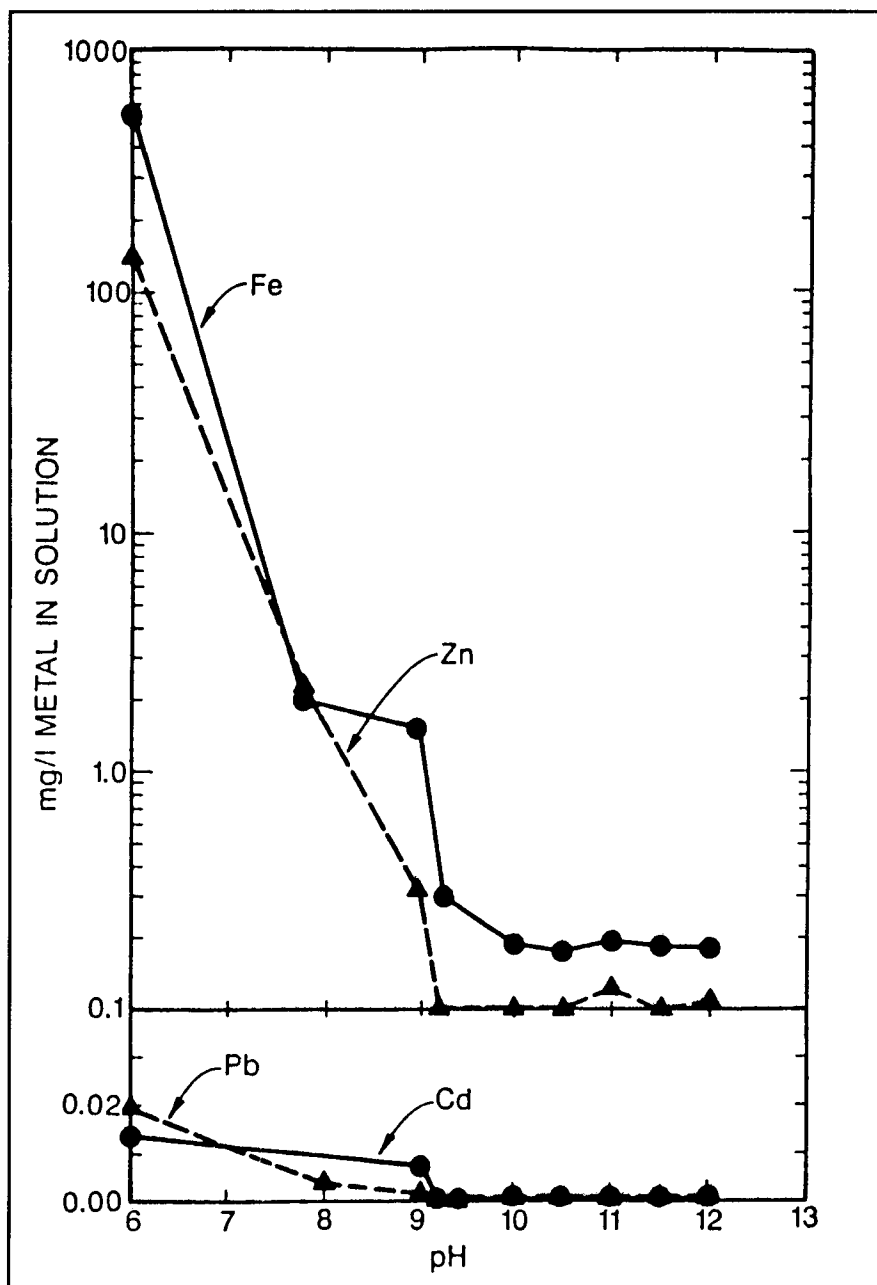


Figure 2. Results from chemical precipitation studies using lime: mg/L metal in solution versus pH—Site 14.

8.25, respectively. Maximum cadmium and lead removals were achieved at pH values greater than 9.

The average initial TDS concentration for samples from sites 4s and 14 were 5346 mg/L and 5660 mg/L, respectively. The TDS and TSS values associated with treated samples for each pH value above 9 and for each site are shown in Tables 3 and 4. As can be seen from the tables, the TSS concentrations are below the 45 mg/L discharge standard. The chemical precipitation process did serve to decrease the TDS concentration, but all resultant values are substantially higher than the 1500 mg/L standard utilized for this study.

The results from the chemical precipitation studies on mine drainage from sites 4s and 14 indicate that, at pH values necessary for the effective removal of zinc, iron can be very efficiently removed without the inclusion of aeration other than that induced by the mixing step. Assuming that combined effluents will be treated, the selected pH should be 10 or above, which will give a maximum removal of all of the metals. Chemical precipitation also produced a settled effluent with a TSS concentration less than the selected standard of 45 mg/L. However, the process was not effective for TDS control.

Chemical Precipitation Plus Polymer Addition

The effects of two polymers on the chemical precipitation process were investigated. Polymers were added to the samples in conjunction with the lime. Figure 3 compares the results obtained when using Cyanamide (Cyn) 1839A and Betz 1100 on the removal of the four heavy metals from the drainage from site 4s. Polymer studies were only conducted at pH values greater than 8, and optimal removals for all four metals when using each of the polymers occurred at pH values of 9 or higher. This pH is lower than that necessary to provide maximum removal for site 4s without the addition of polymers. The polymers, however, did not significantly affect the resultant TDS or TSS concentrations.

Figure 4 compares the effects of the two polymers in treatment efficiencies for site 14. The optimum pH for maximum removal of iron, zinc, cadmium, and lead with Cyn 1839A was 9. Maximum removal with Betz 1100 for iron, cadmium, and lead also occurred at a pH of 9. The sample prepared at a pH of 9, using Betz 1100, was inadvertently not analyzed for zinc, so the first plotted point for zinc was at a pH of 9.8. As noted with samples from site 4s, the utilization of the polymers did not significantly affect the resulting TSS and TDS values for site 14.

Activated Carbon

The use of activated carbon for heavy metal removal was investigated to determine its potential value for treating the discharged mine drainage. Figures 5

Table 3. TDS and TSS Concentrations in mg/L for Chemically Treates Samples from Site 4s

<i>pH</i>	<i>TDS</i>	<i>TSS</i>
9.0	4204	36
9.6	4468	40
9.85	4228	37
10.0	4288	35
10.4	4176	26
10.6	4036	33
11.0	4620	–
11.7	4816	29
12.0	4916	31

Table 4. TDS and TSS Concentrations in mg/L for Chemically Treated Samples from Site 14

<i>pH</i>	<i>TDS</i>	<i>TSS</i>
9.25	4476	29
10.0	4572	31
10.5	4369	30
11.0	4436	33
11.5	4528	32
13.0	4598	31

and 6 show the effects of carbon dose on metal removals for sites 4s and 14, respectively. Doses of one to ten grams of carbon were utilized. Samples from both sites treated with 1-3 grams of carbon exhibited iron oxidation and precipitation resulting in turbid yellowish-orange solutions. At carbon doses greater than 4 grams, this phenomena did not occur, possibly indicating that the carbon dose was sufficiently high to remove the iron by adsorption before it could be oxidized. For site 4s (Figure 5), maximum iron removal was achieved with 4 grams of carbon. The lowest concentration of zinc obtained, 24 mg/L, was observed at an 8 gram carbon dose. The desired effluent concentration for cadmium (0.03 mg/L) was first observed at a carbon dose of 8 grams. At all doses of carbon, effluent lead concentrations ranged from 0.008 to 0.01 mg/L.

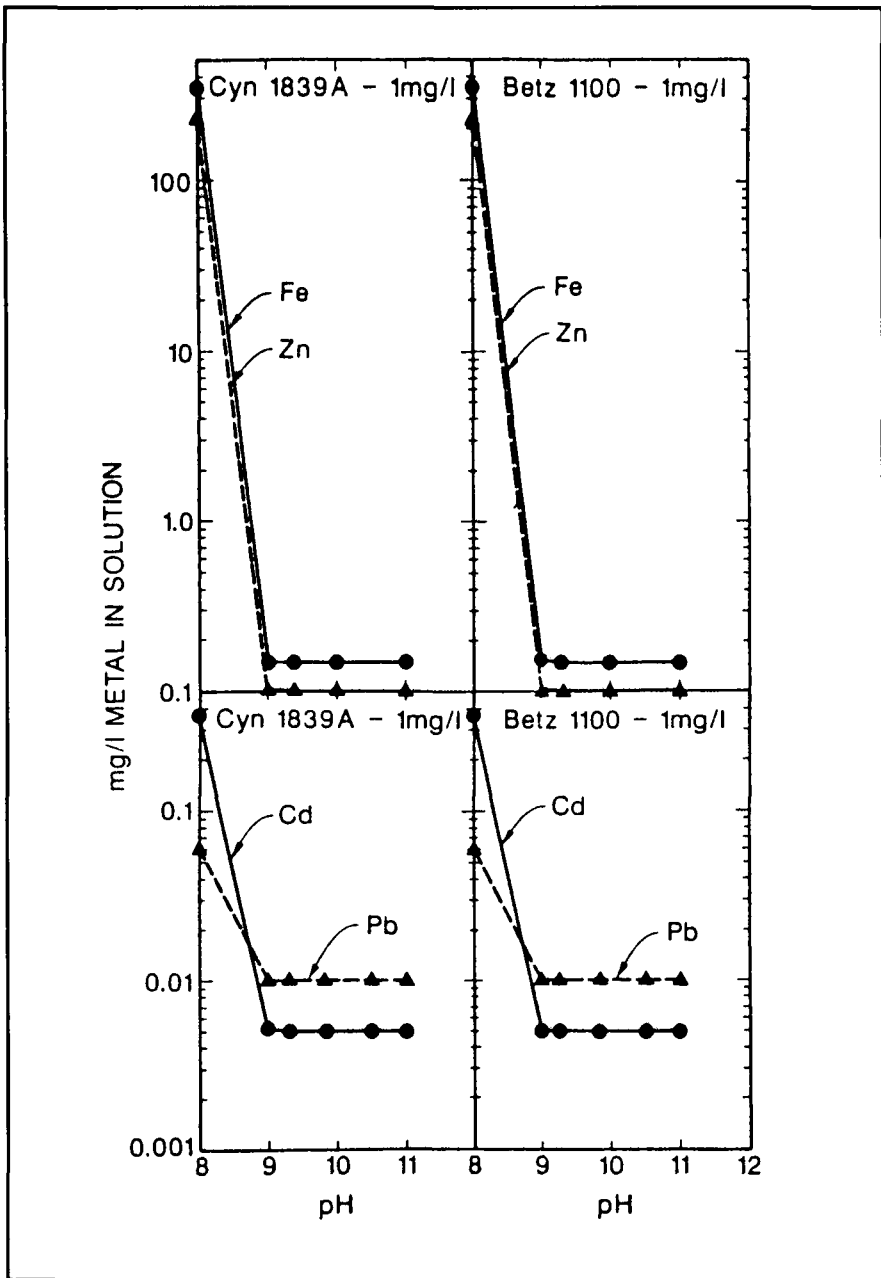


Figure 3. Results from chemical precipitation studies with polymer addition: mg/L metal in solution versus pH—Site 4s.

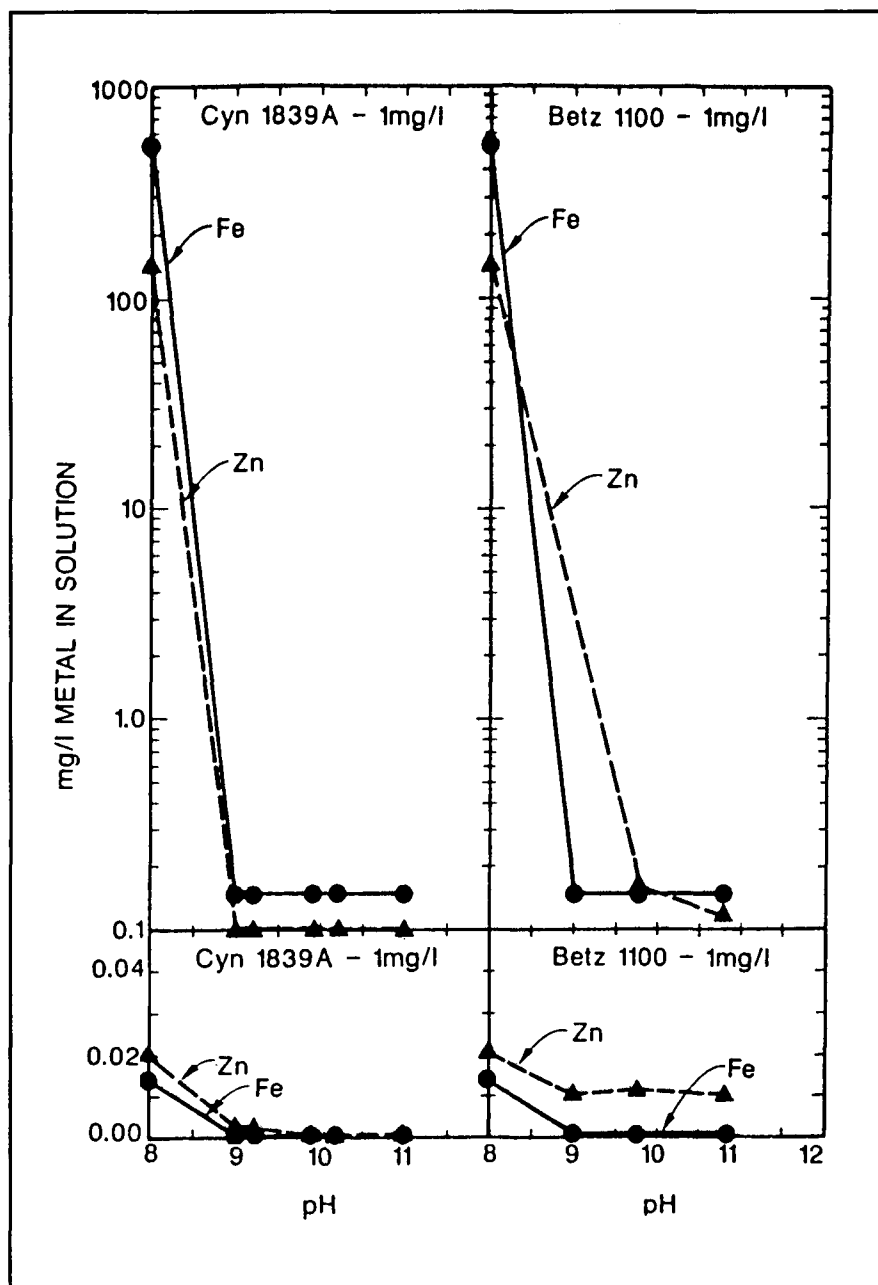


Figure 4. Results from chemical precipitation studies with polymer addition: mg/L metal solution versus pH—Site 14.

For site 14 (Figure 6), it can be seen that maximum iron removal was achieved with carbon doses greater than 2 grams. However, it should be remembered that iron was also removed by oxidation-precipitation at carbon doses of 1-3 mg/L. The zinc concentration decreased with an increase in carbon dose to 10 grams. Maximum removals of Cd and Pb both occurred at all doses of carbon.

Data from the batch studies for iron and zinc at site 4s and for zinc at site 14 were used to develop adsorption isotherms. Isotherms could not be developed for cadmium and lead at either site or for iron at site 14 because the lowest carbon dose of 1 gm/L removed most of the metal. Consequently, the amount of metal remaining in solution for subsequent carbon doses was relatively constant.

The data for iron and zinc at site 4s and for zinc at site 14 were used to plot BET (Brunauer, Emmett, Teller), Freundlich, Langmuir-high and Langmuir-low isotherms. Best fit in all instances occurred with the Langmuir-low which is a plot of C/q vs. C . (C is the concentration of the pollutant remaining in solution while q equals the mass of pollutant adsorbed on the carbon divided by the mass of the carbon.) Figures 7, 8, and 9 show the isotherms developed, and Table 5 tabulates the constants developed for each plot. Q^0 is the total capacity of the adsorbent for the particular metal and b is a constant related to the enthalpy of adsorption [27].

From these preliminary studies, it was concluded that activated carbon is effective in removing heavy metals from the acid mine drainage. Iron seems to be more readily removed than zinc in that the doses utilized easily reduced the iron concentration to below detectable limits, but the concurrent removal of zinc was substantially less. That is not to say, however, that adequate zinc removals cannot be achieved. Increasing bed depths or operation of carbon columns in series can produce higher quality effluents. Figure 10 illustrates breakthrough for zinc using three columns in series each containing approximately two feet of carbon. The third column in the series reached breakthrough, 1 mg/L, after 290 minutes (7.5 bed volumes).

In order to provide some insight into the adsorption process of acid mine drainage by activated carbon, a mass transfer model was used to determine both the internal and external resistance to mass transfer. The model made use of the column data generated in this study and was, therefore, only concerned with zinc sulfate (Figure 10).

Table 5. Constants Developed from Adsorption Isotherms

<i>Site and Metal</i>	<i>b</i>	<i>Q⁰</i>
Site 4s – Fe	5.9	0.0140
Site 4s – Zn	0.0542	0.001
Site 14 – Zn	0.1424	0.0038

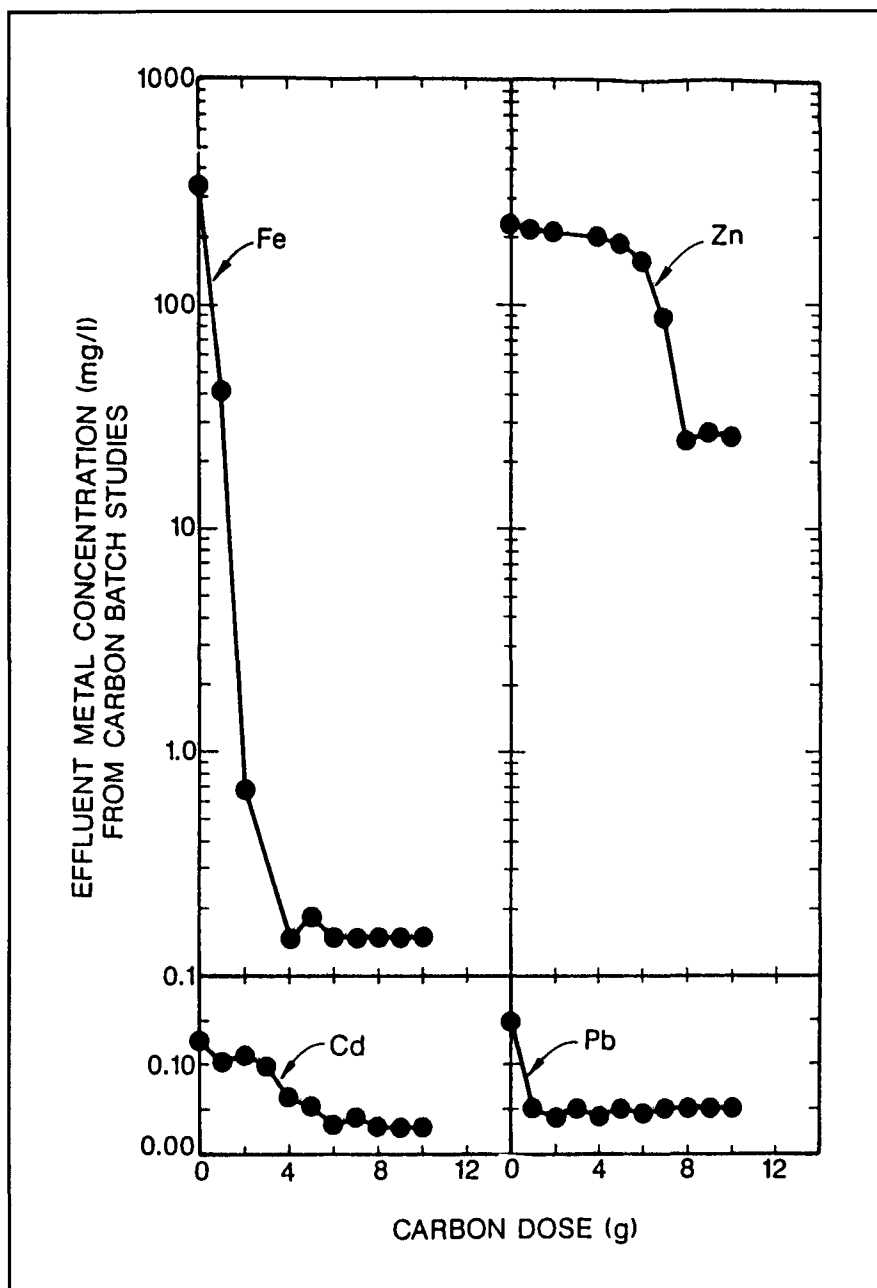


Figure 5. Soluble effluent metal concentration versus carbon dose: batch study—Site 4s.

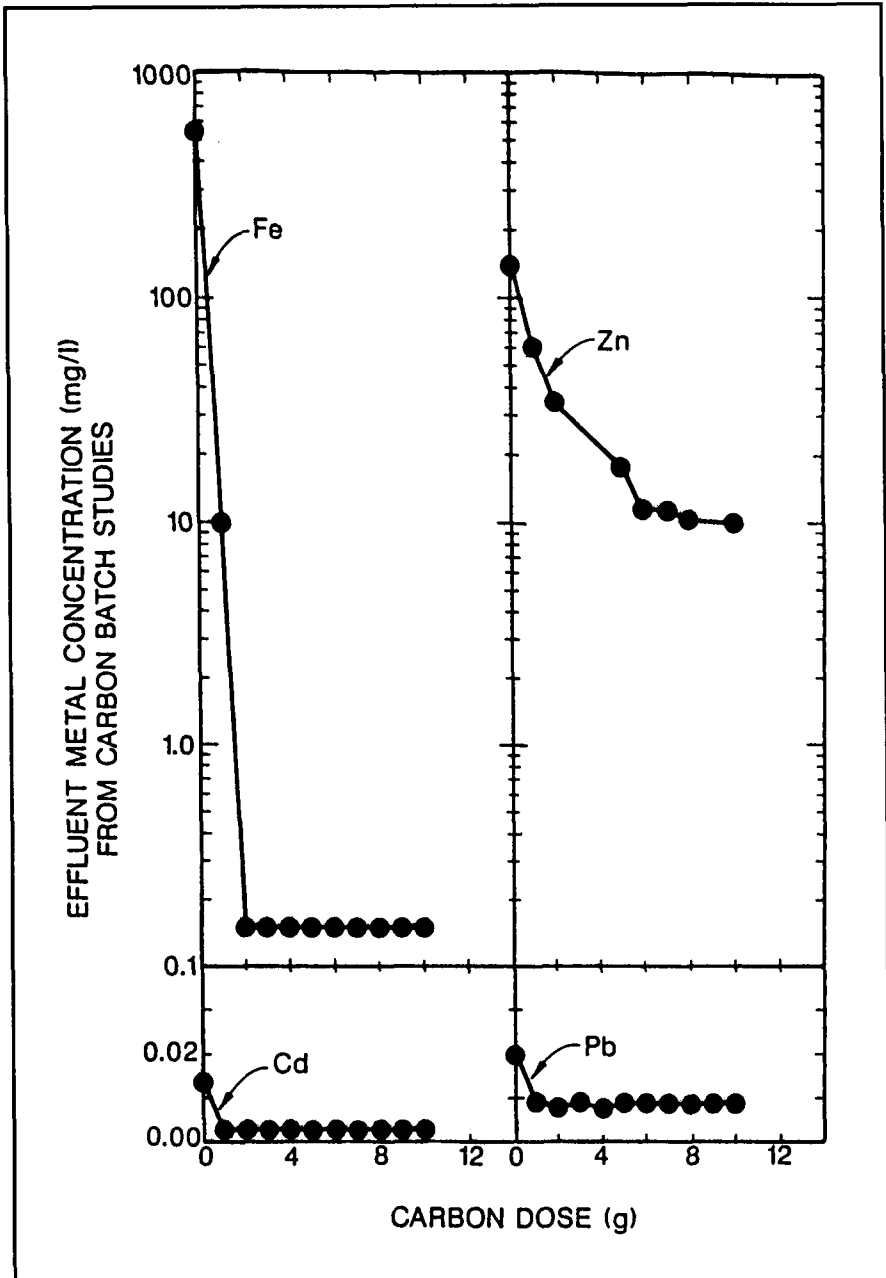


Figure 6. Soluble effluent metal concentration versus carbon dose: batch study—Site 14.

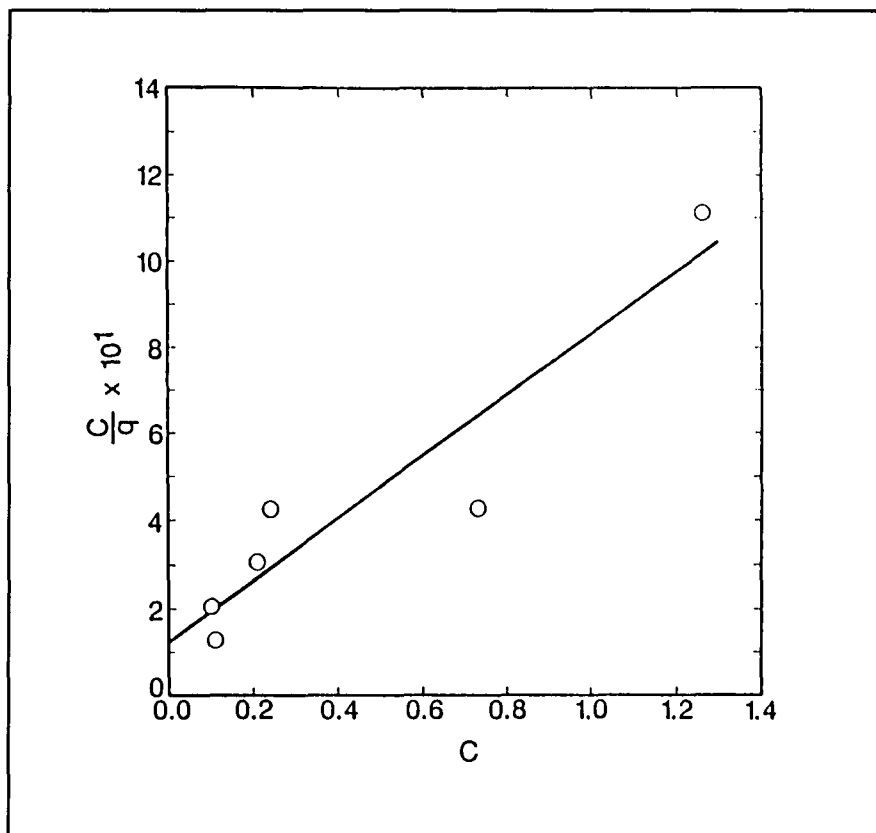


Figure 7. Carbon adsorption isotherm: Langmuir-low for Zn-Site 4s.

The adsorption process is generally considered to consist of three steps [28]:

1. Film diffusion (external diffusion): Transfer of the solute molecule from the bulk liquid phase to the surface of the sorbent;
2. Pore diffusion (internal diffusion): Transfer of the solute from the outer surface of the particle to the inner adsorption sites; and
3. Reaction: Adsorption of the solute onto the inner surface of the sorbent.

The surface reaction step is usually very fast compared to the rates of solute transfer and is therefore neglected. The kinetic behavior of the system can be controlled by either of the two remaining mechanisms.

Resistance values for transport processes were calculated using the method suggested by Summers and Roberts [29]. To calculate resistance, a value for aqueous phase (bulk) diffusivity is needed. A value of bulk diffusivity ($D = 7.39$

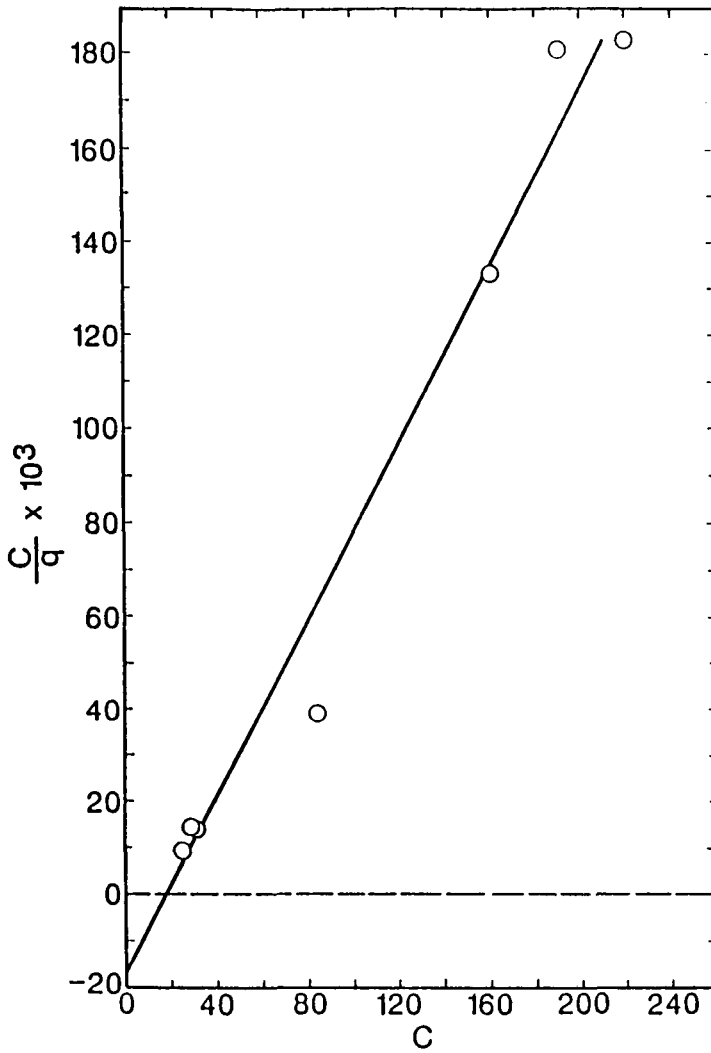


Figure 8. Carbon adsorption isotherm: Langmuir -low for Fe-Site 4s.

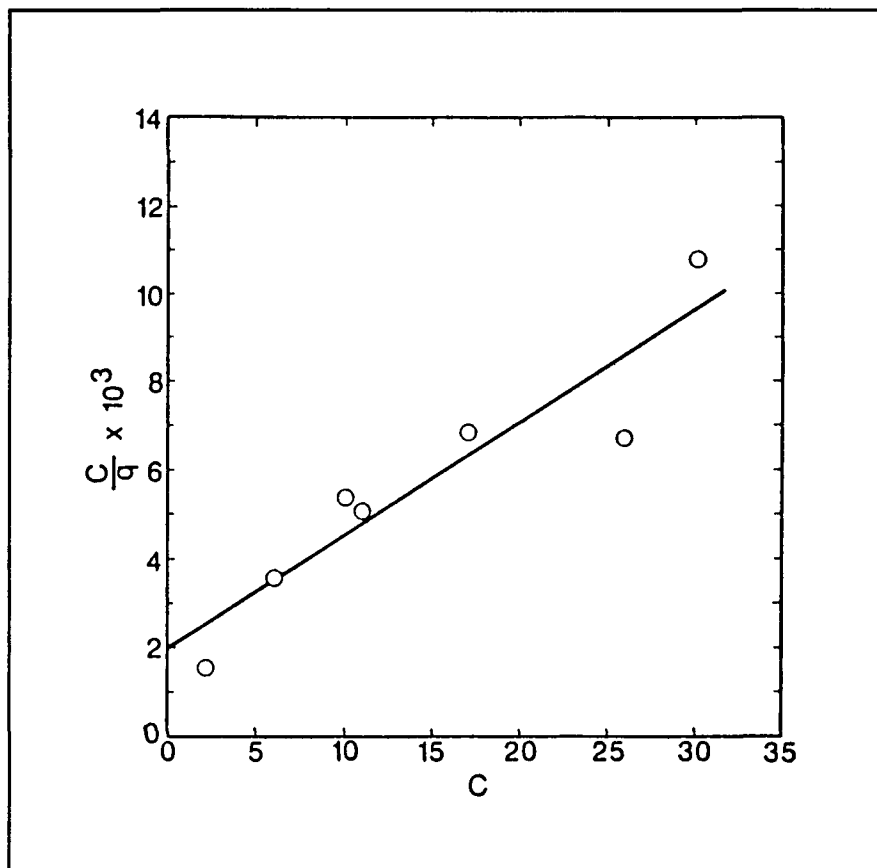


Figure 9. Carbon adsorption isotherm: Langmuir-low for Zn-Site 14.

$\times 10^{-10} \text{ m}^2/\text{s}$) for zinc sulfate at the same molar concentration as used in this study was obtained from the work of Harned and Hudson [30]. The bulk diffusivity coefficient was modified using the following equation in order to account for the porous structure of the carbon;

$$D_p = \frac{D\epsilon_i}{x} \quad (1)$$

in which D_p = effective pore diffusion coefficient, ϵ_i = porosity, and x = tortuosity factor [31]. The internal porosity of the carbon used in this study was calculated to be $0.39 \text{ cm}^3 \text{ pore volume/cm}^3 \text{ particle volume}$. The tortuosity factor accounts for the deviation of the molecules pore diffusional path. Values reported in the literature for the tortuosity factor range from 2-7 [31, 32]. A value of 3.0 was chosen in this work. Substituting the previously stated values for D , ϵ_i ,

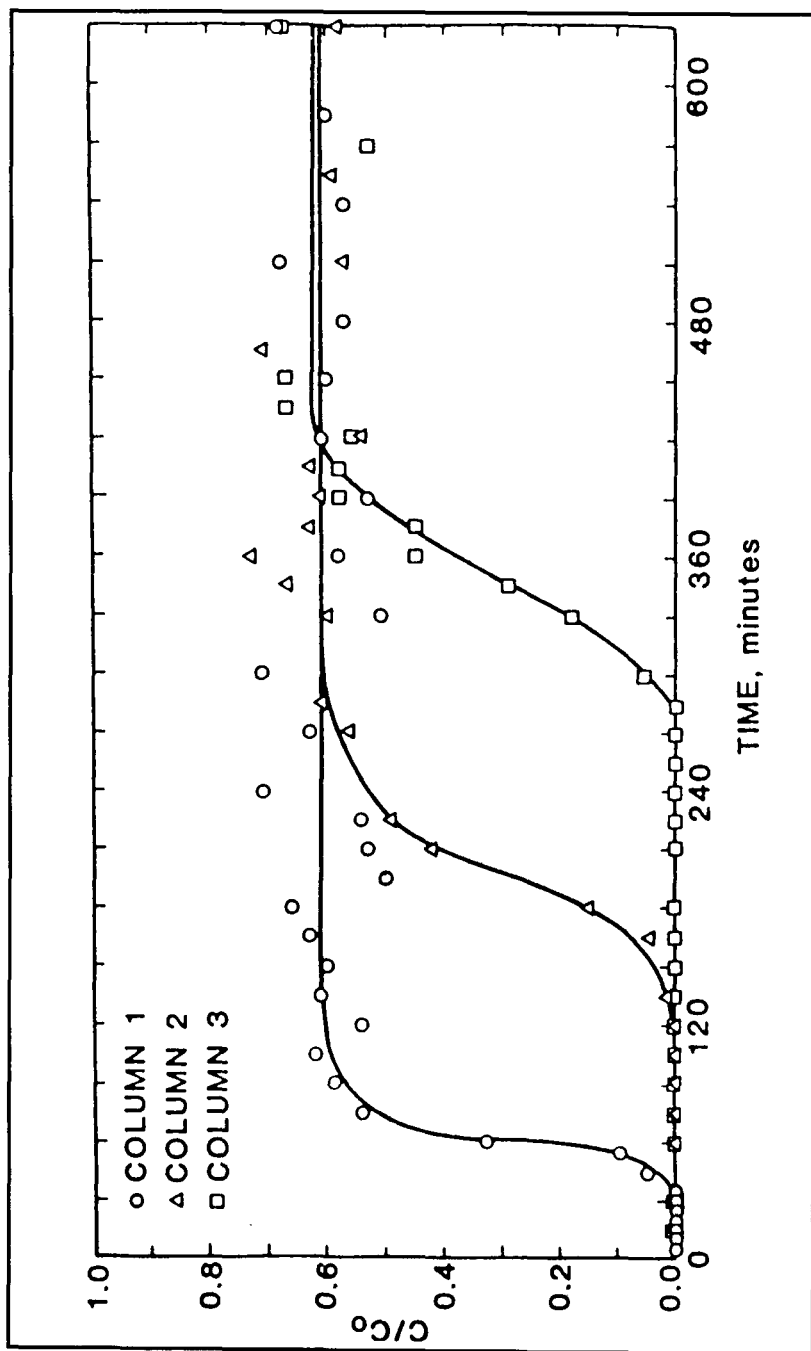


Figure 10. Breakthrough curves: activated carbon column study for Site 4s-Zn.

and x into equation (1) yields a calculated effective pore diffusion coefficient of $9.6 \times 10^{-11} \text{ m}^2/\text{s}$.

An equation presented by Vermeulen [33] was used to calculate the internal resistance to mass transfer (R_p):

$$R_p^{-1} = K_p a = \frac{60 D_p (1 - \epsilon_b)}{d^2}, \quad (2)$$

in which K_p is the pore mass transfer coefficient (m/sec), a is the external surface area of the sorbent particle (m^2/m^3), d is the particle diameter, and ϵ_b equals the bed void fraction. Using average values of $d = 9.15 \times 10^{-4} \text{ m}$ and $\epsilon_b = 0.5$, the internal resistivity due to pore diffusion was calculated to be $R_p = 291$ seconds.

The external resistance to mass transfer was calculated using the relationship presented by Wakao and Funazkri [34].

$$\text{Sh} = 2 + 1.1 (\text{Re})^{0.6} (\text{Sc})^{1/3}, \quad (3)$$

in which $\text{Sh} = \frac{K_f d}{D}$, $\text{Re} = \frac{d v \epsilon_b}{\nu}$, and $\text{Sc} = \nu/D$ with K_f = film mass transfer coefficient (m/s), ν = kinematic viscosity (m^2/s) and V = fluid velocity (m/s). Numerical values used in solving this equation for K_f were: $\nu = 0.937 \times 10^{-6} \text{ m}^2/\text{s}$, $V = 1.74 \times 10^{-4} \text{ m/s}$, and the previously reported values for d and D . The film mass transfer coefficient (K_f) was determined to equal $1.24 \times 10^{-5} \text{ m/s}$. The external resistance to mass transfer (R_f) was calculated using the following equation:

$$R_f = \frac{d}{6K_f}. \quad (4)$$

The value calculated for R_f was 12.3 seconds.

This set of calculations indicates that for the acid mine drainage waste (zinc sulfate component), WV-G carbon system, the rate limiting step is pore diffusion.

ION EXCHANGE

Ion exchange also proved to be effective in removing the heavy metals from the wastewater. Figures 11 and 12 are representative of the data obtained from ion exchange column studies with samples from sites 4s and 14, respectively. The column being fed with water from 4s was operated twenty-four hours. During that time, approximately thirty-nine bed volumes of waste were passed through the column. Within the first hour, iron, cadmium, and lead were reduced to minimum detectable limits (Figure 11). The lowest effluent concentration achieved for zinc occurred in the third hour. The column fed with samples from site 14 was run for twenty-two hours (thirty-six bed volumes). Maximum iron,

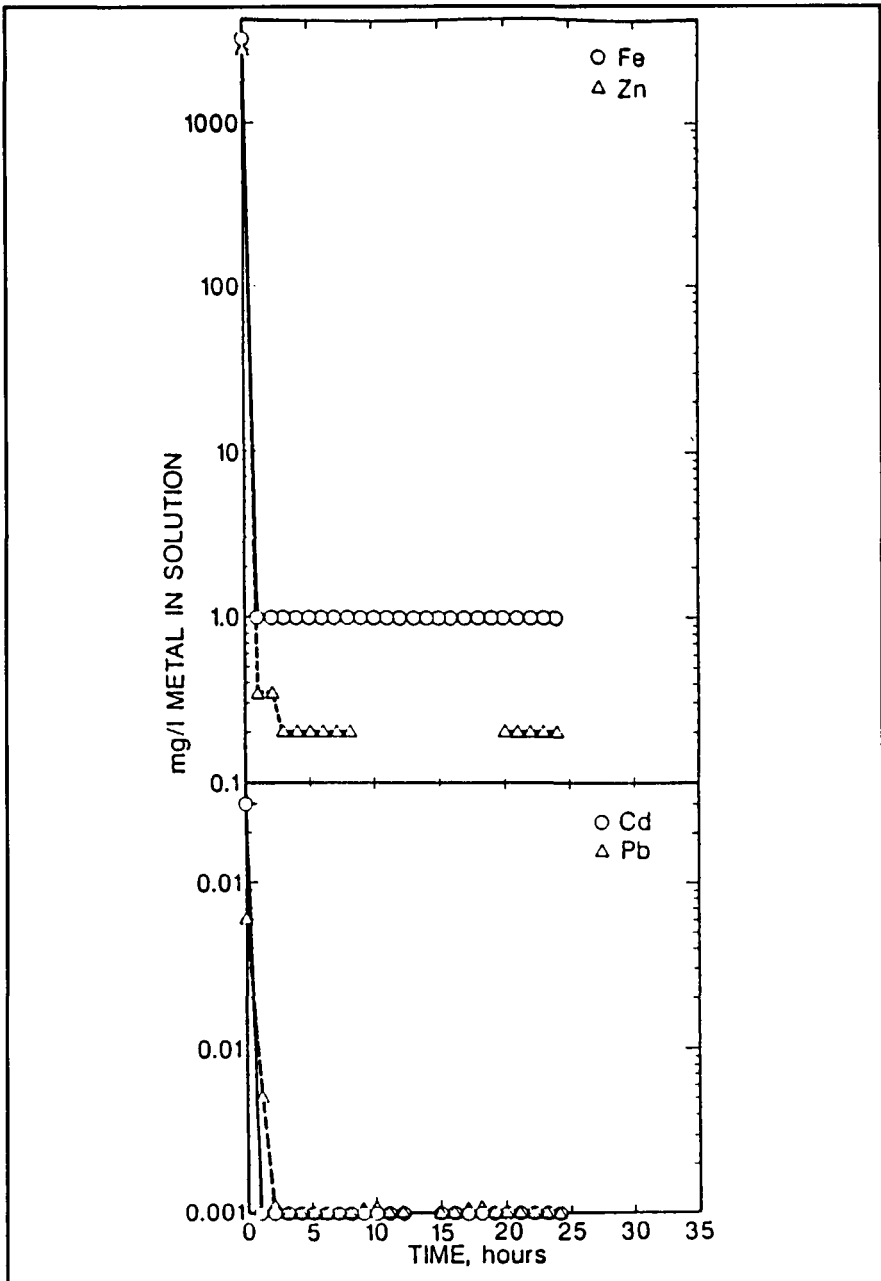


Figure 11. Soluble effluent metal concentration versus time:
ion exchange column studies—Site 4s.

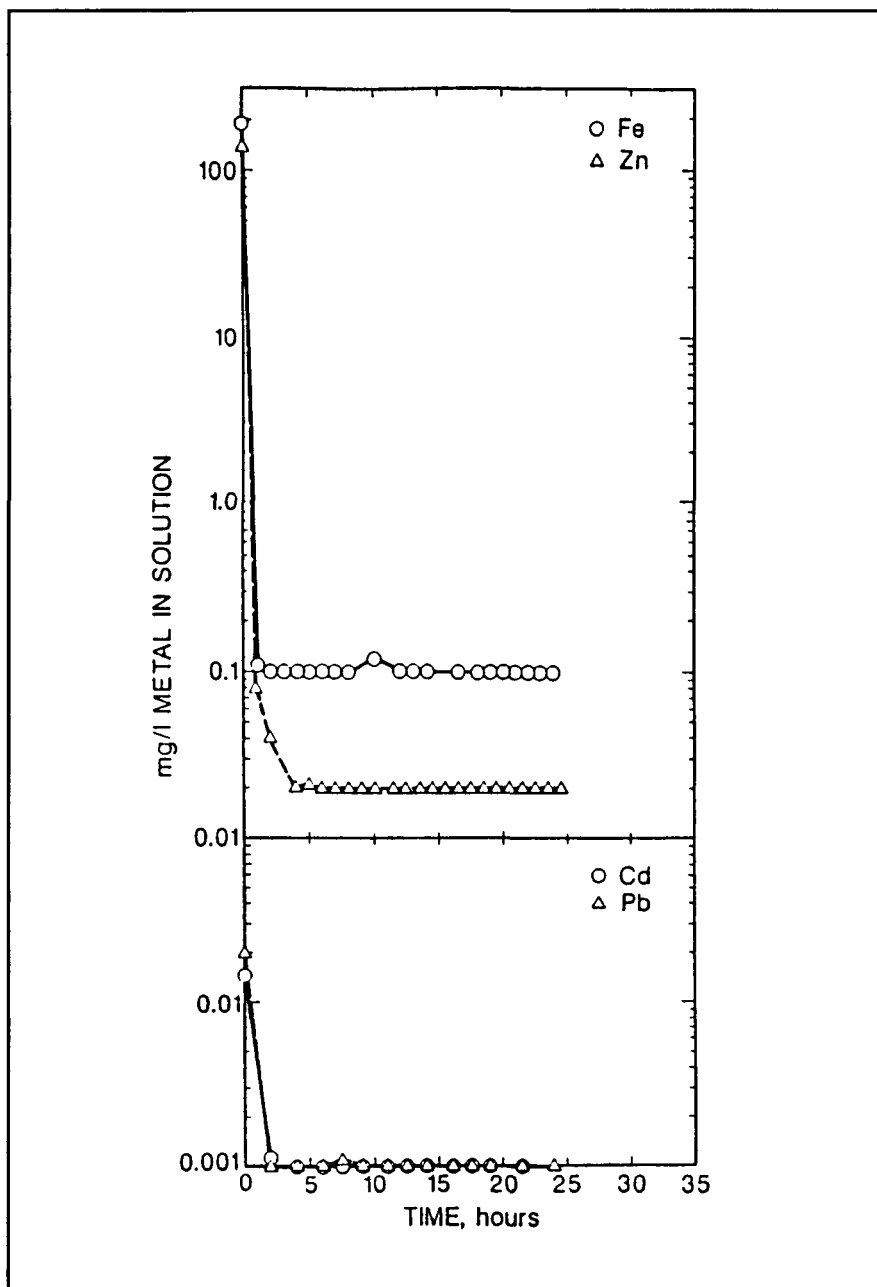


Figure 12. Soluble effluent metal concentration versus time: ion exchange column studies—Site 14.

zinc, cadmium, and lead removals with respect to discharge standards were achieved at two hours, four hours, and one hour, respectively.

For both mine drainages, ion exchange could be utilized to reduce the heavy metals to below the minimal detectable concentrations. In these initial studies, breakthrough was not achieved, meaning that the column was not exhausted with respect to the ion of interest and, therefore, use could have been continued and additional removal could be expected. The results of further ion exchange column studies are illustrated in Figure 13. The second ion exchange column study was conducted using a one-half inch diameter glass column operating at a loading rate of 4.5 gpm/ft² (flow rate of 23 ml/min). The figure shows iron breakthrough after 120 minutes (fifty bed volumes) while zinc breakthrough occurs after 230 minutes (ninety-six bed volumes). It should be noted that zinc breakthrough occurs close to complete exhaustion of the resin with respect to iron. Although ion exchange is a viable alternative, preaeration and filtration would be required to reduce the influent iron concentration to prevent precipitation on the resin.

SUMMARY

This study was one of several conducted to assess various alternatives for managing the Tar Creek Superfund site. At the conclusion of all of the studies, the State of Oklahoma decided to plug the abandoned wells through which the mine drainage was surfacing. During 1987, the drainage again began to surface in new locations, making the need for an alternative management scheme essential. The results from this study indicate that treatment of the accumulated mine drainage by physical-chemical techniques is a viable option. Chemical precipitation, activated carbon, and ion exchange were all found to be effective, and therefore, the prevailing considerations in the choice of a treatment option would be economic. In order to facilitate this choice, estimates of current 1989 costs are presented in Table 6. The costs which were obtained from Neptune Microfloc (chemical precipitation), Calgon (activated carbon), and HOH Systems (ion exchange) represent costs for a package plant for a flow of 350 gpm complete with installation and housing. The 350 gpm flow was based on an estimated discharge of 50,000 gpd made by OWRB [1]. Costs for ion exchange and activated carbon also include resin and carbon costs as well as a package filtration plant for solids removal preceding the ion exchange or activated carbon columns. As can be seen, the initial costs for the three processes appear to be comparable. However, ion exchange and activated carbon become prohibitively expensive with the frequent regeneration needs. Using breakthrough data obtained from the study with the column sizes provided by the manufacturer for both ion exchange and activated carbon, it was determined that breakthrough would occur in less than five minutes for the ion exchange column and in thirty-

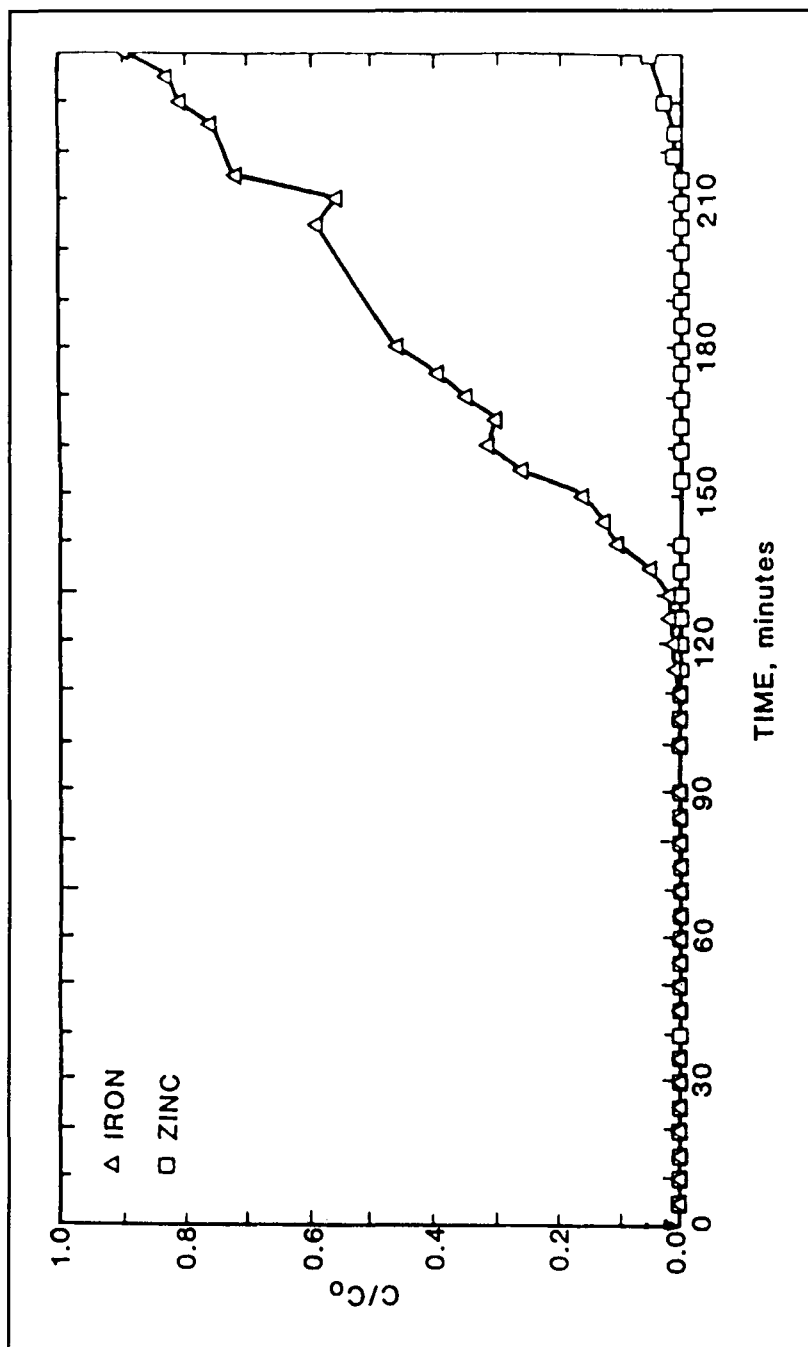


Figure 13. Ion exchange breakthrough for iron and zinc-Site 4s.

Table 6. 1989 Package Plant (350 gpm) Costs for Chemical Precipitation, Ion Exchange, and Activated Carbon

<i>Plant</i>	<i>Cost</i>
Chemical Precipitation	\$420,000
Ion Exchange	\$452,936
Activated Carbon	\$411,066

two minutes for the activated carbon column, thus necessitating either longer columns or columns in series. Ion exchange also incurs a regenerant disposal cost. According to Guter, brine disposal can be assumed to add 30-50 percent to capital and operating costs for an ion exchange plant [35].

Chemical precipitation or chemical precipitation with the aid of polymers would seem to be the most favorable choice. Very good metal removals could be achieved through the addition of lime at a pH of 10. However, when polymers were used in addition to the lime, maximum metal removals occurred at a pH of 9, allowing for a decrease in the lime required for the process.

REFERENCES

1. Oklahoma Water Resources Board, *Tar Creek Field Investigation Task 1.1, Effects of Acid Mine Drainage on the Surface Water Resources in the Tar Creek Area, Ottawa County, Oklahoma*, EPA Grant No. CX 810192-010, 1983.
2. J. S. Whang, et al., Soluble-Sulfide Precipitation for Heavy Metals from Wastewaters, *Environ. Prog.*, 1, p. 110, 1982.
3. K. A. Brantner and E. J. Cichon, Heavy Metals Removal: Comparison of Alternate Precipitation Processes, *Proceedings of the 13th Mid-Atlantic Industrial Waste Conference*, 51, 1988.
4. K. Jurkiewicz, Studies on the Separation of Cadmium from Solutions by Foam Separation II. Precipitate Flotation of Cadmium Hydroxide, *Sep. Sci. Technol.*, 19, p. 1051, 1985.
5. J. P. Gould, et al., Factors Influencing Zinc Cementation of Cadmium, *Proceedings of the Environmental Engineering Division Special Conference*, American Society of Civil Engineers, p. 366, 1985.
6. D. Grosse, et al., Treatment of Aqueous Metal Bearing Hazardous Wastes, 8th AESF/EPA Conference on Pollution Control in the Metallic Finishing Industry, American Electroplaters and Surfacers Society, 1987.
7. A. DuPont, Lime Treatment of Liquid Waste Containing Heavy Metals, *Pollution Engineering*, 19:4, p. 84, 1987.
8. T. Nishimura and K. Tozawa, Removal of Arsenic from Waste Water by Addition of Calcium Hydroxide and Stabilization of Arsenic-Bearing Precipitates by Calcination, *Impurity Control Disposal, Proceedings of the 15th CIM Annual Hydrometallurgists Meeting (G.B.)*, 15, p. 1, 1985.

9. J. Teringo III, Magnesium Hydroxide Reduces Sludge/Improves Filtering, *Pollution Engineering*, 19:4, p. 78, 1987.
10. G. S. Logsdon and J. M. Symons, Mercury Removal by Conventional Water Treatment Techniques, *JAWWA*, 15, p. 554, 1972.
11. M. D. Pandey and M. Chauduri, Removal of Inorganic Mercury from Water by Bitumas Coal, *Water Research*, 16, p. 1113, 1982.
12. M. I. Humenick and J. L. Schnoor, Improving Mercury (II) Removal by Activated Carbon, *Journal of Environmental Engineering Division, Proceedings of the American Society of Civil Engineers*, 100, p. 1249, 1974.
13. L. Thiem, et al., Removal of Mercury from Drinking Water Using Activated Carbon, *JAWWA*, 68, p. 447, 1971.
14. C. P. Huang and P. K. Wirth, Activated Carbon for Treatment of Cadmium Wastewater, *Journal of Environmental Engineering Division, Proceedings of the American Society of Civil Engineers*, 107, p. 1280, 1982.
15. M. O. Corapcioglu and C. P. Huang, The Adsorption of Heavy Metals on Hydrous Activated Carbon, *Water Research*, 21, p. 1031, 1987.
16. H. Koshima and H. Orishi, Adsorption of Metal Ions on Activated Carbon from Aqueous Solutions at pH 1-13, *Talanta*, 33:5, p. 391, 1986.
17. Y. Ku and R. W. Peters, Innovative Uses for Carbon Adsorption of Heavy Metals from Plating Wastewaters, I. AC Polishing Treatment, *Environmental Progress*, 6, p. 119, 1987.
18. C. W. Greer and A. L. Huber, Synthetic Compositions: Effective Treatment of Heavy Metal Containing Wastewaters from the Metal Finishing Industry, *74th Annual AESF Technical Conference, Proceedings of the American Electroplaters and Surfacter Finishers Society*, 1987.
19. W. H. Waitz, Ion Exchange in Heavy Metals Removal and Recovery, *Publication No. 162*, Rohm and Haas Company, Fluid Process Chemicals Department, Philadelphia, Pennsylvania, 1979.
20. A. K. Shcheglov and L. D. Sedova, Ion-Exchange Purification of Sewage for Copper Salt Removal, *Prib. Sist. Upr.*, 1, p. 38, 1986.
21. O. P. Mathur, et al., Removal of Cyanide and Heavy Metals from Industrial Effluent Using Insoluble Functionalized Polysaccharide Derivatives, *Bull. Electrochem.*, 2:2, p. 141, 1986.
22. M. C. Loizidou, Heavy Metal Removal Using Natural Zeolites, *Heavy Metal Environ. International Conference 15th*, 1, p. 649, 1985.
23. American Public Health, *Standard Methods for the Examination of Water and Wastewater*, 15th Edition, APHA, Washington, D.C., 1980.
24. Hach Chemical Company, *Hach Water Analysis Handbook*, Hach Company, Loveland, Colorado, 1982.
25. Oklahoma Water Resources Board, Water Quality Standards, *Publication III*, Oklahoma City, Oklahoma, 1982.
26. N. L. Nemerow, *Scientific Stream Pollution Analyses*, McGraw-Hill Book Company, New York, 1974.
27. W. J. Weber, *Physiochemical Processes for Water Quality Control*, Wiley Interscience, New York, 1972.
28. L. D. Benefield, J. F. Judkins, and B. L. Weand, *Process Chemistry for Water and Wastewater Treatment*, Prentice Hall, Englewood Cliffs, New Jersey, 1982.

29. R. S. Summers and P. V. Roberts, Simulation of DOC Removal in Activated Carbon Beds, *Journal of the Environmental Engineering Division, ASCE*, 110:1, pp. 73-92, 1984.
30. H. S. Harned and R. M. Hudson, The Diffusion Coefficient of Zinc Sulfate in Dilute Aqueous Solution at 25°, *Journal of the American Chemical Society*, 73:8, pp. 3781-3783, 1951.
31. C. N. Satterfield, *Heterogeneous Catalysis in Practice*, McGraw-Hill, New York, 1980.
32. _____, *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Cambridge, Massachusetts, 1970.
33. T. Vermeulen, Separation by Adsorption Methods, in *Advances in Chemical Engineering, Volume II*, T. B. Drew and J. W. Hoopes (eds.), Academic Press, New York, 1958.
34. N. Wakao and T. Funazkri, Effect of Fluid-Dispersion Coefficients on Particle-to-Fluid Mass Transfer Coefficients in Packed Beds, *Chemical Engineering Science*, 33, pp. 1375-1384, 1978.
35. G. A. Guter, Removal of Nitrate from Contaminated Water Supplies for Public Use: Final Report, EPA 600/2-82-042 Municipal Environmental Research Lab., Cincinnati, Ohio, 1982.

Direct reprint requests to:

Prof. Marcia H. Bates
School of Civil Engineering
Oklahoma State University
Stillwater, OK 74078-0327