



Cadmium and lead removal with direct filtration
by Thomas Paul Engleson

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering

Montana State University

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Abstract:

Few studies have investigated trace metal removals with water treatment unit operations and processes. Nowhere in the literature has the author found a reference to trace metal removal with a direct filtration water treatment scheme. To provide this basic information, a direct filtration pilot plant was used to collect cadmium and lead removal data.

The major variables investigated were coagulant dosage and pH. In addition, the effects of coagulant type, polymer, alkalinity and humic materials on cadmium removal efficiencies were studied.

The direct filtration pilot plant was modeled to incorporate many of the design features of operational direct filtration plants. Forty-four pilot plant runs were conducted to collect samples for the following measurements: pH, turbidity, headloss changes and metal concentration. Metal samples were analyzed on a custom built atomic absorption spectrophotometer developed at Montana State University.

Cadmium and lead removals obtained with direct filtration were not significantly different from removals reported in the literature for conventional coagulation water treatment.

Cadmium removal was strongly pH dependent, removals increasing with higher pH. The cadmium MCL was only met above pH 9.

Interestingly, it was discovered that hardness in the experimental water resulted in very low turbidity levels at alkaline pH, outside the thermodynamic boundaries of aluminum. As a result of this phenomenon, it was possible to define, in terms of coagulant dosage and pH, an operating region where both turbidity and cadmium MCLs were met concurrently.

Lead removals were independent of pH and were generally high. The lead MCL was met for all pH and coagulant dosages investigated. Therefore, MCLs for both turbidity and lead were met concurrently whenever the turbidity MCL was satisfied.

Bench-scale tests were conducted to identify the predominant removal mechanism(s) for cadmium and lead. The evidence suggests that a combination of processes may be responsible for the removals obtained within the pilot plant.

Using the operational guidelines delineated in this study, direct filtration is capable of supplying an effluent water that meets turbidity and trace metal MCLs concurrently.

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of

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MONTANA STATE UNIVERSITY
Bozeman, Montana

August 1984

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of a thesis submitted by

Thomas Paul Engleson

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ABSTRACT

Few studies have investigated trace metal removals with water treatment unit operations and processes. Nowhere in the literature has the author found a reference to trace metal removal with a direct filtration water treatment scheme. To provide this basic information, a direct filtration pilot plant was used to collect cadmium and lead removal data.

The major variables investigated were coagulant dosage and pH. In addition, the effects of coagulant type, polymer, alkalinity and humic materials on cadmium removal efficiencies were studied.

The direct filtration pilot plant was modeled to incorporate many of the design features of operational direct filtration plants. Forty-four pilot plant runs were conducted to collect samples for the following measurements: pH, turbidity, headloss changes and metal concentration. Metal samples were analyzed on a custom built atomic absorption spectrophotometer developed at Montana State University.

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Interestingly, it was discovered that hardness in the experimental water resulted in very low turbidity levels at alkaline pH, outside the thermodynamic boundaries of aluminum. As a result of this phenomenon, it was possible to define, in terms of coagulant dosage and pH, an operating region where both turbidity and cadmium MCLs were met concurrently.

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Bench-scale tests were conducted to identify the predominant removal mechanism(s) for cadmium and lead. The evidence suggests that a combination of processes may be responsible for the removals obtained within the pilot plant.

Using the operational guidelines delineated in this study, direct filtration is capable of supplying an effluent water that meets turbidity and trace metal MCLs concurrently.

CHAPTER 1

INTRODUCTION

With the advent of sophisticated techniques and methods for the analysis of trace metals came a better understanding of the health dangers imposed by these substances. One avenue through which people are exposed to metal contaminants is drinking water. Concern over this exposure resulted in the Environmental Protection Agency (EPA) establishing maximum contamination levels (MCL) for ten trace inorganics. Central to this study are the metals lead and cadmium with their respective MCLs of 0.05 and 0.01 mg/L.

The sources and health effects of lead and cadmium are well documented in the literature [2,6,7,9,11] and will not be repeated here. Let it suffice to say that man's industrial and manufacturing activities significantly concentrate these elements. Durum [1] observed that the special difficulty with trace metals is their persistence. This persistence allows metals to be transported for considerable distances oftentimes ending up in surface and underground waters.

Studies of trace metal removal from drinking water are rare. The studies found in the literature evaluate trace metal removal by conventional coagulation and lime softening processes. Nowhere in the literature has the author found a reference to trace metal removal with a direct filtration water treatment scheme. This study investigated trace metal removal with a direct filtration water treatment pilot plant.

Direct filtration has received considerable attention in the past decade. Direct filtration refers to a treatment scheme wherein filtration is not preceded by sedimentation. For many waters, this treatment scheme is an economical alternative to more conventional coagulation treatment.

More information is needed to better categorize those waters that can best be treated by direct filtration. The Direct Filtration subcommittee of the American Water Works Association Filtration Committee published a report [22] in 1980 which included research recommendations. One area of research that was specifically mentioned was the investigation of removal efficiencies for heavy metals and other trace inorganics with direct filtration.

This study was divided into three parts:

1. Pilot plant operation and sampling
2. Trace metal analysis
3. Data evaluation

The pilot plant was designed to incorporate many of the design features of operational, direct filtration plants. Forty-four pilot plant runs were conducted to collect samples for the following measurements: pH, turbidity, headloss, and metal concentration.

The metal samples were analyzed on a Varian AA-5 atomic absorption spectrophotometer with a Woodruff Constant Temperature Furnace. The furnace was developed at Montana State University and has an analytical capability better than many commercially available spectrophotometers.

Results obtained were evaluated with the understanding that metal removal, where required, is only one facet of the water treatment picture. For direct filtration to provide an acceptable effluent water, adequate turbidity removal and metal removal must be accomplished simultaneously. It is hoped that this study will provide information useful in meeting this goal.

CHAPTER 2

THE PROBLEM

The extent to which cadmium and lead enter surface and underground waters is of importance to this study. It is also important to consider the potential magnitude of the problem based upon what is known of natural water chemistry.

Distribution of Lead and Cadmium

Both scattered and intensive surveys [1,11] show that the elements cadmium and lead are widely distributed in low concentrations in the nation's waters. A few of the survey results are included in Table 1.

Table 1. Intensive Survey Results for Lead and Cadmium in Surface and Ground Waters [1,11].

Date	Investigator	No. Samples	Detection Frequency	Ave. Conc.* mg/L	Max Conc. mg/L	Comments
Lead						
1970	Durum et al.	727	63%	0.002	0.890	filtered samples mostly river
1962-1967	Kopp & Kroner	1577	19.3%	0.023	0.14	lakes and rivers
1970	Dutt & McCreary	677	—	—	0.518	ground waters
Cadium						
1970	Durum et al.	727	46%	0.002	0.130	filtered samples mostly river
1962-1967	Kopp & Kroner	1577	2.5%	0.01	0.12	lakes and rivers

*Detectable.

The maximum concentrations encountered are well in excess of established MCLs. To assess the potential extent of trace metal contamination, it is necessary to be familiar with the water quality parameters affecting the distribution of trace metals in natural waters. The pertinent parameters are listed in Table 2 [3,5].

Table 2. Parameters Affecting the Distribution of Trace Metals in Natural Waters [3,5].

-
- | | |
|----|---|
| 1. | pH |
| 2. | Concentration and type of trace metal |
| 3. | Concentration and type of complexing agents |
| | a. inorganic |
| | b. organic |
| 4. | Types of suspended materials (adsorbents) and their surface areas |
| 5. | Oxidation-reduction potential |
| 6. | Temperature |
-

These parameters will control the total soluble metal concentration as well as the fraction transported in insoluble form. For a water incorporating only the more generally applicable parameters from Table 2, it is possible to calculate dissolved metal concentrations using published thermodynamic data. Solubility modeling has been used by many others [3,6,7, 17,30,39] and will be explained in greater detail in Chapter 5.

Lead

Hem and Durum [6] have calculated soluble lead concentrations from solubility diagrams. Calculations indicate that above pH 8.0, the solubility of lead is below 0.01 mg/L regardless of the total soluble inorganic carbon concentration (C_T). Near pH 6.5, however, the solubility of lead could surpass 0.30 mg/L for a water having a low C_T . This concentration is six times the MCL. It is important to note that other complexed species could significantly increase the solubility of lead. In addition, particulate lead and lead adsorbed onto surfaces could greatly increase the gross lead concentration in a water. Based on these calculations and survey findings, lead appears to be a significant threat to water quality.

Cadmium

Similar calculations for cadmium also demonstrate a potential for contamination [7]. For a low C_T , the solubility does not get much below 1.0 mg/L even at pH 10. Another significant discovery is found in Table 1. The survey conducted by Kopp and Kroner detected cadmium in only 40 out of 1577 samples, however, the average concentration of these 40 samples was very close to the MCL. A clear threat to water quality exists.

Research Considerations

Five major considerations led to the decision to investigate trace metal removal with a direct filtration pilot plant.

1. The above discussion demonstrates that the potential for metal contamination exists. A more regional concern is that some towns in Montana have trouble meeting the MCLs for lead and cadmium [9].
2. Direct-filtration has become an attractive alternative to more conventional coagulation treatment due to savings in capital, operation, and maintenance costs [28]. Several direct filtration plants are operating in Montana and are well suited to the relatively low turbidity, color-free water in this region.
3. As mentioned in the introduction, no references were found in the literature that dealt with trace metal removal with direct filtration. This basic information could prove useful in determining the feasibility of this treatment option for a water containing lead and/or cadmium.
4. Research at Montana State University [15] showed that for coagulant dosages suitable for direct filtration, usually less than 20 mg/L, the best turbidity removals occurred within a narrow pH range, pH 6.5 to 7.0. This finding together with theoretical solubility calculations, created doubt as to the feasibility of meeting the MCLs for both metal and turbidity concurrently.

5. The physical differences between a conventional coagulation treatment scheme and a direct filtration treatment scheme could be significant with regard to metal removal. The long detention times in the flocculator and sedimentation basin might prove significant from a kinetics standpoint.

CHAPTER 3

OBJECTIVES

The overall objective of this study is to add to the body of knowledge about direct filtration and thereby better define the capacity for a direct filtration treatment plant to provide a water meeting all of the drinking water standards. The specific objectives were:

1. To evaluate the removal efficiencies for lead and cadmium within a direct filtration pilot plant.
2. To establish operational guidelines that will result in an effluent water that meets both the MCL for turbidity and metal concentration.
3. To identify the predominant removal mechanism(s).
4. To compare results obtained with data found in the literature for conventional treatment schemes.

CHAPTER 4

TRACE METAL REMOVAL IN WATER TREATMENT —AN OVERVIEW

The mechanisms of trace metal removal in conventional water treatment may be either one or a combination of several processes—precipitation, coprecipitation and adsorption. The purpose of this chapter is to introduce some of the common water treatment operations and processes and their associated mechanism(s) for metal removal.

Definitions

In this study the following definitions apply [5]:

Precipitation

Precipitation refers to the addition of a chemical in sufficient quantity that it causes the solubility of the dissolved species in question to be exceeded.

Coprecipitation

Coprecipitation refers to the inclusion in a precipitate of substances that are normally soluble under the conditions of the precipitation. The mechanism of coprecipitation can be (1) surface adsorption in which the coprecipitating species are adsorbed at the surface of the precipitate, or (2) occlusion in which the coprecipitate is mechanically trapped, or otherwise incorporated, in the rapidly forming precipitate. Coprecipitation is a special case of adsorption.

Adsorption

Adsorption refers to the accumulation of substances at a surface or interface.

Coagulation

Coagulation involves the aggregation of colloidal particles due to destabilization and flocculation. Aggregation produces larger particles that can be removed by sedimentation and/or filtration.

Conventional Coagulation Water Treatment

Rarely have water treatment plants been designed with the removal of specific trace metals in mind; however, the operations and processes employed in conventional water treatment do demonstrate some capacity for trace metal removal [4,5,10,11].

The common water treatment operations and processes which show promise of providing some removal of trace metals from drinking water are found in Table 3 [4]. Trace metals are transferred from the liquid (soluble) phase to the solid (insoluble) phase by the mechanisms of precipitation, coprecipitation and adsorption. Trace metals transferred to the solid phase, as well as the trace metal fraction already in the insoluble fraction, are removed by coagulation followed by sedimentation and/or filtration.

Direct Filtration Water Treatment

Some of the same mechanisms of trace metal removal are possible with direct filtration as with conventional water treatment.

Coagulation followed by filtration should effectively remove trace metals associated with the insoluble fraction. The lower coagulant dosages utilized in direct filtration might diminish the importance of coprecipitation as a mechanism for removal.

Precipitation as a result of pH control is possible with direct filtration. It is generally believed that the low solubility limits of the insoluble metal hydroxide and metal carbonate controls cadmium and lead solubility [6,7,10,26,27].

Table 3. Metal Removal With Conventional Water Treatment [4].

Treatment Process	Intended Purpose	Potential Mechanism(s) for Trace Metal Removal
1. Coagulation followed by sedimentation and filtration a. aluminum sulfate b. iron salts c. coagulant aids (clays, silica, polymers)	Turbidity and color removal	<i>Coprecipitation</i> with amorphous, hydrous aluminum and ferric oxides. <i>Adsorption</i> on clays or sediments. Removal of above by coagulation, sedimentation and filtration
2. Precipitation a. lime (CaO) and soda (Na ₂ CO ₃) b. sodium hydroxide (NaOH)	Hardness removal and pH control	<i>Precipitation</i> as oxides, carbonates, sulfides, or phosphates. Possible <i>coprecipitation</i> with CaCO ₃ and Mg(OH) ₂
3. Adsorption a. activated carbon	Taste and odor removal	<i>Adsorption</i> on activated carbon, removal of metallo-organic complexes.
4. Oxidation a. chlorine (Cl ₂) b. potassium permanganate (KMnO ₄) c. ozone (O ₃)	Iron and manganese removal	Oxidation to more insoluble forms that <i>precipitate</i> out. Oxidation of complexing organics that interfere with other coagulation and precipitation reactions.

For a water requiring softening, direct filtration will not be the preferred treatment option due to the large sludge volume generated. However, the solubility of CaCO₃ (s) is sufficiently low that some hardness removal is possible, and, coprecipitation of trace metal may occur [24].

Adsorption onto activated carbon is also quite possible with direct filtration since granular activated carbon can be used in the filters.

If oxidation for iron and manganese removal is required, direct filtration may be used. Oxidation, followed directly by filtration, has been used successfully to treat these waters.

In summary, the removal mechanisms of precipitation, coprecipitation and adsorption are possible within a direct filtration scheme and some level of trace metal removal is anticipated.

CHAPTER 5

PREVIOUS RELATED STUDIES

The previous works related to this study deal with the chemistry of aqueous metals, specifically, the processes mentioned in Chapter 4 which transfer the trace metal from the liquid phase to various solid phases. Data from the literature will be presented in accordance with these potential solubility controlling processes—precipitation, coprecipitation and adsorption.

Trace Metal Distribution

The distribution of the trace metal in a given water is essential for any subsequent discussion of metal removal. The removal processes are directly affected by the chemical form of the metal in solution. Singer [5] lists the more common forms of trace metals in Table 4.

Table 4. Distribution of Trace Metals in Natural Waters [5].

A. Soluble
1. Free metal ion
2. Simple hydroxo complexes
3. Other soluble complexes
a. Organo complexes
b. Inorganic complexes
B. Insoluble
1. Hydrous metal oxides
2. Adsorbed metals on suspended particles
3. Macromolecular organometal complexes

Models

The many constituents of a water are in competition for the available metals and several models are used to handle the simultaneous equilibria that this implies. The more sophisticated models are computer programs such as REDEQL 2 [3], ADSORP [30], and MINEQL [50] which can calculate the relative contribution to metal solubility for several species and can take into account adsorption phenomenon as well. These and other models referenced in this study are equilibrium models using thermodynamic data to predict solubilities.

The use of an equilibrium approach in describing the distribution of trace metal necessitates that precautions be taken in interpreting model results. Weber and Posselt [58] discuss model validity in some detail. They emphasize that the most important limiting factor in many applications of thermodynamic solubility relationships is the slow attainment of equilibrium. Others have observed this as well [17,29,40,46]. Slow reaction kinetics can be especially problematic when applying model results to water treatment processes with their relatively short detention times [11,17].

Parameters Controlling Metal Solubility

The chemical composition of surface waters vary widely with location. Quite commonly anionic species such as hydroxide (OH^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-) are present in sufficient concentration to form complexes with metal ions.

For certain waters, organic ligands are significant and included in the equilibrium model. Humic acids (HA) and fulvic acids (FA) are widely distributed in soils and sediments and form complexes with trace metals upon entering surface waters [41,42,43].

Numerous solids can be suspended in a water and can provide ample surface area for adsorption to occur. These suspended surfaces can include metal oxides, clays/silts and

particulate organic materials. Solids that become part of the bottom sediments continue to play an important role in controlling the distribution of trace metals via adsorption/desorption reactions [19,26,39].

To discuss all the potential interactions is not possible. The remainder of this section will deal with interactions considered important to this study.

Inorganic Ligands. Table 5 lists stability constants for metal-inorganic ligand complexes for cadmium and lead. Stability constants are adjusted for the experimental conditions of ionic strength (I) = 0.003M and temperature (T) = 20°C using the Guntelberg Equation and the van't Hoff-Arrhenius Equation, respectively. These equations are commonly used and explained elsewhere [26].

Table 5. Inorganic Complex Formation Equilibria for Cadmium and Lead.

Complex Reaction	Stability Constant, K*	Reference
$\text{Cd}^{2+} + \text{OH}^- \rightleftharpoons \text{CdOH}^+$	$10^{3.81}$	[39]
$\text{Cd}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_2^0$	$10^{7.72}$	[39]
$\text{Cd}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_3^-$	$10^{8.94}$	[27]
$\text{Cd}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CdSO}_4^0$	$10^{2.40}$	[39]
$\text{Cd}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CdCO}_3^0$	$10^{3.97}$	[29]
$\text{Cd}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CdHCO}_3^+$	$10^{2.3}$	[39]
$\text{Pb}^{2+} + \text{OH}^- \rightleftharpoons \text{PbOH}^+$	$10^{5.98}$	[30]
$\text{Pb}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_2^0$	$10^{10.32}$	[30]
$\text{Pb}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_3^-$	$10^{13.39}$	[30]
$\text{Pb}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_4^{2-}$	$10^{16.27}$	[30]
$\text{Pb}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{PbCO}_3^0$	$10^{5.00}$	[26]
$\text{Pb}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4^0$	$10^{2.70}$	[26]
$\text{Pb}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{PbHCO}_3^+$	$10^{2.80}$	[30]

*For T = 20°C, I = 0.003M.

Organic Ligands. The Bozeman tap water used in this study was an unpolluted surface water with a measured total organic carbon (TOC) content ranging from 1 to 5 mg/L

[44]. The lower limit corresponding to periods of low runoff (turbidity ≤ 1 NTU). Reportedly, the organo-metallic complexes increase metal solubility, interfere with adsorption, prevent agglomeration, and interfere with removal by filtration [4]. Fristoe and Nelson [46] determined conditional constants for cadmium-organic ligand complexes. In principle, the difference in the amount of metal adsorbed onto a cationic resin in the presence and absence of an organic ligand is used to calculate the stability constant for the complex. The conditional stability constants are calculated from Equation (1) and are presented in Table 6.

$$\beta_L = \frac{[M_L]}{[M_{T-L}] \{L\}} \quad (1)$$

where,

β_L = conditional stability constant, L/mg

$[M_L]$ = concentration of metal-organic ligand complex, moles/L

$[M_{T-L}]$ = concentration of total soluble metal minus $[M_L]$, moles/L

$\{L\}$ = organic ligand concentration, mg/L TOC.

Table 6. Conditional Stability Constants for Cadmium-Organic Ligand Complexes [46].

pH	5.0	6.0	6.5	7.0	8.0	9.0
β_L , L/mg (20°C)	0.05	0.18	0.19	0.21	0.05	0.0

Humic Materials. Naturally occurring polyelectrolytes referred to by such names as humic and fulvic acids are widely distributed in soils and sediments where they form water-soluble and water-insoluble complexes with metal ions [41]. A few studies have characterized these natural complexing ligands and conditional complexation stability constants with various metals have been evaluated. Table 7 lists some conditional stability constants for humic-metal complexes.

Table 7. Conditional Stability Constants for Humic-Metal Complexes for pH 7.5.

Metal	$\log \beta_{11}^*$	$\log \beta_{21}^*$	Reference
Pb (II)	6.0	13.2	[41]
Pb (II)	4.7**	—	[30]
Cd (II)	6.0	11.2	[41]
Cd (II)	6.3	11.7	[43]

**From empirical equation $\log \beta_{11}^* = 0.625 \times \text{pH}$.

where,

$$\beta_{11}^* = \frac{\beta_{11}}{\{H\}^x} = \frac{[MHA]}{[M^{2+}][H_x HA]} \quad (2)$$

$$\beta_{21}^* = \frac{\beta_{21}}{\{H\}^y} = \frac{[M_2 HA]}{[M^{2+}]^2 [H_y HA]} \quad (3)$$

and, $[MHA]$ and $[M_2 HA]$ represent metal-humic complexes.

Due to the color causing properties of humic materials, some researchers have developed empirical equations relating the extent of complexation by humic materials to the light absorbing properties of the water. Gardiner [29] developed the following equation for cadmium:

$$\log \frac{[\text{Cd complex}]}{[\text{Cd}^{2+}]} = 0.64 \log A_{400} + 0.20 \text{ pH} - 1.14 \quad (4)$$

where, A_{400} is the absorbance of the filtered solution at a wavelength of 400 nm.

Suspended Solids. Many researchers have treated adsorption surfaces analogous to soluble ligands. Conditional adsorption constants (K_{ads}) have been calculated for various homogeneous and mixed suspensions [3,39,46]. The following equation can be used:

$$K_{\text{ads}} = \frac{MS}{M_T S_T} \quad (\text{L/g}) \quad (5)$$

where, MS = total concentration of metal-solid complexes (mol/L); M_T = total soluble concentration of metal, free and complexed (mol/L); and S_T = total concentration of solid

phase (g/L). The conditional adsorption constant, K_{ads} , is specific for a particular set of chemical and physical characteristics that compose the solid-solution system. In other words, Equation (5) treats implicitly all complex formation equilibria that control constituent species concentrations of MS and M_T .

The experimental data needed to calculate, K_{ads} , and the procedures used are included in References [39] and [46].

Adsorption equilibria data will be presented in a later section.

Generalized Metal Speciation and Distribution Model

Equation (6) has been used to determine the fraction of total metal incorporated in a specific metal-ligand or metal-surface complex [46].

$$\alpha(j)_n = \frac{\beta(j)_n [L(j)]^n}{1 + \sum_j \sum_i \beta(j)_i [L(j)]^i + \sum_m K_{ads} S_m [\alpha_m]^{-1}} \quad (6)$$

where, $\alpha(j)_n$ = species fraction of metal-ligand complex $ML(j)_n$, or metal surface complex, $ML(j)_n S$ (dimensionless); j = ligand-type identifier; i = ligand number; n = stoichiometry of metal-ligand complex; $\beta(j)$ = stability constant for metal ligand complex of type j ; $[L(j)]$ = concentration of complexing ligand of type j (mol/L); S_m = concentration of adsorbing solid of type m (g/L); and $\alpha_m = [M]/[M_T]$ = free metal ion fraction of soluble species.

Using Equation (6), or a modification thereof, it is possible to plot soluble species concentration versus pH. This is done in Figures 1 and 2 for the experimental water used in this study. The procedures and assumptions required in making these diagrams will be discussed in Chapter 7, Speciation and Distribution Model.

Precipitation

Both cadmium and lead combine with various anions in solution to form insoluble compounds. These reactions transferring metal from the liquid phase to the solid phase and

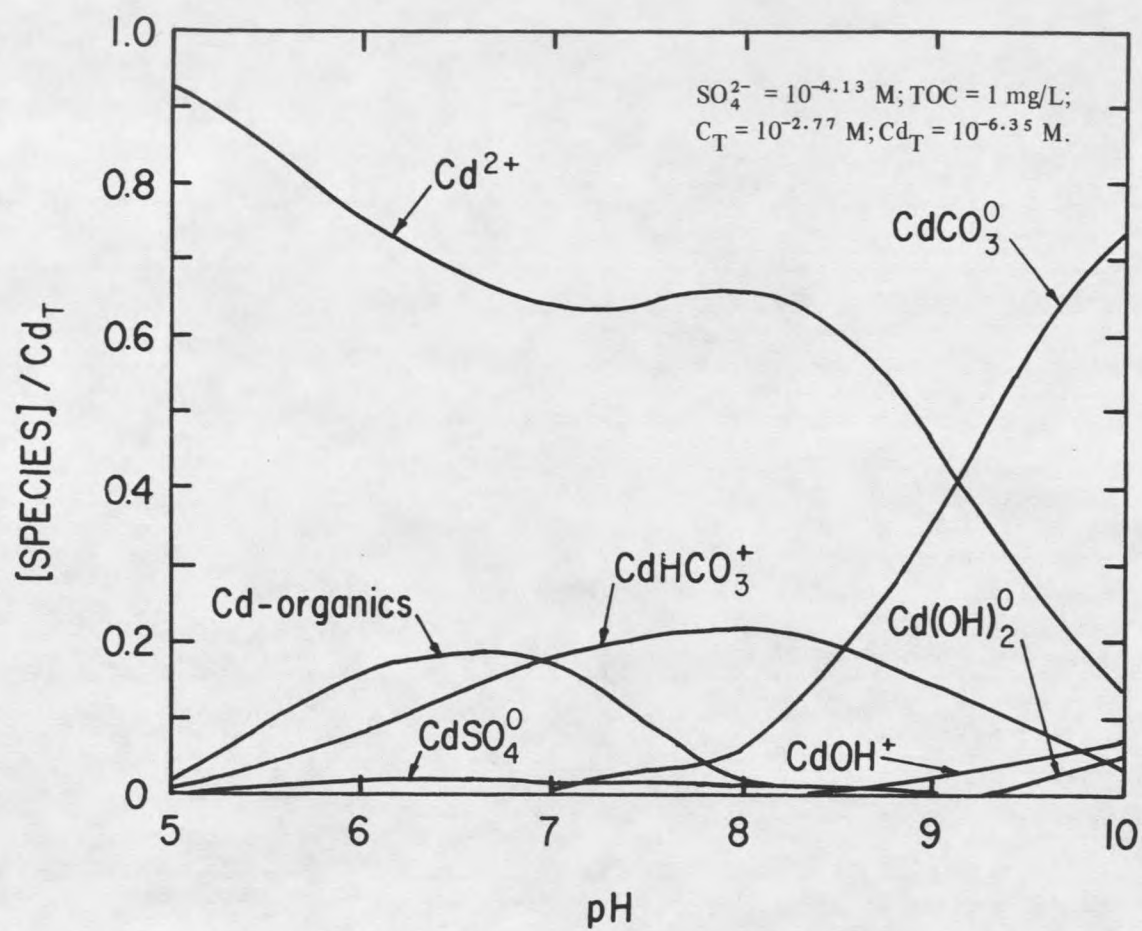


Figure 1. Speciation model for cadmium.

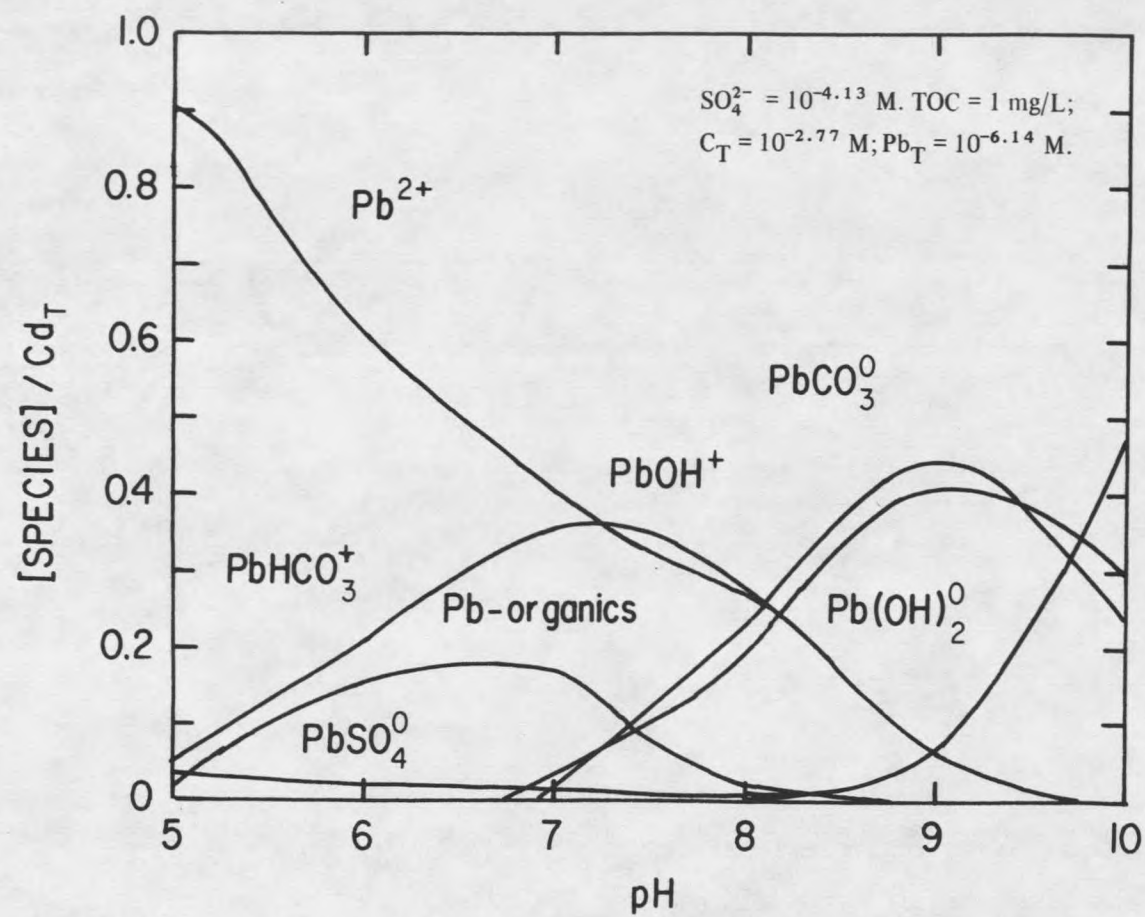


Figure 2. Speciation model for lead.

back to the liquid phase (dissolution) often regulate the concentrations of dissolved metal species. Table 8 lists the more common mineral sources for cadmium and lead along with their solubility products (K_{sp}). Hem's [6,7] calculations indicate that the insoluble compounds of sulfur will not control solubility for pH, total sulfur concentration and redox potential commonly found in oxic waters. In addition, the stability field of the basic carbonate, $Pb_3(CO_3)_2(OH)_2(s)$, occurs over so short a pH range that its contribution can also be omitted without introducing a significant error [6].

Metal-H₂O System

The simplest model used to interpret observed concentrations of trace metal in naturally occurring waters incorporates the metal and the components of pure water—hydrogen ions and hydroxide ions.

Table 8. Mineral Sources of Cadmium and Lead.

Mineral Source	Solubility Product	K_{sp}^*	Reference
$CdCO_3(s)$	$K_{sp} = [Cd^{2+}][CO_3^{2-}]$	; $10^{-10.77}$, $10^{-11.66}$	[19],[7, 26]
$Cd(OH)_2(s)$	$K_{sp} = [Cd^{2+}][OH^-]^2$	; $10^{-13.36}$, $10^{-14.05}$	[17],[7]
$CdS(s)$	$K_{sp} = [Cd^{2+}][S^{2-}]$	; $10^{-27.0}$	[24]
$PbCO_3(s)$	$K_{sp} = [Pb^{2+}][CO_3^{2-}]$	; $10^{-13.54}$, $10^{-13.96}$	[17],[6]
$Pb(OH)_2(s)$	$K_{sp} = [Pb^{2+}][OH^-]^2$	; $10^{-14.85}$, $10^{-19.29}$	[17],[6]
$PbS(s)$	$K_{sp} = [Pb^{2+}][S^{2-}]$	; $10^{-27.5}$	[24]
$PbSO_4(s)$	$K_{sp} = [Pb^{2+}][SO_4^{2-}]$	; $10^{-7.8}$	[26]
$Pb_3(CO_3)_2(OH)_2(s)$	$K_{sp} = [Pb^{2+}]^3[CO_3^{2-}]^2[OH^-]^2$	; $10^{-18.8}$	[17]

*Hydroxides and carbonates adjusted to T = 20°C and I = 0.003M.

Both lead and cadmium salts show varying degrees of acidity when dissolved in water. This observation is explained by the reaction of the metal ion with the solvent water, referred to as hydrolysis. Hydrolysis reactions can be described by either dissociation or complexation reactions and oftentimes occurs in a stepwise manner [26,27]. The general

hydrolysis reactions given below are for a divalent metal and represent the exchange of OH^- for an H_2O molecule from the inner coordinate sphere.



K_1 through K_4 are the stepwise formation constants.

A mass balance for the soluble metal species in the metal- H_2O system is written:

$$\text{M}_{\text{T}_s} = [\text{M}^{2+}] + [\text{MOH}^+] + [\text{M}(\text{OH})_2^0] + [\text{M}(\text{OH})_3^-] + [\text{M}(\text{OH})_4^{2-}] \quad (11)$$

where, M_{T_s} equals the total soluble metal concentration. Substituting the formation constants in Equations (7) through (10) into Equation (11) results in the following equation:

$$\text{M}_{\text{T}_s} = [\text{M}^{2+}](1 + \beta_1 [\text{OH}^-] + \beta_2 [\text{OH}^-]^2 + \beta_3 [\text{OH}^-]^3 + \beta_4 [\text{OH}^-]^4) \quad (12)$$

where, $\beta_1 = K_1$; $\beta_2 = K_1 \cdot K_2$; $\beta_3 = K_1 \cdot K_2 \cdot K_3$; $\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$.

In the divalent metal- H_2O system the maximum solubility is controlled by the insoluble hydroxide species with the stoichiometry $\text{M}(\text{OH})_2$ (s). The corresponding solubility product is found in Table 8. The free-metal concentration can be calculated from Equation (13) below.

$$[\text{M}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} \quad (13)$$

Substituting this value into Equation (12) gives the following expression for solubility, S:

$$S = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} (1 + \beta_1 [\text{OH}^-] + \beta_2 [\text{OH}^-]^2 + \beta_3 [\text{OH}^-]^3 + \beta_4 [\text{OH}^-]^4) \quad (14)$$

Solving Equation (14) for various pH results in theoretical hydroxide solubility curves as shown in Figures 3 and 4. The hydrogen ion and hydroxide ion concentrations are related as follows for $T = 20^\circ\text{C}$, $I = 0.003\text{M}$:

$$[\text{H}^+][\text{OH}^-] = K_w \approx 10^{-14.12} \quad (15)$$

In equation form, pH and hydrogen ion concentration are related by the following expression:

$$\text{pH} = -\log [\text{H}^+] \quad (16)$$

It is convenient to plot these hydroxide solubility curves using equations relating the metal hydroxide solid species in equilibrium with the various soluble species. These equations are presented below and can be derived using Equations (7) through (10), (13) and (15).

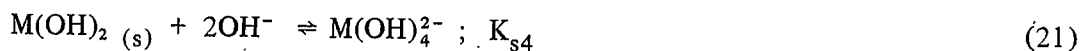
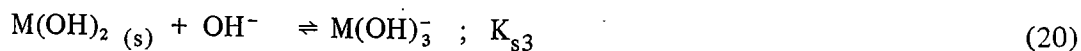
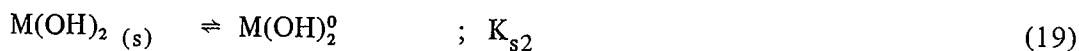
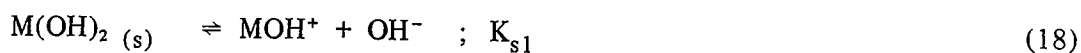
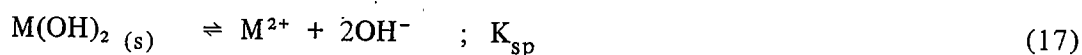


Table 9 lists the hydroxide solubility constants from the various references used in this study. The theoretical hydroxide solubility curves plotted in Figures 3 and 4 give some indication of the variance in thermodynamic data found in the literature.

Metal-H₂O-Carbonate System

Most waters contain appreciable quantities of dissolved carbon species resulting from heterogeneous equilibria with atmospheric carbon dioxide and carbon containing minerals. It is generally believed that together with the insoluble metal hydroxide, insoluble metal carbonate, $\text{MCO}_3 \text{ (s)}$, oftentimes regulates the metal concentration found in natural waters [6,7,11,26]. Modeling a metal-H₂O-carbonate system is complicated by the diprotic nature of carbonic acid as well as equilibria between the two solid phases and the several soluble species.

Modeling water treatment processes with a closed carbonate system, constant C_T , is usually justified [17]. The pertinent equilibria for carbonic acid in aqueous solution are given below for $T = 20^\circ\text{C}$ and $I = 0.003\text{M}$.

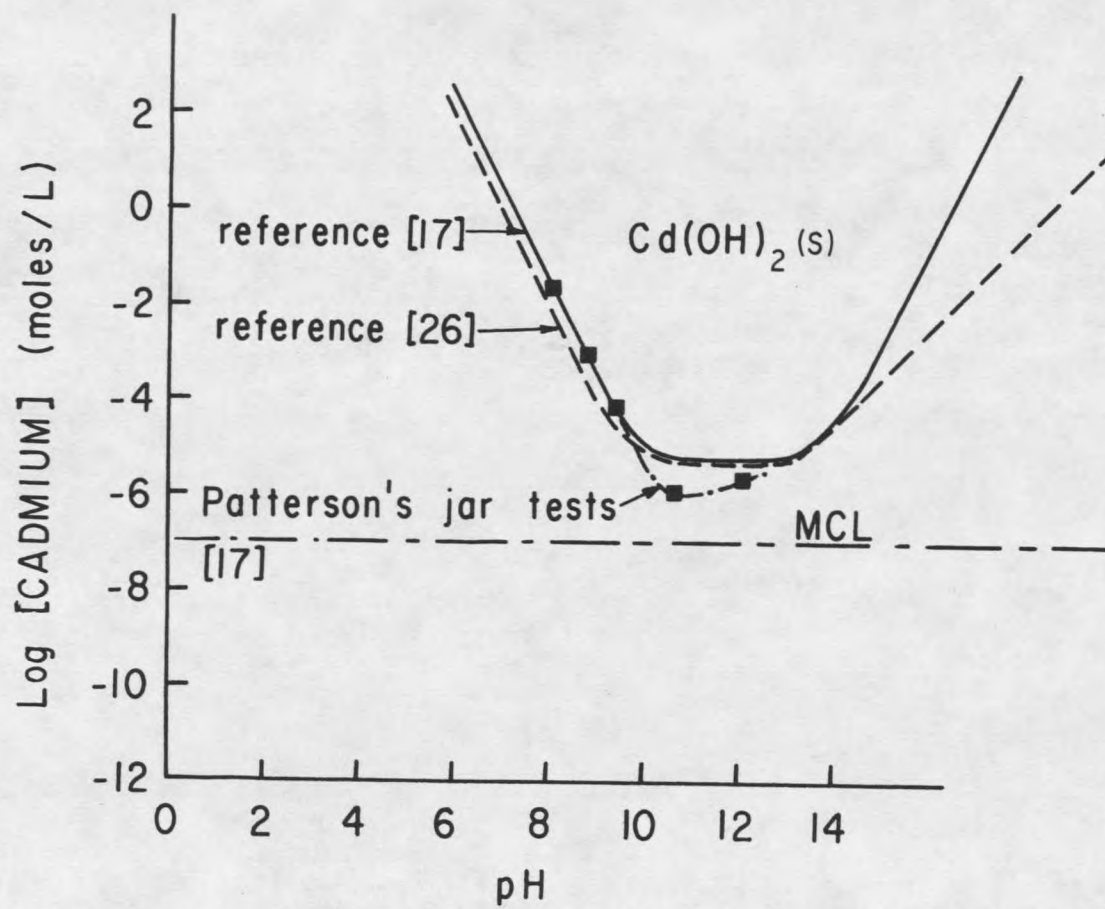


Figure 3. Cadmium hydroxide solubility diagram.

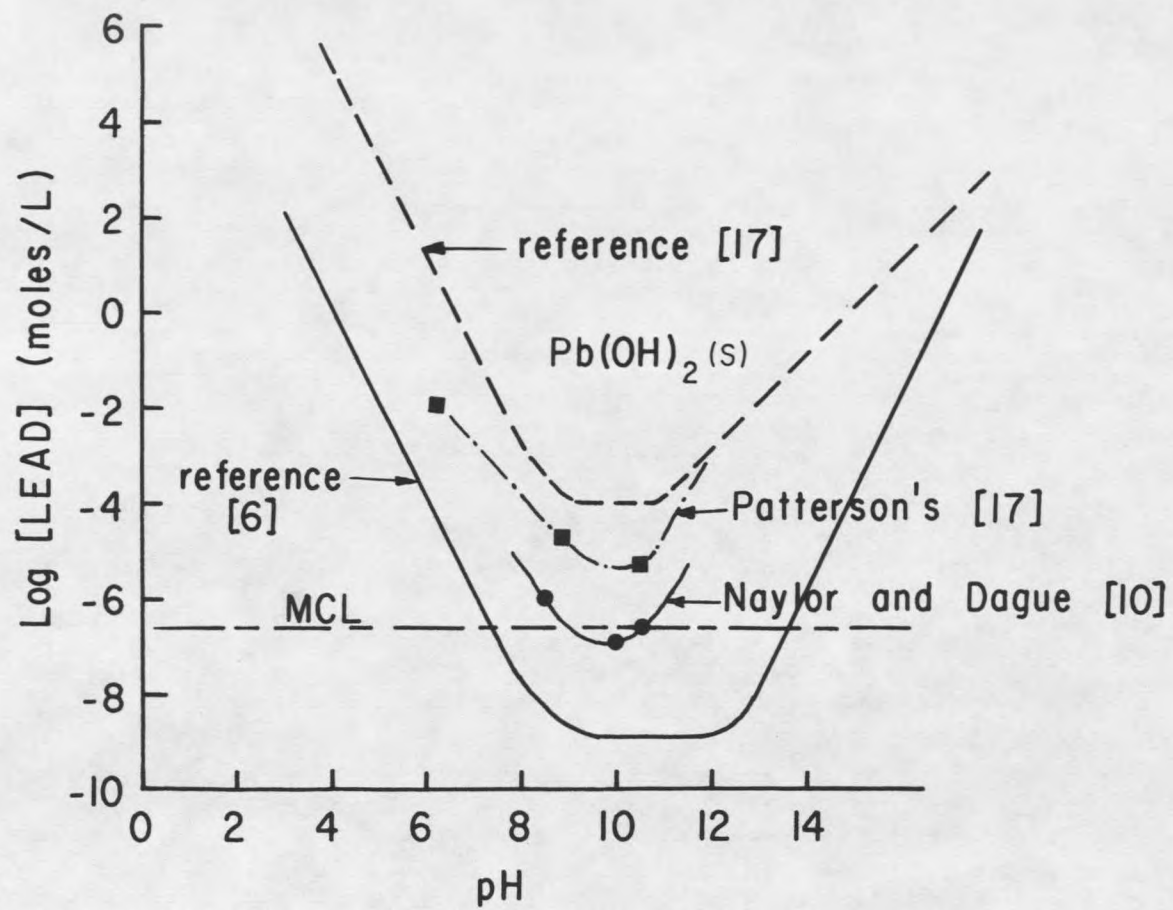
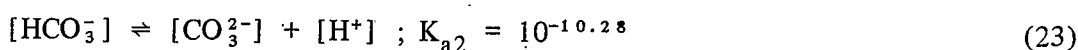
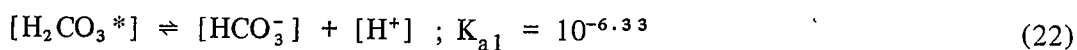


Figure 4. Lead hydroxide solubility diagram.

Table 9. Hydroxide Solubility Constants.

	Reference	K_{sp}	K_{s1}	K_{s2}	K_{s3}	K_{s4}	Source/Comments
Cadmium							
1.*	[17]	-13.7	-9.5	-5.3	-4.6	-4.9	Bard, Feitknecht, Schindler/fresh ppt.
2.	[17]	-14.4	-10.2	-6.0	-5.3	-5.6	aged ppt
3.	[7]	-14.39	-9.78	-5.47	-4.79	—	many sources given
4.*	[26]	-14.2	-9.59	-5.28	-4.60	—	Sillen & Martell 1964 & 1971 pubs.
5.	[25]	-13.6	-9.44	-5.20	(-4.5)	(-4.8)	parenthesis—approximate
6.	[29]	—	-9.06 ± .08	—	—	—	calculated
7.	[24]	-13.65	-9.75	-6.05	-4.95	—	many sources given
8.	[27]	-13.79	-9.20	-4.36	-4.21	—	
Lead							
9.*	[17]	-14.9	-9.1	-4.1	-1.0	—	several sources/fresh ppt.
10.	[17]	-15.3	-9.5	-4.5	-1.4	—	several sources/aged ppt.
11.*	[6]	-19.84	-13.96	-9.0	-5.92	—	Wagman & Faucherre
12.	[26]	-19.9	-13.70	-9.05	-5.32	—	Sillen & Martell 1964 & 1971 pubs.
13.	[30]	-19.9	-13.70	-9.0	-6.0	-3.6	Smith & Martell
14.	[25]	-14.3	—	—	—	—	
15.	[10]	—	—	—	—	—	jar test results only
16.	[27]	-14.93	-9.08	-4.13	-1.01	—	many sources

*Data plotted in Figures 1 and 2.



where, $[H_2CO_3^*]$ is the sum of aqueous CO_2 and free carbonic acid, H_2CO_3 . The distribution of soluble carbonate species for a closed system is shown in Figure 5 for $C_T = 10^{-2.77}$ M. The mass balance for total dissolved carbon can be written:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (24)$$

Neglecting hydrolysis species equilibria, the solubility of a divalent metal in a closed carbonate system can be calculated by direct solution of the following equation:

$$[M^{2+}] = K_{sp}' / [CO_3^{2-}] \quad (25)$$

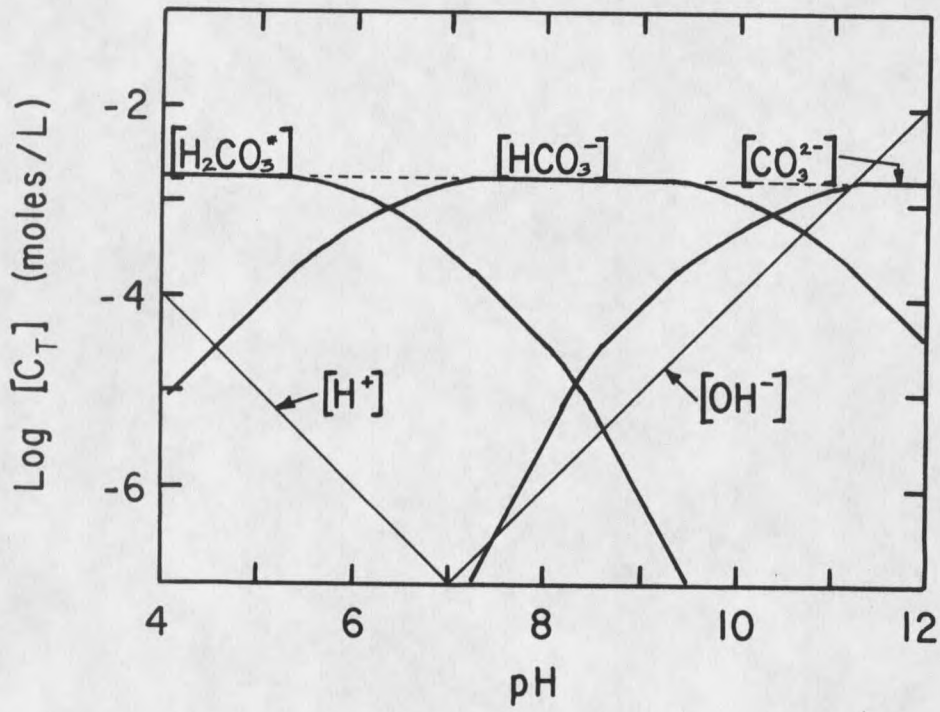


Figure 5. Closed carbonate system. $C_T = 10^{-2.77}$ M.

where, K_{sp}' represents the solubility product for the metal carbonate. Utilizing Equations (15), (22), (23) and (24), the carbonate concentration, $[CO_3^{2-}]$, can be determined from the following equation:

$$[CO_3^{2-}] = \frac{C_T}{\frac{K_w^2}{[OH^-]^2 \cdot K_{a1} \cdot K_{a2}} + \frac{K_w}{K_{a2}[OH^-]} + 1} \quad (26)$$

A better prediction of the metal solubility for this system requires consideration of metal hydrolysis species and the equilibria between these soluble species and the solid metal carbonate. To model these equilibria without unnecessary complication, it is assumed that in the pH ranges separated by points corresponding to the dissociation constants for carbonic acid, K_{a1} and K_{a2} , only one carbon species predominates. Therefore, for

$$pH < pK_{a1}, C_T \approx [H_2CO_3^*]$$

$$pK_{a1} < pH < pK_{a2}, C_T \approx [HCO_3^-]$$

$$pH > pK_{a2}, C_T \approx [CO_3^{2-}]$$

The equilibrium expressions for the metal hydrolysis species and the insoluble carbonate are listed by Patterson [17]. Plotting a solubility curve from these equations and superimposing the hydroxide solubility curve for the particular metal, allows one to predict which system controls solubility; at what pH solubility control transfers from the carbonate to the hydroxide system; and what the predicted soluble metal concentration is. Figures 6 and 7 were constructed in this manner for $C_T = 10^{-2.77}$ M. The thermodynamic data used in these diagrams is found in Tables 8 and 9 and from Equations (15), (22) and (23).

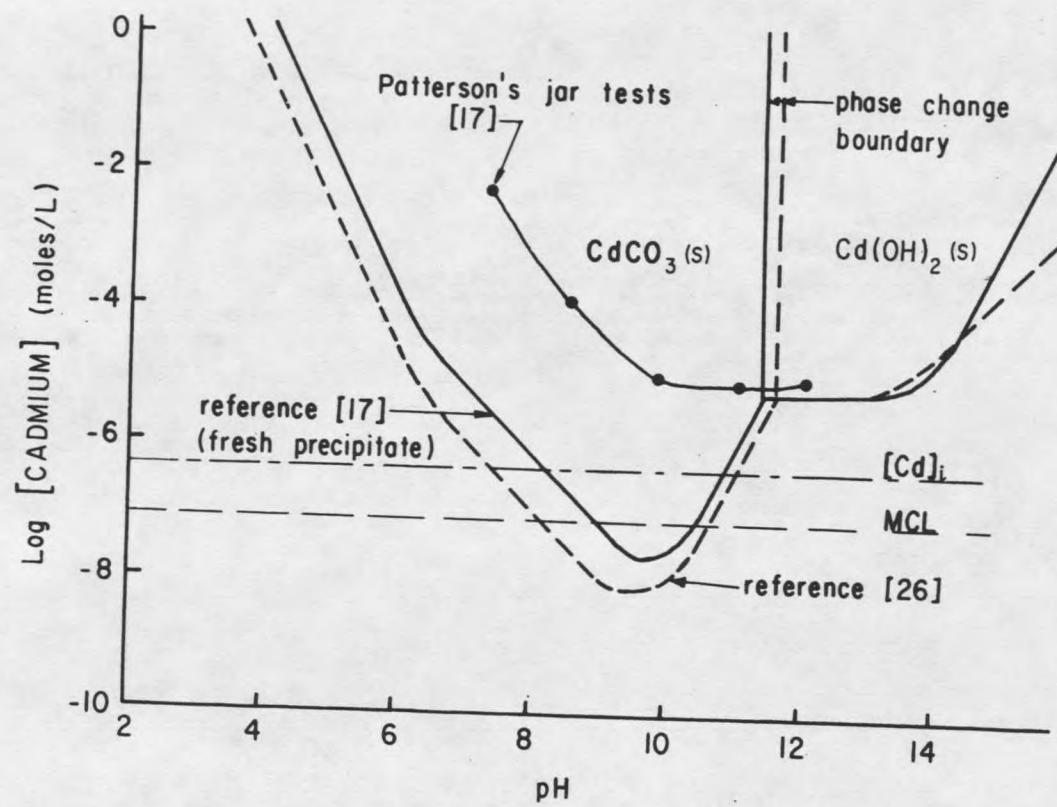


Figure 6. Cadmium phase diagram. $C_T = 10^{-2.77} \text{ M}$.

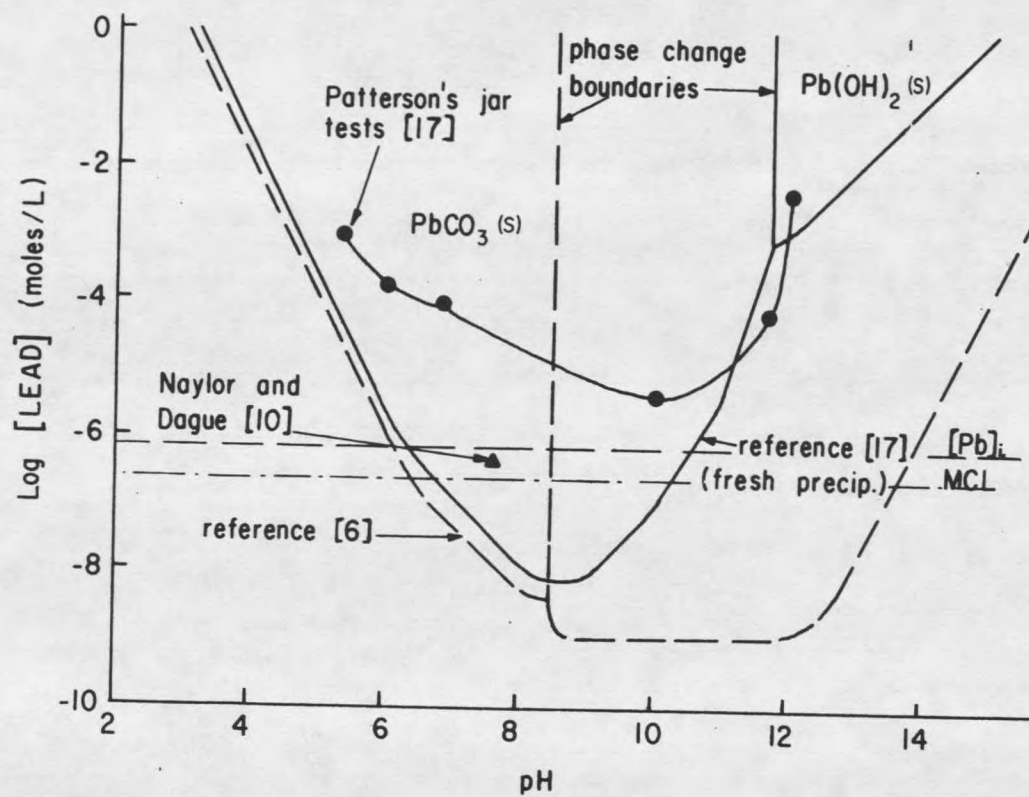


Figure 7. Lead phase diagram. $C_T = 10^{-2.77}$ M.

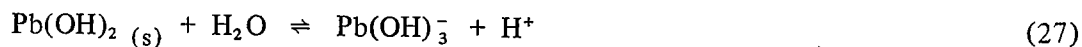
Some Experimental Data from the Literature

A few studies [10,11,17] have conducted laboratory experiments to investigate metal solubility under conditions representative of water treatment unit operations and processes. The results of the studies found are helpful in identifying the important parameters controlling metal solubility.

Lead Hydroxide Precipitation. Figure 4 depicts two sets of solubility data from Table 9 encompassing the range of reported solubilities. All the experimental data cited falls between these theoretical "limits."

Patterson [17] conducted four-hour jar tests to evaluate lead hydroxide solubility. The jars were left open to the atmosphere to simulate actual treatment facility conditions. The data obtained falls below the theoretical solubility curve for a freshly precipitated lead hydroxide. A low residual C_T of $10^{-3.6}$ M was thought to cause the discrepancy. Naylor and Dague [10] conducted jar tests of shorter duration which fell below Patterson's jar test results. Between pH 9.2 and 10.4, the 0.05 mg/L lead MCL was met.

Lime and excess lime-softening jar tests and pilot plant runs were also used to evaluate lead hydroxide solubility. Naylor and Dague demonstrated that the solubility was the same irregardless of whether the pH was controlled with sodium hydroxide or lime addition. Above pH 10.4 the solubility of lead increased due to the following reaction:



When a settled sludge of mixed chemical make-up was used to simulate a solids-contact softening process, nearly complete lead removal was obtained in the 9.5 to 10 pH range [10]. Sorg [11] used a natural water containing alkalinity, hardness and suspended solids to study lead removed with lime softening. Better than 99 per cent removal of 0.15 mg/L lead was observed in the 8.8 to 11 pH range. Sorg did not observe an increase in solubility

beyond pH 10.4 as did Naylor. This was attributed to coprecipitation with the magnesium hydroxide formed ($\text{Mg(II)} = 1.73 \text{ meq/L}$).

Because of the range of theoretical solubility data and differences in test results cited, Figure 4 has little predictive value. Patterson's data predicts no precipitation as the hydroxide at the $10^{-6.14} \text{ M}$ (0.15 mg/L) initial lead concentration used in this study. By contrast, Naylor's data predicts significant lead removal between pH 9.2 and pH 10.4. The lime-softening data appears to support lead hydroxide insolubility (Figure 4, Reference [6] curve), however, the data when compared to solubility data for controlled jar tests strongly implicates other removal mechanisms. Conclusive statements as to the removal mechanism(s) cannot be made.

Cadmium Hydroxide Precipitation. The theoretical and experimental data for cadmium hydroxide are in good agreement as shown in Figure 3. These curves predict that cadmium hydroxide precipitation will not control cadmium solubility at the $10^{-6.35} \text{ M}$ (0.05 mg/L) initial cadmium concentration used in this study.

Sorg [11] also conducted lime and excess lime softening jar tests and pilot plant runs for cadmium removal using a natural water. Essentially 100 per cent removals of cadmium in the 8.5 to 11.3 pH range were observed. These results are considerably better than can be predicted from Figure 3, and other mechanisms of removal are believed to contribute to the high removals.

Lead Carbonate Precipitation. Using thermodynamic data from References [6] and [17], two very different phase diagrams for lead are depicted in Figure 7.

Patterson [17] conducted jar tests with different C_T concentrations to evaluate the effect of carbonate on lead solubility. The four-hour jar tests indicate higher solubilities than either theoretical curve predicts. Patterson's data for $C_T = 10^{-2.77} \text{ M}$ is plotted in Figure 7. The discrepancy between theoretical and experimental data was attributed to the

slow lead carbonate kinetics in dilute solution. Naylor and Dague [10] performed jar tests with varying C_T at constant pH. They reported a lower solubility than observed by Patterson at pH 7.6. Increasing the C_T above $10^{-2.7}$ M had little effect on lead solubility.

Patterson's data predicts that the $10^{-6.14}$ M initial lead concentration will not be regulated by either the lead carbonate nor the lead hydroxide precipitate. Naylor's single data point suggests the strong possibility that the carbonate will regulate the lead solubility. The solubility achieved with $C_T = 10^{-2.7}$ M at pH 7.6 is not achieved in the carbonate free system until pH 8.8 (see Naylor's data Figure 4).

Cadmium Carbonate Precipitation. Figure 6 shows theoretical phase diagrams for the cadmium- H_2O -carbonate system for a $C_T = 10^{-2.77}$ M.

Again, Patterson's jar tests indicate cadmium solubilities much higher than theoretically predicted. The discrepancy is again attributed to the slow kinetics of the metal carbonate. Based on Patterson's jar test results, the $10^{-6.35}$ M initial cadmium concentration used in this study will not be regulated by the cadmium carbonate nor by the cadmium hydroxide precipitate.

Adsorption/Coprecipitation

Adsorption and coprecipitation reactions of possible significance to trace metal removal with direct filtration include: adsorption onto the suspended solids, coprecipitation with the coagulant floc and adsorption onto the filter media(s).

Adsorption Behavior of Hydrolyzable Metal Ions

James and Leckie [59] summarize the general interfacial behavior of hydrolyzable metal ions as follows:

1. There is a critical pH range over which almost 100 per cent adsorption occurs. This pH range is often less than one pH unit wide and is usually only slightly affected by

the type of adsorbent. Critical pH ranges for coprecipitation of selected trace metals on Al(III) and Fe(III) gels are presented in Figure 8 [53]. Benjamin et al. [18] discuss the effects of adsorbent concentration, adsorbate concentration, complexing ligands and competing adsorbates on these adsorption-pH curves.

2. It has been observed that the surface charge of the adsorbate will usually reverse sign when the metal ion hydrolyzes and metal hydroxides are precipitated. Figure 9 depicts the adsorption of lead on quartz. The first sign change corresponds to the original adsorbent becoming coated with hydroxides of the adsorbing metal ion. The charge reversal at higher pH often corresponds to the isoelectric point of the pure oxide of the adsorbing metal ion.

The charge reversals mentioned above are also apparent on the alum-coagulation diagram of Figure 10. The adsorption-destabilization region, particularly well suited for turbidity removal with direct filtration [15] is analogous to the sign reversal corresponding to the amorphous aluminum hydroxide precipitate. A schematic of this process for the negatively charged quartz suspension (Min-U-Sil) used in this study is presented in Figure 11. The negative surface charge for quartz above pH 2.0 is balanced by the charge on the $\text{Al}(\text{OH})_3$ (s) resulting in the dashed zeta-potential-pH curve.

3. Generally, rapid coagulation and settling of the suspended adsorbent occurs when the zeta potential decreases to a low magnitude.

Coprecipitation

The ability of hydrous metal oxides to interact with heavy metals has been known for many years. One method used to concentrate heavy metals from aquatic systems prior to analysis involved coprecipitation with Fe(III) and Al(III) salts [47]. These salts, commonly used in water treatment, are relatively effective in removing some trace metals from drinking waters [4,5,11].

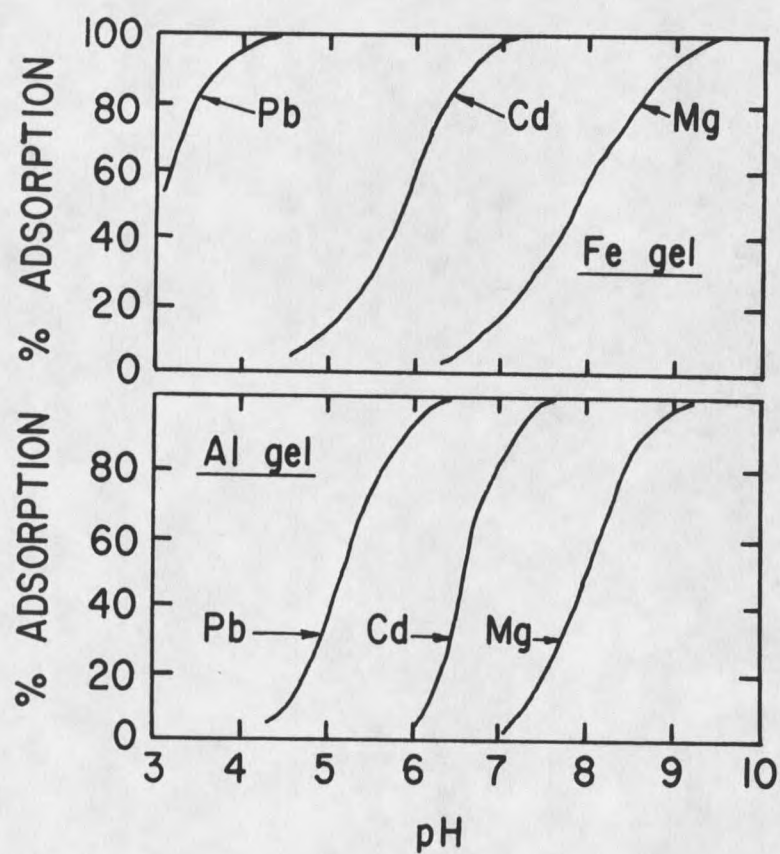


Figure 8. Adsorption of lead and cadmium on Fe(III) and Al(III) precipitate. $[Me]_T = 10^{-3.9} \text{ M}$; $I = 1 \text{ M}$; $Fe(III) = Al(III) = 10^{-1.03} \text{ M}$ [53].

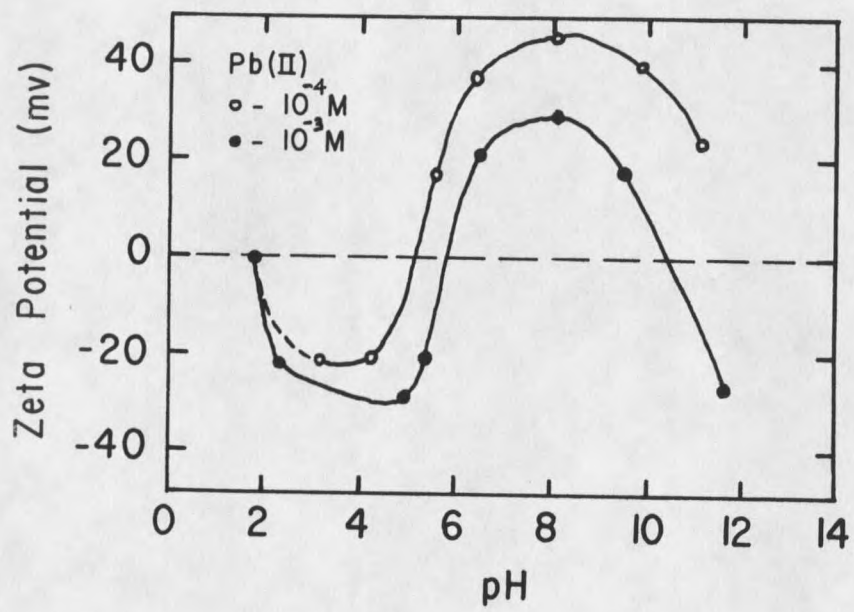


Figure 9. Zeta potential-pH relationship for quartz in the presence of Pb(II) [27].

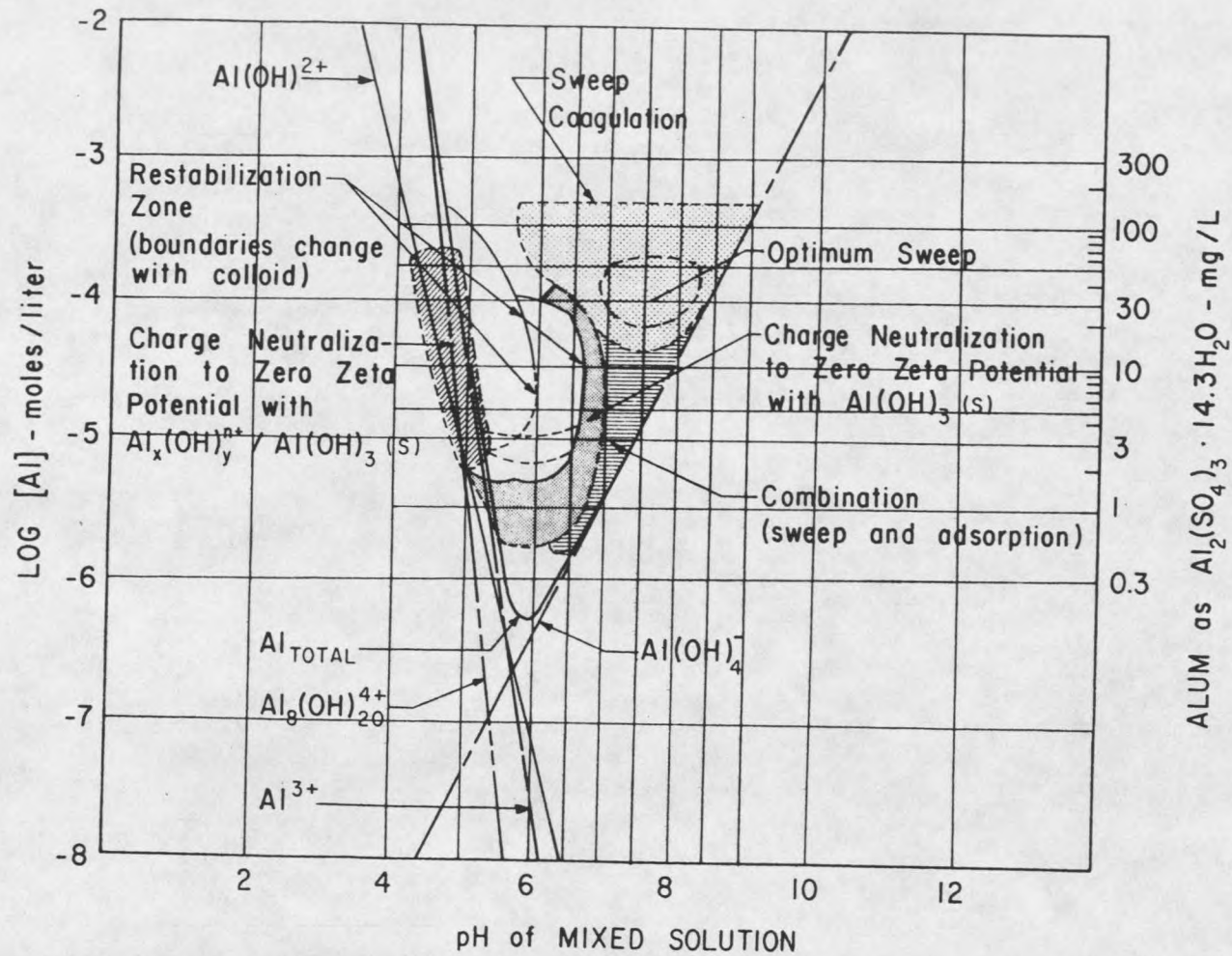


Figure 10. Alum coagulation diagram [35].

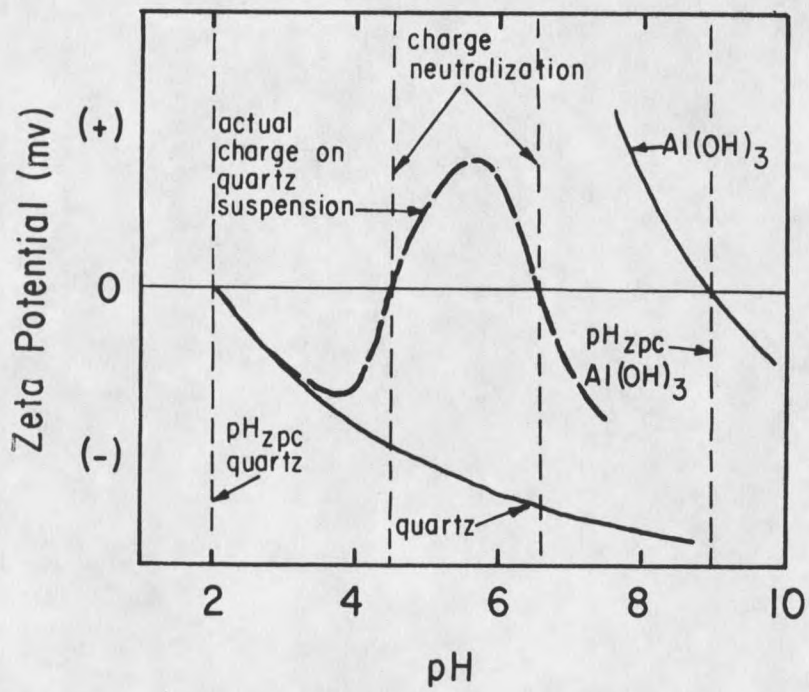


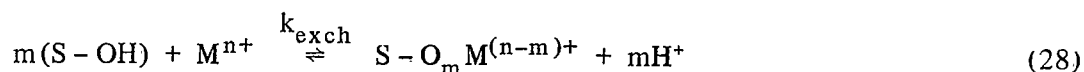
Figure 11. Zeta potential-pH relationship for quartz in presence of aluminum ($\text{Al} \approx 10^{-4.8} \text{ M}$).

Trace metal removal has also been attributed to coprecipitation with calcium carbonate and/or magnesium hydroxide floc in lime-softening processes [5,10,11,12]. However, no results of controlled experiments were found in the literature to evaluate this possible removal mechanism. Gardiner [55] did report large losses of Cd(II) from sample blanks upon precipitation of small amounts of calcium carbonate.

Hydrous Metal Oxides. Singer [5] reported that amorphous aluminum hydroxide and ferric hydroxide exhibit chemisorptive properties for free and complexed metals and as such, function as coprecipitants of trace metals. Others have noted that the metal oxides exhibit ion exchange properties that arise from the existence of pH dependent surface charge.

Interpretation of adsorption phenomena at the oxide surface fall into two general categories: (1) Many studies have examined the importance of ionization of the oxide/water interface in describing adsorption phenomena. The resulting models have successfully described the adsorption of dilute ions from solution [18,30,50]. (2) Other studies have concentrated upon the electrical double layer (EDL) and emphasize the importance of the EDL and physical interactions in controlling the distribution of solutes. EDL models have oftentimes been used to describe the adsorption of major electrolyte ions onto oxide surfaces. More recent models [50,52] develop an integrated approach that considers both chemical and physical interactions simultaneously.

Ion Exchange Models. The ion exchange model is useful conceptually for interpreting the removal of metal ions by oxide surfaces. It is widely accepted that oxide surfaces can act as weak acids and bases in solution, undergoing protonation and deprotonation in response to changes in solution pH [18,27,45,51]. According to the ion exchange model, adsorption on the hydrous oxide surface groups ($\equiv \text{S} - \text{OH}$) replace protons. A generalized equation for ion exchange is written:



where, S can be Al, Si, Fe, etc.; n and m are constants.

Measurements of changes in pH and pM allow calculation of stability constants for this reaction for several metals. However, as Leckie and James [59] point out, ion exchange theory cannot explain certain adsorption phenomena discussed earlier such as surface charge reversal.

The resulting hydrous oxide surface groups can enter into "complexation" reactions with other ions in solution as well. The surface complex formation model treats these surface groups as complex forming species [54]. Possible surface reactions are depicted in Figure 12 [45]. The following types of reactions are depicted:

- a) Acid-base reactions of surface hydroxyl groups
- b) Deprontinated surface hydroxyls coordinate with dissolved metal ions
- c) Surface hydroxyls are replaced by dissolved ligands
- d) and e) are ternary reactions

EDL Models. Many current studies have established that the adsorption of metal ions in the EDL is directly related to the hydrolytic behavior of the particular ion [27,30,50, 53]. These observations have resulted in various adsorption-hydrolysis models and specific adsorption models.

A graph depicting the correlations between surface stability constants and the hydrolysis constants of metals for various surfaces, including $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}_{(\text{am})}$ and SiO_2 , is presented in Reference [30]. Kinniburgh [53] performed coprecipitation tests with Fe(III) and Al(III) gels and found that significant adsorption occurred even when the extent of cation hydrolysis was much less than 1 per cent, and invariably occurred at pH values lower than required for hydroxide precipitation. Figure 8 shows the adsorption-pH

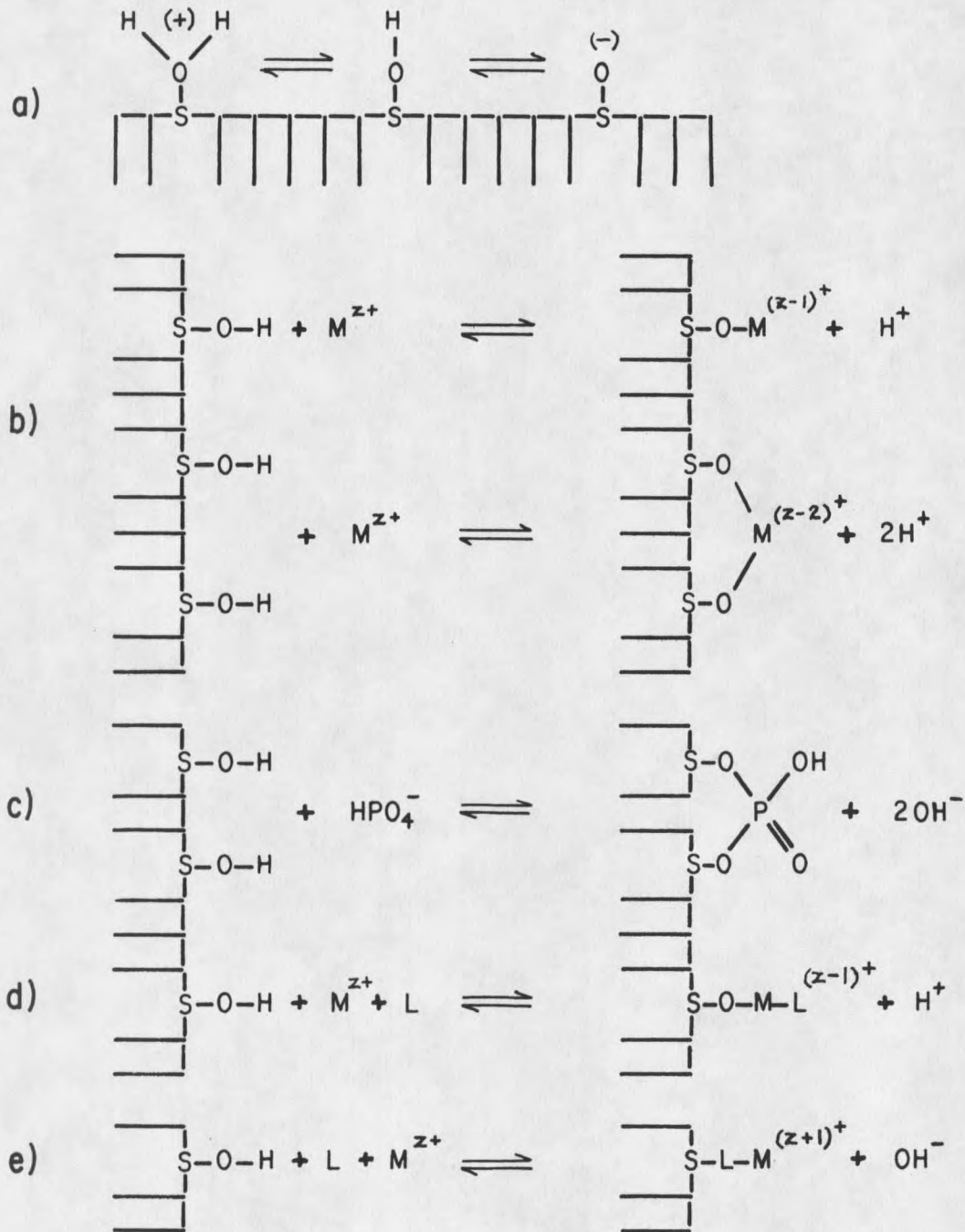


Figure 12. Complexation reactions at oxide-water interface [45].

sequences for the two gels. Shifts in the adsorption edges are significant for the two coprecipitants. Differences in sequencing and other discrepancies indicate that adsorption-hydrolysis models can only provide a qualitative description of adsorption behavior [27].

A general model of adsorption equally applicable to hydrous oxide and nonhydroxylated surfaces was developed by James and Healy [33,34]. The model utilizes EDL theory and considers coulombic, solvation and specific chemical energy interactions as the ion approaches the solid/liquid interface.

Removal Mechanism. As stated in Chapter 4, coprecipitation can be an adsorption process or an occlusion phenomenon. Bruninx [51] noted that it was not likely that occlusion played an important role in coprecipitation with ferric hydroxide. The strong pH dependency of metal accumulation at the ferric hydroxide surface excluded such a mechanism almost entirely. Additionally, tests performed by Benjamin and others [18,51] show the same concentration ratios when the metal is added after the ferric hydroxide precipitate (adsorption) as occurs when added before (coprecipitation). This is depicted in Figure 13. Adsorption appears to be the principal removal mechanism for coprecipitation reactions.

Kinetics of Coprecipitation Reactions. Simple solution equilibria and the simple chemical kinetic approach is essentially nonapplicable to hydrous oxide systems for several reasons [47,48]. Surface impurities, nonstoichiometric reactions, nonreversible reactions and precipitate aging are mentioned in the literature. The effect of aging is particularly complicated since not only is there a change in the total number of adsorption sites with time, but there is also a change in the type of adsorption site [53]. Regardless, kinetic studies and observations have been made. An earlier study of adsorption of metal ions on hydrous manganese dioxide found that the rates of adsorption for all metals studied were rapid, with equilibrium being attained within a matter of several minutes [47]. Benjamin

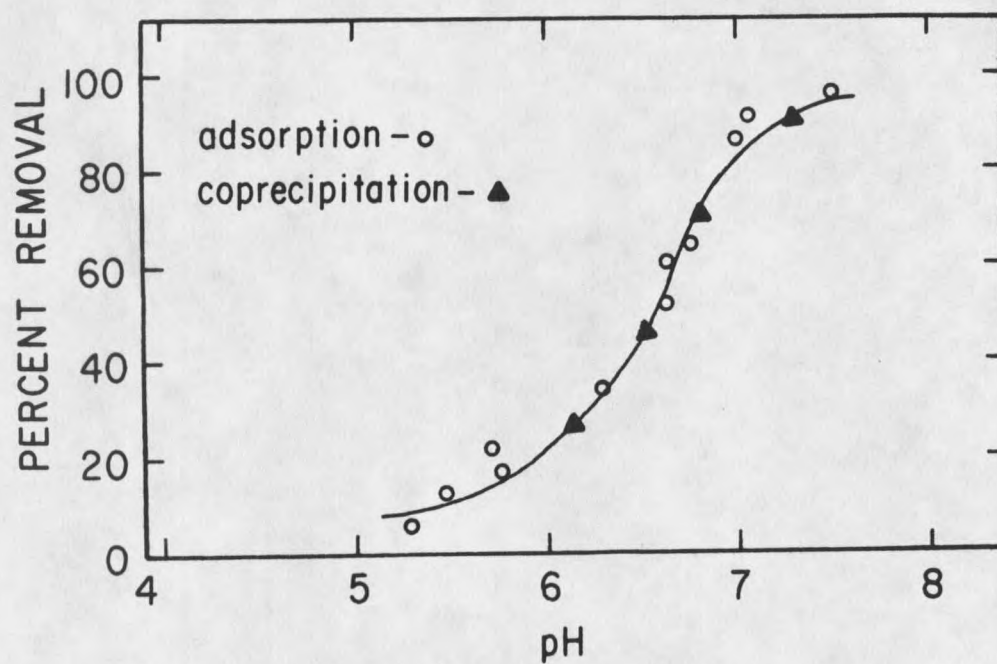


Figure 13. Adsorption/coprecipitation of Cd(II) on Fe(III) gel. $Cd_T = 10^{-6.3}$ M; $Fe_T = 10^{-3}$ M; $I = 0.1$ M; $T = 25^\circ\text{C}$ [18].

et al. [18] found near instantaneous adsorption of several metals including Pb(II) and Cd(II) onto $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}_{(\text{am})}$. Bruninx [51] studied the distribution of three metals including Cd(II) between the solution and coprecipitant as a function of time. Only slight changes in this distribution were noted up to 100 hours with the first measurements made at approximately 3 minutes. Benjamin and Leckie [48] conducted kinetic experiments using $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}_{(\text{am})}$. They also emphasize the fact that $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}_{(\text{am})}$ is not a true stable phase, and true equilibrium cannot be attained in short term experiments. However, their experiments show rapid initial adsorption for Cd(II). A quasi-equilibrium is attained after 1 hour followed by a much slower second step. Of significance to direct filtration treatment schemes is that a large percentage of Cd(II) was adsorbed within the first few minutes. These studies indicate that adsorption onto hydrous metal surfaces will probably be rapid.

Some Experimental Results From the Literature—Cadmium

Sorg [11] conducted both jar tests and pilot plant studies to determine the effects of coagulant type and coagulant dosage on cadmium removal. Some of the data is difficult to analyze as test conditions were not always identical and turbidity removal data was not available. Sorg found that for both a low alkalinity river water (1.2 meq/L) and a high alkalinity ground water (4 meq/L) ferric sulfate resulted in better cadmium removal than alum at the same pH. The high coagulant dosages used, 25 to 30 mg/L for both alum and ferric sulfate, should have resulted in nearly complete turbidity removals, therefore, the differences in removal at a given pH can be attributed to different coprecipitation properties for the two flocs. Other investigators have observed this also [5,53]. Sorg also found that cadmium removal was significantly greater with increasing alum dosage in the range 10 to 50 mg/L at pH 8.3. For the low alkalinity river water, cadmium removal increased from around 10 per cent for an alum dosage of 10 mg/L to 60 per cent with an alum dosage of

50 mg/L. Sorg's jar tests also revealed that for river water with turbidities below 20 NTU, alum coagulation resulted in decreasing cadmium removal above pH 8.0 to 8.5. This was attributed to the poor quality of the alum floc above pH 8.0. This pH corresponds roughly to the right thermodynamic boundary for $\text{Al}(\text{OH})_3 (s)$ precipitate (see Figure 10). To the right of this boundary, the soluble $\text{Al}(\text{OH})_4^-$ species will predominate with a subsequent decrease in floc formation. Without turbidity removal data, which may or may not be poorer outside the thermodynamic boundary, the mechanism of removal cannot be identified unambiguously.

Some Experimental Results From the Literature—Lead

Sorg's [11] jar test and pilot plant data show alum and ferric sulfate coagulation to be very effective for lead removal. Near 100 per cent removal was achieved in the pH range 6 to 10 for both coagulants. The only exception was alum coagulation of low-turbidity well water which showed a pH dependency with lead removal increasing with increasing pH. Removals increased from 78 per cent at pH 6.6 to 96 per cent at pH 9.6. Additional jar tests with varying water turbidities indicated that lead was easily adsorbed by the turbidity. The relative contributions of turbidity and coagulant to the removal of lead were not thoroughly investigated.

Naylor and Dague [10] found that varying the alum dosage resulted in increased lead removal with increased dosage, however, the increases were not appreciable. At $\text{pH} \approx 7.0$, lead solubility was reduced from 1.7 mg/L with about 10 mg/L alum to 0.75 mg/L lead at 200 mg/L alum. In the turbidity free synthetic water utilized, lead removal showed the pH dependency also observed by Sorg [11]. Removals ranged from 85 per cent at pH 6.4 to 97.5 per cent at pH 8.2 for a water containing 4 meq/L alkalinity with an alum dosage of 50 mg/L. The removals obtained were similar to those obtained as a result of carbonate alkalinity without any coagulant present, and were unlike the removals obtained with alum

in a carbonate free water. From this data, Naylor concluded that alum would not significantly improve lead removals since lead was already quite insoluble in the pH range investigated. Nilsson [31] observed that the more soluble metals are more affected by coprecipitation with aluminum hydroxide than are the more insoluble metals; the latter being readily removed by filtration and sedimentation unit operations.

Adsorption Onto Suspended Solids

Various studies have quantified adsorption reactions onto suspended solids. However, the quartz suspension used in this study has not received much attention. Since quartz is an oxide much of the previous discussion on hydrous metal oxides applies.

Using published thermodynamic data, Vuceta and Morgan [3] modeled complex aquatic systems with SiO_2 (s) (not specified as quartz) as the principal adsorbent. In inorganic systems, no more than 8 per cent adsorption of lead and 1 per cent adsorption of cadmium was predicted.

Gardiner [55] used the Freundlich isotherm to quantify cadmium adsorption onto various surfaces.

$$C_s = KC_l^{1/n} \quad (29)$$

where,

C_s = the concentration of adsorbed species on the solid, mg/kg

K = a constant, L/g

C_l = the concentration of the solute remaining in solution after adsorption has occurred, $\mu\text{g/L}$

n = a number measured empirically.

Equation (29) was simplified by assuming $n = 1$, resulting in the following equation:

$$K = \frac{C_s}{C_l} \quad (30)$$

where, K now becomes a concentration factor.

Gardiner's adsorption experiments on river muds indicated very fast reactions with adsorption nearly completed after 2 minutes. An increase in the proportion adsorbed with increasing suspended-solids concentration was observed. Vuceta and Morgan [3] also observed this (see Figure 14). Also, the proportion of the total cadmium adsorbed decreased steadily with increasing cadmium concentration. Competition between the adsorbing solid and the aqueous ligands was demonstrated by a decrease in K with increasing EDTA concentration. To determine which component of river mud was most responsible for the adsorption observed, concentration factors were determined for silica (precipitated), clay and humic materials. The concentration factor for humic material was close to those obtained for the muds and it is therefore probable that humic constituents of mud are principally responsible for its adsorptive properties. For the silica a $K = 430 (\pm 40)$ was measured compared to $K = 14,000 (\pm 2000)$ for humic material. The experimental water used by Gardiner contained approximately twice the alkalinity and comparable pH to Bozeman tap water. Assuming the same K for quartz Equation (30) predicts approximately 6 per cent adsorption of cadmium ($[Cd]_0 = 0.05 \text{ mg/L}$) onto silica at pH 7.5. It is reported that freshly precipitated oxides have a greater surface activity [5], therefore, the actual adsorption onto quartz may be less.

Wiley and Nelson [39] determined that the contribution of clays and sand to the adsorption of cadmium on river sediments was negligible even though they compose most of the sediment mass. Indirectly, they can be important as matrices for coatings of iron and manganese oxides and organic materials [19,39,55].

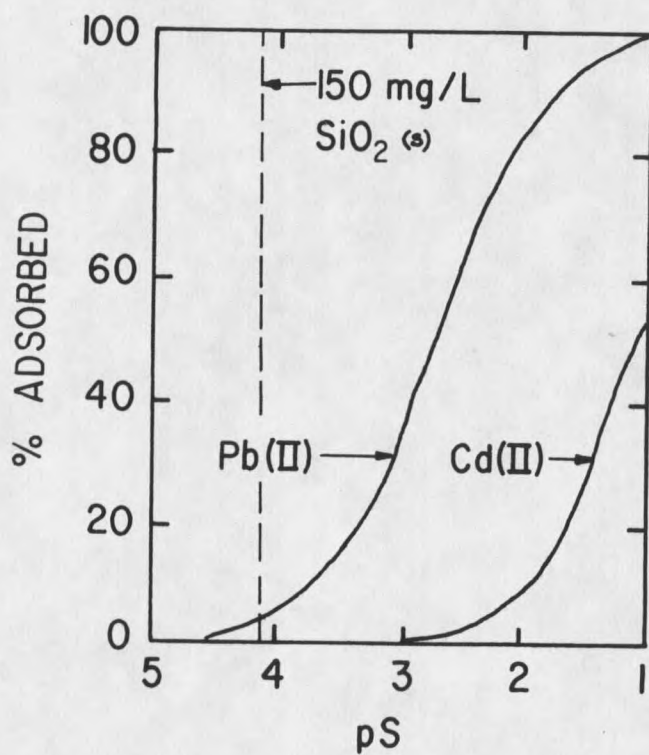


Figure 14. Adsorption onto $\text{SiO}_2(s)$ as a function of surface area, S . $\text{pH} = 7.0$; $p\epsilon = 12$; $P_{\text{CO}_2} = 3.5$; $pM_T = 4.16$ [3].

Mouvet [30] determined that most of the lead, 80 to 100 per cent, was readily adsorbed onto river sediments, however, the sediments were not analyzed as to their makeup.

Suzuki [19] found that cadmium correlated well with ignition loss of river sediments and therefore the cadmium was adsorbed predominately onto the organic fraction. The inorganic fraction, however, could not be ignored and accounted for some adsorption.

Sorg [11] noted that cadmium will be found mainly as the free ion Cd^{2+} and other complexed dissolved forms such as CdCO_3 (aq) and Cd-humic complexes. Adsorption onto inorganic suspended-solids was not reported as being too significant. Lead, by contrast, readily adsorbed onto suspended materials and was easily removed from high turbidity surface waters. Figure 15 [11] illustrates this. The suspended-solids were not characterized in Sorg's study.

Davis and Leckie [50,52] found that more than one stoichiometric surface reaction was usually necessary to describe the adsorption behavior of dilute heavy metal ions onto hydrous oxides. In their site-binding model, mass law equations for surface reactions of metal ions are corrected for effects of the EDL. The significant surface reactions for an α -quartz suspension were determined to be:

Cadmium



Lead



By fitting model calculations with experimental adsorption data for quartz, the intrinsic surfaces complexation constants in Table 10 were determined.

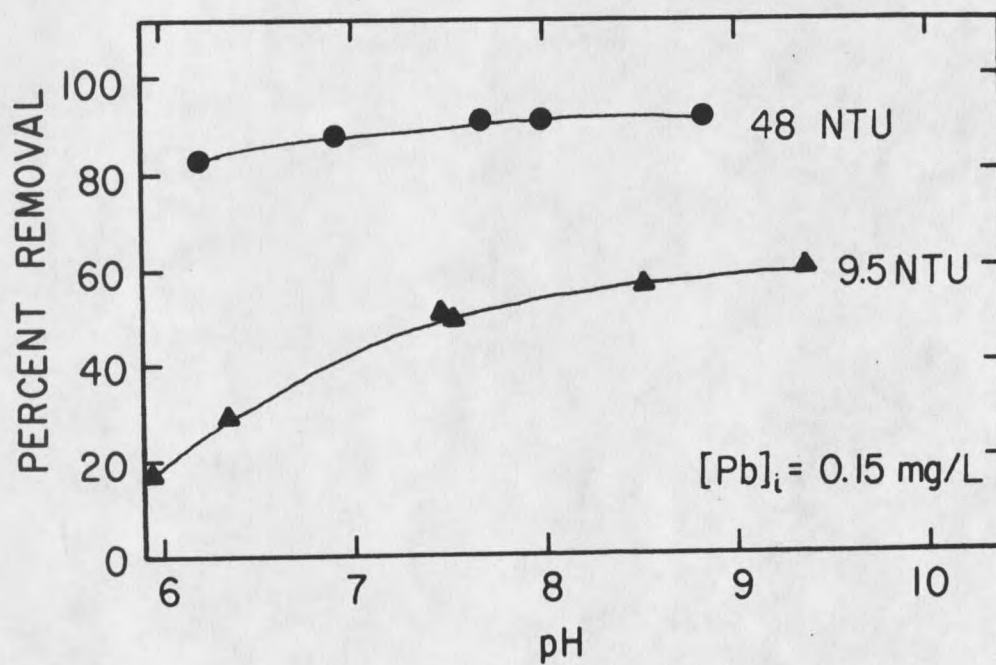


Figure 15. Effect of turbidity and pH on lead removal by settling [11].

Table 10. Intrinsic Surface Complexation Constants for Quartz [50].

Oxide	Metal	$\log K_{Me^{2+}}^{int}$	$\log K_{MeOH^+}^{int}$	Total Metal Concentration
α -quartz	Cadmium	— *	5.0	5×10^{-7} M
α -quartz	Lead	4.6	7.8	5×10^{-7} M

*Unable to determine since model calculations were adequate with the monohydroxo complex as the only adsorbing species.

Lead forms stronger bonds with the quartz surface than does cadmium. It was also noted that the intrinsic constants of heavy metal ions with a silica surface are considerably smaller than with other oxide surfaces [3,39,50]. The total metal concentration is reported in Table 10 because it was found that the pH-adsorption relationships of several metal ions, e.g., Pb(II) and Cd(II), on some hydrous oxides are dependent on the total metal concentrations, even at low adsorption density. Benjamin and Leckie [48] attributed this to an array of oxide surface sites of variable complexation strength for metals.

Adsorption Onto Filter Media

No literature data was found describing trace metal adsorption onto anthracite coal. While Sorg [11] reports some removal in the dual media filters the actual method of removal cannot be ascertained. Removal of suspended-solids, coagulant floc and/or adsorption to surfaces already attached to the filter media can all be significant to the removals reported. Coating of the filter media by $Al(OH)_3 (s)$ and $Fe(OH)_3 (s)$ could control the adsorption characteristics of the media surfaces at pH values conducive to floc formation [39].

CHAPTER 6

EXPERIMENTAL WORK

Plan

The intent of the experimental work was to investigate lead and cadmium removals under conditions simulating a direct filtration water treatment plant. To accomplish this, a direct filtration pilot plant designed to incorporate many characteristics commonly found in operating treatment plants was utilized.

Forty-four, five to eight hour, direct filtration pilot plant runs were conducted to collect data on metal concentration, pH, turbidity and headloss variations. In addition, supplemental benchscale tests were conducted in order to identify the mechanism(s) of metal removal.

The major parameters investigated were pH and coagulant dosage. These two parameters can be important in producing a high quality water with respect to turbidity and metal removal [10,11,15].

Turbidity Removal

The Coagulation Diagrams shown in Figures 10 and 16 define regions of turbidity removal within the thermodynamic boundaries of aluminum, Al(III), and iron, Fe(III). The ordinate and abscissa are coagulant dosage (aluminum and iron salt) and pH, respectively. An earlier study [15] has demonstrated the suitability of the charge-neutralization region at near neutral pH as being especially suited to direct filtration. In this region a colloidal suspension can be destabilized with relatively low coagulant dosage. This is important in a treatment scheme wherein all solids are removed in the filtration unit.

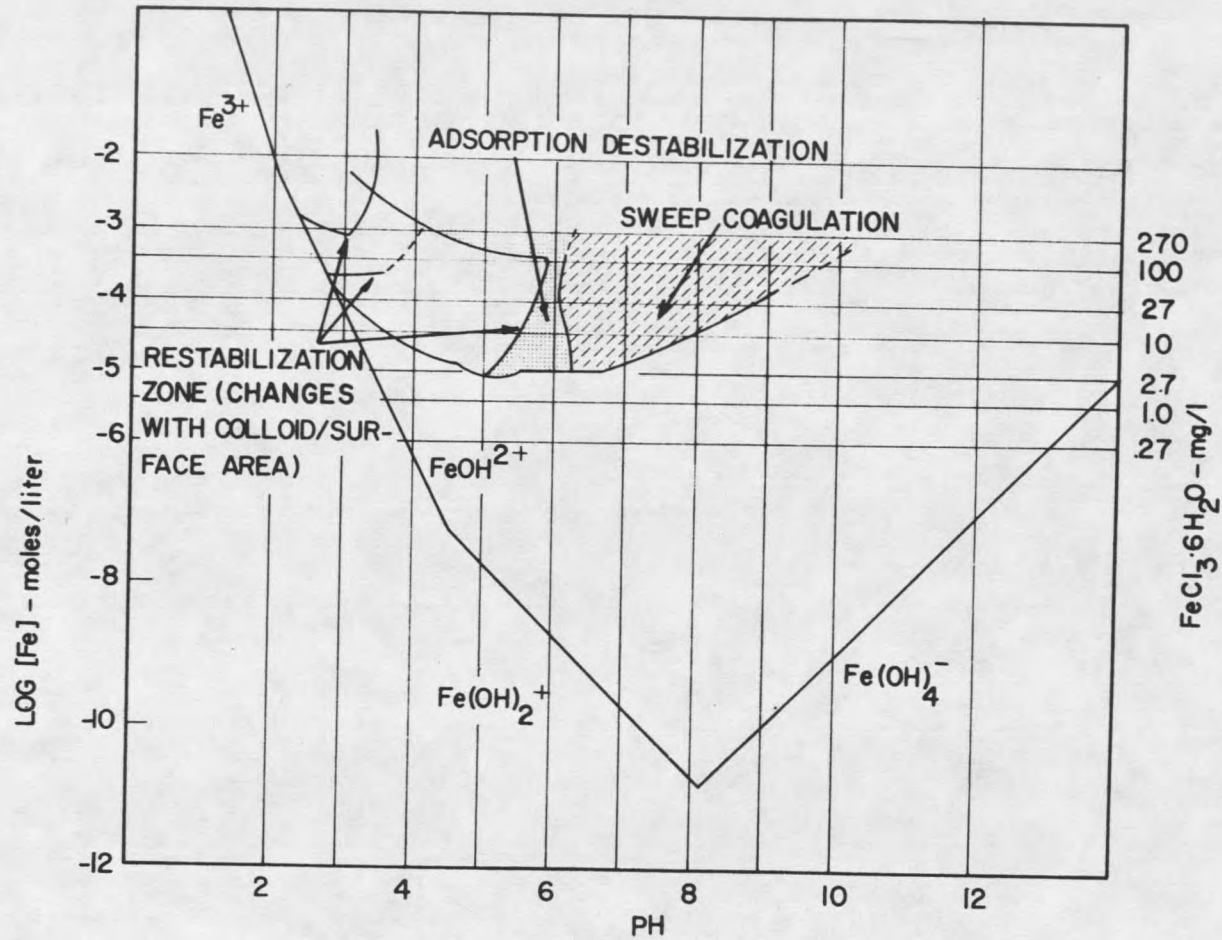


Figure 16. Iron (III) coagulation diagram [60].

Theory relating to colloid destabilization was discussed in Chapter 5, section entitled "Adsorption Behavior of Hydrolyzable Metal Ions."

Trace Metal Removal

As discussed in Chapter 5, pH is an important variable in controlling the solubility of trace metals in natural waters. References cited in Chapter 5 have shown that trace metals can adsorb strongly onto hydrous oxide surfaces. Freshly precipitated hydrous aluminum and ferric hydroxide, used in water treatment as coagulants, provide large and active surfaces for this attachment to occur.

To produce an acceptable effluent water, both turbidity and trace metal removal must be accomplished concurrently. The approach taken in this study was to run the pilot plant within a range of variables suitable for turbidity removal and to evaluate trace metal removal in this context. Both turbidity and metal removal data were collected to identify operating regions on the coagulation diagrams that resulted in attainment of the MCLs for both metal and turbidity.

Direct Filtration Pilot Plant

The constant rate direct filtration pilot plant used in this study is diagrammed in Figure 17. A constant flow of 1 L/min (0.264 g/min) was maintained throughout all pilot plant experiments. The 220 L/min/m² (5.4 g/min/ft²) filtration rate falls towards the upper end of rates reported in a questionnaire survey of operating direct filtration plants [22]. The constant rate was maintained with variable head influent control.

The pilot plant consists of four major sections: the raw water reservoir (C), the rapid-mix unit (D), the chemical feed reservoirs (A and B), and the filter unit (E).

A-COAGULANT STOCK
 B-POLYMER STOCK
 C-RAW WATER RESERVOIR
 D-RAPID MIX
 E-DUAL MEDIA FILTER
 F- FLOWMETER
 G-SAMPLING PORTS
 H-MANOMETER TAPS
 M-MIXER
 P-PUMP
 X- VALVE

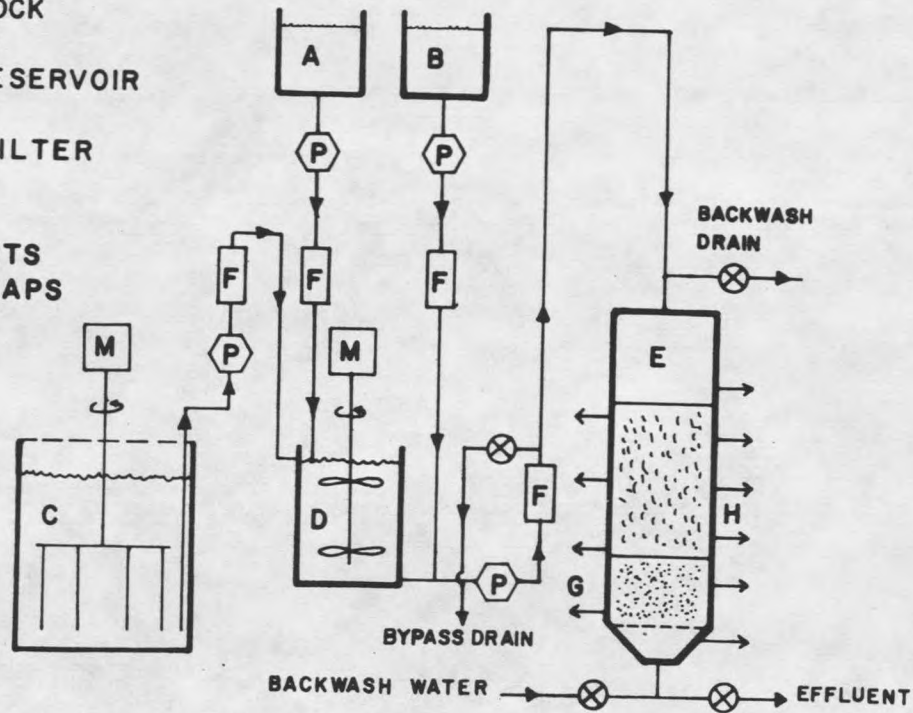


Figure 17. Direct filtration pilot plant flow diagram.

Raw Water Reservoir

A 200 L lined drum with a variable speed mixer was utilized as the raw water reservoir. Mixing was sufficient to provide a uniform influent water. The reservoir was covered to minimize carbon dioxide exchange.

Raw Water Preparation. Unless otherwise specified, Bozeman, Montana tap water was used in all pilot plant runs. Water temperature was maintained at 20°C (68°F) by adjustment of the cold and hot water taps at the time of filling. The significant chemical characteristics of Bozeman tap water are given in Table 11.

Table 11. Bozeman Tap Water.

Parameter	Concentration
Alkalinity (mg/L as CaCO ₃)	80
Sulfates (mg/L)	8
Hardness (mg/L as CaCO ₃)	100
Phosphates (mg/L)	< 0.2
Turbidity (NTU)	0.5 - 1.0
pH	7.4 - 7.7
Color (CU)	8
TDS (mg/L)	150
TOC (mg/L)	< 5

Measurements over the years show these parameters to be fairly constant. Seasonal changes occurred during the spring runoff period when tap water turbidity occasionally surpassed 10 NTU. Attempts at treatment during the runoff period indicated a water that was significantly different. However, by operating the pilot plant only when the tap water had a turbidity ≤ 1 NTU, seasonal changes were avoided and the data collected was reproducible throughout the experimental period July 1982 to December 1983.

Since Bozeman water contains immeasurable concentrations of cadmium and lead, both were added to the raw water. Initial metal concentration was not a variable in this

study. The initial trace metal concentrations decided upon were 0.05 mg/L for cadmium and 0.15 mg/L for lead, five and three times the MCL respectively.

Turbidity was added in the form of Min-U-Sil 30 (M30). This quartz suspension has been used in previous studies [15,38] and is a product of the Pennsylvania Glass Sand Corporation. A particle size distribution [38] is included in Figure 18. It was found that 150 mg/L M30 resulted in an unsettled turbidity of approximately 25 NTU. This initial turbidity was kept constant for all runs.

Control of raw water pH was achieved using hydrochloric acid (Baker Reagent, 37% HCl) or sodium hydroxide (Baker Reagent, 98.8% NaOH pellets). The pH was controlled in the raw water reservoir to give the desired effluent pH. It is the effluent pH which is reported in all subsequent results.

Rapid-Mix Unit

The raw water prepared as described above was pumped to a constant head arrangement on the influent side of the rapid-mix unit. The rapid-mix unit was comprised of a cylindrical baffled vessel with a single motor driven shaft. The shaft rotated two propeller type impellers at a constant rate. A detention time of 1 minute was maintained by a rotometer on the influent side of the mixer. The level of mixing and detention time resulted in a measured velocity gradient, or G value, of approximately 4900 s^{-1} . The method of measurement is explained in a previous study [15] and is calculated from the following expression:

$$G = \left[\frac{P}{\mu V} \right]^{1/2} \quad (34)$$

where, P = power input to the water, μ = dynamic viscosity of water at 20°C , and V = the volume of water in the rapid-mix vessel. The rationale for using such a high G value stems from another study [35] on rapid-mix design conducted at Montana State University.

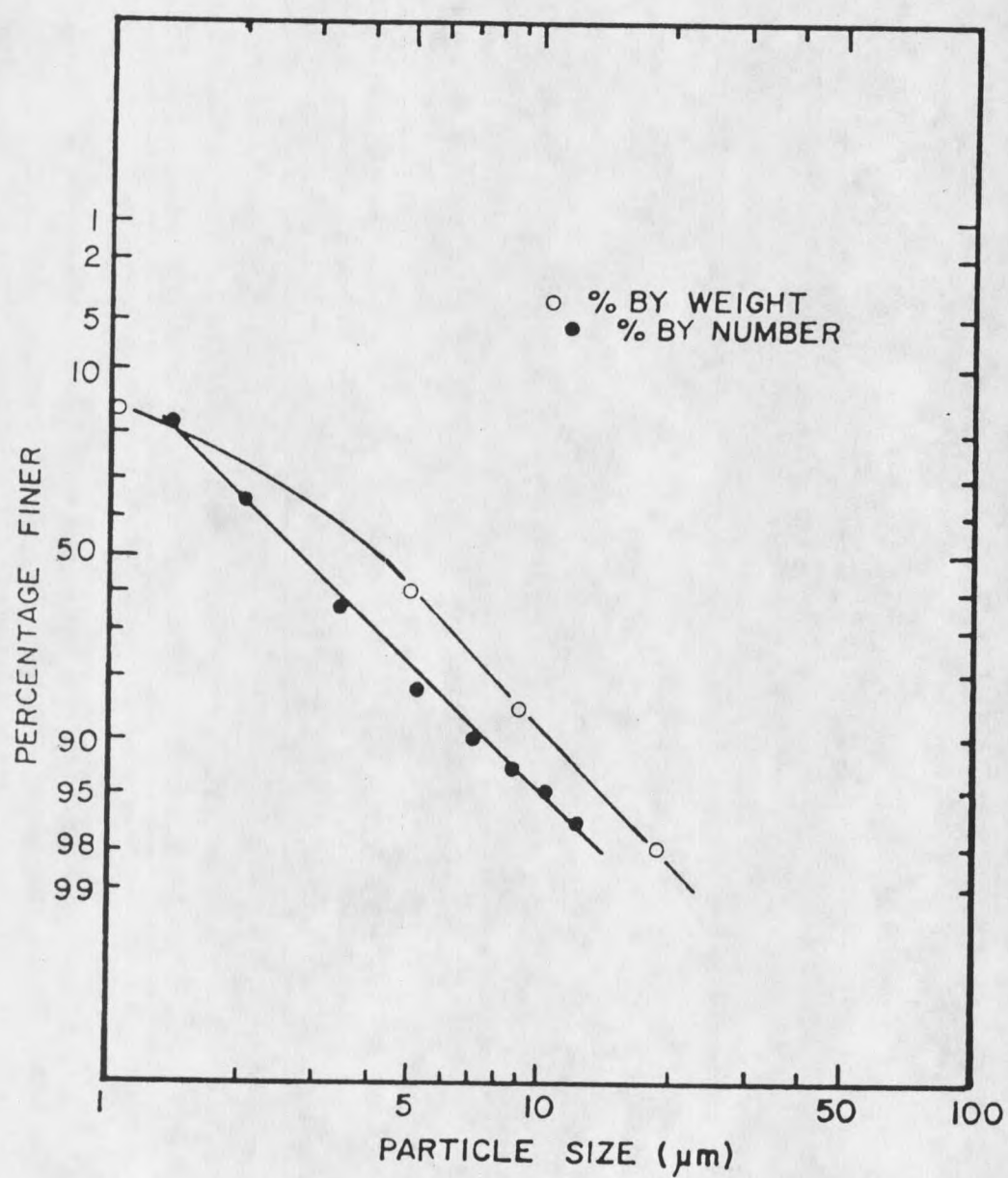


Figure 18. Particle size distribution for Min-U-Sil 30 [38].

Coagulant Feed

Aluminum Sulfate, 16-hydrate (alum) (Baker Reagent, 99.8% crystal) was the coagulant used in all runs unless otherwise specified. An alum stock solution concentration of 1 mg/ml had a pH of 3.5. According to Sanks [23] this stock concentration results in approximately 76% of total aluminum as the free ion, $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Alum dosages used in this study correspond to equivalent amounts of $\text{Al}_2(\text{SO}_4)_3 \cdot 14.3 \text{ H}_2\text{O}$ so that the alum coagulation diagram can be used directly. Coagulant was added directly to the rapid-mixer from a constant head arrangement. In those runs where a polyelectrolyte was used, addition of the polymer occurred after the rapid-mix as illustrated in Figure 17.

Filtration Unit

A constant rate, influent controlled, filter was used in this study. The filter consisted of a 3 inch diameter by 48 inch long cylindrical plexiglass column filled with 16 inches of anthracite coal and 8 inches of silica sand. Size characteristics of the media are given in Table 12.

Table 12. Size Characteristics of Filter Media.

Size Characteristic	Sand	Coal
D_{10} , effective size	0.46	0.86
D_{60}	0.62	1.25
D_{90}	0.70	1.52
U_C , uniformity coefficient	1.35	1.46

The effluent from the rapid-mixer was pumped onto the filter via a one inch rise tube. As the filter clogged during a run, the water level in this tube increased and the filtration rate was kept constant. Monometer ports were located above and below the media bed and at depths of 3, 9, 15 and 21 inches within the bed. At these same bed depths, drip sample taps were also installed. These taps were adjusted at the start of a run to allow turbidity

sampling within the bed. The combined flow from these taps was always less than 20 per cent of the total flow.

Prior to each pilot plant run, the filter was backwashed for 30 minutes during which all tubing was thoroughly flushed. The backwash was accomplished by expanding the media bed 29 per cent by reversing flow through the filter. This same procedure was repeated at the end of each run, thus, the filter was essentially backwashed twice between each operation.

Sampling Procedures

All metal samples were collected in acid washed (25 per cent HCl) 20 ml stoppered Pyrex test tubes. Turbidity and pH samples were collected in capped Nalgene bottles that were rinsed with distilled water between samplings.

Metal samples were collected every one-half hour from start of the run at the constant head vessel on the influent side of the rapid-mix (influent) and at the filter underdrain (effluent). For selected runs, metal samples were also collected at various depths within the filter bed. All metal samples were acidified with nitric acid (Baker Reagent, 70.9% HNO_3) as per recommendations in References [26] and [37]. This depressed the pH to around 2.4. Most metal samples were analyzed within 24 hours of sampling. Samples prepared in this way showed no measurable change in concentration over a two week storage period.

Turbidity samples were also collected every one-half hour at the influent, effluent, and at the four filter sampling taps. Turbidity was measured immediately upon sampling with a Hach 2100 turbidimeter.

Measurements of pH were made at frequent intervals to prevent deviations from the desired effluent pH. Influent and effluent pH were recorded every one-half hour. A Beckman Altex Φ 30 pH meter was used for all pH measurements. The instrument was checked

for standardization against known buffer solutions every two hours during pilot plant operation.

Headloss data was obtained directly from the monometer board every one-half hour.

Atomic Absorption Spectrophotometer

Atomic absorption spectroscopy (AAS) is the preferred technique for the analysis of individual trace elements in complex mixtures where matrix materials are present in relatively high concentrations [13]. The method is simple, rapid and applicable to a large number of metals. A custom built atomic absorption spectrophotometer (AA) was used for all metal analysis in this study. The atomizer used in conjunction with a Varian AA-5 photo-multiplier (shelf item) was a Woodriff Constant Temperature Furnace (WCTF) developed at Montana State University. To aid the operator in the analysis for gross metal concentration, an Apple II computer, video monitor and floppy disc reader were linked to the AA. The program used greatly speeded analysis by integrating the absorbance curve, an example of which is depicted in Figure 19. The significance of absorbance area is discussed in subsequent paragraphs. The computer program allowed the operator to visually monitor the absorbance curve and its significant parameters—peak height and absorbance area. An assessment of data quality and operator consistency was inferred from the computer generated data.

Woodriff Constant Temperature Furnace

The WCTF has a demonstrated analytical capability superior to many commercially available spectrophotometers. Table 13 contains results from a recent study [13] defining the optimum working ranges for the furnace. Only wavelengths used in this study are listed.

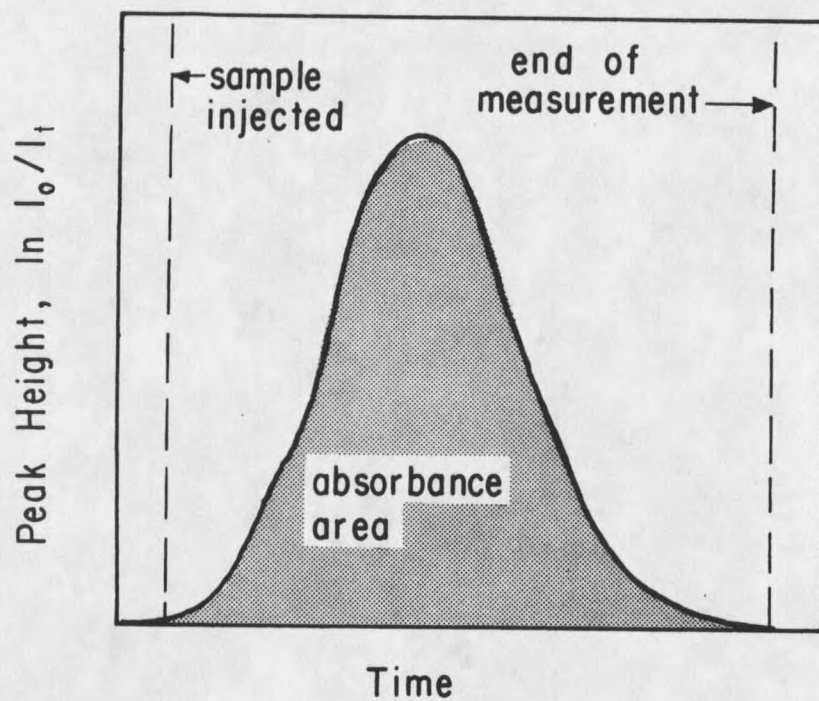


Figure 19. Atomic absorption spectrophotometer absorbance curve.

Table 13. Optimum Working Ranges for the Woodriff Constant Temperature Furnace [13].

Wavelength (nm)	Slit Width (μm)	WCTF Optimum Working Range (ng)	Standard* Error (%)	WCTF Optimum** Working Range (mg/L)	Flame*** Spectroscopy Optimum Range (mg/L)
<u>Cadmium</u>					
228.8	151.5	0.02 - 0.1	5.42	0.000125 - 0.02	0.5 - 2.0
<u>Lead</u>					
217.0	300	0.05 - 1.25	4.95	0.00031 - 0.25	5 - 20

*Regression analysis of linear portion of absorption plot had a standard error of x% at 95% confidence.

**Values determined from min and max sample sizes, 5 and 160 μl , respectively.

***From Analytical Methods for Flame Spectroscopy. Varian Techtron, Australia (1972).

Beer's Law

Subsequent discussion will be facilitated by examining Beer's Law as it relates to AAS.

$$I_t = I_o e^{-(k'cl)} \quad (35)$$

where, I_o = intensity of incident radiation

I_t = intensity of transmittal radiation

k' = absorption coefficient at given wavelength

c = concentration of absorbing atoms

l = length of the absorption path

Rearranging and taking the logarithm results in the following:

$$\ln \frac{I_o}{I_t} = k'cl \quad (36)$$

This expression is defined as the absorbance and it is proportional to the analyte concentration for a given path length, l and wavelength, λ . Injection of the metal sample into the furnace and subsequent absorbance is a time variant process. Initially the concentration of metal (absorbing atoms) is high and absorbance increases to a maximum. As the number of

absorbing atoms decreases due to depletion and flushing from the furnace (constant argon flow), the transmitted radiation, I_t , will return to the initial baseline value, I_0 . Plotting $\ln I_0/I_t$ against time results in the absorbance curve of Figure 19. The area under the curve is proportional to the concentration of absorbing atoms, c .

Metal Analysis

Practical applications of AAS take advantage of the linear relationship between absorbance and the concentration of absorbing atoms as defined by Equation (36). The absorbing atoms are, in turn, proportional to the total analyte present in a given sample.

Typically, a plot of absorbance versus analyte mass will be linear at lower absorbance, when only a small fraction of the incident radiation is absorbed, and will curve or flatten out at higher absorbance [13]. When this occurs, sensitivity is lost. Ideally, analysis is based on absorbance values corresponding to the most linear portion of the absorbance plot.

The first step in the analysis of lead and cadmium was the construction of standardization absorbance plots shown in Figures 20 and 21. For both metals studied, the most sensitive wavelength as listed in Reference [36] was utilized. The choice of wavelength was based on the anticipated range of metal concentrations to be measured.

The absorbance plots in Figures 20 and 21 plot analyte mass (ng) on the abscissa axis and absorbance number on the ordinate axis. Analyte mass was used to prevent confusion. Samples were transferred to the atomizer in small graphite cups that had a maximum capacity of 150 μ l. Various size samples were transferred depending upon the sample concentration anticipated. It was easier to think in terms of analyte mass rather than concentration as all samples were dried prior to injection into the furnace. Absorbance number is generated by the computer integration of the absorbance curve and is proportional to the amount of analyte as predicted by Equation (36).

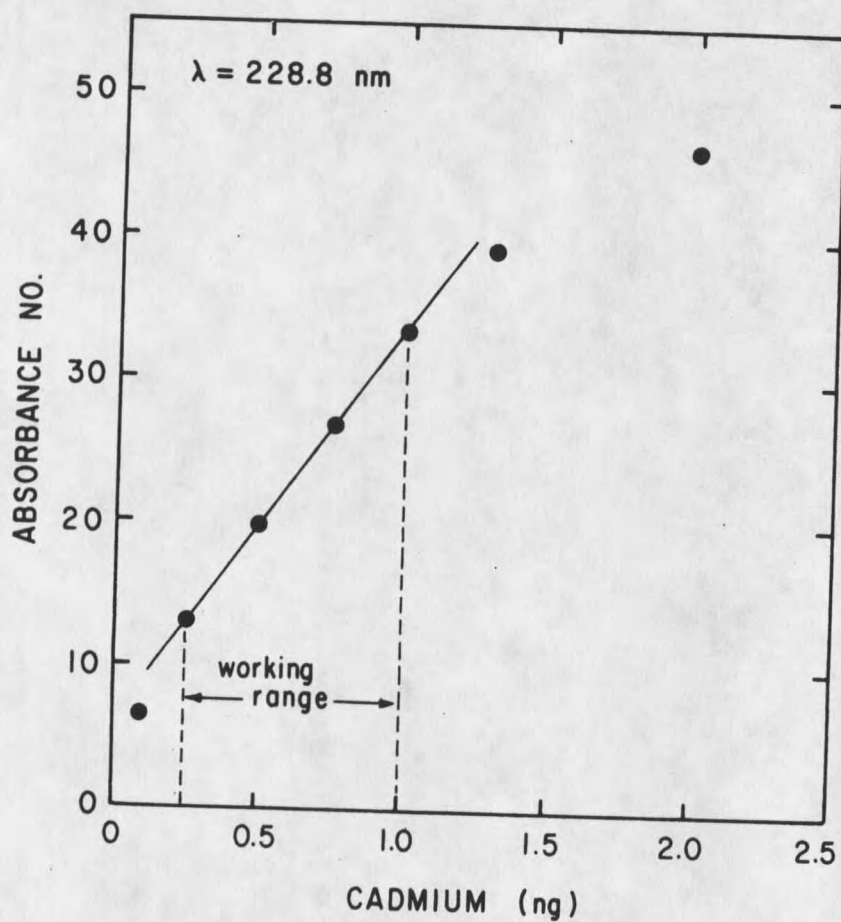


Figure 20. Typical standardization curve and working range for cadmium at 228.8 nm wavelength.

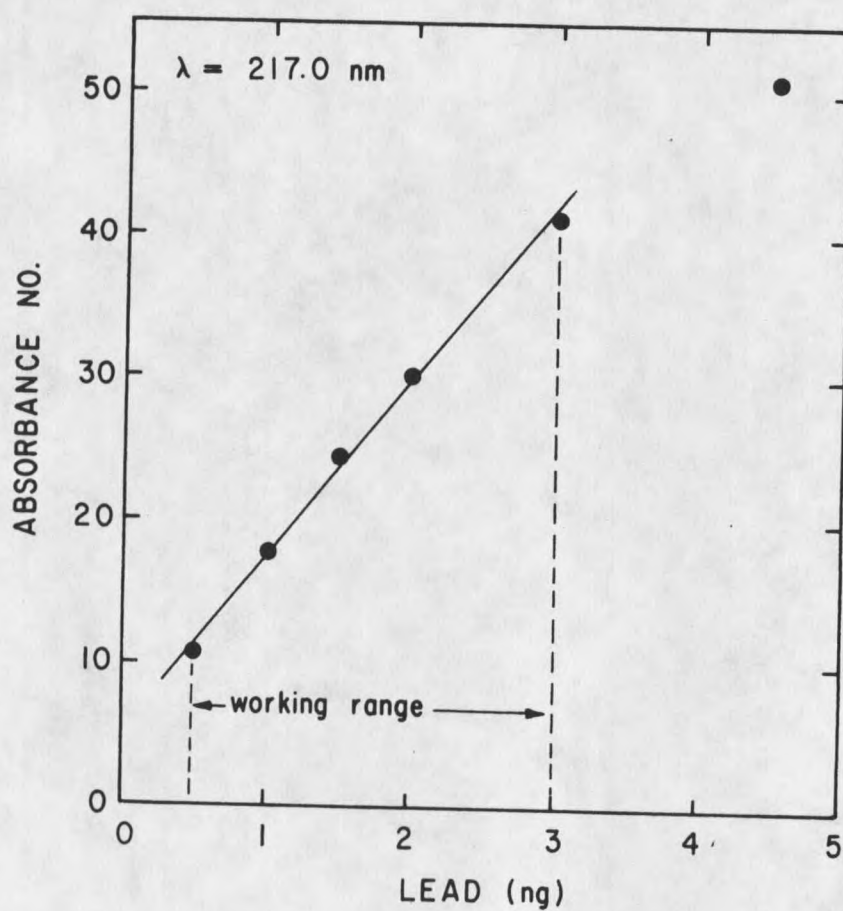


Figure 21. Typical standardization curve and working range for lead at 228.8 nm wavelength.

Standardization Curves

The absorbance plots for cadmium and lead show the characteristic divergence from linearity at higher absorbance numbers. Also a non-linear response was observed at the very lowest absorbance readings. The portion of linear response was called the working range and all samples to be analyzed were manipulated by choice of sample size to fall on this portion of the curve. Dilution was not required in this study.

Each time the AA was operated a standard curve was constructed and unknown samples were compared against it. The standard curve contained four points that fell within the working range described above. Each point of the standard curve was the average of three samples of known analyte mass. Standard solutions were prepared from metal salts, lead nitrate crystal (Baker Reagent, 99.6% $\text{Pb}(\text{NO}_3)_2$) and cadmium nitrate 4-hydrate (Baker Reagent, 99.0%, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$).

Cadmium. The working range chosen for cadmium was 0.25 ng to 1.0 ng. This portion of the absorbance plot had a correlation coefficient greater than +0.99. For a sample size range from 10 to 150 μl , this working range equates to a concentration range of 0.0017 mg/L to 0.10 mg/L. This was sufficient for all measurements. For the initial cadmium concentration of 0.05 mg/L the lower end of the concentration range equates to a 96.6% removal of cadmium.

Lead. The working range for lead was 0.5 ng to 3.0 ng. The correlation coefficient for this range was greater than +0.99. The concentration range 0.003 mg/L to 0.3 mg/L was more than adequate for all measurements. For the initial lead concentration of 0.15 mg/L, the lower end of the concentration range equates to measurement of 97.8% lead removal.

CHAPTER 7

SPECIATION AND DISTRIBUTION MODELS

To better define the experimental water used in this study, speciation and distribution models were developed for cadmium and lead in Bozeman tap water. The distribution of a particular trace metal between the soluble and insoluble fractions (see Table 4) can be useful information in designing systems to meet the MCL.

The models developed in this chapter were used to predict the amount of metal associated with the quartz suspension. The adsorption model used [50] identified specific surface reactions and, therefore, concentrations of these surface active species were required to calculate the adsorbed metal.

The model described in subsequent paragraphs provides for simultaneous solution of the soluble species concentrations as well as the metal fraction adsorbed.

Model Constituents

For both cadmium and lead the following constituents were used in the model: $[C_T] = 10^{-2.77}$ M; $[SO_4^{2-}] = 10^{-4.13}$ M; 150 mg/L quartz suspension; and organics = 1.0 mg/L TOC. The metal inorganic ligand complexes considered and their formation constants are listed in Table 5. The conditional complexation constants for the organic ligands present, measured as mg/L TOC, are included in Table 6. Intrinsic adsorption constants for specific quartz surface reactions are found in Table 10.

Major Assumptions

The following major assumptions were made:

1. It was assumed that only the previously mentioned constituents were needed to describe the speciation and distribution of cadmium and lead in the experimental water.

2. It was assumed that the kinetics of carbonate precipitate were insufficiently rapid to regulate cadmium and lead solubilities. This was based upon Patterson's [17] test results depicted in Figures 6 and 7, the initial metal concentration and the average detention time of the raw water reservoir and pilot plant. Tests performed by Naylor and Dague [10] indicate that this assumption may not be valid for lead. Their data indicate lead solubilities less than $10^{-6.14}$ M above pH 8.

3. The conditional complexation constants for organic complexation with cadmium were assumed equal for organic complexation with lead. As these constants were derived for an entirely different water [46], the assumption is made that the chemical structure, and therefore the complexing ability, of the soluble organics in the water described in Reference [46] were comparable to those of the organic ligands present in Bozeman tap water.

3. Many assumptions were necessary to incorporate the Min-U-Sil adsorptive surface into the model. The surface reactions shown in Table 10 require calculation of moles per liter ($\equiv \text{SiO}^-$) sites as well as the molar concentration of the surface active metal species.

In determining the former, the following parameters and equilibria were used:

1. 150 mg/L M30 added to experimental water.
2. M30 surface area equal to $0.54 \text{ m}^2/\text{gm}$ [57].
3. $\equiv \text{SiOH}$ surface site density equal to 5 sites/ $100 \text{ \AA}^2$ [45].
4. Avogadro constant equal to $6.0225 \times 10^{23}/\text{mole}$ [26].
5. pK_{int}^2 for SiO^2 surface ionization equal to 6.77 [27].

With the above information, the $[\equiv\text{SiO}^-]$ is determined from the following equation:

$$[\equiv\text{SiO}^-] = K_{\text{int}}^2 [\equiv\text{SiOH}] / \text{H}^+ \quad (37)$$

where, $K_{\text{int}}^2 = 10^{-6.77}$; $[\equiv\text{SiOH}] = 10^{-8.17}$ M.

Speciation and Distribution Model for Cadmium

The total cadmium concentration can be calculated from the following equation:

$$\begin{aligned} \text{Cd}_T = & [\text{Cd}^{2+}] + [\text{CdOH}^+] + [\text{Cd}(\text{OH})_2^0] + [\text{CdSO}_4^0] + [\text{CdCO}_3^0] \\ & + [\text{CdHCO}_3^+] + [\equiv\text{SiO}^- - \text{CdOH}^+] + [\text{Cd-organics}] \end{aligned} \quad (38)$$

Upon substitution of appropriate constants from Tables 5, 6 and 10, Equation (38) becomes,

$$\begin{aligned} \text{Cd}_T = & [\text{Cd}^{2+}] \left\{ 1 + 10^{3.81} [\text{OH}^-] + 10^{7.72} [\text{OH}^-]^2 + 10^{2.4} [\text{SO}_4^{2-}] \right. \\ & \left. + 10^{3.97} [\text{CO}_3^{2-}] + 10^{2.3} [\text{HCO}_3^+] + 10^{5.0} [\text{CdOH}^+] [\equiv\text{SiO}^-] \right\} + [\text{Cd-org}] \end{aligned} \quad (39)$$

where, Cd_T = total cadmium, $[\text{CdOH}^+] = 10^{3.81} [\text{Cd}^{2+}] [\text{OH}^-]$.

One simplifying assumption used in Equation [39] pertains to leaving the Cd-organic complexes outside the brackets. The Cd-organic complex concentrations were determined using Equation (1) and the conditional complexation constants found in Table 6. The Cd-organic complex concentrations were calculated assuming that the 0.05 mg/L cadmium concentration added to the experimental water remained in a soluble state. This was later verified, but, had a significant fraction of the added cadmium been insoluble, adjustments to Equation (38) would be necessary.

Solving Equation (39) for various pH, and subsequently various $[\text{OH}^-]$, $[\text{HCO}_3^-]$, $[\text{Cd-organics}]$, $[\text{CO}_3^{2-}]$ and $[\equiv\text{SiO}^-]$ results in the α -pH curves of Figure 1. Alpha values relate to the following ratio, $[\text{cadmium species}]/\text{Cd}_T$.

Results

The predominant cadmium species are Cd^{2+} below pH 9 and CdCO_3^0 above this pH. Adsorbed cadmium is insignificant with less than 1 per cent adsorption predicted at all pH. The results of this model compare favorably with other cadmium speciation and distribution models cited [3,39].

The same procedures were used in developing the lead model shown in Figure 2. The predominant lead species below pH 7.2 is Pb^{2+} ; PbHCO_3^+ is significant between pH 7 and pH 8.1; PbOH^+ and PbCO_3^0 are the main species predicted between pH 8.1 and 9.5; and Pb(OH)_2^0 becomes significant only above pH 9.5. Adsorbed lead is not significant for the quartz surface area used in this study.

The models depicted in Figures 1 and 2 are for the raw water (Bozeman tap water plus Min-U-Sil and metal) and, therefore, do not describe the experimental water upon addition of coagulant. The models can, however, predict metal speciation resulting from pH control which was accomplished in the raw water reservoir.

CHAPTER 8

RESULTS AND DISCUSSION

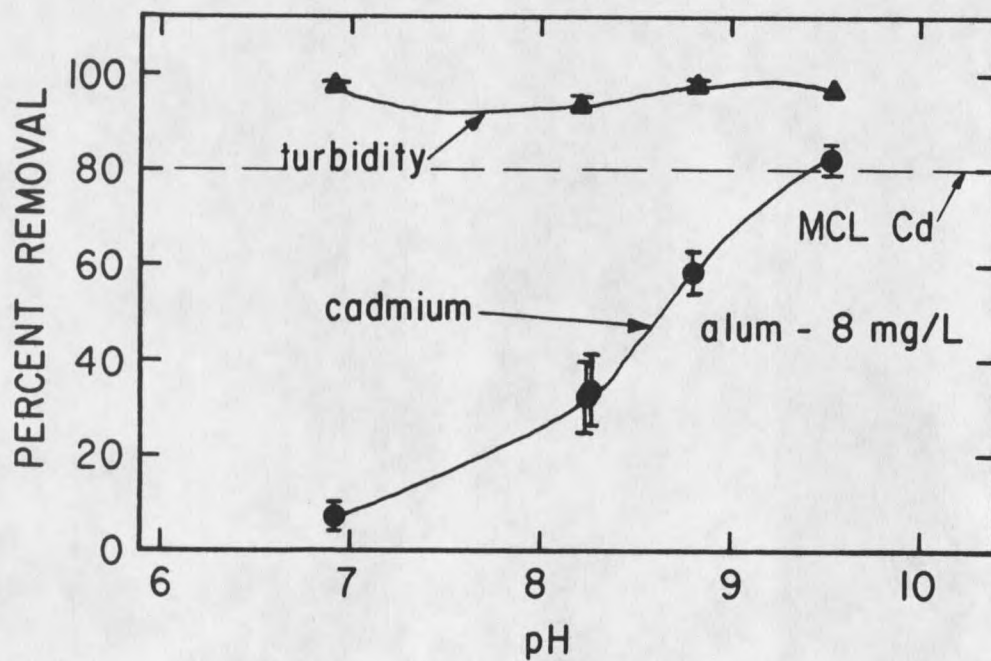
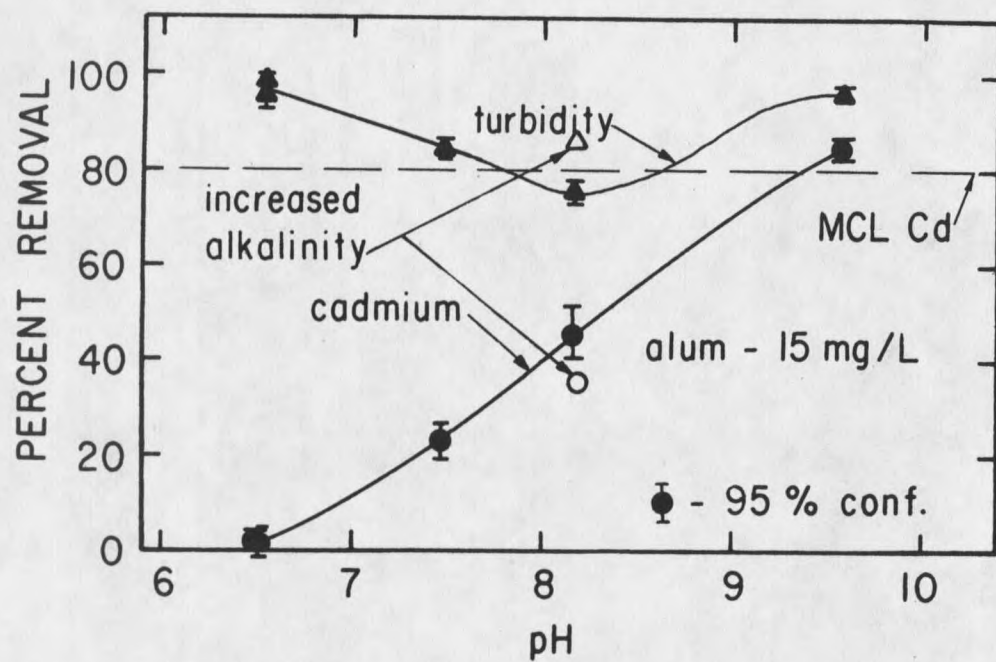
The data obtained from pilot plant runs and jar tests will be presented and discussed in accordance with the objectives stated in Chapter 3. Evaluation of removal efficiencies within a direct filtration pilot plant was the primary objective of this study. Establishment of operational guidelines to satisfy metal and turbidity MCLs was accomplished by plotting measured removals upon the alum coagulation diagram and constructing isoremoval lines. Identification of the predominant removal mechanism(s) proved difficult. Some statements concerning removal mechanisms, however, are possible using experimental data and previous studies. Finally, the results obtained will be compared with data from the literature, much of which has already been presented in Chapter 5.

Removal Efficiencies

Cadmium and lead removal efficiencies were measured for various pH and alum dosages. Since cadmium proved more difficult to remove, it received more attention. In addition to the major parameters, the effects of coagulant type, alkalinity, humic acids and polymers were evaluated for cadmium removal.

Cadmium

Figures 22, 23 and 24 present cadmium and turbidity removal data as a function of pH for three different alum dosages. The 95 per cent confidence intervals shown are for seven measurements taken during each 5-hour pilot plant.



Figures 22 and 23. Turbidity and cadmium removals for 15 and 8 mg/L alum. $Cd_i = 0.05$ mg/L; $turb_i = 25$ NTU.

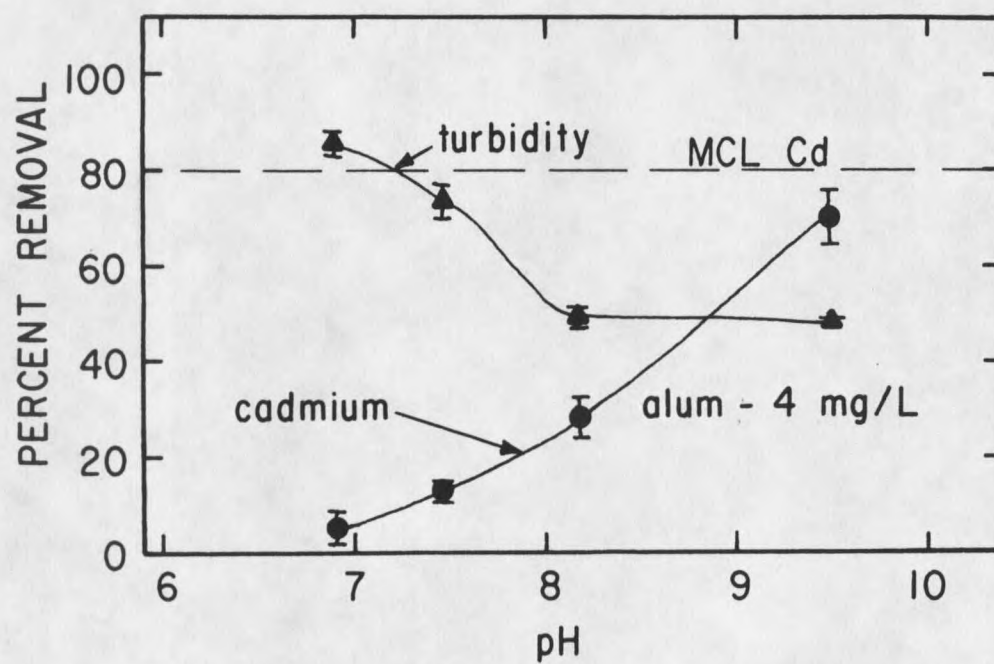


Figure 24. Turbidity and cadmium removals for 4 mg/L alum. $Cd_i = 0.05$ mg/L; $turb_i = 25$ NTU.

pH. The removal of cadmium is strongly pH dependent with increased removals corresponding to higher pH. This behavior of hydrolyzable metal ions can be observed as a consequence of precipitation and/or adsorption. Figure 6 indicates that cadmium becomes less soluble with increasing pH in the pH range investigated.

The cadmium MCL, for 15 and 8 mg/L alum dosages, was not satisfied until the pH was elevated above pH 9.0. The best removal obtained with 4 mg/L alum was 70 per cent removal at pH 9.5. This does not meet the MCL.

Coagulant Dosage. Cadmium removal increased slightly with increased alum dosage. Figure 25 is a composite of the cadmium removals for the three alum dosages used. The cadmium MCL is only met with the higher alum dosages and then only at elevated pH.

Turbidity. Cadmium removal correlates poorly with turbidity removal as shown in Figure 26. A correlation coefficient, r , equal to +0.1167 is obtained from a linear regression of the data. For all alum dosages investigated, greater than 80 per cent turbidity removal is achieved at pH 6.9. However, there is little or no cadmium removal at this pH. For pH greater than 8, cadmium removal is comparable for all alum dosages, however, turbidity removals are quite variable. Alum dosages of 15 and 8 mg/L result in greater than 80 per cent turbidity removal, while a 4 mg/L alum dosage results in only 50 per cent removal above pH 8. Most likely the smallest particles with the greatest surface area are passing the filter. If cadmium is significantly associated with the M30, the high cadmium removal and poor turbidity removal, observed at pH 9.5 using 4 mg/L alum, would not occur concurrently.

Ferric Chloride. A series of pilot plant runs was made with ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) as a comparison against an equal molar concentration of alum. Figure 27 depicts results for 8 mg/L coagulant dosages ($10^{-4.57}$ M Al(III) and Fe(III)). The cadmium MCL

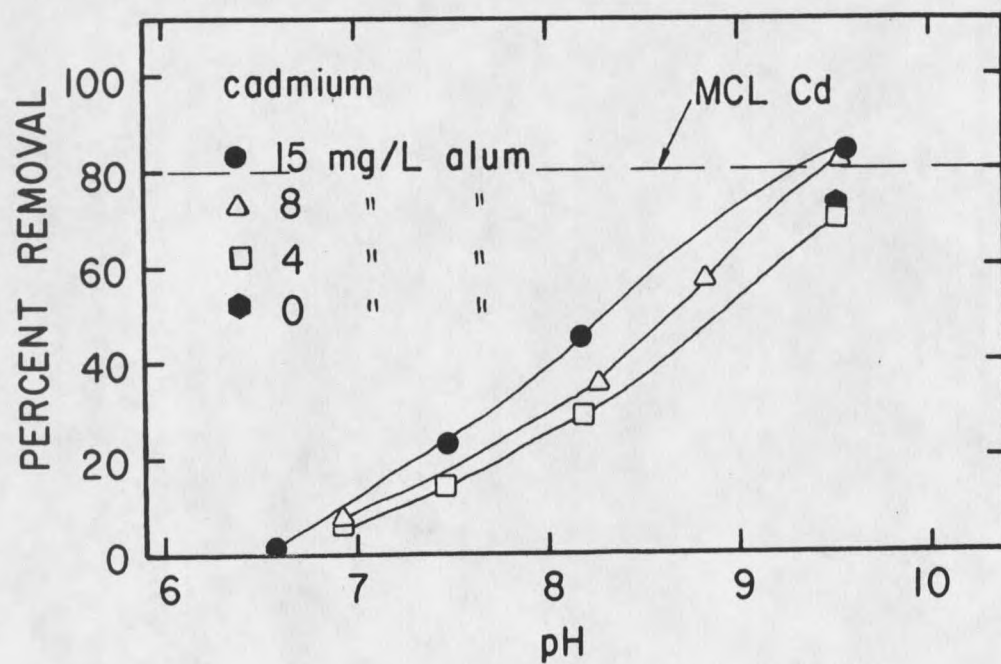


Figure 25. Cadmium removal composite. $Cd_i = 0.05$ mg/L.

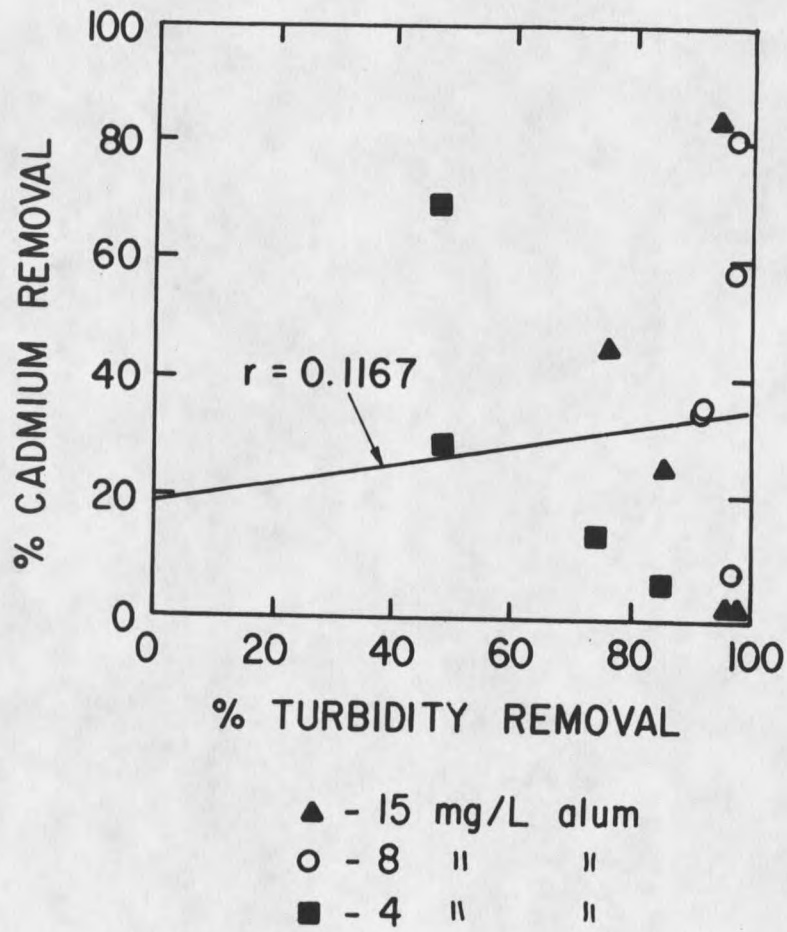


Figure 26. Correlation between cadmium and turbidity removals.

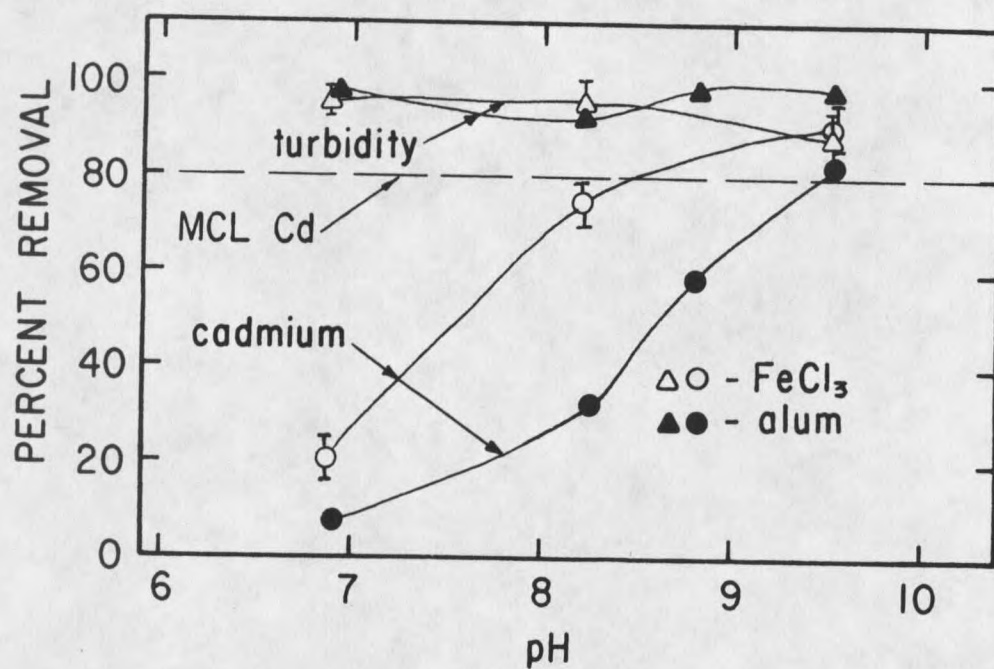


Figure 27. Comparison—Cadmium removals with Fe(III) coagulation. $Cd_i = 0.05$ mg/L; $turb_i = 25$ NTU; coagulant = 8 mg/L.

was met at pH 8.5 using the ferric chloride, whereas, elevating the pH to 9.5 was required to achieve the same removal efficiency with alum. Turbidity removals were comparable. The head loss rates for the ferric chloride runs were significantly greater as shown in Figure 28. This could prove troublesome in a direct filtration application where filter run length is an important design criteria. Lower ferric chloride dosages were not evaluated and could conceivably reduce headloss rates significantly while still providing adequate removal.

Polymer. Figure 29 compares removals for runs conducted with and without 0.4 mg/L cationic polymer (Calgon Corp. CAT-FLOC T). CAT-FLOC T was chosen because it is a medium molecular weight, cationic polymer recommended for direct filtration [16]. The 0.4 mg/L dosage utilized was determined from jar tests; lower dosages did not provide adequate turbidity removal when used in conjunction with 4 mg/L alum. Use of the polymer resulted in much improved turbidity removals (turbidity MCL met at all pH) and slightly better cadmium removals. With the proper use of polymers, meeting the cadmium MCL becomes the primary challenge to providing an adequate effluent water.

Humic Acid. The effect of humic acid on cadmium removal was assessed with two pilot plant runs plotted on the alum coagulation diagram of Figure 30. Humic Acid (4 mg/L) was added to the raw water reservoir having an average detention time of 90 minutes. The color removals observed were in good agreement with a previous study [14]. At pH 6.8, the removals measured were 8 per cent cadmium and 100 per cent color (initial color = 70 CUs). At pH 8.2, 40 per cent cadmium and 0 per cent color removals occurred. These cadmium removal efficiencies are comparable to removals obtained with 15 mg/L alum without HA present (see Figure 22). Cadmium removal was not significantly affected by the presence of HA indicating little if any complexation under the test conditions.

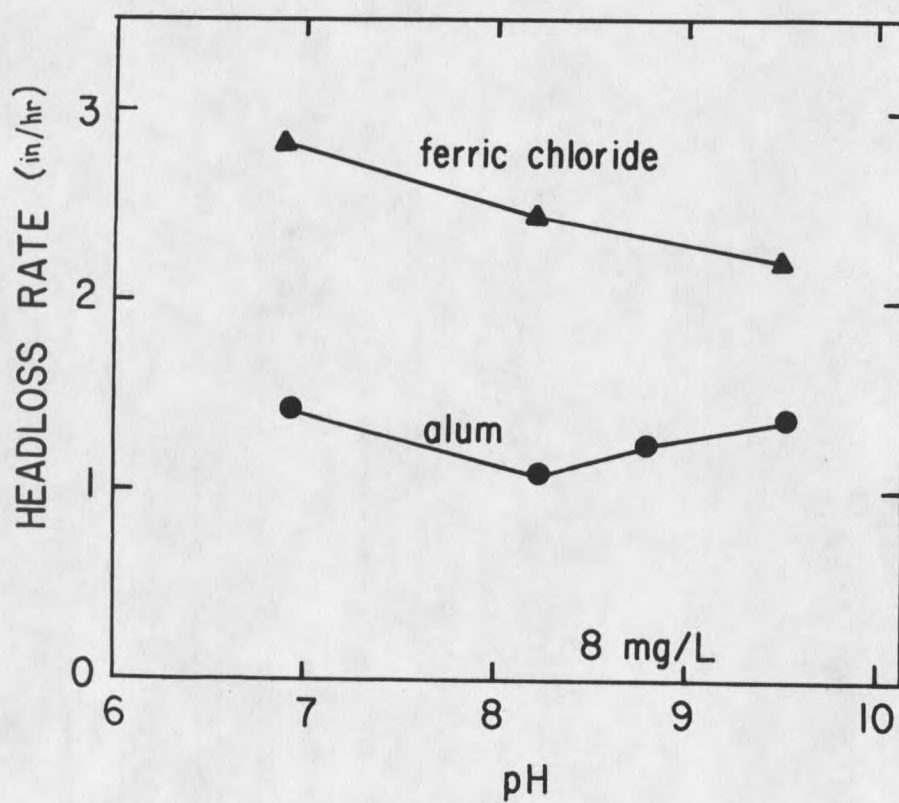


Figure 28. Headloss rates for pilot plant filter. $\text{Fe(III)} = \text{Al(III)} = 10^{-4.57} \text{ M}$.

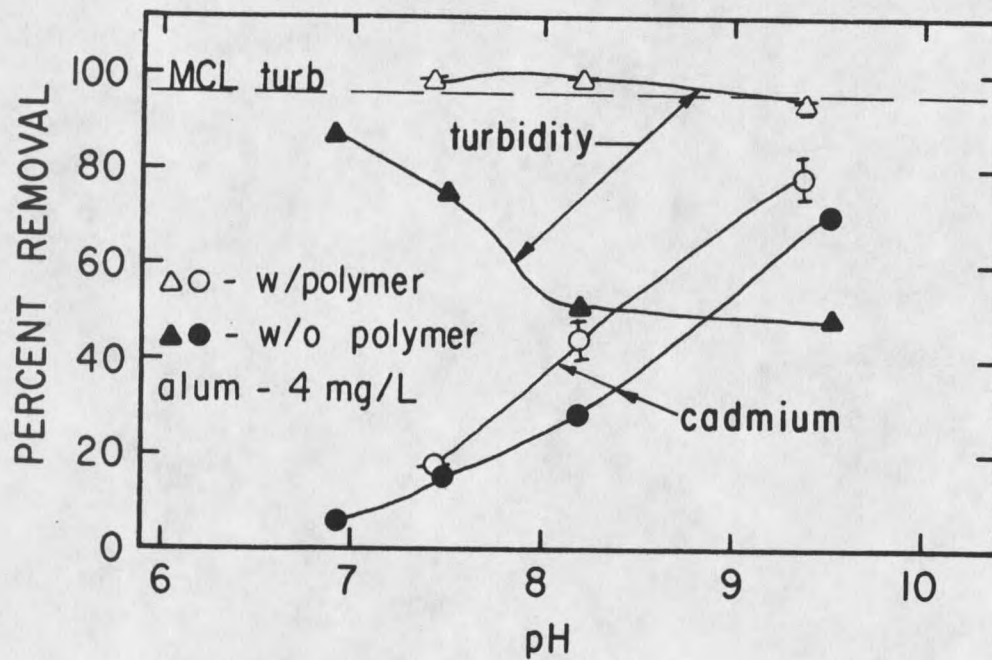


Figure 29. Comparison—Cadmium removals with polymer (0.4 mg/L CAT-FLOC T). $Cd_i = 0.05$ mg/L; $turb_i = 25$ NTU.

Alkalinity. A single pilot plant run was conducted at an increased alkalinity. The alkalinity was raised from 1.5 meq/L to 4.5 meq/L with the results plotted on Figure 22. There were no significant changes in turbidity and cadmium removals.

Lead

Figures 31, 32 and 33 present lead and turbidity removal data as a function of pH for three different alum dosages.

pH. For the 15 and 8 mg/L alum dosages, lead and turbidity removals are essentially independent of pH. Between 80 and 90 per cent lead removals were observed for all pH values investigated. Lead removal is also fairly independent of pH for an alum dosage of 4 mg/L with somewhat lower removals, 60 to 80 per cent, observed. The highest removal at pH 6.9 corresponds to charge neutralization of the M30 suspension within the adsorption-destabilization region of the alum coagulation diagram. Figure 34 shows that the MCL for lead is satisfied for all pH and alum dosages used.

Turbidity. Lead removal correlates well with turbidity removal as shown in Figure 35. A +0.8674 correlation coefficient is obtained from a linear regression of the data. Many studies [4,5,11] have concluded that good particulate removal is the key to good lead removal.

For quick comparisons between cadmium and lead removals, Figures 36, 37 and 38 are presented.

Operational Guidelines

The alum coagulation diagram is useful in graphically depicting the regions of effective metal and turbidity removal.

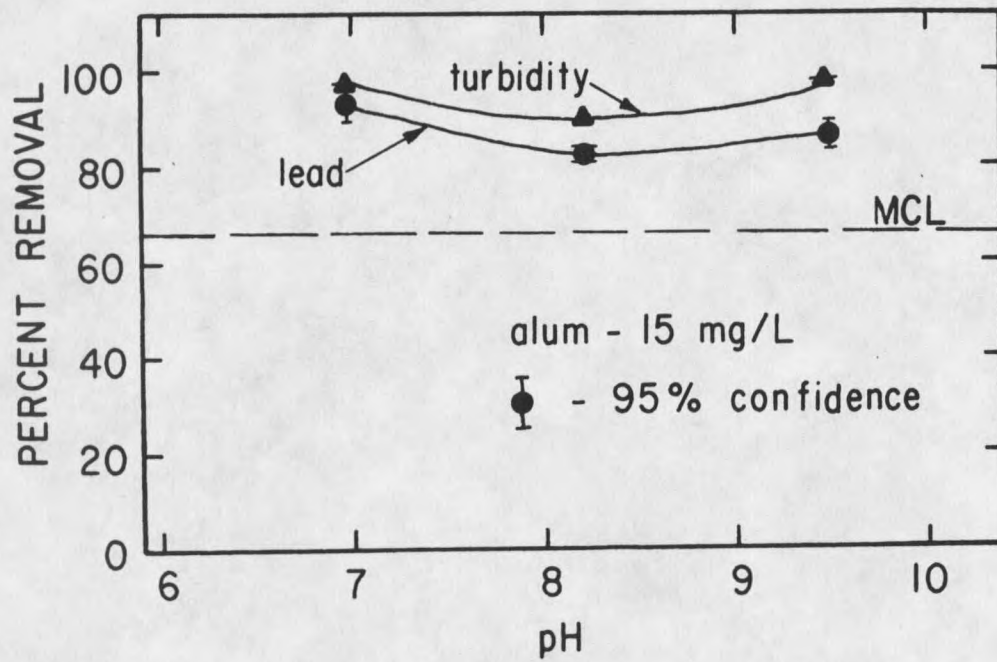
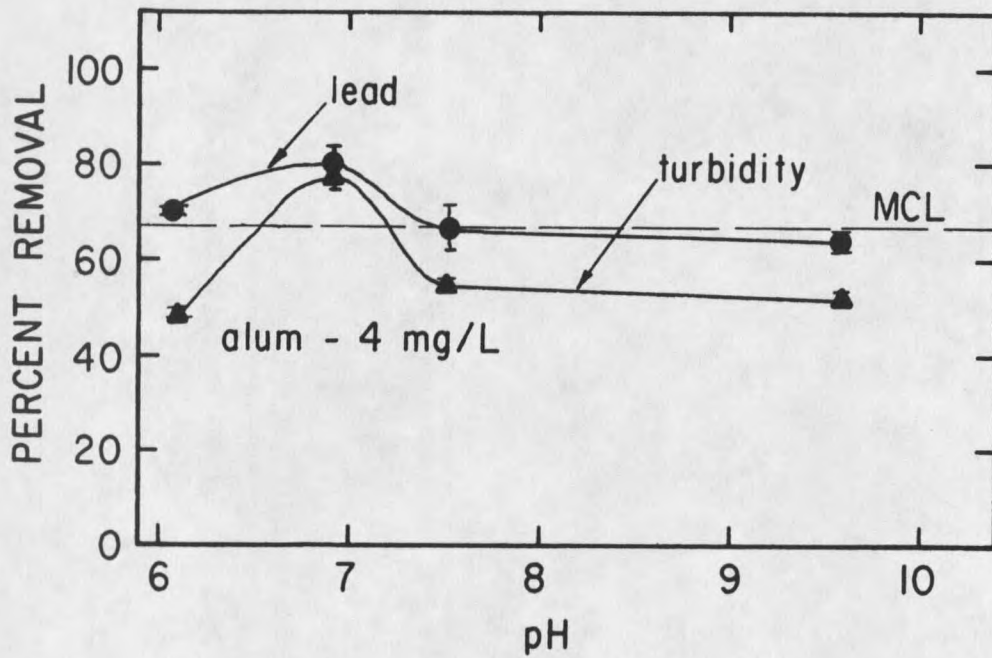
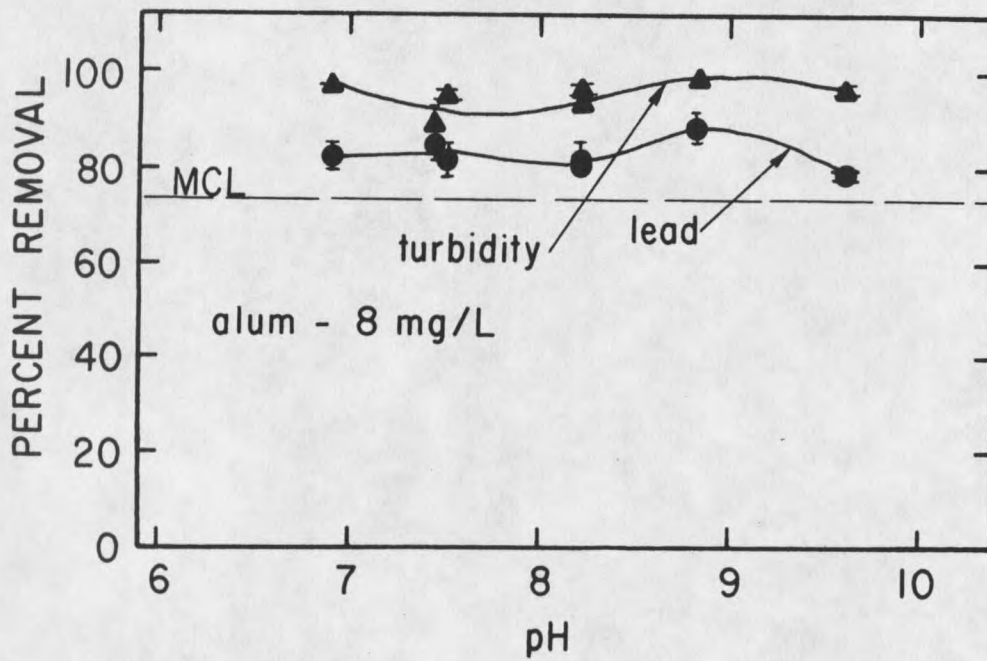


Figure 31. Turbidity and lead removals for 15 mg/L alum. $Pb_i = 0.15$ mg/L; $turb_i = 25$ NTU.



Figures 32 and 33. Turbidity and lead removals for 8 and 4 mg/L alum. $Pb_i = 0.15$ mg/L; $turb_i = 25$ NTU.

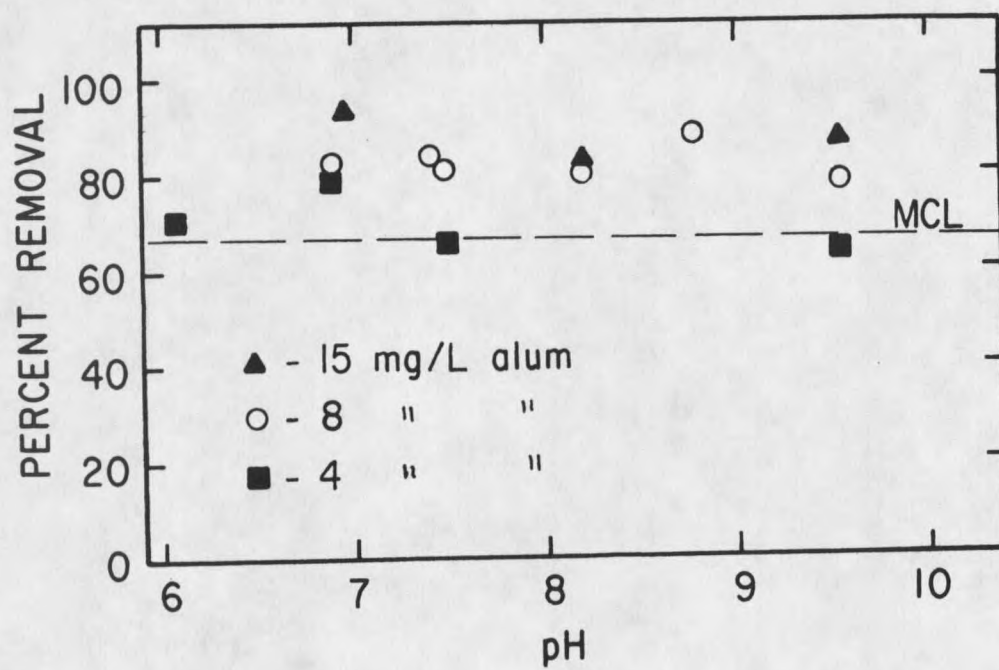


Figure 34. Lead removal composite. $Pb_i = 0.15$ mg/L.

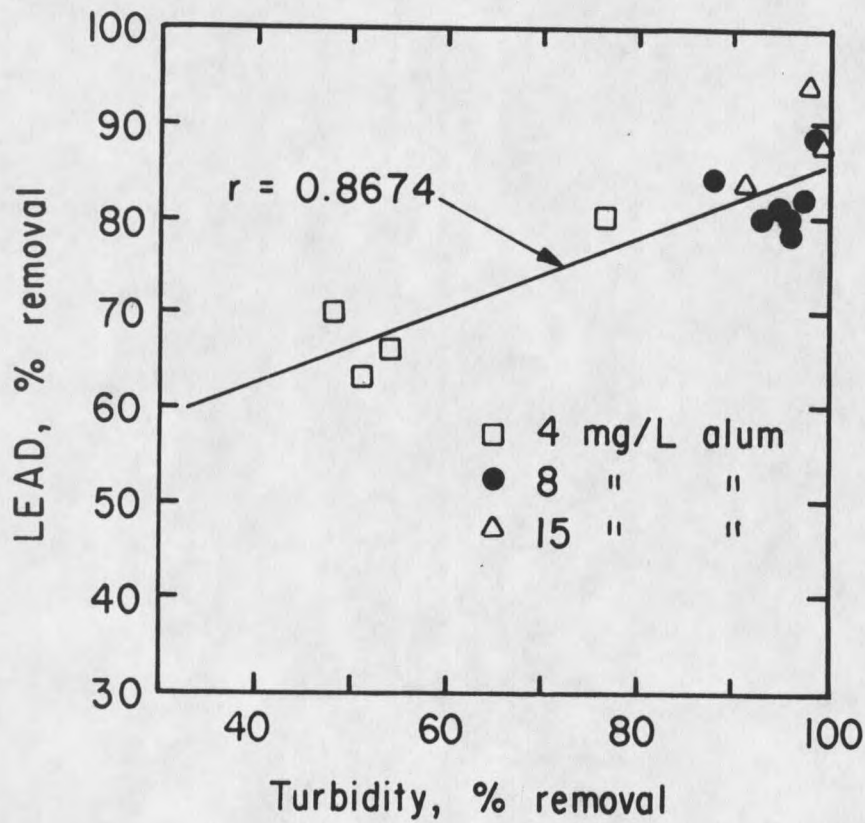


Figure 35. Correlation between turbidity and lead removals. $Pb_i = 0.15$ mg/L; $turb_i = 25$ NTU.

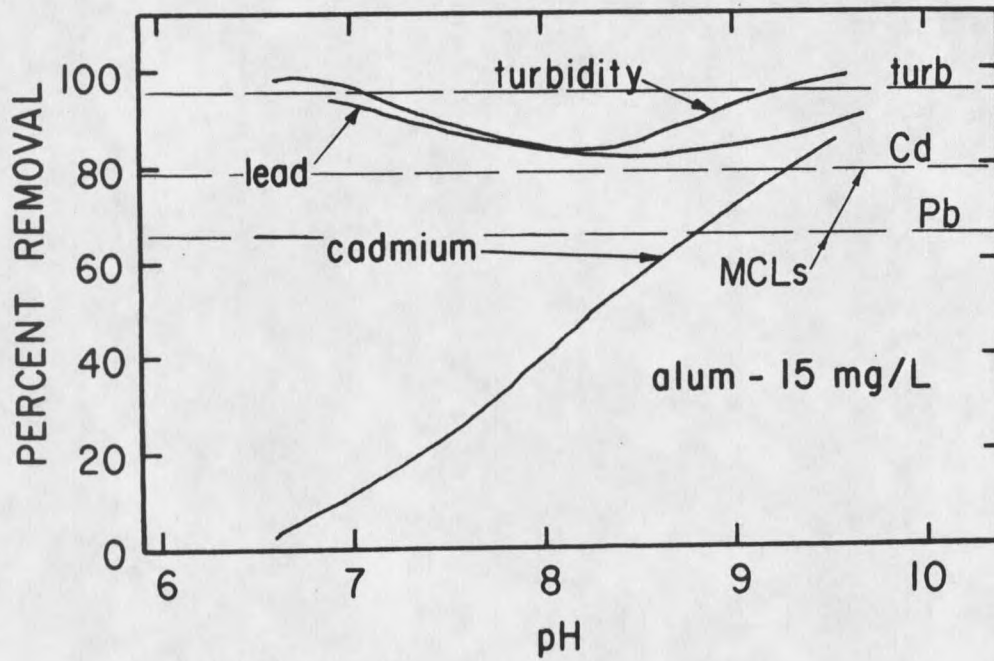
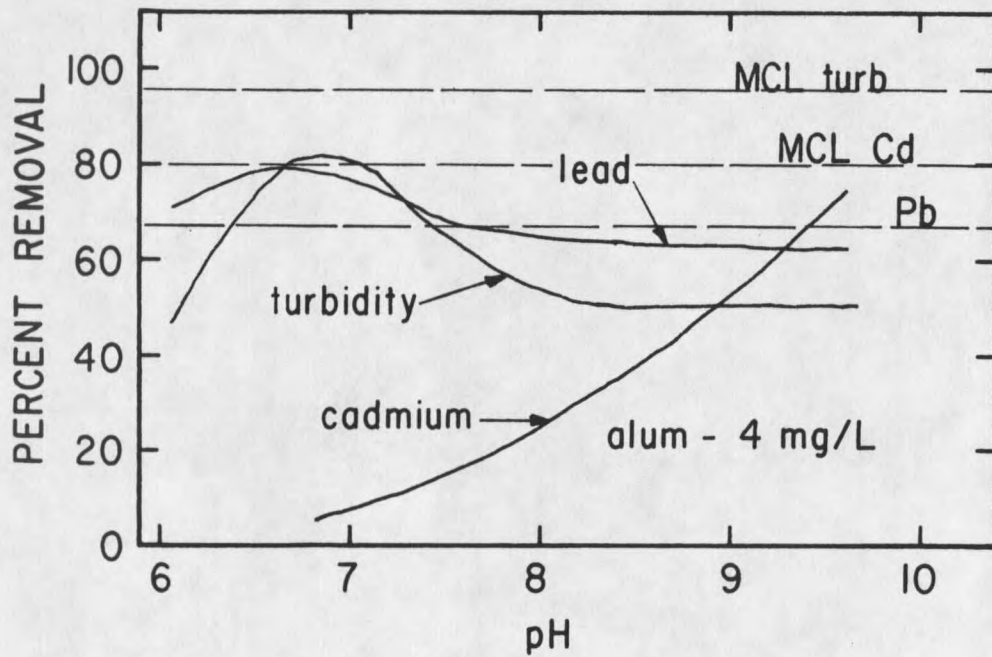
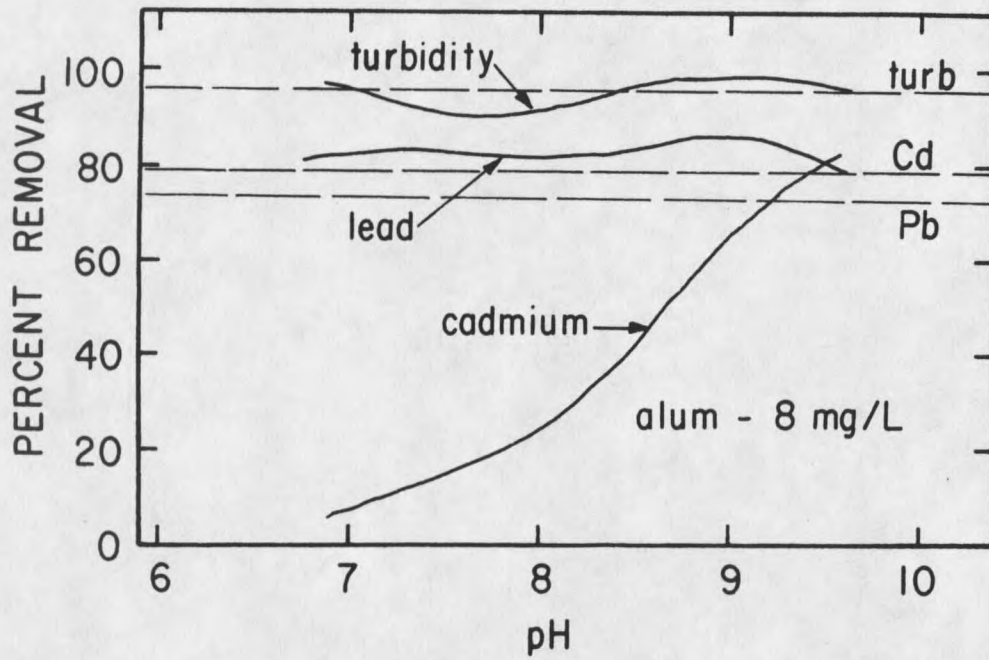


Figure 36. Comparison between lead and cadmium removals for 15 mg/L alum. $Cd_i = 0.05$ mg/L; $Pb_i = 0.15$ mg/L; $turb_i = 25$ NTU.



Figures 37 and 38. Comparison between lead and cadmium removals for 8 and 4 mg/L alum. $Cd_i = 0.05$ mg/L; $Pb_i = 0.15$ mg/L; $turb_i = 25$ NTU.

Cadmium

The isoremoval lines for cadmium and turbidity are presented in Figure 39. When operating at a pH and alum dosage that coincides with the shaded areas, the MCL for turbidity (1 NTU) will be met. The hatched region ensures compliance with both cadmium and turbidity MCLs. To meet the MCLs for both cadmium and turbidity one should operate above pH 9.3 and with an 8 mg/L or higher alum dosage.

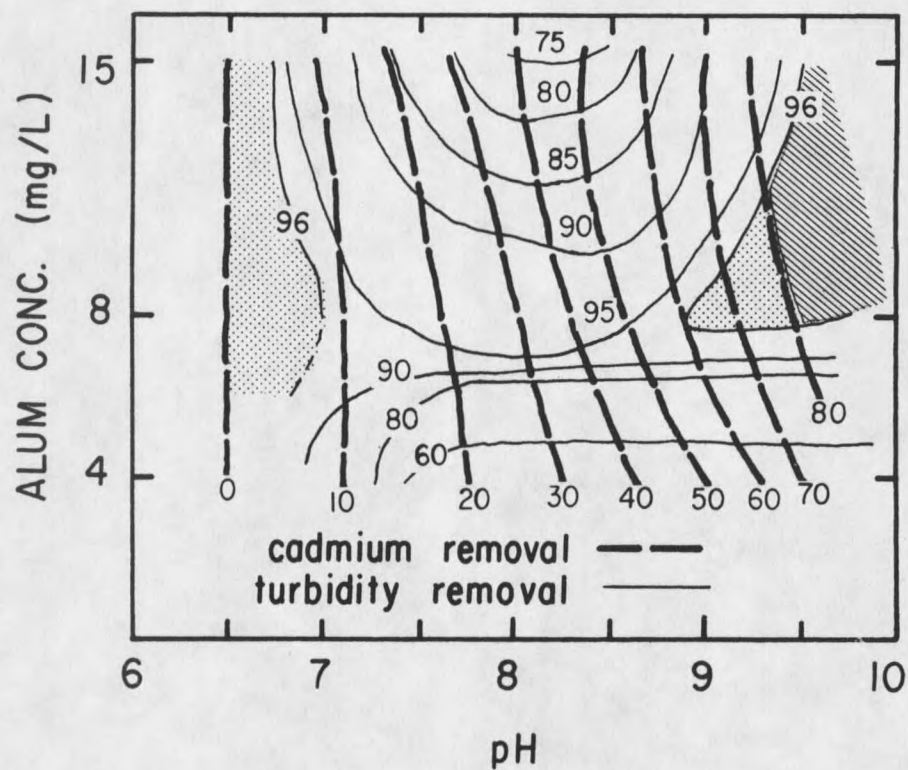
Figure 40 plots some of the same data on the coagulation diagram with the thermodynamic boundaries for aluminum shown. If operating at the recommended pH and alum dosage, one will be operating outside of the thermodynamic boundaries of Figure 40. While not investigated in this study, concern is growing over residual aluminum in the effluent water. The low alum dosages utilized (≤ 15 mg/L) will result in a maximum residual of 1.35 mg/L as aluminum. This is significantly higher than the 0.05 mg/L goal set by the American Water Works Association.

The iron (III) coagulation diagram of Figure 16 predicts that no such problem is likely to occur with Fe(III) coagulation since $\text{Fe}(\text{OH})_3$ (s) precipitates over a much wider pH range.

The operating region described above is only applicable to waters similar (see Table 11) to the experimental water. The high turbidity removals outside the thermodynamic boundaries of aluminum are due to the hardness component. The investigation of this is discussed later in this chapter.

Lead

Figure 41 plots isoremoval lines for lead and turbidity. The shaded areas represent 70 per cent or greater lead removal. This amount of removal satisfies the MCL for lead. The hatched regions represent pH and alum dosages that satisfy both turbidity and lead MCLs. Though not investigated, the use of polymers should result in effective lead removal at all



▨ turbidity MCL met

▨ turbidity and cadmium MCLs met

Figure 39. Operating regions for cadmium and turbidity removal. $Cd_i = 0.05$ mg/L; $turb_i = 25$ NTU.

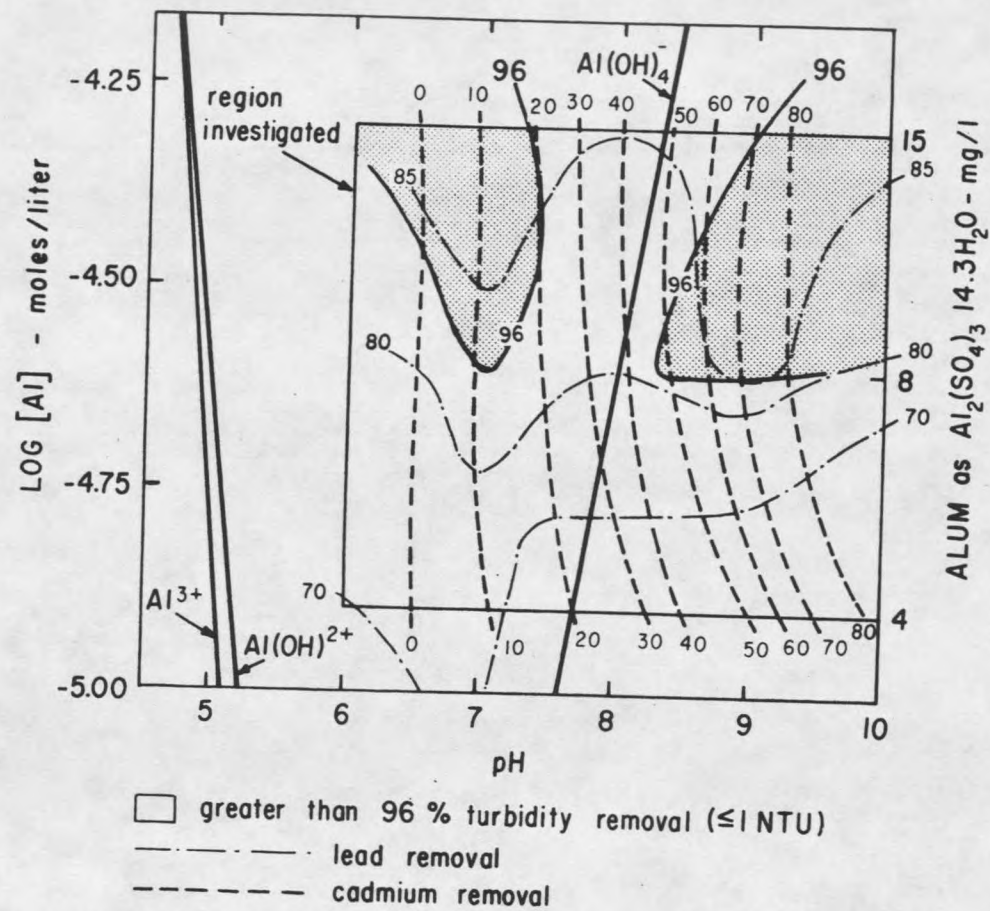


Figure 40. Cadmium, lead and turbidity isoremoval lines on the alum coagulation diagram.

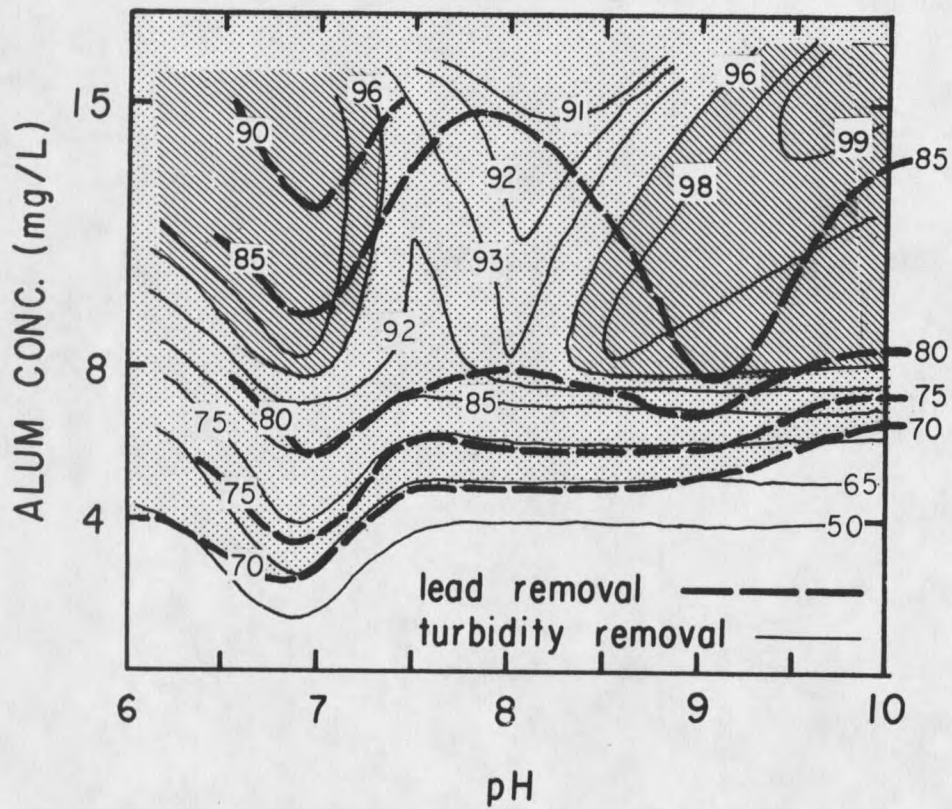


Figure 41. Operating regions for lead and turbidity removal. $Pb_i = 0.15$ mg/L; $turb_i = 25$ NTU.

pH and alum dosages utilized in this study. The turbidity removals shown in Figure 29 support this.

Contribution of Hardness to Turbidity Removal

The excellent turbidity removal observed outside the thermodynamic boundaries of aluminum was not anticipated. This phenomenon did provide an operating region for simultaneously meeting the MCLs for cadmium and turbidity and was therefore investigated further. Figure 42 shows the results of a pilot plant run performed for the purpose of investigating what, if any, role calcium (Ca(II)) and magnesium (Mg(II)) played in turbidity removals at elevated pH. The vertical dashed lines of Figure 42 separate periods when different experimental waters were used. Initially, a synthetic water containing 1.5 meq/L alkalinity (NaHCO_3) and no hardness was run through the pilot plant. With an effluent pH of 9.5 and an alum dosage of 8 mg/L, between 20 and 30 per cent turbidity removal was observed. Cadmium removal was apparently unaffected by the absence of hardness ions and approximately 96 per cent was removed. A little more than 3 hours into the run the raw water was switched to a second synthetic water (synthetic water II) containing 1.5 meq/L alkalinity and 2.0 meq/L hardness (CaCl_2). Immediately the turbidity removal improved to roughly 90 per cent. After the fifth hour of the run the raw water was again switched, this time to Bozeman tap water. The 96 per cent cadmium and 90+ per cent turbidity removals continued relatively unchanged for the remainder of the run.

The dramatic improvement to turbidity removal is clearly due to the presence of the major divalent cation, Ca(II), in the second synthetic water. To further investigate this phenomenon, total hardness was measured in influent and effluent samples using the EDTA titrimetric method from Standard Methods [37]. The influent hardness for synthetic water II was measured at 105 mg/L as CaCO_3 , while the effluent hardness was determined to be 64 mg/L as CaCO_3 . Therefore, a hardness removal of 41 mg/L as CaCO_3 .

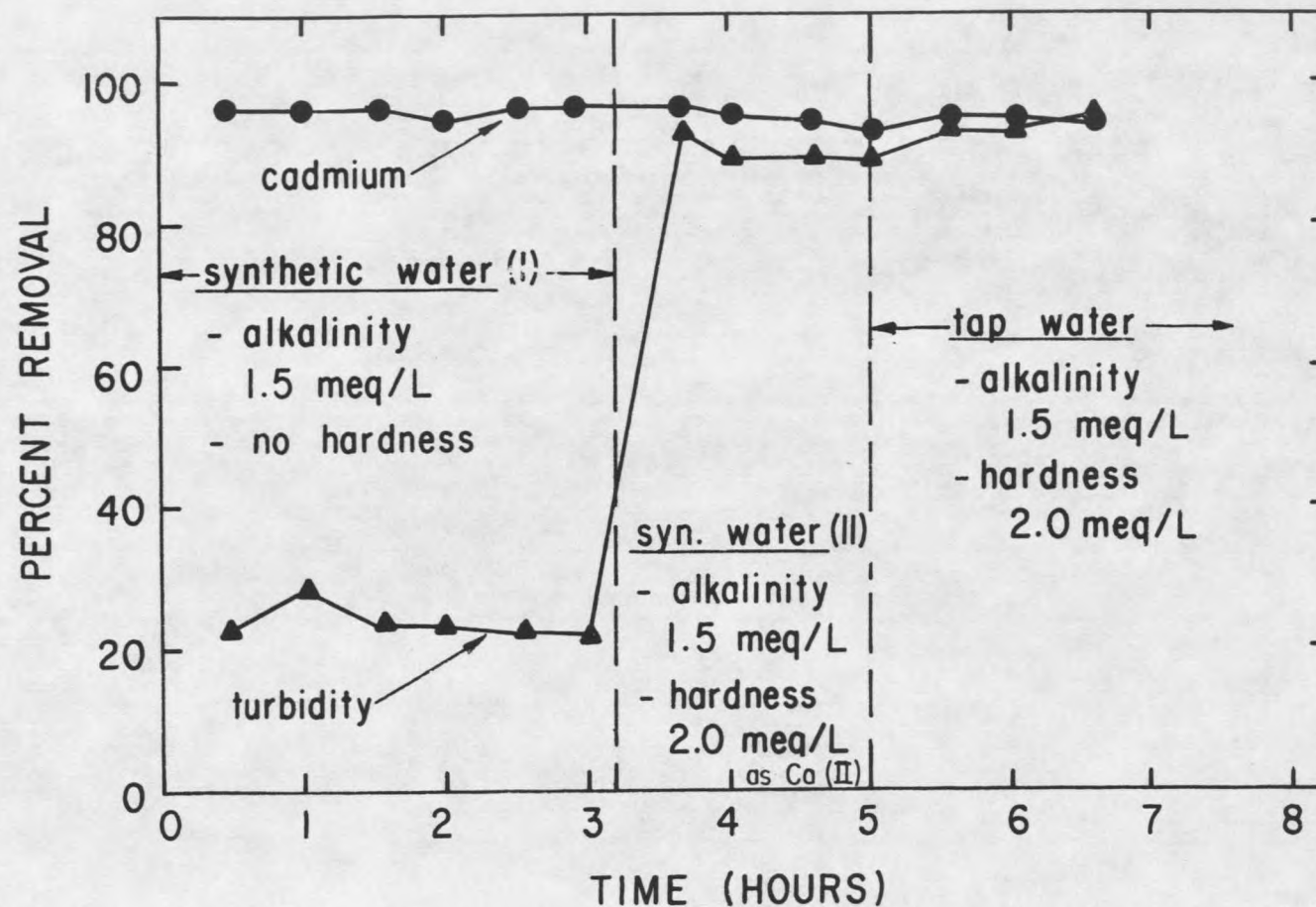


Figure 42. Role of hardness in turbidity removal at elevated pH. 8 mg/L alum; 25 NTU turb; $Cd_i = 0.05$ mg/L; pH = 9.5.

occurred through the pilot plant. A pilot plant run made to evaluate lead removal at pH 9.5 also showed measurable hardness removal, however, not to the extent observed with the synthetic water. The initial hardness of 92 mg/L as CaCO_3 was reduced to 85 mg/L, a hardness removal of 7 mg/L as CaCO_3 . The different extent of hardness removal for the two waters was not investigated, but, may have to do with the kinetics of CaCO_3 (s) precipitation. It is also possible that mixed calcium-aluminate precipitates are being formed.

Another interesting observation with respect to the role of hardness in turbidity removal at elevated pH pertains to the alum dosage. As can be seen in Figure 24, the improved turbidity removal at $\text{pH} > 8$ does not occur for the 4 mg/L alum dosage nor the run conducted without alum. The removal is better than the 20 to 30 per cent removal, shown in Figure 42, however, turbidity removal does not improve above 50 per cent. Although not investigated in this study, apparently a certain minimum alum dosage acts in conjunction with the hardness ions to destabilize and/or sweep the turbid suspension. This evidence would seem to support the formation of mixed calcium-aluminate precipitates mentioned above.

Mechanisms of Removal

Chapter 4 introduces several possible processes by which trace amounts of cadmium and lead can be removed from solution in a direct filtration treatment scheme. Identification of the more significant removal mechanism(s) could prove useful in designing unit processes and/or establishing operating procedures to effectively treat waters containing trace amounts of metal.

Cadmium

The various possible removal mechanisms will be evaluated in light of the pilot plant data presented above. Supplemental bench-scale test data will also be presented.

Adsorption Onto Silica Suspension. Any cadmium adsorbed onto the turbid suspension should be readily removed by coagulation followed by filtration [4,5,11]. The literature cited in Chapter 5, however, indicates a minor or negligible contribution from a quartz suspension for surface areas consistent with this study. This is reflected in the speciation model developed in Chapter 7.

As shown in Figure 26, a very weak correlation exists between turbidity removal and cadmium removal. In addition to the incongruencies between cadmium and turbidity removals already discussed, Figure 42 shows another situation where the cadmium removal is independent of the turbidity removal achieved. In this case the Ca(II) hardness component of synthetic water II is responsible for a dramatic increase in turbidity removal, an increase from 25 to 90 per cent. The cadmium removal remains unchanged.

Jar tests performed by mixing a turbid suspension (20 NTU Min-U-Sil) and a turbidity free water of the same chemical makeup further suggests the insignificance of the suspension in removing cadmium. Jars were mixed for 15 minutes at 80 rpm, then centrifuged at 10,000 rpm for 10 minutes. The results obtained are shown in Figure 43. The apparent high adsorption onto the test apparatus was not accounted for, however, the differences between the turbid and non-turbid waters are insignificant.

Precipitation Due to pH Control. The gradual increase in cadmium removal with increasing pH would appear to support evidence of a precipitation reaction in controlling cadmium solubility. As stated in Chapter 5, many researchers have used the low solubilities of the cadmium hydroxide and cadmium carbonate to explain observed removals and/or the low concentrations of cadmium found in natural waters. Short duration solubility tests, e.g., Patterson's [17] 4 hour jar tests, however, are strong evidence that the kinetics of the carbonate precipitation reaction are slow in dilute solutions. Even Patterson's theoretical

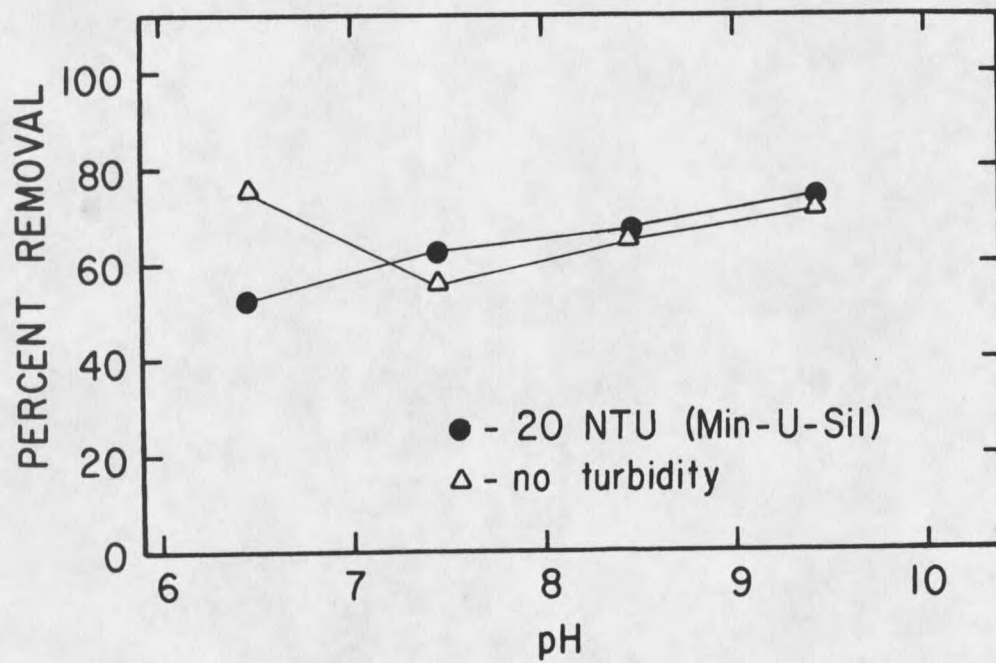


Figure 43. Effect of turbidity on cadmium removal (jar test data). $Cd_i = 0.05$ mg/L.

phase diagram for a fresh precipitate (see Figure 6) does not predict $\text{CdCO}_3 (s)$ precipitation below pH 8 for the initial cadmium concentration used in this study. It is, therefore, highly unlikely that the 25 to 40 per cent removals, shown in Figure 25 for pH 8.0, are a result of $\text{CdCO}_3 (s)$ precipitation.

To assess whether the cadmium was being removed by a precipitation process, a series of 90 minute pilot plant runs were performed. Figure 44 indicates that much of the cadmium is already in the insoluble fraction prior to filtration. Samples were collected above the filter with the metal analysis consisting of a comparison between centrifuged (10,000 rpm for 10 minutes) and uncentrifuged portions. Since turbidity and alum coagulant were present in those runs, additional experiments were necessary to isolate the mechanism(s) of removal.

Figure 45 gives the results of 90 minute pilot plant runs performed without alum. Also included are data for 4, 8 and 15 mg/L alum measured at 90 minutes. Surprisingly, the removals achieved without alum are somewhat higher. Although not very significant, chemical differences between Bozeman tap water and the synthetic water may be responsible. Regardless, coprecipitation of cadmium with alum does not appear to be that significant.

Adsorption of cadmium onto the Min-U-Sil suspension has already been discussed and discounted.

Analyzed together, the data presented in Figures 43, 44 and 45 would support a precipitation reaction as regulating the cadmium concentration.

Because a precipitation reaction is contrary to much of the evidence presented in Chapter 5, especially the evidence supporting slow carbonate precipitation, additional bench-scale tests were performed. The tests for cadmium are presented in Figure 46. Parallel tests were conducted at pH 7.5 and 9.5 for each parameter investigated. Tests were either 30 minutes or 5 minutes as indicated.

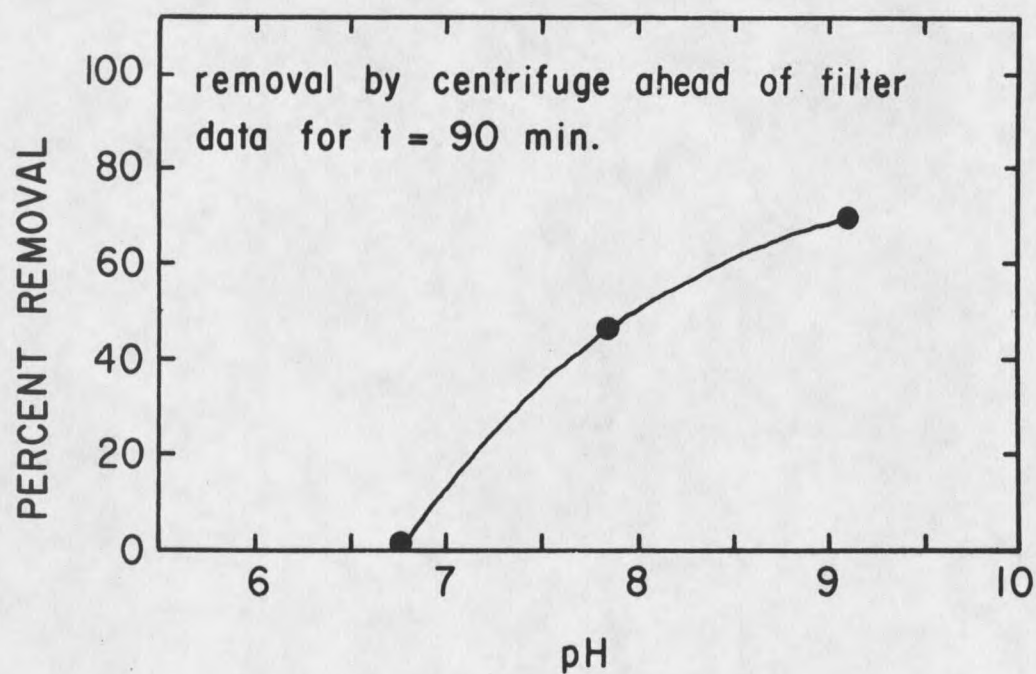


Figure 44. Cadmium removals ahead of filter. Alum = 8 mg/L; turb_i = 25 NTU; Cd_i = 0.05 mg/L.

Synthetic water:

- 1.5 meq/L alkalinity
- 2.0 meq/L hardness

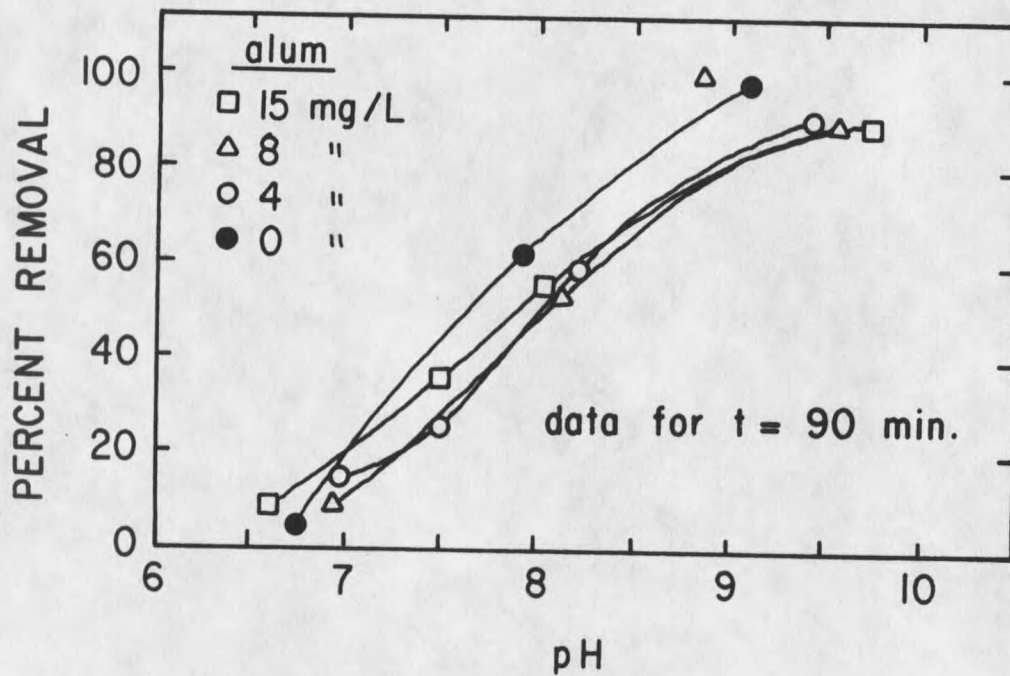


Figure 45. Cadmium removals at $T = 90$ min. Data for no alum using synthetic water: 1.5 meq/L alkalinity; 2.0 meq/L hardness; $Cd_i = 0.05$ mg/L.

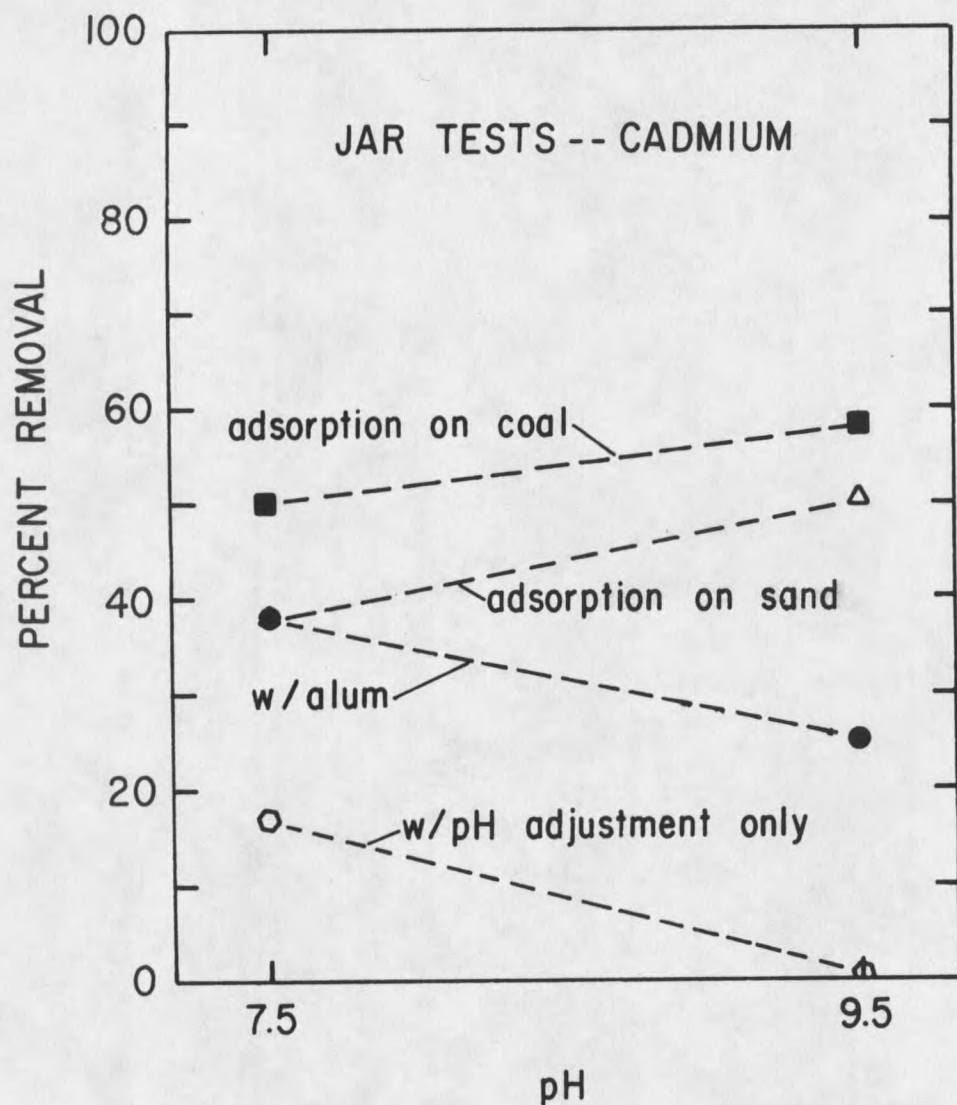


Figure 46. Bench-scale tests for cadmium. Coal and sand—5 min duration; all others—30 min duration; $Cd_i = 0.03$ mg/L.

The tests performed by pH adjustment only showed low cadmium removals. Surprisingly, the removal measured at pH 9.5 was less than the removal measured at pH 7.5. This is not explained and may be an indication of the insensitivity of these tests. Regardless, the data is not evidence of a precipitation reaction.

Coprecipitation with Coagulant. Figure 25 shows that somewhat higher cadmium removals occur with increased alum dosage. Sorg [11], using a wider range of alum dosages on a river water, found cadmium removals to increase from 10 to 60 per cent when the dosage was varied from 10 to 50 mg/L at pH 8.3. The alum dosages used in this study fall at or below the lower end of this range. The minor role of alum towards cadmium removal as evidenced by data presented in Figure 45, therefore, is not inconsistent with Sorg's results.

Assuming that coprecipitation with alum is an important removal mechanism for cadmium, removals should be affected at or near the aluminum hydroxide thermodynamic boundary. This is not observed in the pilot plant data. Removals increase to pH 9.5, the highest pH investigated.

Bench-scale jar tests depicted in Figure 46 demonstrated increased (as compared to pH adjustment alone) removals when 15 mg/L alum was used. The parallel tests at pH 7.5 and 9.5 are not significantly different, and this is evidence against a strong coprecipitation reaction between alum and cadmium. While substantial aluminum hydroxide formation should occur at pH 7.5 (see Figure 10), no precipitate is expected outside the thermodynamic boundaries of aluminum at pH 9.5.

Coprecipitation with Hardness. This potential removal mechanism for cadmium is insignificant as demonstrated by the experimental results shown in Figure 42. The 95+ per cent cadmium removal is unchanged for waters with and without Ca(II) hardness.

Adsorption Onto Filter Media. Figure 47 plots cadmium removal results for synthetic waters collected ahead of and after the filter. The difference between the two curves can be interpreted as removal within the filter. The removal data collected after the filter was for a water without coagulant treatment, therefore, the differences may be conservative, and the role of the filter media understated. It is probable that the aluminum hydroxide floc stored in the filter will provide additional surface area for cadmium adsorption.

The high removals obtained during 5 minute jar tests with anthracite coal and silica sand were not anticipated. The tests were conducted with used media taken out of the pilot plant filter. When the media was acid washed, the cadmium removals obtained were essentially unchanged. The cadmium removals measured for coal were higher than removals obtained with the silica sand.

The pH dependence of these jar test results may contribute significantly to higher removals at elevated pH. Figure 47 shows that removal of cadmium within the filter is highest at the upper end of the pH range investigated.

Lead

Fewer bench-scale and pilot plant experiments were conducted to identify the predominant removal mechanism(s) for lead.

Adsorption Onto the Silica Suspension. The speciation and distribution model developed for this study predicts insignificant adsorption onto the quartz suspension. Other studies, however, indicate that lead has a high adsorption potential [6,10,11] for naturally occurring suspended solids.

The strong correlation between turbidity removal and lead removal does not unequivocally show that lead is associated with the suspended solids present. If lead were predominantly insoluble due to other processes, it could also show this high correlation with

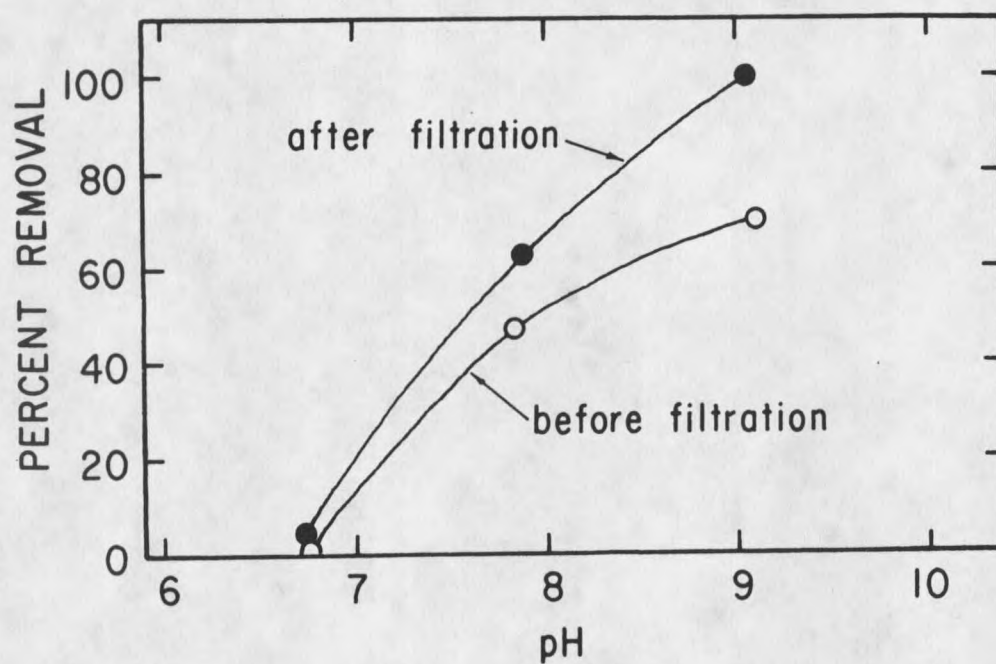


Figure 47. Cadmium removal within filter. $Cd_i = 0.05$ mg/L.

turbidity removal. In either situation, lead removal efficiency would be a function of the effectiveness of particulate removal within the filter.

The bench-scale test results for lead are presented in Figure 48. The 30 minute jar tests with a 25 NTU M30 suspension indicate high removals at pH 7.5 and pH 9.5. The removals are significantly higher than those obtained with pH adjustment only. A slight increase in removal was observed with pH 9.5.

The lead adsorbed onto the test apparatus was 30 per cent at both pH 7.5 and 9.5. If the adsorption onto the jars is neglected, lead removal at pH 7.5 is not increased over the removal measured with pH adjustment alone. Removals observed at pH 9.5 are 25 per cent greater. These results are in qualitative agreement with Davis and Leckie's site binding model [50]. At higher pH the available ($\equiv\text{SO}^-$) sites will increase and the surface complexation reaction will increase as $[\text{PbOH}^+]$ increases above pH 8 (see Figure 2).

Precipitation with pH Control. The pH independent removals observed for lead are not indicative of a precipitation control mechanism, however, they do not necessarily preclude it. If lead is sufficiently insoluble at all pH investigated, removals may be more a function of particulate removal as discussed earlier. It is also possible that other removal mechanisms mask a pH dependent solubility.

Lead removals for jar tests performed on waters adjusted for pH only are shown in Figure 48. As was the case with cadmium, removals were low and, surprisingly, lowest for pH 9.5.

Inconsistencies in the literature, e.g., Sorg's [11] jar test results versus Naylor and Dague's [10] jar test results, together with the lack of data collected in this study, preclude any conclusive statements with regard to lead precipitation.

Coprecipitation with Coagulant. The high lead removals at low pH (< 8) are readily explained by the affinity that alum has for lead. Figure 48 shows removals obtained with

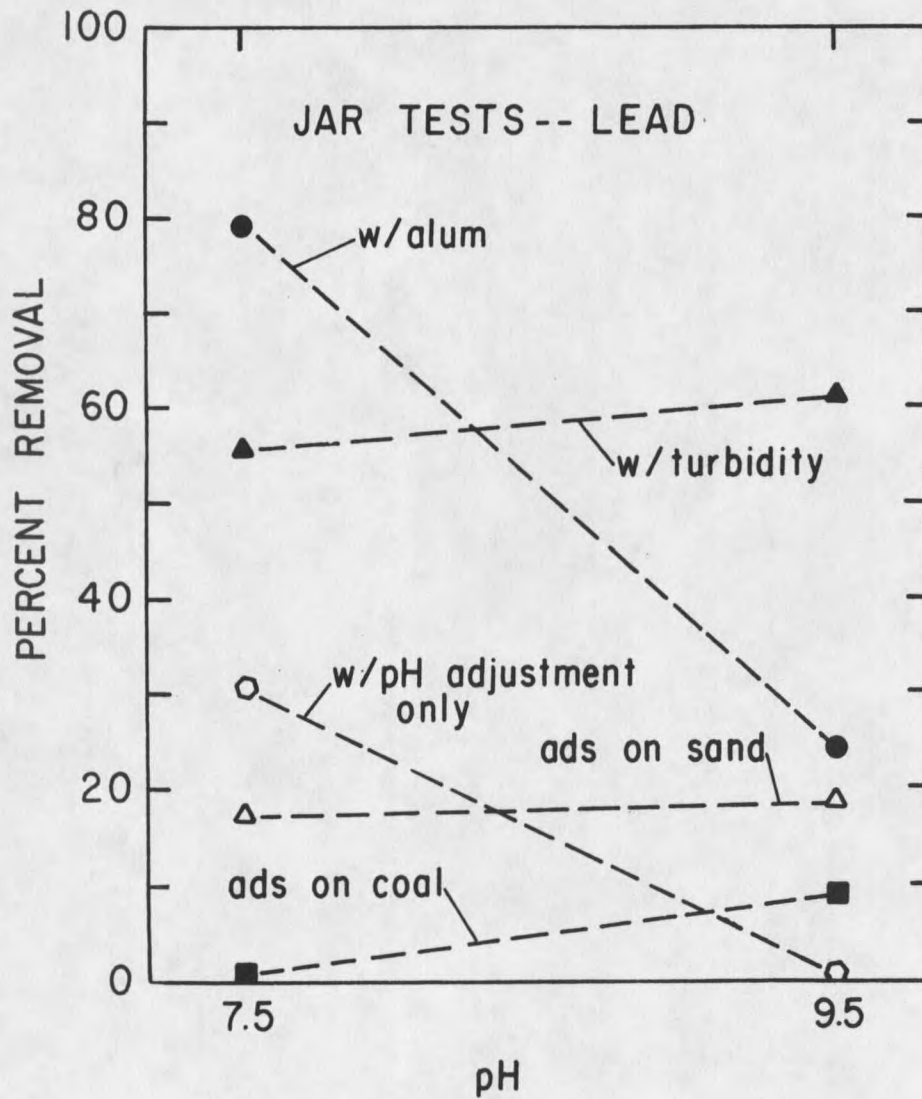


Figure 48. Bench-scale tests for lead. Coal and sand—5 min duration; all others—30 min duration; $Pb_i = 0.10$ mg/L.

15 mg/L alum at pH 7.5 and 9.5. Approximately 80 per cent of the lead was removed at pH 7.5, where substantial aluminum hydroxide floc formation occurs. This is compared to 24 per cent removal at pH 9.5.

The high affinity between lead and alum floc is further evidenced by comparing lead removals obtained with alum to cadmium removals obtained with alum. This is done in Figure 49. Lead is removed to a much greater extent.

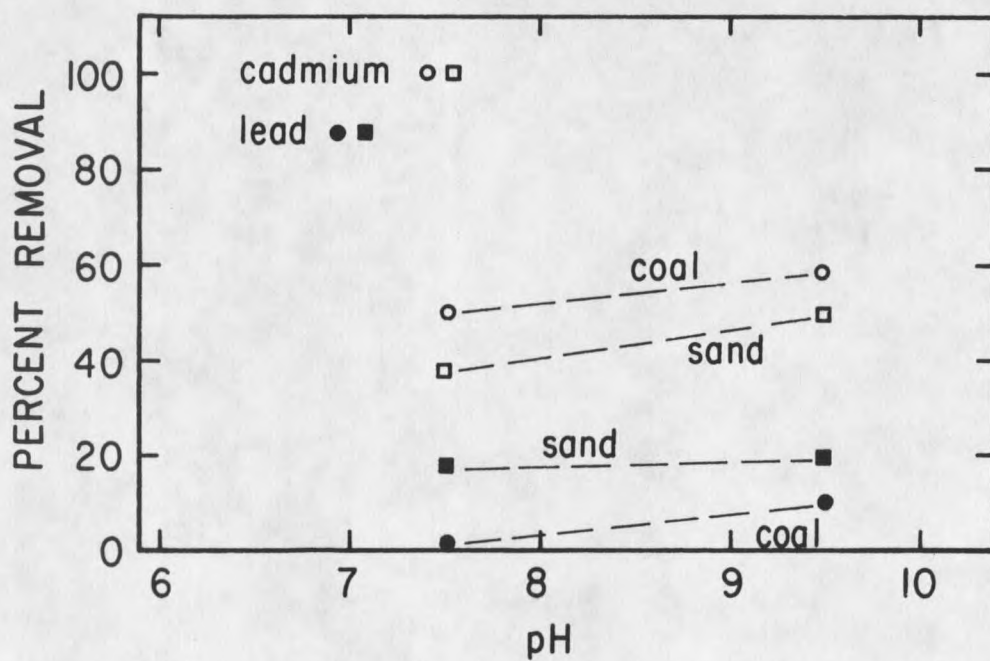
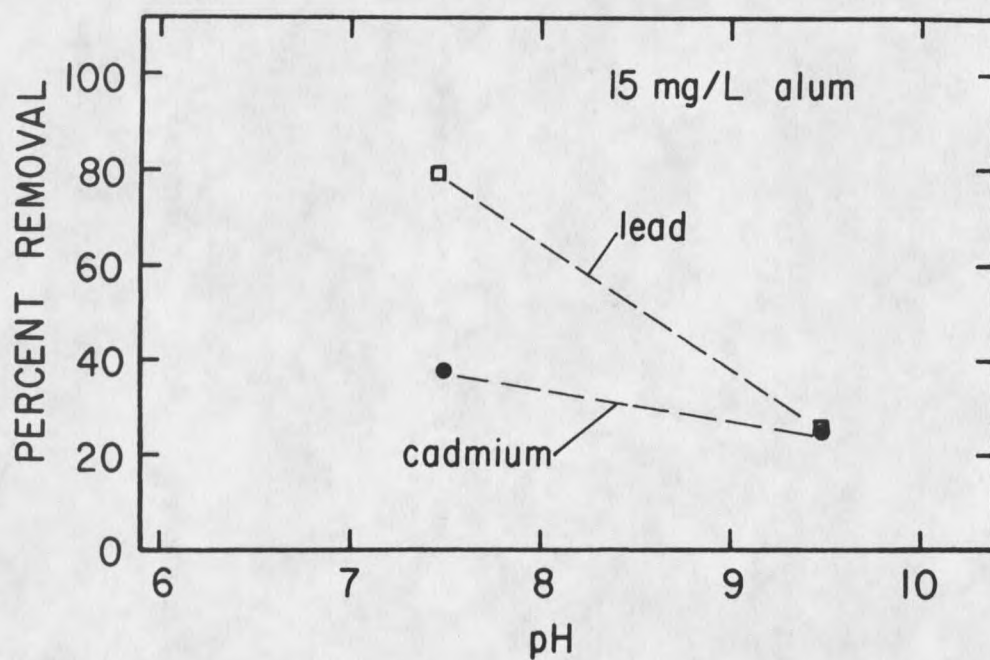
Adsorption Onto Filter Media. Figure 50 indicates that adsorption onto the filter media may not be as significant for lead as it appears to be for cadmium. However, based upon the discussion of the generalized adsorption behavior of hydrolyzable metal ions presented in Chapter 5, it is unlikely that lead would have a greater affinity for aluminum hydroxide and a lower affinity for the filter media. This probably is another indication of the insensitivity of these tests and the data should be interpreted cautiously.

Comparison of Results

Lead and cadmium removals obtained with a direct filtration pilot plant are similar to removals reported in the literature for conventional coagulation pilot plant and bench-scale tests. Much of the literature data has been presented in Chapter 5. Only the more significant findings are reviewed in this section.

Cadmium

Sorg [11] reported cadmium removals increasing from 10 to 85 per cent in the pH range 6.5 to 9. Somewhat higher removals were obtained with ferric sulfate coagulant. Anywhere from 50 to 90 per cent of the 0.03 to 0.05 mg/L initial cadmium concentration was removed by settling prior to filtration. Sorg concluded that pH was the most significant variable in the removal of cadmium.



Figures 49 and 50. Comparison—Jar test results for lead and cadmium. $Cd_i = 0.03 \text{ mg/L}$; $Pb_i = 0.10 \text{ mg/L}$.

Cadmium removals obtained with the direct filtration pilot plant are plotted in Figure 25. Removals increased from zero to 85 per cent in the pH range 6.5 to 9.5. The same strong pH dependency is observed. Pilot plant runs using ferric chloride coagulant resulted in superior removals, as compared to alum, at all pH values. No significant differences in cadmium removals are observed with direct filtration and conventional coagulation treatment schemes.

Lead

Both Sorg [11] and Naylor and Dague [10] investigated lead removals in simulated conventional coagulation treatment plants.

Sorg's lead removals, obtained with pilot plant and bench-scale tests were independent of pH with nearly 100 per cent of the 0.08 to 0.16 mg/L initial lead concentration removed in the pH range 6 to 10. Alum coagulation of low-turbidity well water was the only exception with pH dependent lead removal. Removals increased from 78 to 96 per cent in the pH range 6.6 to 9.6.

Naylor and Dague performed jar tests to investigate lead removal. Their tests came closest to simulating direct filtration by using 0.45 μ m membrane filter paper to simulate the solids separation steps of sedimentation and filtration. The results of these tests indicate that alum has only a small effect on lead solubility. The removals obtained were similar to removals observed with alkalinity variations alone. One significant difference between Naylor and Dague's tests and Sorg's tests was the initial lead concentration. Naylor and Dague used a 2 mg/L initial lead concentration. This concentration is sufficiently high to precipitate lead (see Figure 7) and, thus, the similarity between lead removal as a result of pH adjustment of a water containing alkalinity and lead removal with coagulation of the same water. Both resulted in less than 0.05 mg/L lead.

Lead removals obtained with the direct filtration pilot plant are plotted in Figure 34. Removals are relatively pH independent ranging from 65 to 95 per cent in the pH range 6 to 9.5. The lowest lead removals correspond to the 4 mg/L alum dosage used. Higher alum dosages generally resulted in higher lead removals. The superior removals observed by Sorg probably result from higher coagulant dosages (≈ 30 mg/L alum) and suspended solids with a greater affinity for lead (see Figure 15). All in all, Sorg's results compare favorably with data from this study.

Naylor and Dague's results are not directly comparable with this study. Between pH 7.0 and 9.5, lead solubility was ≈ 0.05 mg/L. This corresponds to 97.5 per cent removal for the initial lead concentration used. Sorg [11] performed jar tests which demonstrated that initial lead concentration has an effect on the lead concentration remaining in solution after coagulation. If this is considered, Naylor and Dague's data is not inconsistent with other data presented above.

CHAPTER 9

CONCLUSIONS

Removal Efficiencies

The metal and turbidity removals obtained in this study are adequately summarized in Chapter 8. Cadmium and lead demonstrate considerably different removal characteristics.

Cadmium removal is pH dependent with removals increasing gradually from 6.9 to 9.5 (the pH range investigated). While this characteristic is commonly observed with precipitation and adsorption reactions, the pH-adsorption curve typically increases from zero adsorption to 100 per cent adsorption over a narrower pH range, oftentimes less than 1 pH unit wide.

Lead removal, by contrast, is pH independent with removals ranging from 65 to 95 per cent. The higher removals corresponded to higher alum dosages, and combinations of alum dosage and pH that produced the best turbidity removals.

Turbidity removals are highest at near neutral pH and above pH 9.0. The high removals observed at neutral pH correspond to the charge-neutralization of the colloidal suspension (see Figure 10). High removals above pH 9 result from the hardness in the water. Increasing the alum dosage from 4 to 15 mg/L produced a lower effluent turbidity. However, more rapid clogging of the filter with the 15 mg/L dosage led to earlier effluent degradation, and subsequently the average removal observed over the 5-hour run was at times inferior to that obtained with the 8 mg/L dosage.

Operational Guidelines

As a result of the different removal characteristics described above, the proposed operational guidelines for lead and cadmium are quite different.

Cadmium and turbidity MCLs are met concurrently when the pilot plant operates above pH 9.3 with an alum dosage ≥ 8 mg/L (see Figure 39). Using polymers will undoubtedly provide the required turbidity removal at all alum dosage and pH investigated, therefore, operating at a pH that provides effective cadmium removal should satisfy both MCLs.

Lead and turbidity MCLs are met concurrently whenever the turbidity MCL is met. This includes the region of excellent turbidity removal at near neutral pH in addition to the excellent removals observed at elevated pH (see Figure 41). The use of polymers will most likely result in simultaneous achievement of both lead and turbidity MCLs for the range of pH and alum dosages used in this study.

Removal Mechanisms

Cadmium

Cadmium removals apparently result from a combination of several removal mechanisms.

Adsorption onto the silica suspension and coprecipitation with aluminum hydroxide floc are not responsible for the observed removals, however, they undoubtedly contribute.

Precipitation of cadmium as CdCO_3 (s) is doubtful, but, not disproved by the data collected in this study.

Adsorption of cadmium onto the filter media contributes to observed removals, and, may be significant. Jar tests indicate that the process is pH dependent with greater removals occurring at higher pH. This is consistent with the experimental data and especially with

results of supplementary pilot plant runs shown in Figure 47. Those experiments show that removals of soluble cadmium within the filter increase with pH?

Pilot plant data indicates that cadmium is to a large extent already in an insoluble state (at elevated pH) ahead of the filter. Experiments performed to determine the cause of this insolubility discounted coprecipitation with the coagulant and adsorption onto the silica suspension. It is possible some other adsorption phenomenon and/or precipitation is responsible.

Benes and Kopicka [56] discovered cadmium to be somewhat insoluble in dilute solutions, 1×10^{-7} M to 5×10^{-7} M cadmium. Using dialysis, centrifugation and electromigration techniques they attributed the observed insolubilities to adsorption onto "impurities" in the experimental waters. The authors referred to these separable solids as pseudocolloids. As the impurities were not characterized, little consideration was given to the experimental results obtained. Results of centrifugation experiments are, however, presented in Figure 51 for two reasons: (1) they are in qualitative and quantitative agreement with experimental results obtained in this study, and (2) further investigation of these reported results may provide the answer to questions raised in this section as to the removal mechanism(s) for cadmium.

In support of the contention that more than one removal mechanism is responsible for observed cadmium removals, the jar test data plotted in Figure 46 is considered. The results, while not easily interpreted, do indicate that all the various surfaces considered have a capacity to remove cadmium from solution.

Lead

The pH independent results observed appear to be a result of a combination of several removal mechanisms. Again, the results of jar tests presented in Figure 48 suggest that all of the surfaces investigated are capable of reducing lead concentrations.

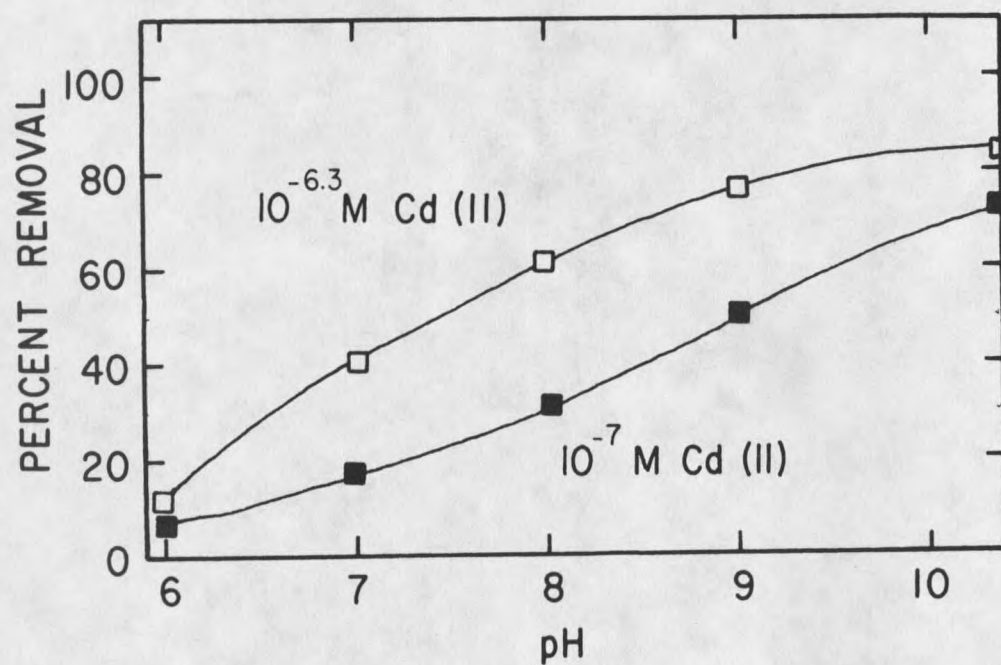


Figure 51. Cadmium removal as a result of pseudocolloid formation [56].

Precipitation reactions may also contribute to the removals observed. However, the evidence is contradictory.

Coprecipitation of lead with coagulant floc is apparently significant and probably accounts for the high removals observed at low pH. As discussed earlier, alum floc has a greater affinity for lead than for cadmium.

It is likely that lead attaches to the silica suspension and other colloidal particles present in the experimental water. The strong correlation between turbidity and lead removals is the best evidence of this. Additionally, the jar tests show considerable adsorption onto the M30 suspension.

The combination of coprecipitation with the coagulant and adsorption onto particulates could account for the observed removals. Insolubility due to a precipitation reaction could also account for observed removals. In either case the extent of lead removal would be a function of the filter efficiency, and, thus, the strong correlation observed between turbidity and lead removals.

Suggestions for Further Study

Additional research into two topics are encouraged as a result of this study.

Effect of Hardness on Turbidity Removal

This study identified hardness as an important parameter in providing excellent turbidity removal at elevated pH, outside the thermodynamic boundary for aluminum. Information such as minimum hardness concentrations required, nature of precipitate formed, contribution of alum, etc., would be useful. Practical applications could include designing treatment facilities for concurrent turbidity and hardness removals. Possible savings in capital, chemical and operating costs can be envisioned.

Removal Mechanisms for Metals

More rigorous experimentation to unambiguously identify the predominant removal mechanisms for metals used in this study and others would be useful design and/or operational information.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Durum, W. H. "Occurrence of Some Trace Metals in Surface Waters and Groundwaters." *Proceedings, 16th Water Quality Conference*, U. of Illinois, 1975.
2. McCabe, L. J. "Problems of Trace Metals in Water Supplies." *Proc. 16th Water Qual. Conf.*, U. of Illinois, 1975.
3. Vuceta, J. and Morgan, J. J. "Chemical Modeling of Trace Metals in Fresh Waters: Role of Complexation and Adsorption." *Environmental Science and Technology*. 12 (Nov. 1978): 1302-1308.
4. O'Connor, J. T. "Removal of Trace Inorganic Constituents by Conventional Water Treatment Processes." *Proc., 16th Water Qual. Conf.*, U. of Illinois, 1975.
5. Singer, P. C. "Chemical Processes for the Removal of Trace Metals from Drinking Water." *Proc., 16th Water Qual. Conf.*, U. of Illinois, 1975.
6. Hem, J. D. and Durum, W. H. "Solubility and Occurrence of Lead in Surface Water." *Journal of the American Water Works Association*. 65 (Aug. 1973): 562-568.
7. Hem, J. D. "Chemistry and Occurrence of Cadmium and Zinc in Surface Water and Groundwater." *Water Resources Research*. 8 (June 1972): 661-679.
8. Linstedt, K. D., et al. "Trace Element Removals in Advanced Wastewater Treatment Processes." *Journal of the Water Pollution Control Federation*. 43 (July 1971): 1507-1513.
9. Montana State Department of Health. *Chemical Analyses of Community Water Supplies*. May 1981.
10. Naylor, L. M. and Dague, R. R. "Simulation of Lead Removal by Chemical Treatment." *J. AWWA*. 67 (Oct. 1975): 560-565.
11. Sorg, T. J., et al. "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics." *J. AWWA*. 71 (Dec. 78): 680-691.
12. Argo, D. G. and Culp, G. L. "Heavy Metal Removal in Wastewater Treatment Processes." *Water and Sewage Works*. 62 (Aug. 1972): 62-65.
13. Boyd, T. C. "Determinants of Optimum Working Ranges for Flameless AA Spectroscopy." Unpublished Professional Paper—Montana State University. May 1982.

14. Edwards, G. A. and Amirtharajah, A. "Color Removal Domains on the Alum Coagulation Diagram." *Proceedings, Part 2, Annual Conference of the American Water Works Association*. June 1982: 1129-1145.
15. Amirtharajah, A. and Suprenant, B. K. "Direct Filtration Using the Alum Coagulation Diagram." Presented at the *Annual Conference of the American Water Works Association*. June 1984, Dallas, TX.
16. Yeh, H. and Ghosh, M. M. "Selecting Polymers for Direct Filtration." *J. AWWA*. 73 (Apr. 1981): 211-218.
17. Patterson, J. W., et al. "Carbonate Precipitation for Heavy Metals Pollutants." *Journal of the Water Pollution Control Federation*. 49 (Dec. 1977): 2397-2410.
18. Benjamin, M. M., et al. "Removal of Toxic Metals from Power-Generation Waste Streams by Adsorption and Coprecipitation." *J. WPCF*. 54 (No. 1982): 1472-1480.
19. Suzuki, M., et al. "Sorption and Accumulation of Cadmium in the Sediment of the Tama River." *Water Research*. 18 (July 1978): 57-63.
20. McCormick, R. F. and King, P. H. "Factors Affecting Use of Direct Filtration in Treatment of High Quality Surface Waters." *Proc., Ann. Conf. AWWA*. June 1979: 973-977.
21. Wagner, E. G. and Hudson, H. E. Jr. "Low-Dosage High-Rate Direct Filtration." *American Water Works Association Seminar Proceedings: Coagulation and Filtration: Back to the Basics*. June 1981: 139-153.
22. Committee Report. "The Status of Direct Filtration." *J. AWWA*. 72 (July 1980): 405-411.
23. Sanks, R. L., ed. *Water Treatment Plant Design*. Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1980.
24. Stumm, W. and Morgan J. J. *Aquatic Chemistry*. New York: Wiley-Interscience, 1981.
25. Snoeyink, V. L. and Jenkins, D. *Water Chemistry*. New York: John Wiley & Sons, 1980.
26. Pagenkopf, G. K. *Introduction to Natural Water Chemistry*. New York: Marcel Dekker, Inc., 1978.
27. Rubin, A. J. *Aqueous-Environmental Chemistry of Metals*. Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1974.
28. Hutchison, W. R. "High-Rate Direct Filtration." *J. AWWA*. 68 (June 1976): 292-298.
29. Gardiner, J. "The Chemistry of Cadmium in Natural Waters—I: A Study of Cadmium Complex Formation Using the Cadmium Specific-Ion Electrode." *Water Research*. 8 (June 1973): 23-30.

30. Mouvet, C. and Bourg, C. M. "Speciation (Including Adsorbed Species) of Copper, Lead, Nickel and Zinc in the Meuse River." *Water Res.* 17 (Mar. 1982): 641-649.
31. Nilsson, R. "Removal of Metals by Chemical Treatment of Municipal Waste Water." *Water Res.* 5 (July 1970): 51-60.
32. Weber, W. J. Jr. *Physicochemical Processes: For Water Quality Control*. New York: Wiley-Interscience, 1972.
33. James, R. O. and Healy, T. W. "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface-II." *Journal of Colloid and Interface Science.* 40 (July 1972): 53-64.
34. James, R. O. and Healy, T. W. "Adsorption of Hydrolyzable Metal Ion at the Oxide-Water Interface-III." *J. Coll. Interf. Sci.* 40 (July 1972): 65-76.
35. Mills, K. M. and Amirtharajah, A. "Rapid-Mix Design for Mechanisms of Alum Coagulation." *J. AWWA.* 74 (Apr. 1982): 210-216.
36. *Varian Techtron: Analytical Methods for Flame Spectroscopy*. Varian Techtron Pty: Melbourne, Australia, 1972.
37. *Standard Methods for the Examination of Water and Wastewater*. 13th Edition, American Public Health Association, 1971.
38. Trusler, S. "Turbulent Rapid Mixing in Direct Filtration." Unpublished Master's Thesis—Montana State University. May 1983.
39. Wiley, J. O. and Nelson, P. O. "Cadmium Adsorption by Aerobic Lake Sediments." *Journal of Environmental Engineering.* 110 (Feb. 1984): 226-243.
40. Florence, T. M. "Trace Metal Species in Fresh Water." *Water Res.* 11 (Nov. 1976): 681-687.
41. Stevenson, F. J. "Stability Constants of Cu^{2+} , Pb^{2+} , and Cd^{2+} Complexes with Humic Acids." *Soil Science Society of American Journal.* 40 (June 1976): 665-672.
42. Brady, B. and Pagenkopf, G. K. "Cadmium Complexation by Soil Fulvic Acid." *Canadian Journal of Chemistry.* 56 (1978): 2331-2335.
43. Whitworth, C. and Pagenkopf, G. K. "Cadmium Complexation by Coal Humic Acid." *Journal of Inorganic Nuclear Chemistry.* 41 (Aug. 1978): 317-321.
44. Turakhia, M. and Bakke, R. (June 1984). Personal communication.
45. Anderson, M. A. and Rubin, A. J. *Adsorption of Inorganics at Solid-Liquid Interface*. Ann Arbor, MI: Ann Arbor Science Pub., 1981.
46. Fristoe, B. R. and Nelson, P. O. "Equilibrium Modelling of Heavy Metals in Activated Sludge." *Water Res.* 17 (Apr. 1982): 771-777.

47. Lee, F. G. "Role of Hydrous Metal Oxides in the Transport of Heavy Metals in the Environment." *An International Conference: Heavy Metals in the Aquatic Environment*. New York: Pergamon Press, 1975.
48. Benjamin, M. M. and Leckie, J. O. "Multi-Site Adsorption of Cd, Cu, Zn and Pb on Amorphous Iron Oxyhydroxide." *J. Coll. Interf. Sci.* 79 (Jan. 1981):
49. Benjamin, M. M. and Leckie, J. O. "Effects of Complexation by Cl, SO₄ and S₂O₃ on Adsorption Behavior of Cd on Oxide Surfaces." *Environmental Science and Technology*. 16 (1982): 162-169.
50. Davis, J. A. and Leckie, J. O. "Surface Ionization and Complexation at the Oxide/Water Interface—I." *J. Coll. Interf. Sci.* 63 (Mar. 1978): 480-499.
51. Bruninx, E. "The Coprecipitation of Zn, Cd and Hg with Ferric Hydroxide." *Philips Research Reports*. 30 (Aug. 1975): 178-191.
52. Davis, J. A. and Leckie, J. O. "Surface Ionization and Complexation at the Oxide/Water Interface—II." *J. Coll. Interf. Sci.* 67 (Oct. 1978): 90-107.
53. Kinniburgh, A. G., et al. "Adsorption of Alkaline Earth, Transition, and Heavy Metal Cations by Hydrous Oxide Gels of Iron and Aluminum." *Soil Science Society of America Journal*. 40 (1976): 796-799.
54. Hohl, H. and Stumm, W. "Interaction of Pb²⁺ with Hydrous γ -Al₂O₃." *J. Coll. Interf. Sci.* 55 (May 1976): 281-288.
55. Gardiner, J. "The Chemistry of Cadmium in Natural Water—II." *Water Res.* 8 (Sept. 1973): 157-164.
56. Benes, P. and Kopicka, K. "The State and Adsorption Behavior of Traces of Cadmium in Aqueous Solutions." *J. Inorg. Nuclear Chem.* 38 (June 1974): 2043-2047.
57. Tobiason, J. E. "Packed Bed Filtration: Experimental Investigation and Conceptual Analysis of a Filter Ripening Model." Master's Thesis—University of North Carolina, 1979.
58. Weber, W. J. Jr. and Posselt, H. S. "Equilibrium Models and Precipitation Reactions for Cadmium (II)." *Aqueous-Environmental Chemistry of Metals*. Ann Arbor, MI: Ann Arbor Science Publ., Inc., 1974.
59. Leckie, J. O. and James, R. D. "Control Mechanisms for Trace Metals in Natural Waters." *Aqueous-Environmental Chemistry of Metals*. Ann Arbor, MI: Ann Arbor Science Publ., Inc., 1974.
60. Johnson, P. N. and Amirtharajah, A. "Ferric Chloride and Alum as Single and Dual Coagulants." *J. AWWA*. 75 (May 1983): 232-239.



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