

THE REMOVAL OF HEAVY METALS FROM
MUNICIPAL WASTEWATERS BY
LIME-MAGNESIUM COAGULATION

by

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ABSTRACT

The evidence of heavy metal build up in the aquatic environment near sewage treatment plant outfalls around Vancouver, coupled with the generally held theory that secondary treatment is not required in this area, leads to the conclusion that a treatment method is required that is primarily aimed at heavy metal removal.

In this study, jar tests were performed to evaluate the heavy metal removal efficiency of the lime-magnesium coagulation process. Five heavy metals (Cr^{3+} , Cu^{2+} , Pb^{2+} , Ni^{2+} and Zn^{2+}) were all tested at initial concentrations of .5, 2.5 and 5.0 mg/l individually and in combination. The experiments were performed on prechlorinated primary effluent and raw sewage at the natural alkalinity levels (120-130 mg/l as CaCO_3), and some work was done at elevated alkalinity (190-200 mg/l). The need for filtration in the process was also researched.

Results of the study indicated that the heavy metal removal efficiency was enhanced by the presence of Mg^{2+} at a given lime dosage for all of the heavy metals except nickel. A comparison indicated that intermediate lime treatment (220 mg/l) coupled with 33 mg/l Mg^{2+} might be a more attractive process than just straight high lime treatment (400 mg/l).

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CHAPTER 1

INTRODUCTION

There has been an increasing concern in recent years over the problems associated with heavy metal build-up from cultural sources in the aquatic environment. The realization of these problems has moved many governments to bring in stricter pollution control standards.

A study of the lower Fraser River system conducted by Benedict et al. (5) found BOD values of ≤ 1 mg/l and 2-4 mg/l and dissolved oxygen levels of $> 90\%$ and $> 80\%$ of saturation for the Main Arm and North Arm/Middle Arm respectively. This information, coupled with river flow data, has led most researchers to conclude that secondary treatment of Vancouver municipal wastewaters is not highly cost-effective.

The precipitation of heavy metals by lime coagulation is a well documented process (11). A slight modification, the lime-magnesium process, involves the precipitation of magnesium ion *insitu* during lime coagulation. This process has been shown to be effective for the removal of cadmium as well as COD, SS and colour (8). The main objective of the research reported herein is to establish the heavy metal removal efficiency of this process for Vancouver municipal sewage. The specific objectives are as follows:

- 1) To develop a method to evaluate heavy metal removal by the lime-magnesium process (Appendix A).
- 2) To evaluate the removal efficiency of individual heavy metals (i.e. Cr^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+}) at various initial concentrations in prechlorinated primary effluent (PPE) (Section 7.1).
- 3) To evaluate the need for filtration in the process (Section 7.2).
- 4) To evaluate the removal efficiency of mixed metals in PPE and compare

these removals with the individual metal data (Section 7.3).

5) To compare the removal efficiency from PPE to that from raw sewage (Section 7.4).

6) To evaluate the effect of alkalinity on the removal efficiency (Section 7.5).

The experimentation program is summarized in Table 1.

TABLE 1
EXPERIMENTATION PROGRAM

Test Conditions	Chromium PPE	Copper PPE	Lead PPE	Nickel PPE	Zinc PPE	Σ PPE	Σ RS
pH 10.0 Alk: natural	X	X	X	X	X	X	X
pH 10.70 Alk: natural	X	X	X	X	X	X	X
pH 11.40 Alk: natural	X	X	X	X	X	X	X
pH 10.70 Alk: 180-200 mg/l as CaCO ₃	X	X	X	X	X	X	X

- Notes: 1) Individual metal runs were all performed starting with the following initial metal concentrations - .5 mg/l, 2.5 mg/l, 5.0 mg/l.
- 2) Mg²⁺ dosage: 0, 8, 17, 33 and 50 mg/l.
- 3) PPE - prechlorinated primary effluent.
- 4) RS - raw sewage.
- 5) Natural alkalinity: 120-130 mg/l as CaCO₃.
- 6) Σ indicates a combination of all five metals each with initial concentration of .5 mg/l.

CHAPTER 2

HISTORY OF THE HEAVY METAL PROBLEM2.1 Toxicity

The major areas of concern with respect to the heavy metal problem in the aquatic environment is that of toxicity to biological organisms at low concentrations. The build-up of heavy metals in Vancouver street sediments and in the river sediments near Vancouver sewage treatment plant outfalls has become an area of increasing concern (4,5,12,13).

The factors that contribute to the problem of toxicity of heavy metals are as follows:

- 1) being elements, heavy metals do not degrade and hence tend to build up in the environment (stream sediments).
- 2) some heavy metals are susceptible to food chain concentration.
- 3) most heavy metals are toxic to living organisms in fairly low concentrations.

The toxicities of the five heavy metals used in this study (Cr, Cu, Pb, Ni, Zn) are summarized in the following paragraphs.

a) Chromium. The USPHS Drinking Water Standard (19) for hexavalent chromium is .05 mg/l, although it does not appear to have any physiological effects on humans and is not retained in the body. Similarly, hexavalent and trivalent chromium have no significant effect on animals at dosages of the order of 25 mg/l (19). Fish are relatively tolerant of chromium salts, but lower forms of aquatic life are extremely sensitive. McKee and Wolf (19) conclude that concentrations above 1.0 mg/l for fish and .05 mg/l for other aquatic life will have toxic effects. The concentration of radioactive chromium by algae has been found to be in the range of 100 to 500 times (19) that present in the water.

b) Copper. McKee and Wolf (19) state that "Chronic copper poisoning among human beings has never been proved, even among people in copper industries who have absorbed enough copper through their skin to be colored green". The USPHS Drinking Water Standards recommend 1.0 mg/l and this is primarily for taste considerations. Toxicological studies on a wide range of commercial crops indicates that .1 mg/l of copper is beneficial in irrigation water (19). The major area of concern with respect to copper toxicity appears to be with the lower biological forms. The toxicity of copper to aquatic organisms varies significantly with species and with physical and chemical characteristics of the water. McKee and Wolf (19) indicate that .02 mg/l for fresh water and .05 mg/l for sea water are beneficial copper concentrations. Studies indicate that plankton concentrate copper by factors of 1000 to 5000.

c) Lead. Lead is not considered essential to the nutrition of human beings or other animals and is a cumulative poison to both. Due to the fact that lead may enter the body through food and air sources as well as from water, the USPHS Drinking Water Standard has been set at .05 mg/l. Most authorities agree that .05 mg/l is a maximum safe limit for lead in a potable supply for animals. Lead concentrations as low as .1 mg/l have been deleterious to fish life especially in soft water (19).

d) Nickel. The toxicity of nickel to man is believed to be very low. The USPHS has not set a drinking water standard for nickel. Although not a great deal of data exists, nickel appears to be quite injurious to plants even at low concentrations. Nickel is toxic to fish and other aquatic life at about 1.0 mg/l (19). Concentrations of nickel salts in the 10-15 mg/l range caused a 50 percent reduction in the bacterial oxygen utilization from synthetic sewage (19).

e) Zinc. Zinc has no known physiological effects upon man or animals, except at high concentrations, and the USPHS Drinking Water Standard of 5 mg/l was set due mainly to taste threshold considerations. It is toward fish and aquatic organisms that zinc, especially in water lacking calcium hardness, exhibits its greatest toxicity (19). In soft water, concentrations of zinc from 0.1 to 1.0 mg/l have been reported toxic. Copper appears to have synergistic effect on the toxicity of zinc. Zinc is quite toxic to shellfish and it has been shown that they have been able to concentrate Zn-65 by a factor of 100,000 (19).

From the above discussion of heavy metal toxicity one major conclusion can be drawn - all five metals exhibit an injurious effect on the aquatic environment and in combination with one another the overall effect is, in all probability, one of synergism rather than antagonism.

2.2 Heavy Metal Concentrations in the Urban Environment

The uses of the five heavy metals studied are numerous and it is therefore not surprising that they are present in measureable amounts in the combined sewer discharges from the city of Vancouver. In a Westwater Research Centre survey (13) the concentrations of eleven trace metals were determined in samples collected from Vancouver street surfaces. This data was compared to Environmental Protection Agency (E.P.A.) data for several cities in the United States. The data is shown in Table 2. The data for Seattle is shown separately since this west coast city has a similar climate to Vancouver. As would be expected, the highest degree of metal contamination is in the industrial and commercial areas for all three sets of data. Hall et al. (13) also concluded that lead contamination was not only a function of land use but also of traffic volume.

A study by Tanner et al. (25) on the characteristics of Vancouver

Table 2: Average Trace Metal Concentrations in Street Surface Contaminants^a
from 8 U.S. Cities (from Hall et al. (13))

Study Area	Land Use	Number of Stations	Ag	Cd	Co	Cr	Cu	Fe	Hg ^b	Ni	Mn	Pb	Zn
Vancouver, B.C. (Brunette River Basin)	Industrial	8	0.6	1.5	87	208	780	18,200	62	44	220	1,243	296
	Commercial	6	0.7	2.4	9.5	141	212	20,400	117	34	232	1,415	702
	Residential	8	0.5	1.2	6.3	140	133	18,500	40	46	195	710	404
	Green Space	4	0.3	1.2	8.9	144	117	16,850	22	27	226	100	246
	Overall	26	0.5	1.6	32.2	163	347	18,590	62	35	216	867	415
Seattle, Washington ^c	Industrial	1	-	1.4	-	239	110	27,000	-	20	490	1,100	480
	Commercial	2	-	1.9	-	206	136	37,000	-	40	435	4,000	445
	Residential	4	-	1.6	-	244	76	36,500	-	37	455	2,450	497
	Overall	7	-	1.5	-	247	97	35,000	-	35	454	2,700	480
United States ^c (8 cities)	Industrial	38	-	4.1	-	279	120	28,000	-	37	590	1,600	360
	Commercial	19	-	5.1	-	226	170	24,000	-	52	400	3,600	520
	Residential	22	-	3.1	-	189	91	21,000	-	26	370	1,600	380
	Overall	79	-	3.8	-	209	120	24,000	-	34	440	2,000	400

^a concentrations as mg/kg dry weight of sediment

^b Hg concentrations as ug/kg dry weight of sediment

^c Pitt and Amy (1973)

wastewaters concluded that the majority of the sewers contain sufficient contaminants to be toxic to fish. The researchers measured heavy metal and organic contaminant concentrations and indirectly concluded that the heavy metals were partially responsible for the toxicity.

Due to the toxic effect of heavy metals on the aquatic environment, an area of prime concern has been the build-up of heavy metal concentrations in the Fraser River sediments, especially at the outfalls of sewage treatment plants. A comparison of the heavy metal concentrations in the sediments of the Iona Island sewage treatment plant to concentrations at four other locations is presented in Table 3. There is no build-up of heavy metals at the Lulu Island sewage treatment plant outfall due to the high velocity of the river at this point and also due to the fact that the plant has only been operational for three years. Around the Iona Island sewage treatment plant outfall there appears to be increases in heavy metal concentrations in the sediments from 1.25 to 20 times the natural background concentrations. Grieve and Fletcher (12) in a study concerned with heavy metal concentrations as a function of sediment grain size on the Fraser River Delta also found increases in copper, lead and zinc at the outfall of the Iona Island Sewage Treatment Plant.

2.3 Heavy Metal Removal Processes

At the present time there are a number of different heavy metal removal processes being researched. The three most familiar processes are:

- i) removal during biological treatment
- ii) carbon adsorption
- iii) lime coagulation.

2.3.1 Biological Treatment

It is generally felt that the removal of heavy metals during biological treatment can proceed by either of three mechanisms:

TABLE 3

A comparison of the heavy metal concentrations* in the Iona Dyke sediments to those in four other locations around Vancouver.

Location	Chromium	Copper	Lead	Nickel	Zinc
(1) Iona Dyke	200	183	55	157	170
(2) Lulu Is. S.T.P. Outfall**	18	21	34	4	25
(3) Roberts Bank	-	274	39	4	60
(4) Woodward Is. (Main Arm)	-	39	62	6	50
(5) North Arm of Fraser River	-	34	40	16	72
(6) Average of 2,3,4,5	18	30	44	8	52
Increase in Iona Dyke Concentrations over 6	11x	6x	1.25x	20x	3.25x

* Concentrations in mg/Kg of sediments.

** High velocity of river at this point does not allow sedimentation.

i) Precipitation of metal hydroxides or carbonates with subsequent entrapment in the biological floc.

ii) Some form of sorption by the organic solids.

iii) Biological cell uptake.

The removal efficiency for heavy metals by biological waste treatment has been studied by several researchers and a summary of their results is presented in Table 4. The removal efficiency appears to be somewhat unpredictable. This is best shown by comparing the three different sewage treatment plants studied by Barth et al. (7) over a 14 day sampling period. They found removal ranges of 37 to 82%, 16-73%, 8-78% and 53-85% for hexavalent chromium, copper, nickel and zinc respectively.

Barth et al. (6) studied the effects of copper, chromium, nickel and zinc, individually and in combination, on activated sludge treatment. Pilot plant studies indicated that a total heavy metal concentration of 10 mg/l either singly or in combination, would reduce the overall plant efficiency by about 5%. They further concluded that nitrification was inhibited by heavy metals and that there was no acclimation of the nitrifying organisms to the metals.

From the previous discussion two conclusions can be drawn concerning heavy metal removal during biological treatment.

i) The removal efficiency is unpredictable and therefore cannot be designed into the system.

ii) High metal concentrations appear to have adverse effects on the treatment efficiency.

2.3.2 Carbon Adsorption

Carbon adsorption has been used as a polishing step to remove the refractory organics that conventional biological treatment processes fail to remove. In the past few years research has been carried out to apply this

TABLE 4

Heavy Metal Removal during
Biological Waste Treatment

Researcher	% Removal			
	Cr	Cu	Ni	Zn
Jenkin et al. (2)	50-70 .5ppm*	-	-	60-80 10-100ppm*
McDermott et al. (2)	-	50-79 .4-25ppm*	30	95-74 2.5-20ppm*
Moore et al. (2)	>99 .05ppm*	-	-	-
Barth (7)	a) 40	16	12	58
	b) 82	73	78	85
	c) 37	23	8	53
	d) 80	-	-	-

a) Grand Rapids, Michigan 14 day sample

b) Richmond, Indiana 14 day sample

c) Rockford, Illinois 13 day sample

d) Bryon, Ohio (50 lb. slug dose)

*initial concentration range

process to heavy metal removal.

Westvaco (22) reported mercury levels < 50 ppb when an activated carbon process was applied to a caustic waste stream from a pulp mill. Although the mercury was present in several forms (metallic droplets, inorganic salts and organic forms) the removal was still quite high. Smith (22) concluded that carbon adsorption might be attractive for the removal of other trace metals for the following reasons:

i) Carbon is an effective removal agent even at very low solution concentrations.

ii) The removal action is relatively non-specific, that is, the carbon has a capacity for the metal in several different forms.

iii) Carbon can be regenerated and reused.

Linstedt et al. (8) in carbon adsorption pilot plant studies obtained removals of 97.1%, 98.8%, 96.96%, and 43.2% for silver, cadmium, chromium and selenium respectively. The mechanism of this inorganic removal was speculated to be caused by the adsorption of metal organic compounds rather than the adsorption of the metals as inorganic ions.

The Orange County Water District operated a pilot plant consisting of lime coagulation, ammonia stripping and activated carbon adsorption to remove heavy metals from secondary treated effluent (3). The pilot plant obtained average removals of 95%, 77%, 30% and 78% for hexavalent chromium, copper, lead and zinc respectively.

It should be noted that in both of the previously mentioned pilot plant studies carbon adsorption was used as a polishing step after the gross metal removal was performed by coagulation and filtration.

2.3.3 Lime Coagulation

The precipitation of metal hydroxides is dependent upon the

concentration of the metal ion in solution and the pH of the solution. The following equation indicates the interdependency of pH, metal concentration and metal solubility; as pH increases the solubility of the metal hydroxide decreases.

$$\frac{[M^{+n}][OH^{-}]^n}{[M(OH)_n]} = k_{sp}$$

Table 5, taken from Brouzes (10), lists the solubility products of some heavy metal oxides or hydroxides. Theoretically, of the metals studied, Cr^{3+} should yield the best removal when precipitated with lime alone and the removals of Cu^{2+} , Pb^{2+} and Zn^{2+} should be about the same. As will be seen in Section 7 this was the case.

Table 6, reproduced from Argo and Culp (11) gives the results of lime coagulation treatment of a number of different types of municipal and domestic wastes. It appears that for the majority of the metals tested lime coagulation is reasonably effective.

TABLE 5
Solubility Products of Cationic Heavy
Metal Oxides or Hydroxides

<u>Compound</u>	<u>K_{sp}</u>
SnO	1×10^{-61}
Au(OH) ₃	8.5×10^{-45}
Ti(OH) ₃	1×10^{-40}
Fe(OH) ₃	6×10^{-38}
Cr(OH) ₃	1×10^{-30}
HgO	3×10^{-26}
Cu(OH) ₂	3×10^{-19}
Zn	4.5×10^{-17}
Fe(OH) ₂	1.8×10^{-15}
Pb ₂ O(OH) ₂	1.6×10^{-15}
Cd(OH) ₂	2×10^{-14}
Mn(OH)	2×10^{-13}
BiOOH	3×10^{-11}
BaSO ₄	1×10^{-10}
BaCO ₃	1.6×10^{-9}
Ag ₂ O	2×10^{-8}

TABLE 6: LIME COAGULATION AND RECARBONATION

Metal	Concentration Before Treatment mg/l	Concentration After Treatment mg/l	Final pH	Percent Removal
Antimony ¹			11	~90
Arsenic ¹			11	<10
Barium ¹		~1.3(sol) ²	11	
Bismuth ¹		0.0002(sol)	11	
Cadmium	Trace		11	~50
	0.0137	0.00075	>11	94.5
Chromium (+6)	0.056	0.050	>11	11
Chromium (+3)	7.400	2.7	8.7	99.9+
Copper	15.700	0.79	8.7	
	7	1	8	86
	7	0.05	9.5	93
	302	Trace	9.1	99+
Gold ¹		<.001(sol)	11	90+
Iron	13	2.4	9.1	82
	17	0.1	10.8	99+
	2.0	1.2 ³	10.5	40
Lead ¹		<.0001(sol)	11	90+
Manganese	2.3	<0.1	10.8	96
	2.0	1.1 ³	10.5	45
	21.0	0.05	9.5	95
Mercury ¹		Oxide soluble		<10
Molybdenum	Trace		8.2	~10
Nickel	160	0.08	8.7	99.9+
	5	0.5	8	90
	5	0.5	9.5	90
	100	1.5	10.0	99
Selenium	0.0123	0.0103	>11	16.2
Silver	0.0546	0.0164	>11	97
Tellurium ¹ 4		(<0.001?)	11	(?90+)
Titanium ¹ 4		(<0.001?)	11	(?90+)
Uranium ⁵		?		?
Zinc		.007(sol)	11	90+

1. The potential removal of these metals was estimated from solubility data.
2. Barium and lead reductions and solubilities are based upon the carbonate.
3. These data were from experiments using iron and manganese in the organic form.
4. Titanium and Tellurium solubility and stability data made the potential reduction estimates unsure.
5. Uranium forms complexes with carbonate ion. Quantitative data were unavailable to allow determination of this effect.
6. Temperature: Ambient 20-25°C.

CHAPTER 3

MAGNESIUM SOLUBILITY

Stumm and Morgan (21) studied the system of $\text{Mg}-\text{CO}_2-\text{H}_2\text{O}$ from two points of view: 1) a system which is open to the atmosphere and is therefore in equilibrium with $\text{CO}_2(\text{g})$. 2) a system which is closed to the atmosphere (they considered only the solid phase and the solution phase, that is, H_2CO_3 was treated as a non-volatile acid).

A predominant species diagram for $\log(\text{Mg}^{2+}) = 0$ and -3 is presented in Figure 1 for the open $\text{Mg}-\text{CO}_2-\text{H}_2\text{O}$ system. At a partial pressure of CO_2 corresponding to that of the atmosphere ($\log P_{\text{CO}_2} = -3.5$) the predominant specie over the entire coagulation range of 10.0 to 11.4 would be hydromagnesite ($\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}(\text{s})$) if the system was at equilibrium with respect to CO_2 .

A solubility diagram ($-\log(\text{Mg}^{2+})$ vs pH) for the closed $\text{Mg}-\text{CO}_2-\text{H}_2\text{O}$ system is shown in Figure 2. In this case brucite ($\text{Mg}(\text{OH})_2$) is the least soluble above pH 9.

The predominant specie under the coagulation conditions is most probably $\text{Mg}(\text{OH})_2$ for the following reasons:

1) The alkalinity in the wastewater will be used up initially to precipitate lime as CaCO_3 and to precipitate hydroxide carbonates (e.g. hydromagnesite $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) and carbonates of multivalent cations present. The CO_3^{-2} source is generally limited to the initial alkalinity because there is usually insufficient time to convert $\text{CO}_2(\text{g})$ to CO_3^{-2} . Assuming that the reaction rate for $\text{Mg}(\text{OH})_2$ is not slower than the jar test reaction time, $\text{Mg}(\text{OH})_2$ will predominate due to the abundance of hydroxide. Other magnesium forms will be present but in lesser amounts.

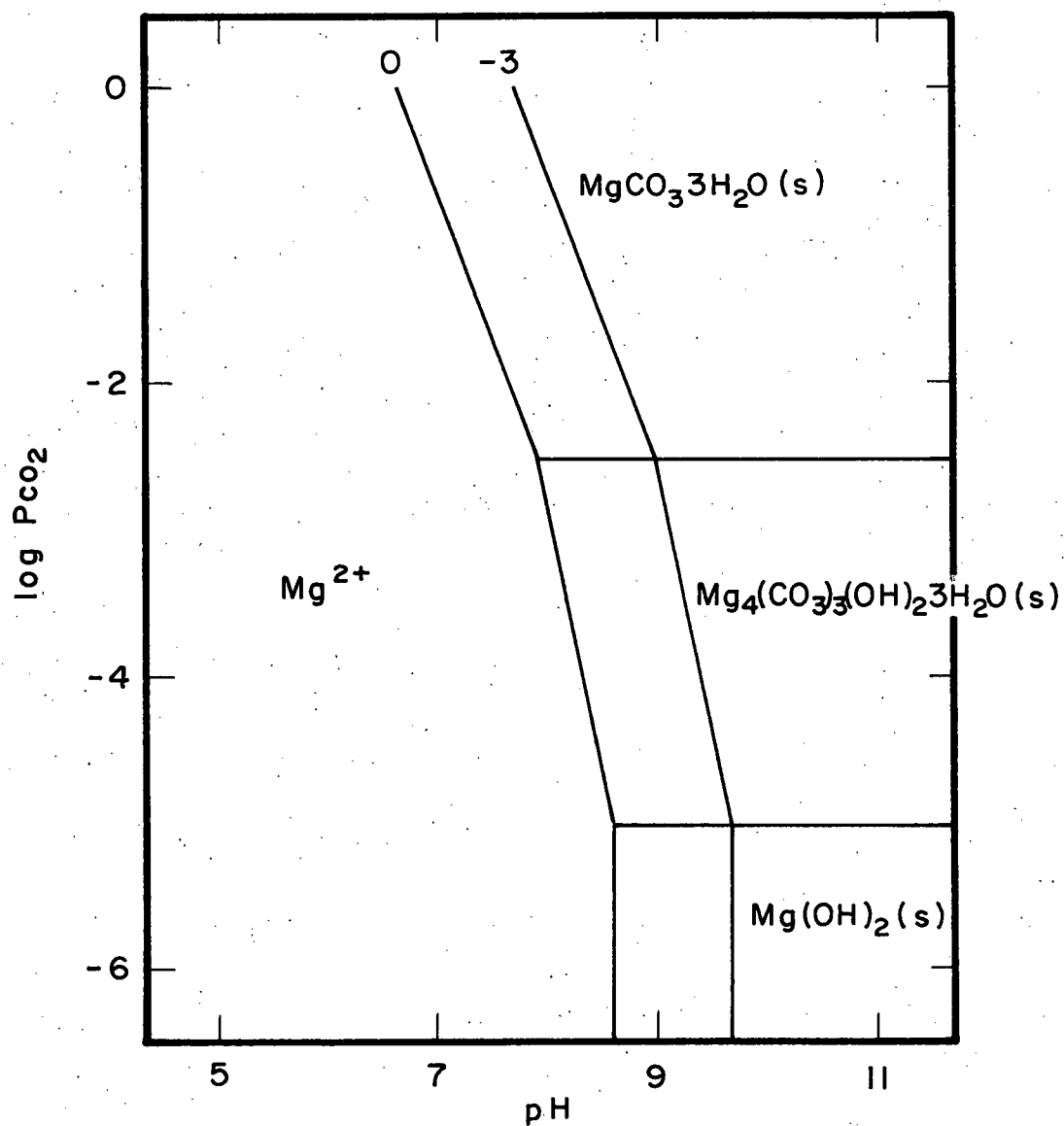


FIGURE 1 PREDOMINANCE DIAGRAM FOR $\text{Log}(\text{Mg}^{2+}) = 0$ AND -3 (STUMM AND MORGAN, 1970).

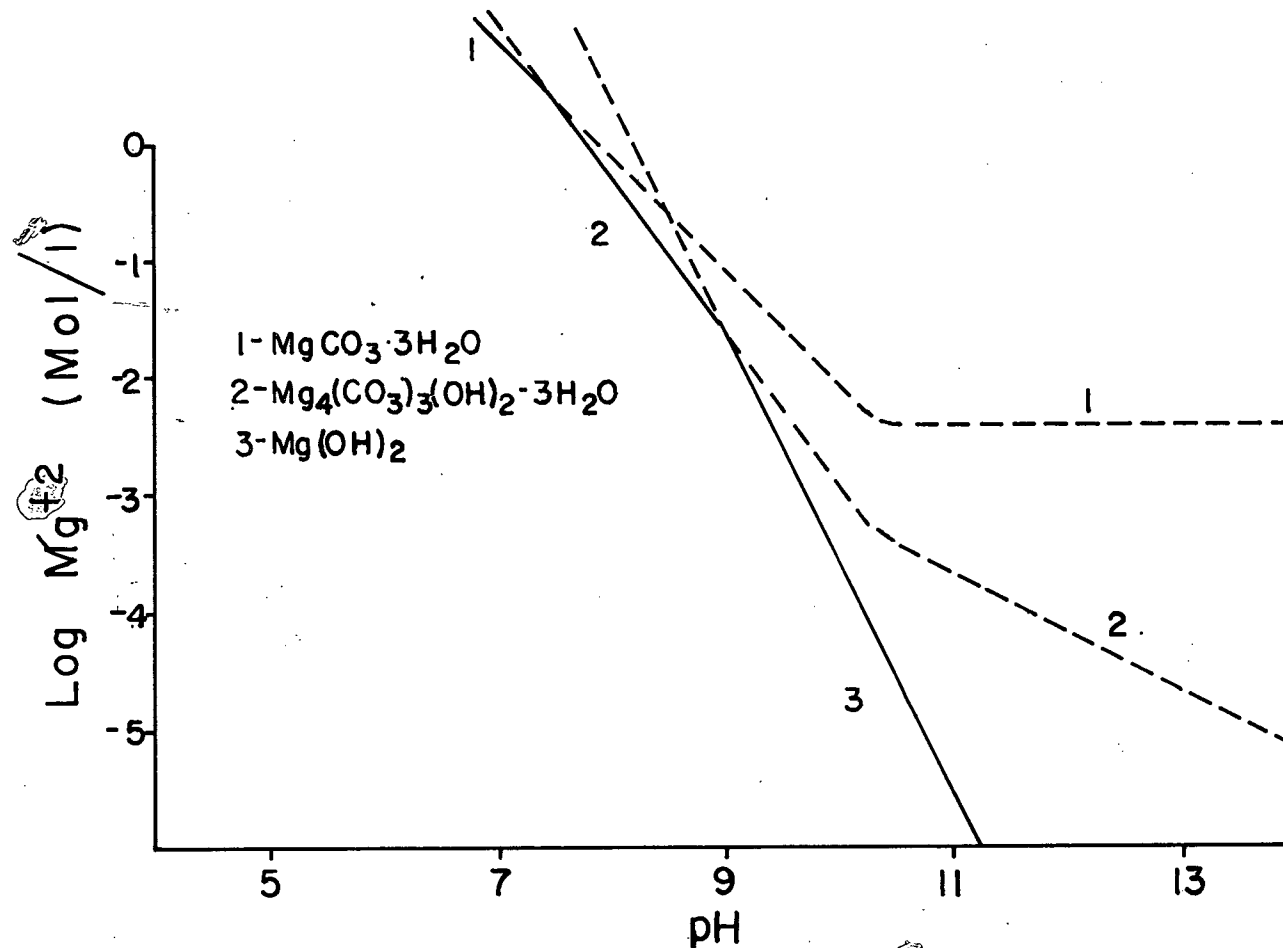


FIGURE 2 SOLUBILITY DIAGRAM FOR MAGNESIUM IN WATER AT ATMOSPHERIC CONDITIONS.
 TOTAL CARBONATE = 10^{-3} M.
 (STUMM AND MORGAN, 1970).

2) The affinity of natural aquatic ligands other than OH^- and CO_3^{2-} (e.g. S^{2-} and PO_4^{3-}) might form more stable forms than $\text{Mg}(\text{OH})_2$. At the precipitation pH these other species will usually be present in much lower concentrations than OH^- and therefore the $\text{Mg}(\text{OH})_2$ will predominate.

Larson et al. (16) used solubility product constants of Travers and Nouvel (27) to show the influence of temperature and pH on the solubility of magnesium as shown in Figure 3. From the work of Langlier (15) it has been established that the solubility curves in Figure 3 would move up slightly with increasing alkalinity. That is to say that the solubility would be increased with increasing alkalinity.

In practice, the amount of Mg^{2+} in aqueous solution under a given set of conditions (i.e. pH, temperature, alkalinity, TDS) is higher than that predicted from theory. This comes about for several reasons.

1) The system is not at equilibrium.

2) The formation of soluble hydroxo complexes (e.g. MgOH^+) will increase the overall metal solubility. The metal solubility (M_t) can be expressed by the following equation:

$$M_t = [\text{M}^{2+}] + \sum_1^n [\text{M}(\text{OH})_n^{z-n}]$$

3) The presence of foreign ligands (L^{-y}) will form soluble complexes $(\text{M L})_{p p}^{z p - y p}$, which will further increase the metal solubility.

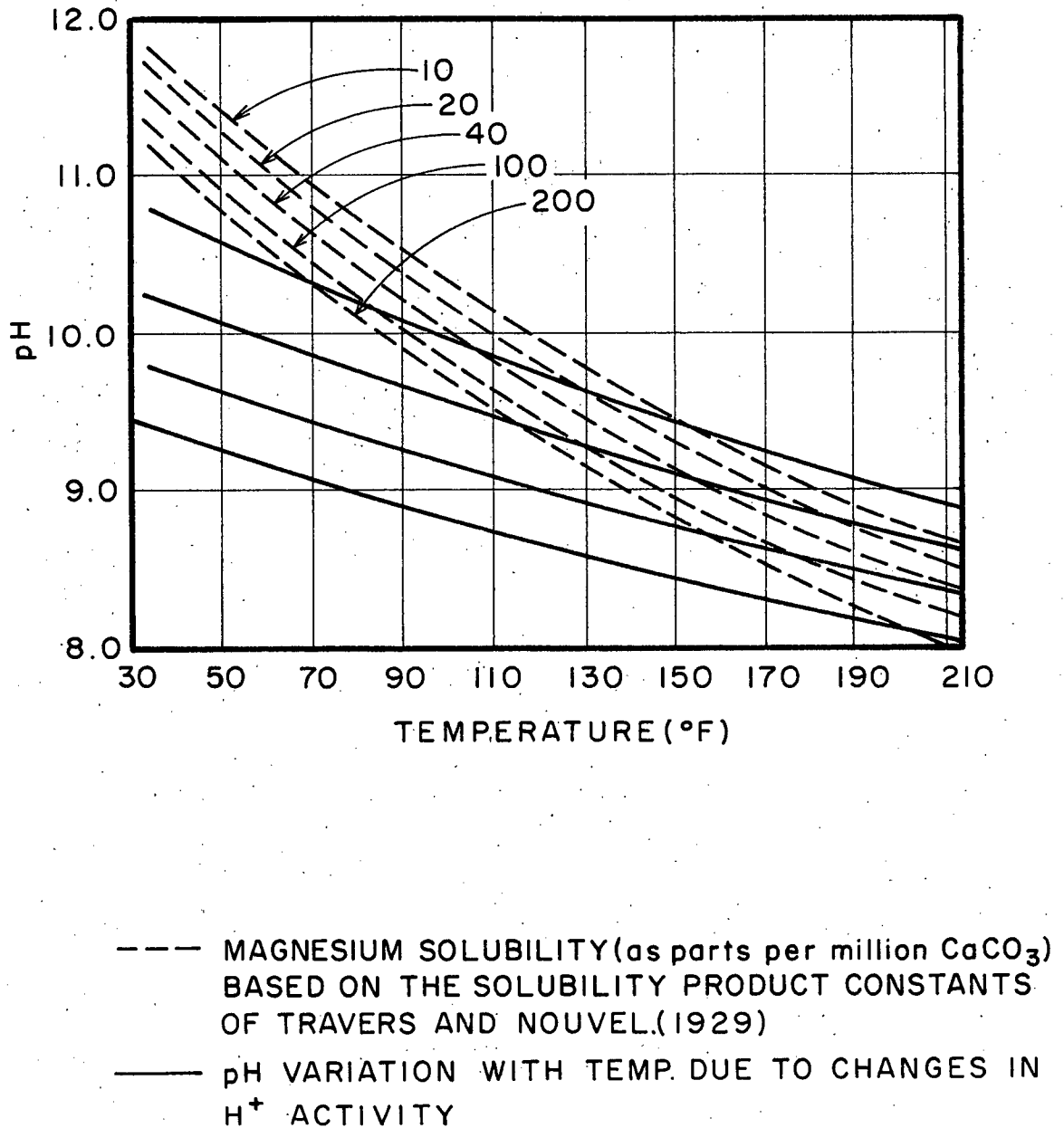


FIGURE 3 TEMPERATURE INFLUENCE ON
 MAGNESIUM SOLUBILITY.
 (LARSON ET AL, 1959) (16)

CHAPTER 4

RESEARCH RATIONALE4.1 History of the Lime-Magnesium Process for Water Renovation

The use of magnesium ion, precipitated in situ as $\text{Mg}(\text{OH})_2$, has been established as a successful coagulant for the removal of dissolved, colloidal and suspended material.

Thompson et al. (26) demonstrated that MgCO_3 , precipitated with lime, would remove organic colour and turbidity from natural waters. Black et al. (8) found an increased removal efficiency for COD, suspended solids and colour when using lime and MgCO_3 as compared with lime alone. Black and Thompson (9) showed that cadmium removal was greatly enhanced by using magnesium in conjunction with lime. They also found that cadmium was not released in any significant amounts on carbonation to resolubilize the magnesium as MgCO_3 . Rush (21) showed that a combination of low magnesium and low lime could achieve a better decolourization of Kraft mill effluents than 3-5 times as much lime alone.

The hydrated $\text{Mg}(\text{OH})_2$ precipitate has a gelatinous nature and the removal mechanism is probably some combination of adsorption, precipitation, complexation, flocculation and entrapment.

4.2 Application of the lime-magnesium process to Vancouver wastewaters

It has been fairly well documented by Hall et al. (15) that BOD and suspended solids in Vancouver's sewage are not of prime concern due primarily to high dissolved oxygen levels in the Fraser River. As was previously discussed, secondary treatment of wastewater is designed primarily for BOD and suspended solids removal, with the unpredictable side benefit of heavy metal removal. In the Vancouver area a more practical process might be one aimed at predictable heavy metal removal, with the side benefit of BOD and suspended solids removal.

It was felt that research was warranted to see if a coagulation type process could achieve this end.

A lime-magnesium coagulation was chosen over just a straight lime coagulation because of the low natural magnesium levels in the surrounding waters (< 5 mg/l (5)). In areas where the natural magnesium levels are high, there is already a source of Mg^{2+} and therefore an enhancement in removal efficiency caused by a further Mg^{2+} addition would not be expected. However, it was felt that for low magnesium waters such as in Vancouver, the effect of magnesium might prove significant.

CHAPTER 5

EXPERIMENTAL METHODS AND MATERIALS5.1 Selection of Effluent

The majority of the research was carried out using prechlorinated primary effluent (PPE) from the Annacis Island Sewage Treatment Plant. A series of experiments was also done on raw sewage (RS) from the same plant in order to compare the removal efficiencies of the two waste streams. Effluent from the Annacis Island sewage treatment plant was chosen because this plant contributes a large flow into the Fraser River estuary and there are a number of industrial waste streams tied into its sewer system.

5.2 Sampling Procedure

Prechlorinated primary effluent was obtained by sampling the overflow at the discharge end of the primary sedimentation basin using a plastic bucket on a rope. A sample of about 10 Imperial gallons was taken every Monday morning which was adequate for the week's testing.

Initially, a one litre sample of raw sewage was taken for an alkalinity titration. As the research program progressed, the sample size was changed to 10 Imperial gallons, to provide sufficient sample for the raw sewage experimentation. These samples were taken prior to the comminutors as this was the most convenient location.

In order to eliminate dilution effects caused by storm water flows, no sampling was done within 8 hours of the completion of a rain storm within the sewer catchment area. This precaution was deemed necessary because a large part of the sewage collection system is comprised of combined sewers. Dilution was assumed to be present if the alkalinity of either sample was below the normal value of 120-130 mg/l as CaCO_3 .

5.3 Sample Storage

All samples were stored at 3°C. Prior to a coagulation test the samples were warmed to 20°C in a 35°C incubator which usually took about 1½ hours.

5.4 Chemical Preparations

5.4.1 Heavy Metal Spike Solutions

In order to test the heavy metal removal efficiency over a range of initial concentrations (.5, 2.5 and 5.0 mg/l M^{n+}) a set of stock solutions of the various heavy metals were prepared each having a concentration of 1000 mg/l. A volume of 200 ml was prepared for each metal from the following compounds:

Heavy Metal	Compound
Cr ³⁺	CrCl ₃ ·6H ₂ O
Cu ²⁺	CuSO ₄ ·5H ₂ O
Ni ²⁺	Ni(NO ₃) ₂ ·6H ₂ O
Zn ²⁺	ZnSO ₄ ·7H ₂ O

The stock solution concentration was not checked, but for each experiment a spiked sewage sample was analysed to obtain an exact metal ion concentration.

5.4.2 Atomic Absorption Standard Solutions

The atomic absorption standard solutions were prepared by accurately diluting Fisher Certified A.A. standards to the range .05 mg/l to 5.0 mg/l.

5.4.3 Lime

Dry reagent grade Ca(OH)₂ was chosen for this study as the preferred method of lime addition. Immediately prior to usage the Ca(OH)₂ powder was weighed accurately on a Sartorius Model 2442 balance. Selection of the method for lime addition is discussed in Appendix A.

5.4.4 Magnesium ion

A 10^4 mg/l Mg^{2+} solution was carefully prepared from $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The exact concentration was not obtained by analysis because it was felt that the chemical purity would be accurate enough, considering the small volumes used. A concentration of 10^4 mg/l Mg^{2+} was selected to minimize dilution of the coagulation test sample ($1 \text{ ml} \equiv 16.7 \text{ mg/l } \text{Mg}^{2+}$). The decision to add magnesium in an ionic form rather than as $\text{Mg}(\text{OH})_2$ is discussed in Appendix A.

5.4.5 Sodium Bicarbonate

A 10^4 mg/l as CaCO_3 solution of NaHCO_3 was prepared and was used to increase the alkalinity from the normal 120-130 to approximately 200 mg/l as CaCO_3 for certain tests.

5.5 Analytical Techniques

5.5.1 Alkalinity

Alkalinity was measured using the potentiometric titration method described in "Standard Methods" (1).

5.5.2 Heavy Metal Analysis

Analysis of heavy metal concentrations was done following the atomic absorption procedures described in "Standard Methods" (1) with the exception of the pretreatment procedure. A digestion consisting of adding $1\frac{1}{2}$ ml of HNO_3 and 1 ml of HCl to a 50 ml sample and then boiling for about 15 minutes was used in place of the more time consuming technique described in "Standard Methods" (1). Tests comparing the two digestion procedures produced identical results.

Digestion procedures for samples containing lead were slightly different. It was found necessary to concentrate the samples by a factor of four in order to increase AA sensitivity.

All samples except zinc were run on the Jarrall-Ash Model 810 Atomic Absorption Spectrophotometer. Zinc was run on the Jarrall-Ash Model 500 due to availability. Table 7 summarizes the A.A. operating parameters.

5.5.3 pH

The pH was measured on an Accumet Model 810 pH meter which was standardized daily at pH 10.

5.6 Lime-magnesium Coagulation Test Procedure

The development of the test procedure is detailed in Appendix A.

TABLE 7

Instrument Operating Parameters

Metal	Lamp Current	λ	Nonabsorbing λ	Flame	Instrument
Cr	10 ma	3579	3520	reducing	Järrall-Ash 810
Cu	7 ma	3247	N/A	slightly reducing	"
Pb	10 ma	2320	2316	oxidizing	"
Ni	8 ma	2170	2204	slightly reducing	"
Zn	7.5 ma	2138	N/A	oxidizing	J.A. 500

Misc. 1) Scale expansion used in all cases.

2) Flame: air/acetylene.

3) Pb samples concentrated 4x by boiling.

4) Background correction not required for Cu and Zn.

CHAPTER 6

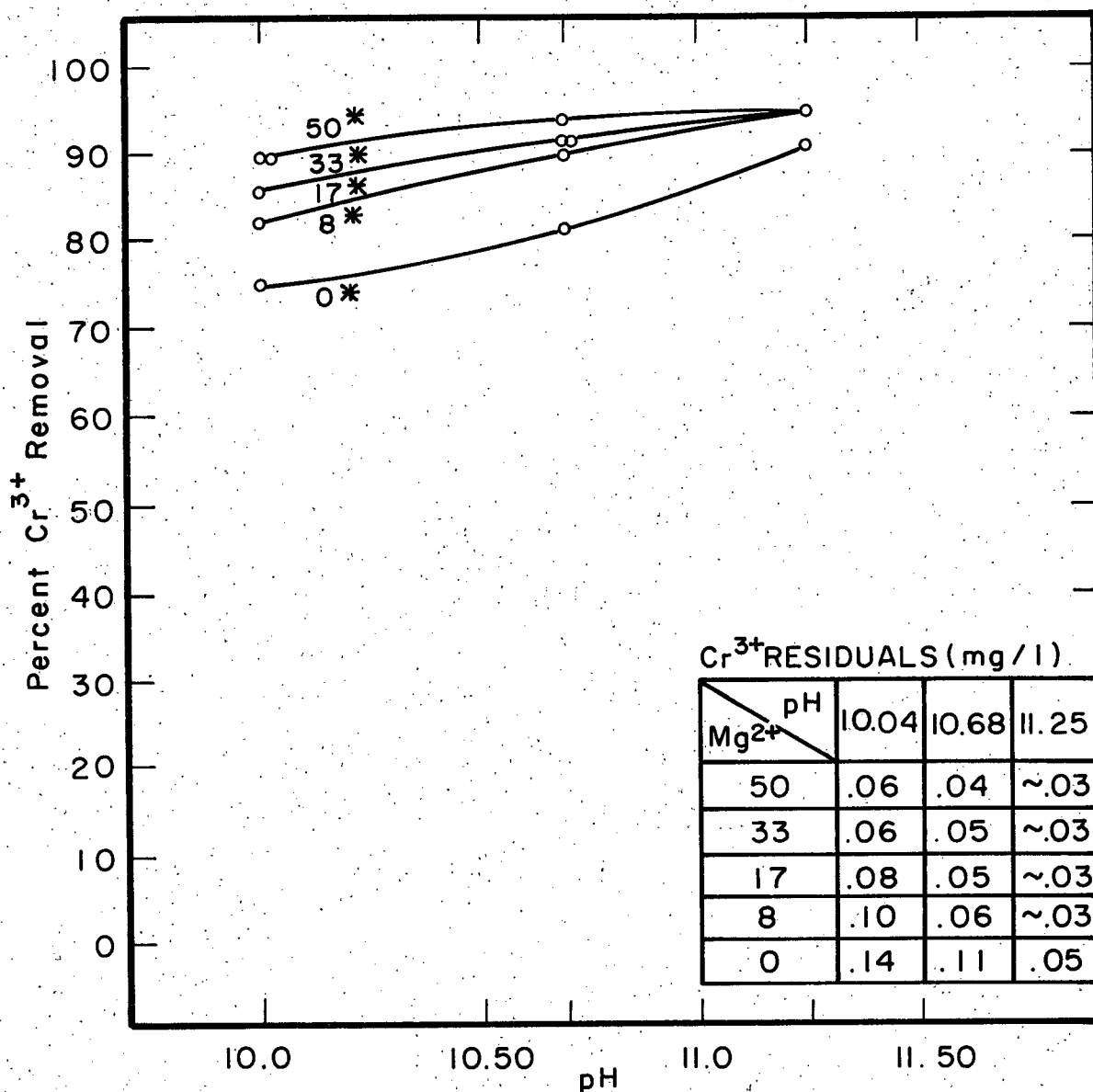
RESULTS AND DISCUSSION6.1. The removal efficiency of individual heavy metals from PPE - UnfilteredResults6.1.1 Chromium

Figures 4, 5 and 6 show the removal of Cr^{3+} from PPE with increasing pH and at different Mg^{2+} dosages. The average lime dosage is also shown. At a given lime dosage, the pH tended to drop as the Mg^{2+} concentration was increased. The drop in pH was about .1 pH units at the low lime dosage (pH 10) and about .4 pH units at the high lime dosage (pH 11.4). This was the case for all five metals studied.

The effect of Mg^{2+} on Cr^{3+} removal was most significant at the lowest initial Cr^{3+} concentration ($[\text{Cr}^{3+}]_i$). At $[\text{Cr}^{3+}]_i = .5 \text{ mg/l}$ a removal of 75% was obtained by raising the pH to 10.04. The additional 33 mg/l of Mg^{2+} enhanced this removal to 89%. The removal was not significantly increased by further Mg^{2+} addition at this pH. At pH 10.68 the Cr^{3+} removal was enhanced from 80 to 91% by the addition of 17 mg/l of Mg^{2+} and with only minor improvement at higher Mg^{2+} dosages. At pH 11.25 the addition of 8 mg/l Mg^{2+} reduced the residual to approximately .03 mg/l Cr^{3+} . This could only be approximated due to a lack of A.A. sensitivity at this concentration range. For Mg^{2+} additions $\geq 8 \text{ mg/l}$, the Cr^{3+} residuals at the higher levels of $[\text{Cr}^{3+}]_i$ were approximated at this same value.

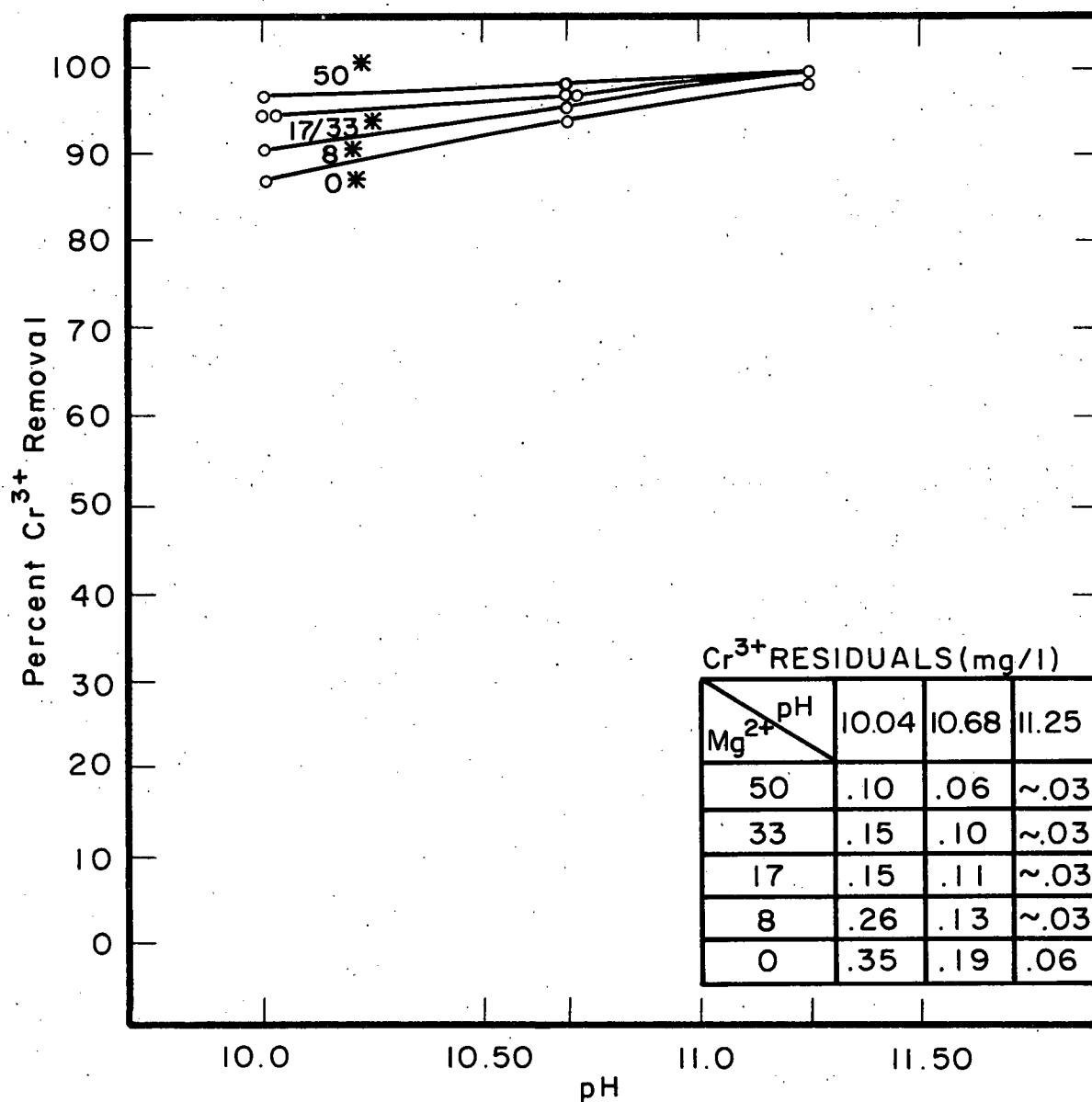
At $[\text{Cr}^{3+}]_i = 2.5 \text{ mg/l}$ the effect of Mg^{2+} is most significant at pH 10.04. About 17 mg/l Mg^{2+} enhanced the Cr^{3+} removal from 87 to 94% and at higher pH's the effect diminishes.

At $[\text{Cr}^{3+}]_i = 5.0 \text{ mg/l}$ the removal is very high and 8 mg/l Mg^{2+} appears to increase the removal by about 2% over the entire pH range. An increase in removal by a Mg^{2+} addition greater than 8 mg/l did not occur



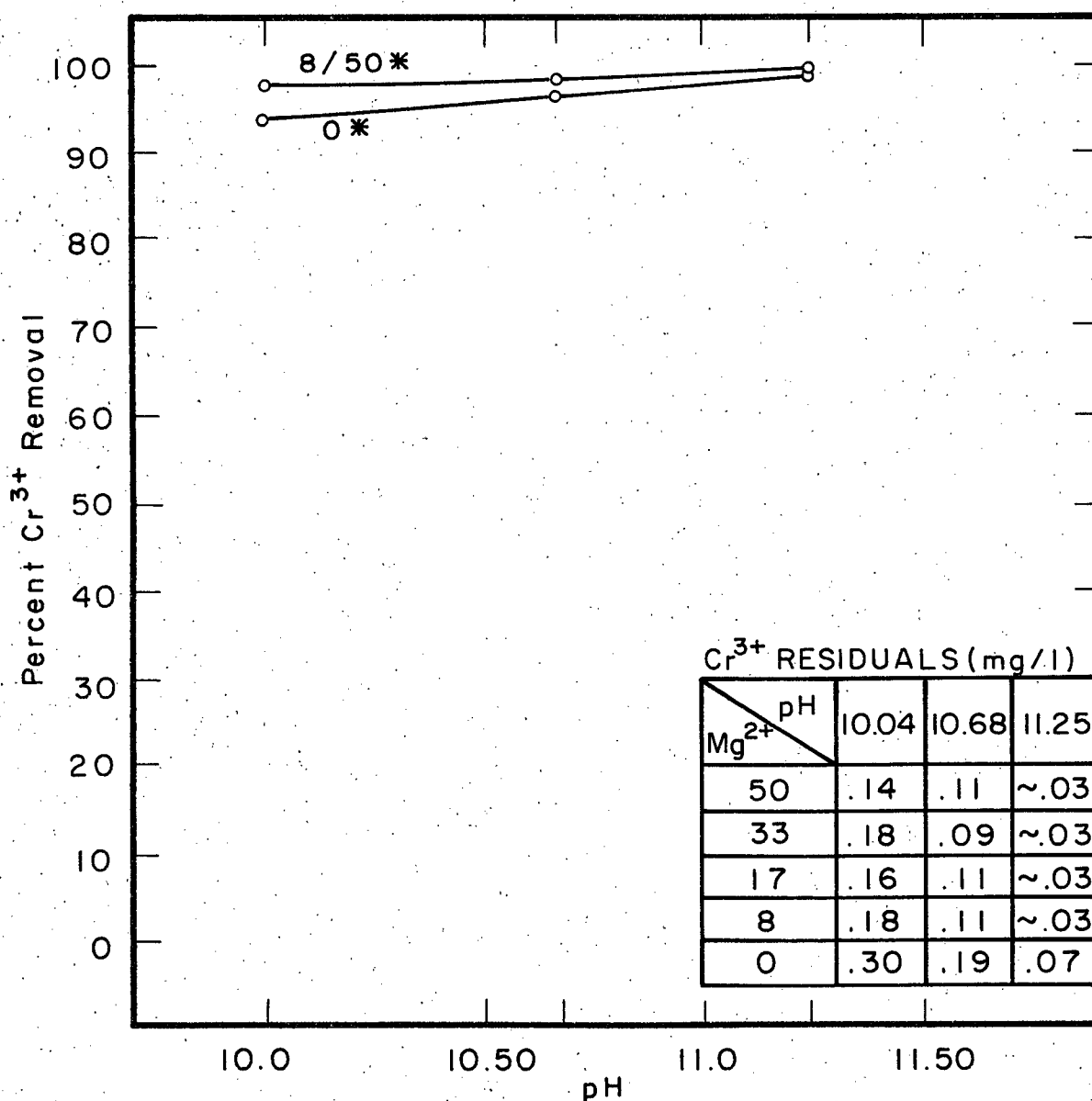
LIME DOSE (mg/l)	163	236	415
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FIGURE 4 PERCENT Cr^{3+} REMOVAL vs. pH AND LIME DOSAGE FOR $[\text{Cr}^{3+}]_i = 0.50 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)



LIME DOSE(mg/l)	163	236	415
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FIGURE 5 PERCENT Cr^{3+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[\text{Cr}^{3+}] = 2.50 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)



LIME DOSE(mg/l)	163	236	415
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FIGURE 6 PERCENT Cr^{3+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[\text{Cr}^{3+}]_i = 5.00 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)

because additional Mg^{2+} did not further reduce the residual at a given pH.

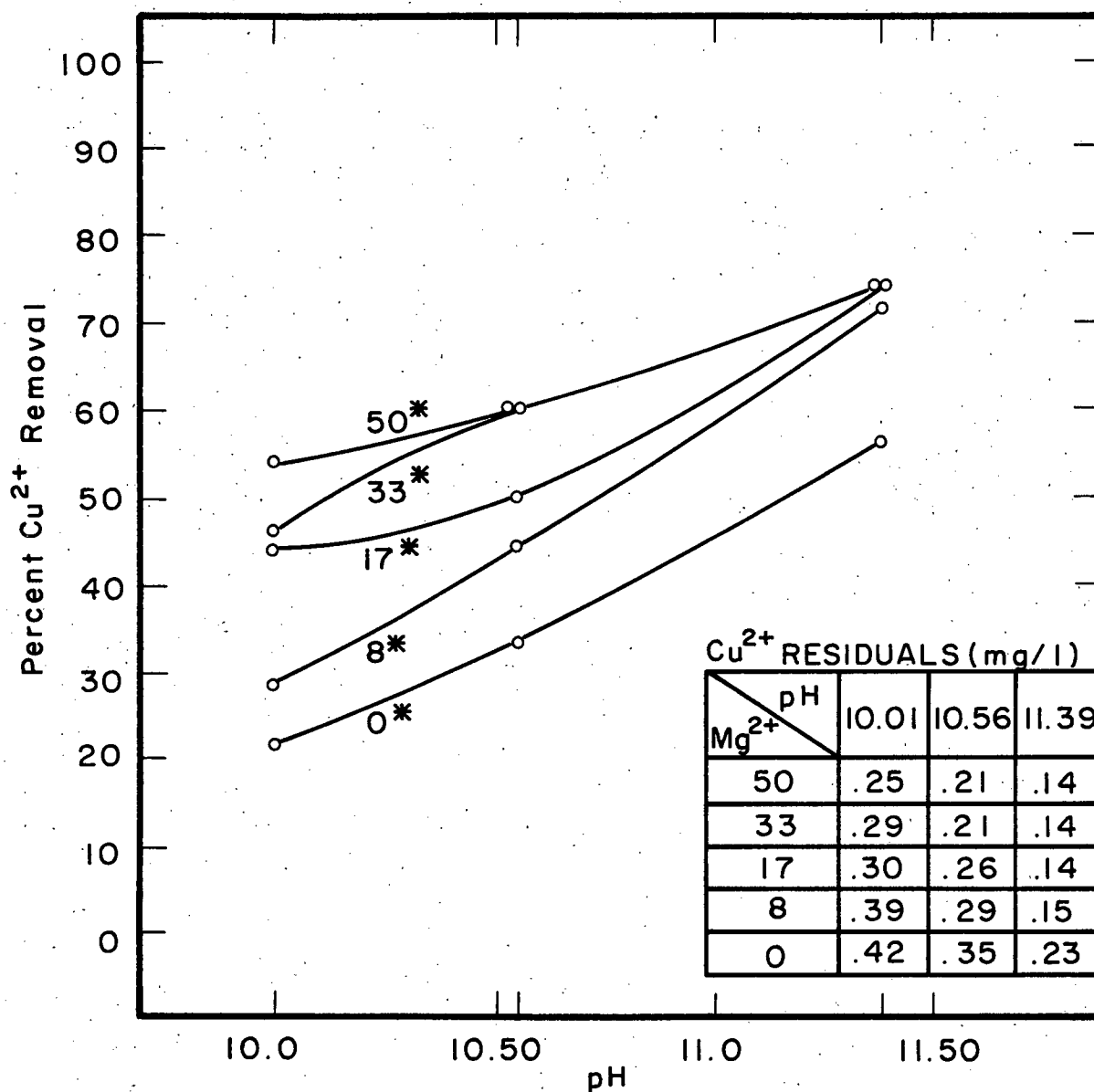
6.1.2 Copper

Figures 7, 8 and 9 show the percent Cu^{2+} removal from PPE with increasing pH and at different Mg^{2+} dosages. The effect of Mg^{2+} on Cu^{2+} removal appeared to be significant throughout the entire pH range tested. The data indicated that, as the pH is increased, a lesser amount of Mg^{2+} is required to achieve the maximum practical removal. The maximum practical removal is defined as the removal beyond which there is only minor improvement with increased Mg^{2+} dosages.

At pH 10.01 for all three initial copper concentrations, there is still improvement in removal up to at least 33 mg/l Mg^{2+} . Removal increases of 22 to 46%, 33 to 54% and 50 to 69% were obtained for initial copper concentrations $[\text{Cu}^{2+}]_i$ of .5, 2.5, 5.0 mg/l respectively, as a consequence of a Mg^{2+} addition of 33 mg/l. These results indicate that the effect of Mg^{2+} is most significant at lower initial copper concentrations. This conclusion is further demonstrated at pH 10.56 where removal increases of 21.5 to 60%, 54 to 75% and 63 to 82% were obtained in order of increasing $[\text{Cu}^{2+}]_i$ as a consequence of adding 33 mg/l Mg^{2+} . The maximum practical removal at pH 10.56 is at 33 mg/l Mg . The trend of increased removal with increased $[\text{Cu}^{2+}]_i$ at constant pH and Mg^{2+} dosage was found to be true for all metals studied.

At pH 11.39 only 8 mg/l Mg^{2+} appeared to achieve the maximum practical removal. As the $[\text{Cu}^{2+}]_i$ was increased from .5 to 5.0 mg/l removal increases of 58 to 70.5%, 84 to 92% and 88 to 95% were obtained respectively.

Cu^{2+} residual appeared to reach a minimum value of .14 - .16 mg/l at pH 11.39 and Mg^{2+} dosage greater than 17 mg/l. This constant residual appeared to be independent of the initial copper concentration within the range studied.



LIME DOSE(mg/l)	168	216	395
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FIGURE 7 PERCENT Cu^{2+} REMOVAL vs. pH AND LIME DOSAGE FOR $[\text{Cu}^{2+}]_i = 0.50 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)

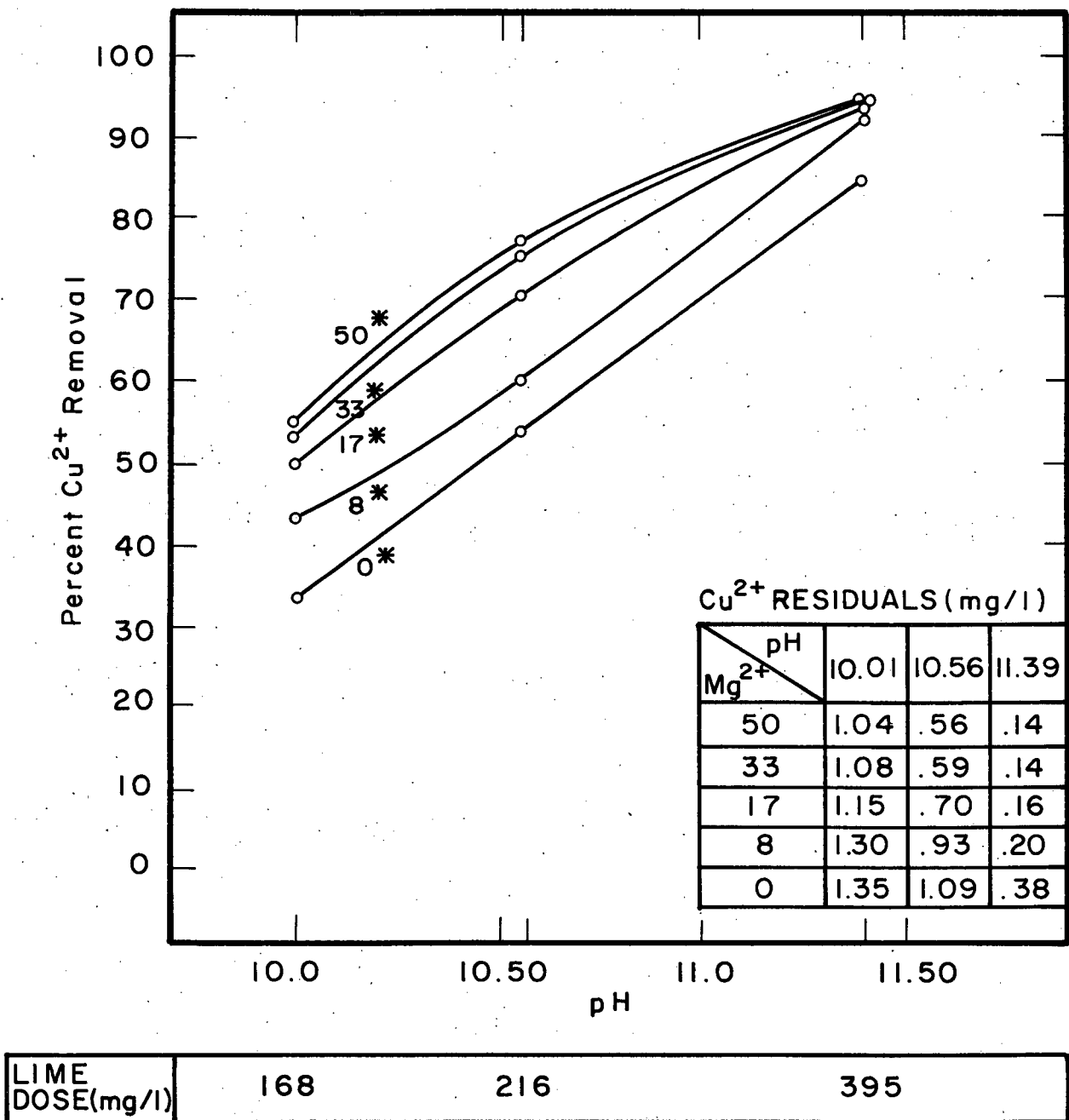
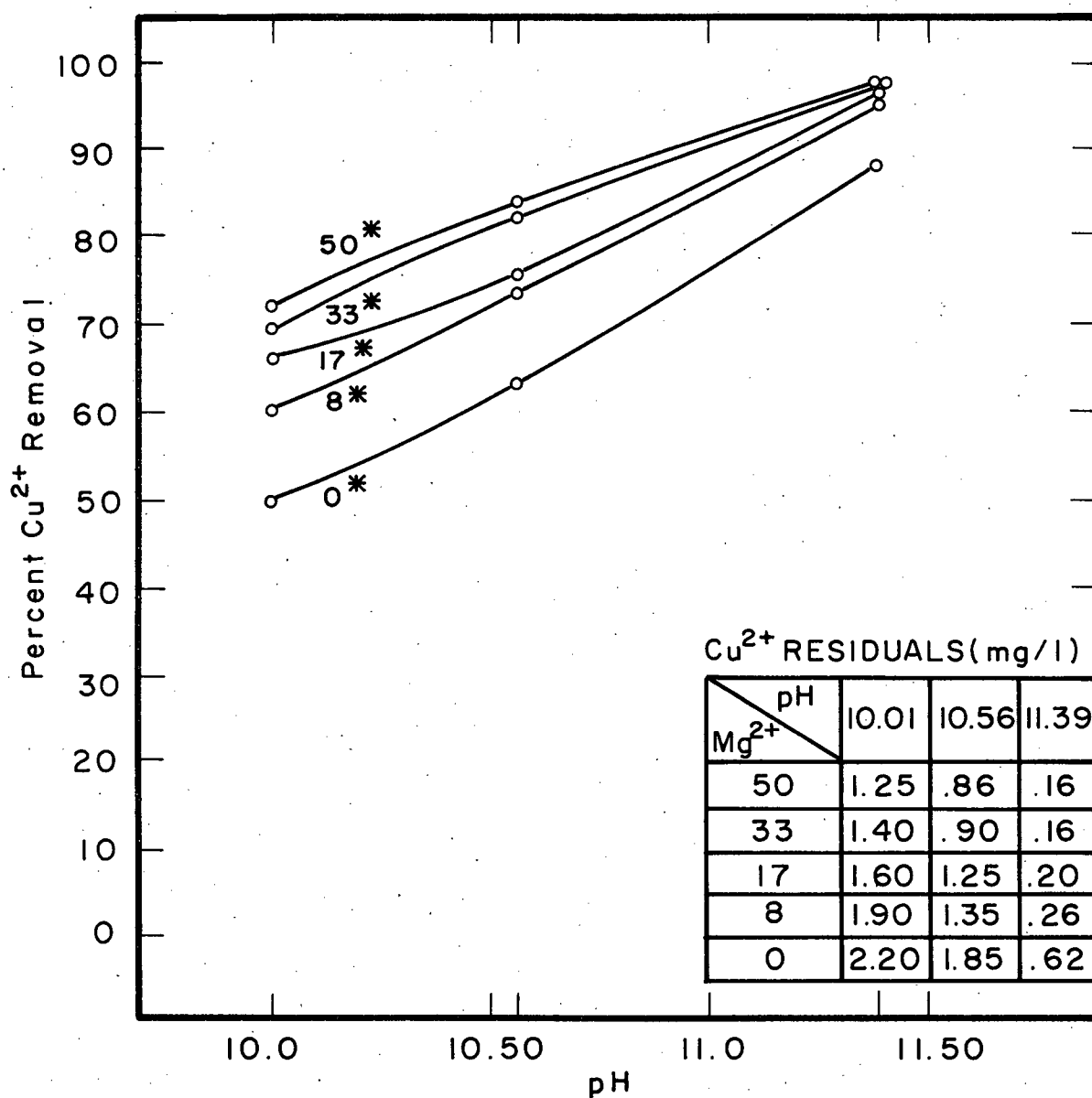


FIGURE 8 PERCENT Cu^{2+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[\text{Cu}^{2+}]_i = 2.50 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)



LIME DOSE(mg/l)	168	216	395
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FIGURE 9 PERCENT Cu^{2+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[\text{Cu}^{2+}]_i = 5.00 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)

6.1.3 Lead

Figures 10, 11 and 12 show percent Pb^{2+} removal with increasing pH and at different Mg^{2+} additions. As was the case with Cu^{2+} , the effect of Mg^{2+} on Pb^{2+} removal is most significant at the low pH range. At pH 9.86 the Pb^{2+} removal was increased from about 40% to about 75% by the addition of 33 mg/l Mg^{2+} . This increase in removal appeared to be independent of initial Pb^{2+} concentration ($[\text{Pb}^{2+}]_i$) over the range studied.

At pH 10.56 the addition of between 17-33 mg/l Mg^{2+} increased the Pb^{2+} removal by about 8% and this appeared to be independent of $[\text{Pb}^{2+}]_i$.

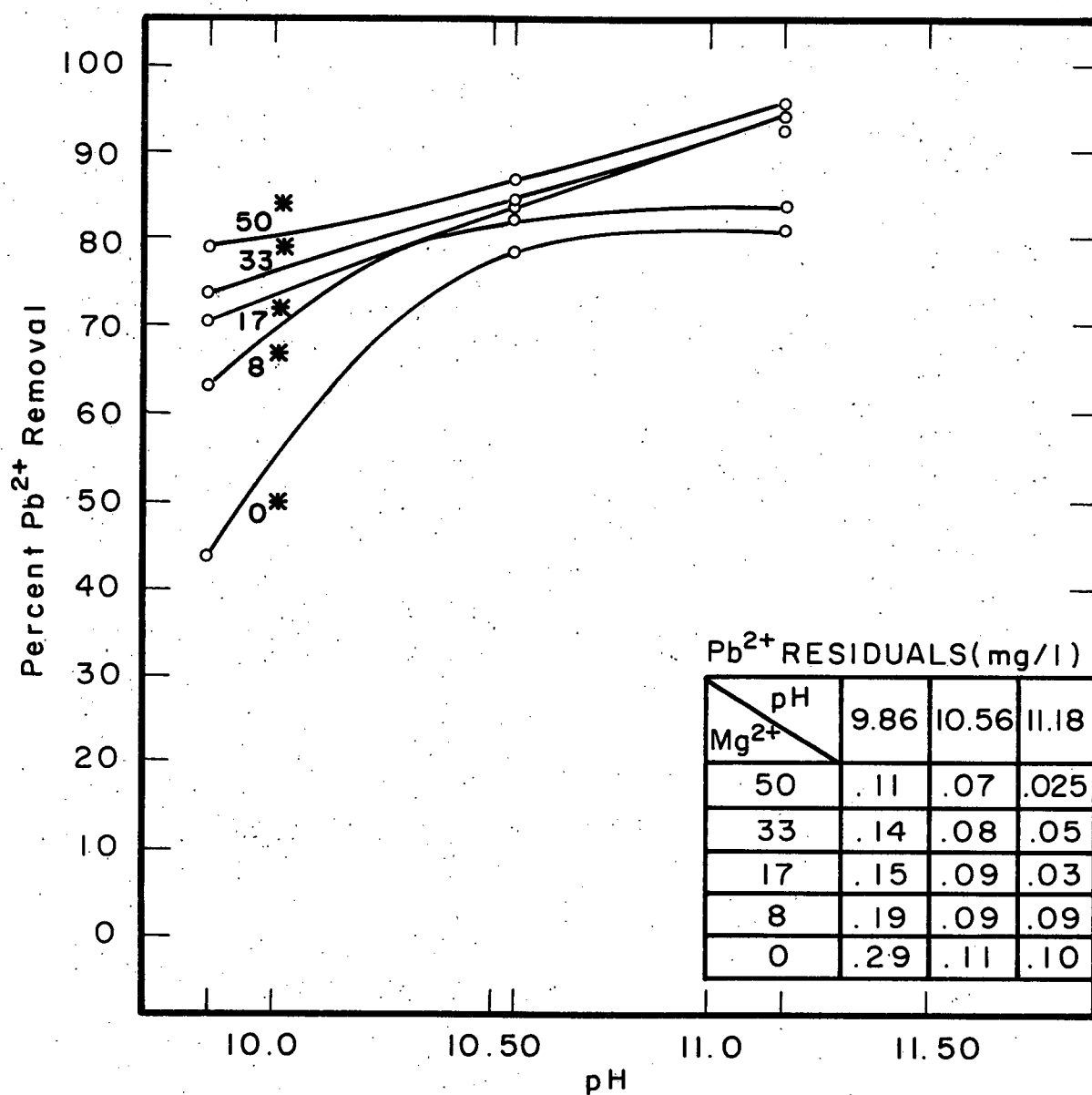
At pH 11.18 the effect of Mg^{2+} was minimal. At $[\text{Pb}^{2+}]_i = 2.5$ and 5.0 mg/l, the addition of 8 mg/l increased the removal by about 2%. At $[\text{Pb}^{2+}]_i = .5$ mg/l the data was inconsistent and may in fact be in error due to sample contamination. The residuals obtained for Mg^{2+} dosages of 0 and 8 mg/l were the same at pH 10.56 and 11.18. (Figure 10). This is in disagreement with all other results obtained for any of the five metals at any initial concentration.

6.1.4 Nickel

Figures 13, 14 and 15 show the removal of Ni^{2+} from PPE with increasing pH and at different Mg^{2+} dosages. The removal of Ni^{2+} increased with increasing pH but it was hardly affected at all by the addition of Mg^{2+} . The only removal enhancement of any significance was for the high pH treatment of the sample with an initial Ni^{2+} concentration of .5 mg/l. In this case the removal was increased from 45 to 57% with the addition of 8 mg/l or more of Mg^{2+} . As was the case with Cu^{2+} , the effect of Mg^{2+} on Ni^{2+} removal is most significant at low initial Ni^{2+} concentrations.

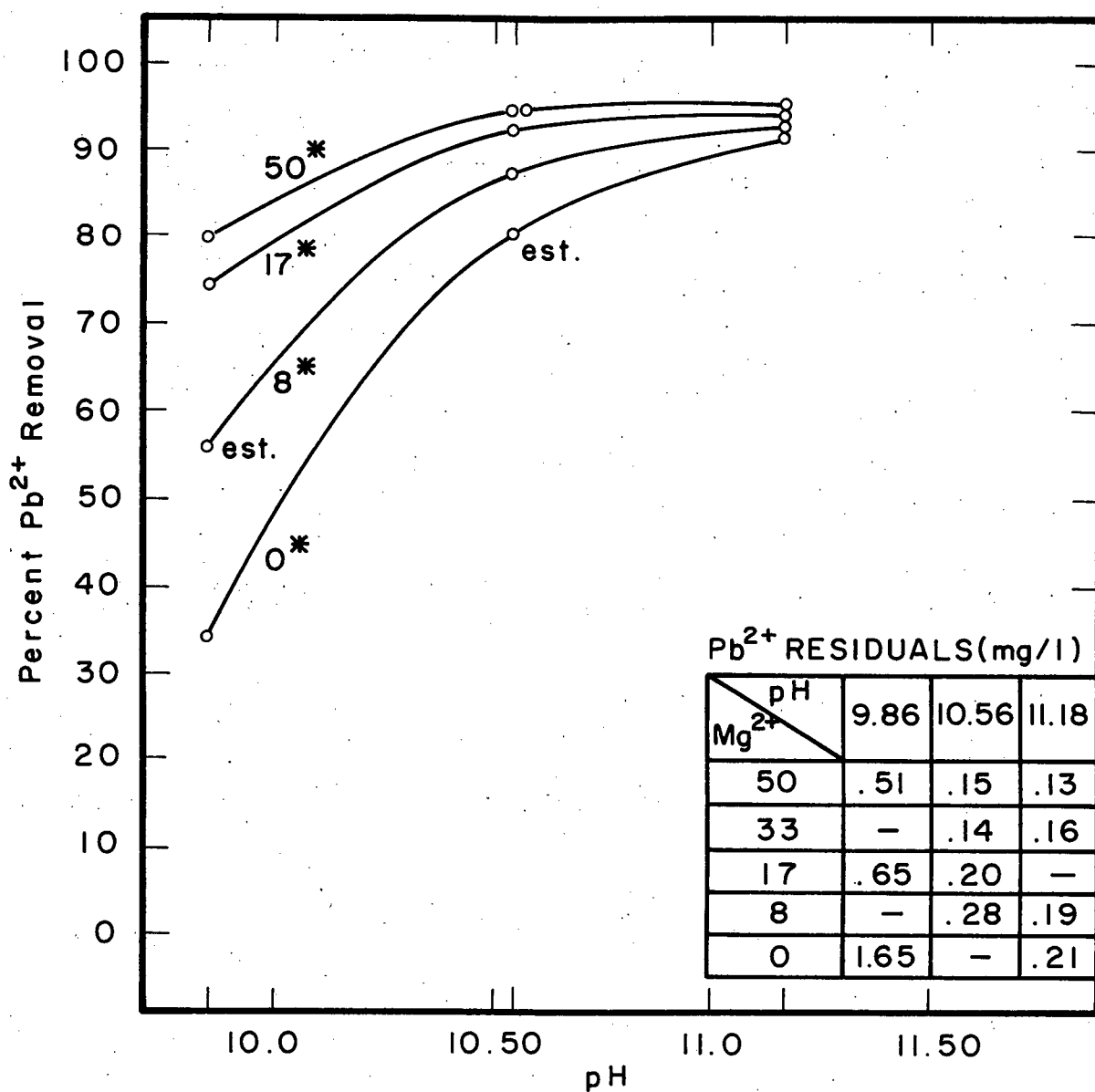
6.1.5 Zinc

Figures 16, 17 and 18 show the removal of Zn^{2+} with increasing pH.



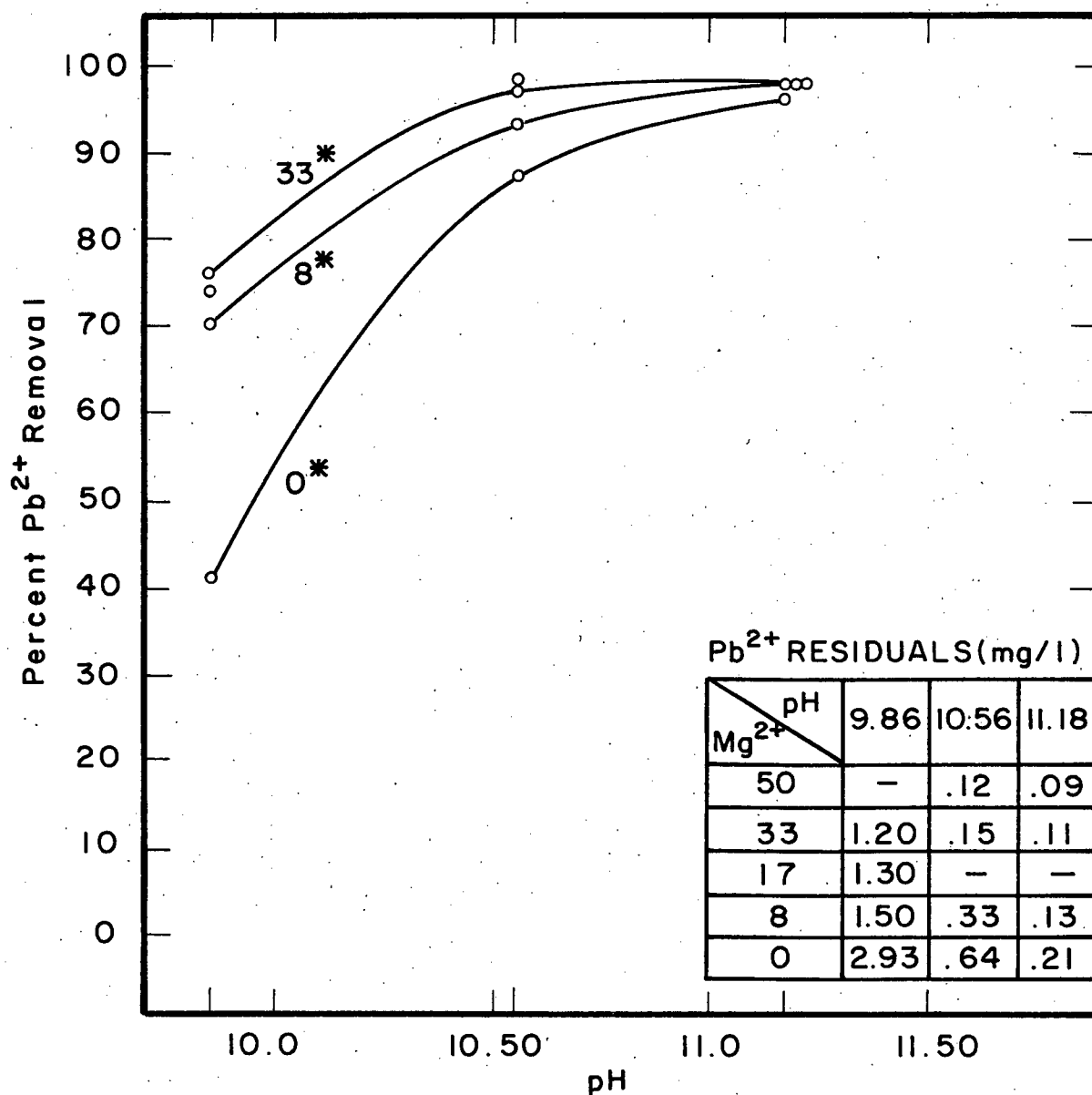
LIME DOSE(mg/l)	144	228	327
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FIGURE 10 PERCENT Pb^{2+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[Pb^{2+}]_i = 0.50 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg / l)



LIME DOSE(mg/l)	144	228	327
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FIGURE II PERCENT Pb^{2+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[Pb^{2+}]_i = 2.50 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg / l)



LIME DOSE(mg/l)	144	228	327
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FIGURE 12 PERCENT Pb^{2+} REMOVAL Vs. pH AND
 LIME DOSAGE FOR $[Pb^{2+}]_i = 5.00 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg / l)

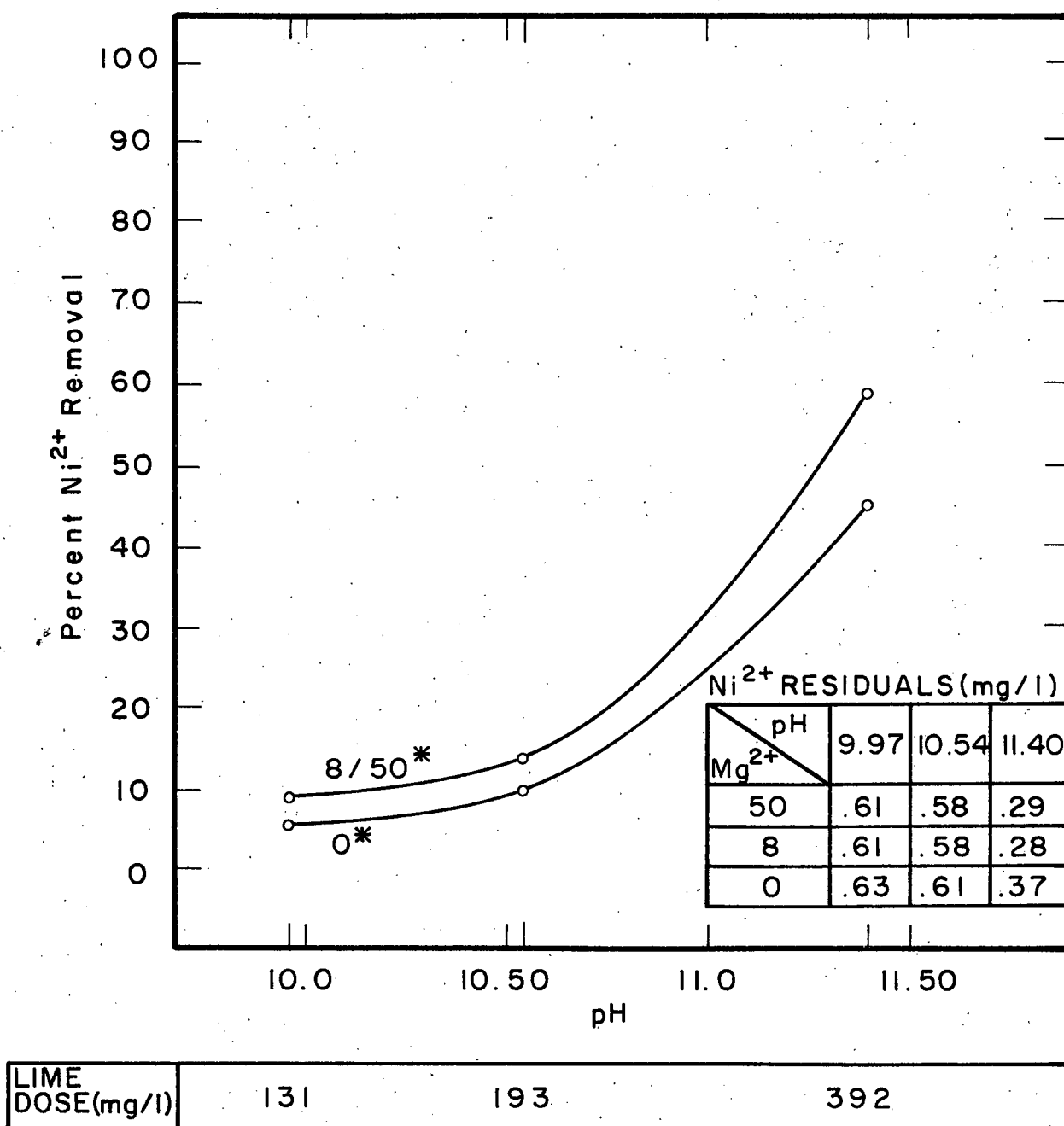
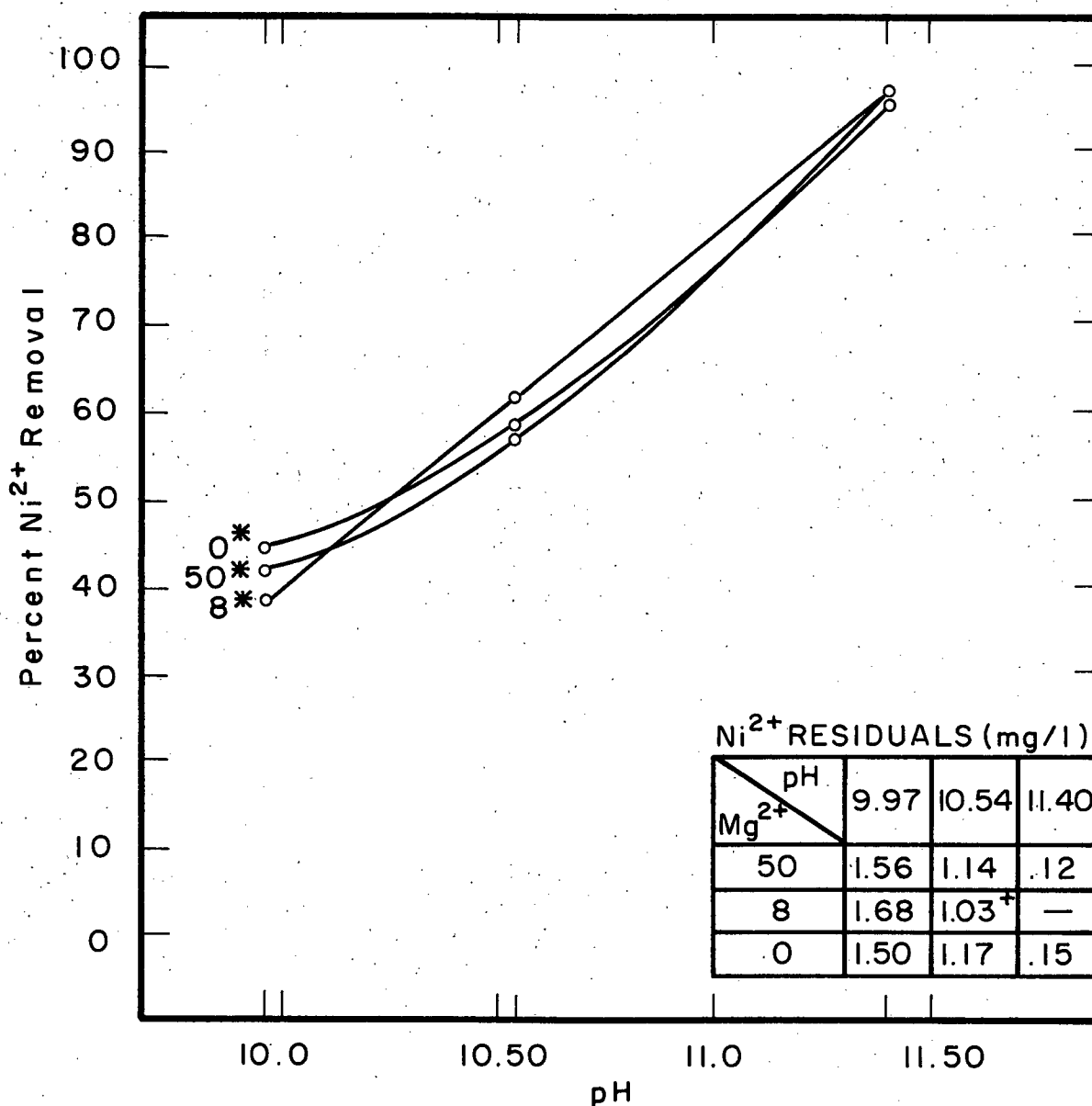
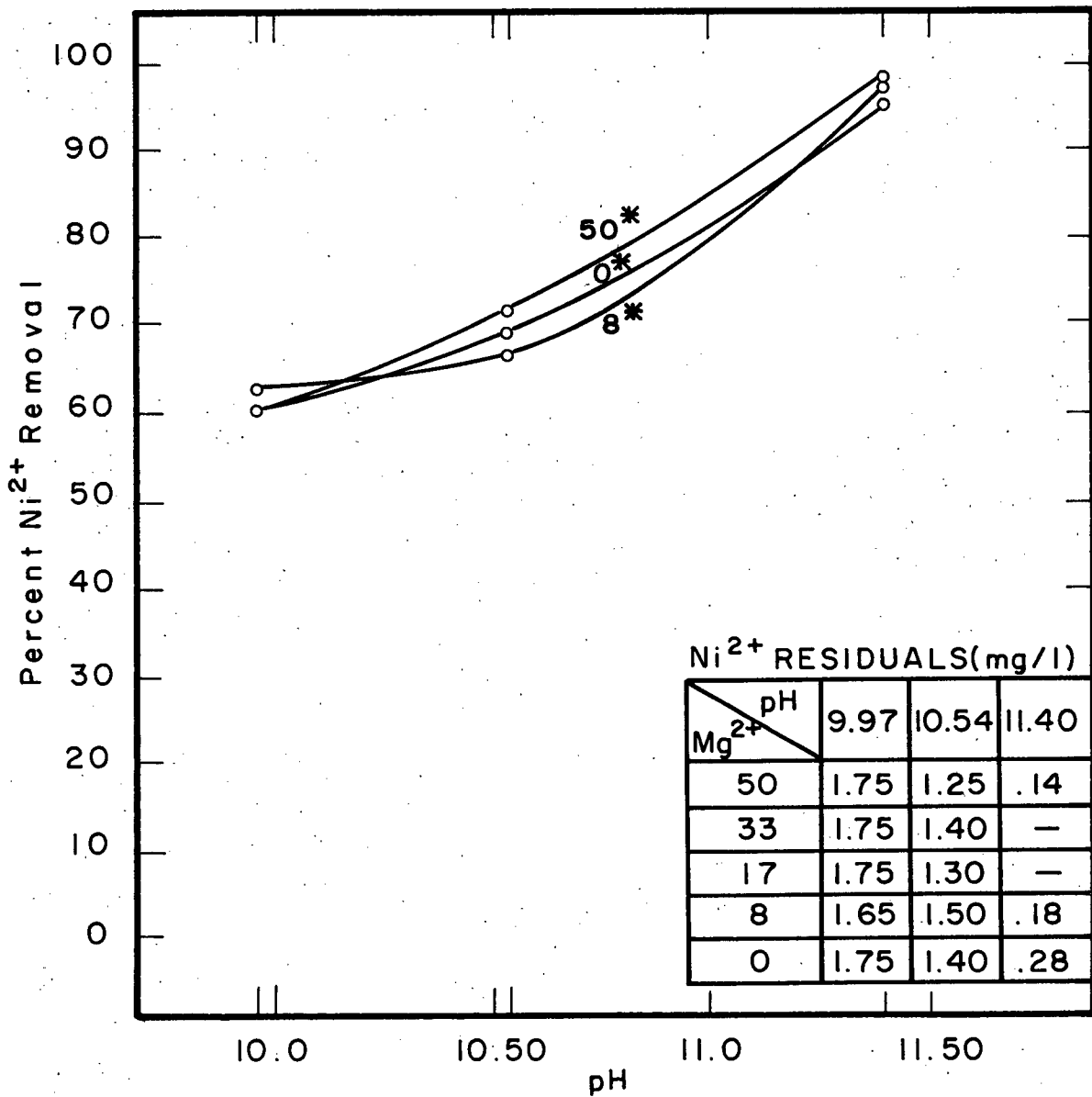


FIGURE 13 PERCENT Ni^{2+} REMOVAL Vs. pH AND
 LIME DOSAGE FOR $[\text{Ni}^{2+}]_i = 0.50 \text{ mg/l}$
 $^* \text{Mg}^{2+}$ DOSAGE (mg / l)



LIME DOSE(mg/l)	131	193	392
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FIGURE 14 PERCENT Ni^{2+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[\text{Ni}^{2+}]_i = 2.50 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)
 + ABNORMALLY HIGH pH VALUE (10.92)



LIME DOSE(mg/l)	131	193	392
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FIGURE 15 PERCENT Ni^{2+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[\text{Ni}^{2+}]_i = 5.00 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)

and at different Mg^{2+} dosages.

The removal of Zn^{2+} was similar to Cu^{2+} in that it was affected by the addition of Mg^{2+} over the entire range of pH tested, but the effect was most significant in the low pH range. At pH 10.07 the increases in removal due to the addition of 50 mg/l of Mg^{2+} were the largest of any of the 5 metals tested. For initial Zn^{2+} concentration $[Zn^{2+}]_i$ of .5, 2.5 and 5.0 mg/l the increases in percent removal were from 20 to 62, from 40 to 86.5 and from 18 to 77 respectively. At this pH the constant Mg^{2+} dosage curves show no indication of converging at high Mg^{2+} concentrations. This indicates that dosages greater than 50 mg/l Mg^{2+} might be required in order to reach the maximum practical removal.

At pH 10.59 the maximum practical removal was obtained with a Mg^{2+} dosage in the 33-50 mg/l range. The increase averaged 13.5 percentage points for the three initial concentrations.

At pH 11.36 the maximum practical removal for $[Zn^{2+}]_i$ of 2.5 and 5.0 mg/l was obtained with a Mg^{2+} dosage of 8 mg/l. The increase averaged 9.0 percentage points. The residuals obtained for $[Zn^{2+}]_i = .5$ mg/l at pH 11.36 were approximately .04 mg/l. Due to a lack of A.A. sensitivity no significant improvement was noticeably by the addition of Mg^{2+} .

6.1.6 Summary

The degree to which the addition of magnesium ions improves the removal of tested heavy metals has been shown to be dependent upon the following: species of metal ion; concentration of metal ion; and reactions pH. To provide some idea of the worth of magnesium addition, Table 8 summarizes the Mg^{2+} additions required to obtain the maximum practical removal for each different set of experimental conditions.

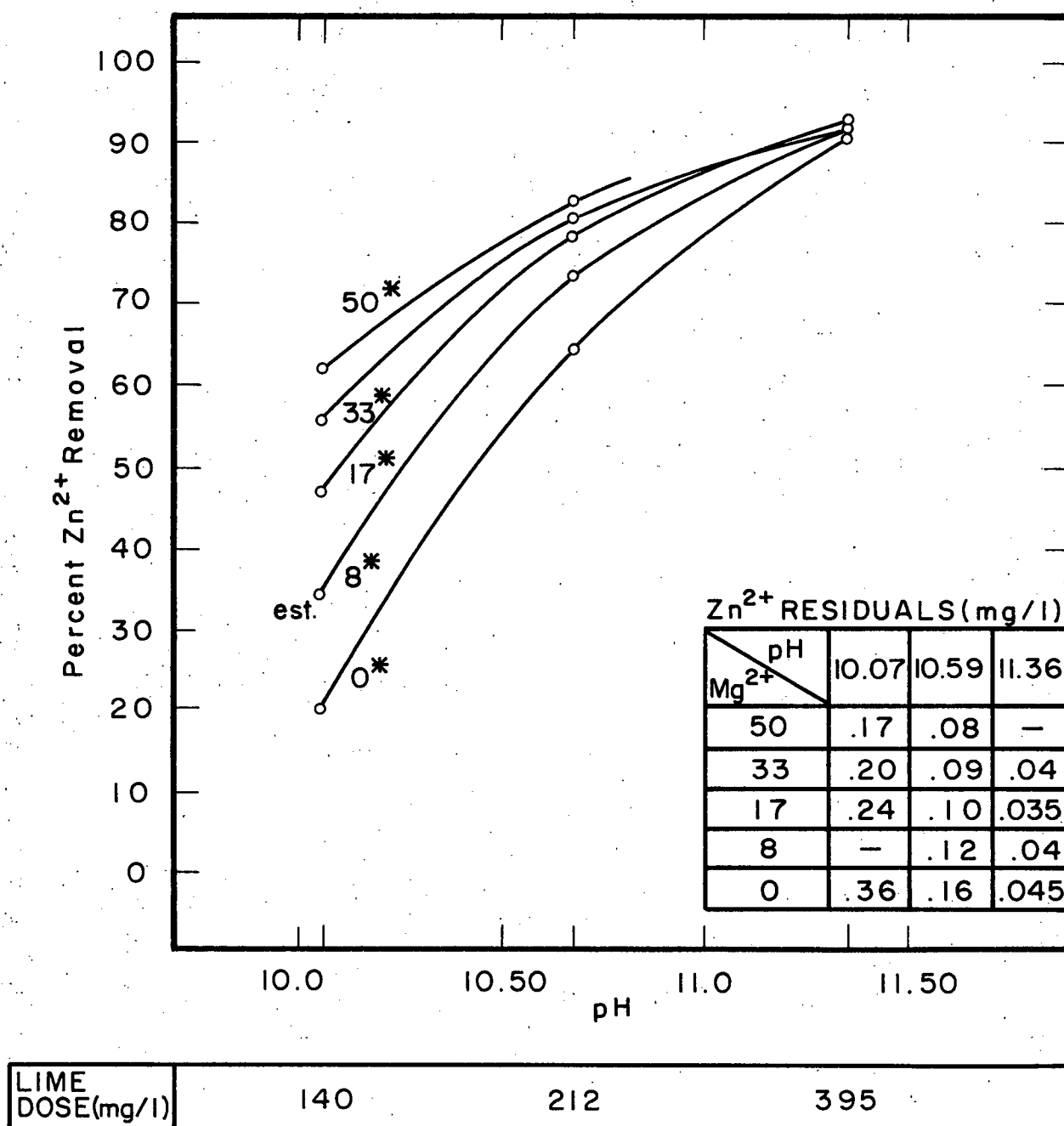
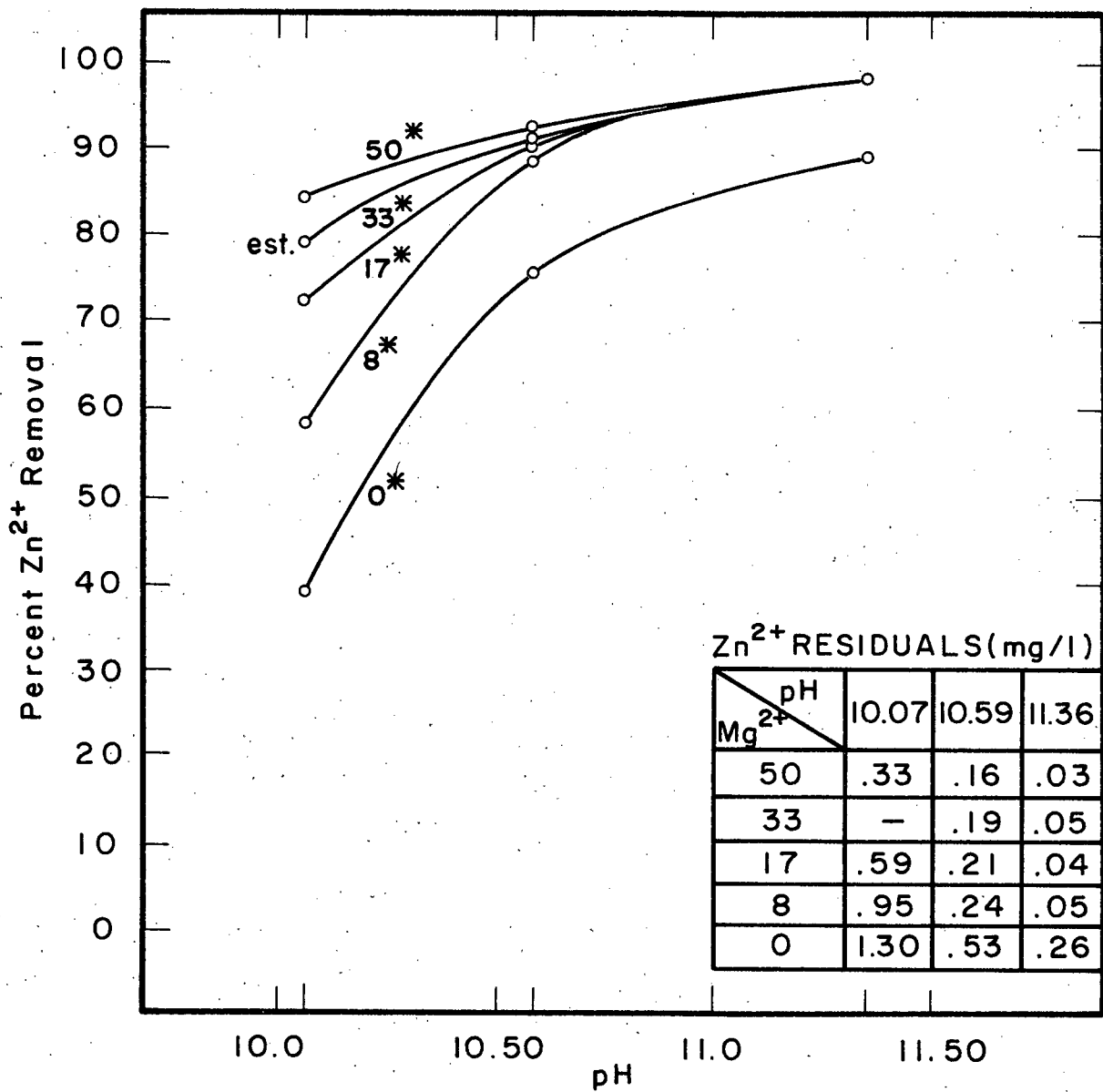


FIGURE 16 PERCENT Zn²⁺ REMOVAL Vs. pH AND
LIME DOSAGE FOR [Zn²⁺]_i = 0.50 mg/l

* Mg²⁺ DOSAGE (mg/l)



LIME DOSE(mg/l)	140	212	395
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FIGURE 17 PERCENT Zn^{2+} REMOVAL Vs. pH AND LIME DOSAGE FOR $[Zn^{2+}]_i = 2.50 \text{ mg/l}$
 * Mg^{2+} DOSAGE (mg/l)

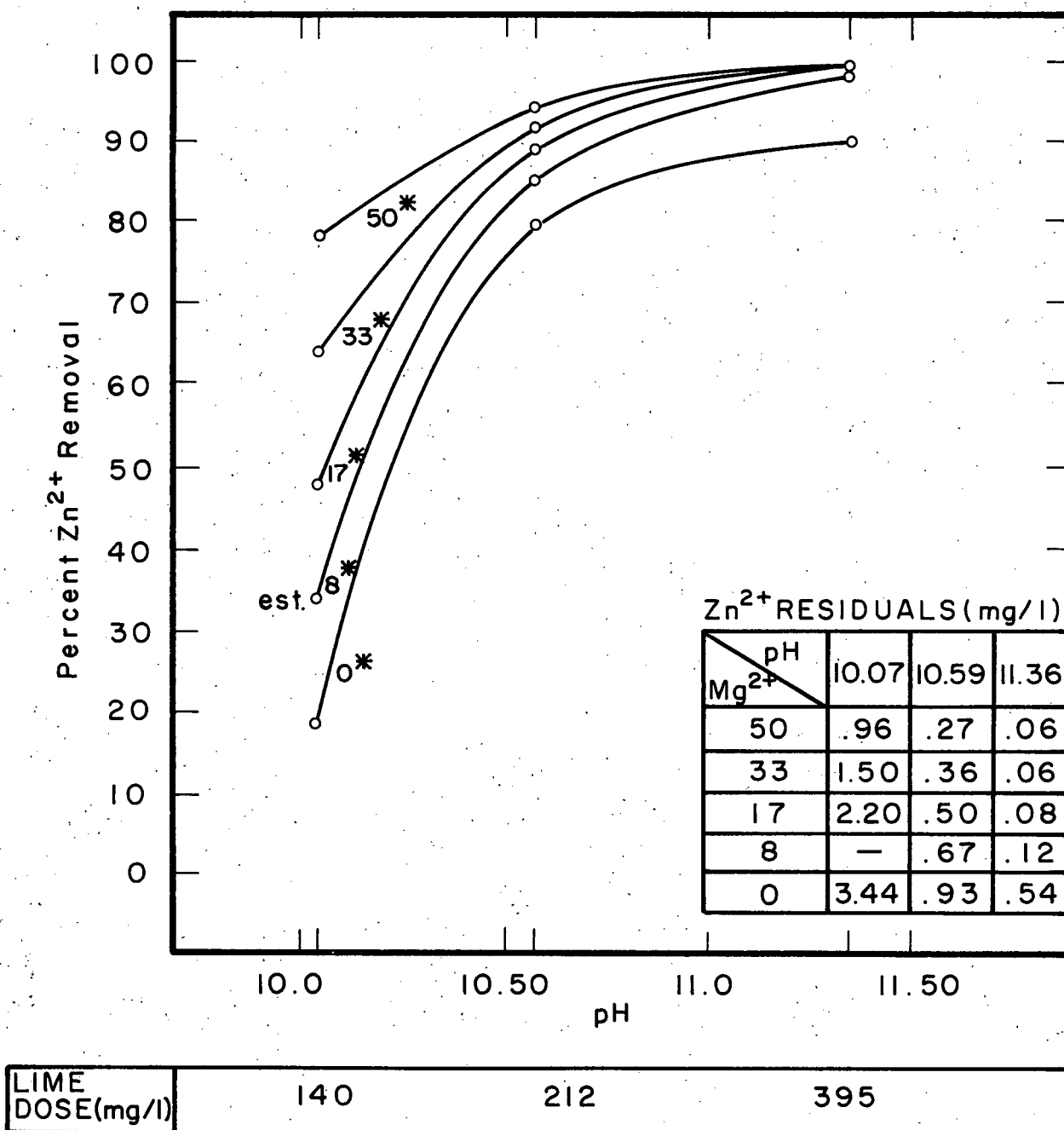


FIGURE 18 PERCENT Zn²⁺ REMOVAL Vs. pH AND
LIME DOSAGE FOR $[Zn^{2+}]_i = 5.00 \text{ mg/l}$
* Mg²⁺ DOSAGE (mg/l)

TABLE 8

Effective Mg^{2+} Dosages for
the Five Heavy Metals under Different
Conditions of $[M^{n+}]_i$ and pH

		Chromium			Copper			Lead			Nickel			Zinc		
Initial Concentration		.5	2.5	5.0	.5	2.5	5.0	.5	2.5	5.0	.5	2.5	5.0	.5	2.5	5.0
pH																
10.0		33	17	<8 ⁺	33	33	33	~33	~33	33	8	0	0	≥50	≥50	50
10.6		17	8-17	<8 ⁺	33	33	33	17	17	38	8	8	8	33	17-33	17-33
11.4		8 ⁺	8 ⁺	<8 ⁺	8	8	8	?	8-17	8	8	0	0	8	8	8

⁺ minimal improvement (only practical where optimum removal required)

6.2 The removal efficiency of individual metals in PPE - Filtered vs

Unfiltered Results

A comparison of the removal efficiencies obtained with filtered and unfiltered settled final effluent is shown in Tables 9, 10 and 11. These tables indicate that the removal efficiency is only improved about 1 to 2 percent with the addition of a filtration step (#2 Whatman filter paper) in the process. The only exception appears to be that of Zn^{2+} . The improvement caused by filtration was about 8 percentage points at pH 10, 4.4 at pH 10.6 and 5.4 at pH 11.4.

6.3 The removal efficiency of mixed metals from PPE - Unfiltered and

Filtered Results

A set of experiments was performed on effluent that had been spiked to approximately .50 mg/l M^{n+} with each of the five metals previously tested. Unfortunately, the Pb^{2+} was underspiked to .125 mg/l so these results could not be compared to the individual metal runs.

The results of these experiments were compared to the results of the .50 mg/l individual metal runs previously performed. The comparisons are shown in Tables 12, 13 and 14. Of the 12 comparisons shown, the only three that did not compare very well are Zn^{2+} at pH 10 and Ni^{2+} at pH 10.6 and 11.4. The reason for these differences is unknown but it may be related to the slight differences in initial concentrations of the individual and mixed heavy metal experiments.

Table 15 gives a comparison of the percentage removals of heavy metals from filtered and unfiltered samples for the experiments performed with mixed heavy metals in PPE. As was the case with the individual metals, there appears to be only minor improvement in removal due to filtration.

TABLE 9

Percent Removals for Filtered and Unfiltered Samples
of Individual Heavy Metals in Prechlorinated Primary
Effluent at Initial Concentration = .5 mg/l.

pH 10.0										
Mg ²⁺ Dose (mg/l)	Chromium		Copper		Nickel		Zinc		Lead	
	Filtered	Unfiltered	F	Unf	F	Unf	F	Unf	F	Unf
0	75	75		22	6	6	31	20	50	44
8.33	84	82		28	9	9	51	47	62	63
16.66	-	86		44	-	-	56	47	71	71
33.33	89	89		46	-	-	67	56	73	74
50.0	89	89		54	9	9	69	62	78	78
pH 10.6										
0	-	80	37	33	13.4	9	Contaminated	67	78	78
8.33	-	89	48	44	13.4	13.4		75	82	82
16.66	-	91	52	50	-	-		81	83	83
33.33	-	91	60	60	-	-		81	84	84
50.0	-	93	62	60	13.4	13.4		83	86	87
pH 11.4										
0	>95	>95	60	56	42	45	89	90	83	80
8.33	>95	>95	73	71	55	58	93	91	93	83
16.66	>95	>95	-	-	-	-	93	92	95	94
33.33	>95	>95	73	73	-	-	92	91	95	93
50.0	>95	>95	75	73	55	57	-	-	95	95

TABLE 10

Percent Removals for Filtered and Unfiltered Samples of
Individual Heavy Metals in Prechlorinated Primary Effluent
at Initial Concentration = 2.5 mg/l

pH 10.0

Mg ²⁺ Dose (mg/l)	Chromium		Copper		Nickel		Zinc		Lead	
	Filtered	Unfiltered	F	Unf	F	Unf	F	Unf	F	Unf
0	88	87	33	33	39	44	Contaminated	40	45	34
8.33	91	90	47	43	42	39		58	78	-
16.66	95	94	52	50	-	-		73	81	74
33.33	93	94	60	53	-	-		73	85	-
50.0	95	96	61	55	-	42		85	88	80

pH 10.6

0	93	93	55	54	57	58	75	70	-	-
8.33	95	95	63	60	62	63	89	78	89	87
16.66	96	96	71	70	-	-	90	85	92	-
33.33	96	96	77	75	-	-	91	89	95	-
50.0	97	97	77	76	58	-	92	91	94	94

pH 11.4

0	97	97	85	84	87	94	93	84	95	92
8.33	99	99	92	92	94	87	96	82	96	93
16.66	99	99	93	93	-	-	96	86	97	-
33.33	99	99	94	94	-	-	93	86	-	94
50.0	99	99	94	94	95	96	94	87	98	95

TABLE 11

Percent Removals for Filtered and Unfiltered Samples
of Individual Heavy Metals in Prechlorinated Primary
Effluent at Initial Concentration = 5.0 mg/l

pH 10.0

Mg ²⁺ Dose (mg/l)	Chromium		Copper		Nickel		Zinc		Lead	
	Filtered	Unfiltered	F	Unf	F	Unf	F	Unf	F	Unf
0	95	94	56	50	56	60	31	18		42
8.33	97	97	62	60	63	63	40	18		70
16.66	97	97	68	66	60	60	57	48		74
33.33	97	97	72	69	60	60	70	64		76
50.0	98	97	75	72	60	60	81	77		-

pH 10.6

0	97	96	66	63	68	68	85	79	90	87
8.33	98	98	74	73	67	66	89	85	94	94
16.66	98	98	78	75	71	71	94	89	96	-
33.33	99	98	83	82	71	68	-	92	98	97
50.0	98	98	84	83	74	72	75	94	98	98

pH 11.4

0	99	99	89	88	95	95	Contaminated	89	-	96
8.33	99	99	95	95	97	97		98	98	97
16.66	99	99	96	96	-	-		98	93	-
33.33	99	99	97	97	-	-		99	99	98
50.0	99	99	-	97	97	97		99	99	98

TABLE 12

Comparison of the Individual Metal Removals to the Combined Metal Removals at pH 10.0 (Approx.)

Mg ²⁺ Dose (mg/l)	Chromium				Copper				Nickel				Zinc			
	Individual		Combination		Ind		Comb		Ind		Comb		Ind		Comb	
	Residual	Removal	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem
0	.14	75.0	.14	73.1	.42	22	.38	34.5	.63	6.0	.47	16.1	.36	20	.26	51.9
8.33	.10	82.1	.09	82.7	.39	28	.34	41.4	.61	9.0	.47	16.1	.24	46.7	.20	63.0
16.66	.08	85.7	.09	82.7	.30	44	.34	41.4	-	-	.47	16.1	.24	46.7	.18	66.7
33.33	.06	89.3	.07	86.5	.29	46	.32	44.8	-	-	.47	16.1	.20	55.6	.10	81.5
50.0	.06	89.3	.07	86.5	.25	54	.34	41.4	.61	9.0	.47	16.1	.17	62.2	.12	77.8
Initial Conc.	.56		.52		.54		.58		.67		.56		.45		.54	
Avg pH	10.04		9.94		10.01		9.94		9.97		9.94		10.07		9.94	

TABLE 13

Comparison of the Individual Metal Removals to the Combined
Metal Removals at pH 10.60 (Approx.)

Mg ²⁺ Dose (mg/l)	Chromium				Copper				Nickel				Zinc			
	Individual		Combination		Ind		Comb		Ind		Comb		Ind		Comb	
	Residual	Removal	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem
0	.11	80.4	.04	92.7	.35	33	.26	56.1	.61	9	.49	15.5	.16	66.7	.19	61.4
8.33	.06	89.3	.05	90.9	.29	44	.24	60	.58	13.4	.46	20.7	.12	75	.10	80
16.66	.05	91.1	<.03	>95	.26	50	.23	61.7	-	-	.40	31	.09	81	.08	84
33.33	.05	91.1	<.03	>95	.21	60	.25	58.3	-	-	.40	31	.09	81	.09	82
50.0	.04	92.8	<.03	>95	.21	60	.23	61.7	.58	13.4	.38	34.5	.08	83.3	.07	86
Initial Conc.	.56		.55		.52		.60		.67		.58		.49		.50	
Avg pH	10.68		10.56		10.56		10.56		10.54		10.56		10.59		10.56	

TABLE 14

Comparison of the Individual Metal Removals to the Combined Metal Removals at pH 11.4 (Approx.)

Mg ²⁺ Dose (mg/l)	Chromium				Copper				Nickel				Zinc			
	Individual		Combination		Ind		Comb		Ind		Comb		Ind		Comb	
	Residual	Removal	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem
0	-.05	91	<.02	>96	.23	56	.20	66.7	.37	44.7	.30	48.3	.045	90	.045	91
8.33	~.03	>95	<.02	>96	-	-	.19	68.3	.28	58.2	.32	44.8	.040	91.1	.045	91
16.66	~.03	>95	<.02	>96	.15	71	.175	70.8	-	-	.27	53.4	.035	92.2	.045	91
33.33	~.03	>95	<.02	>96	.14	73	.17	71.7	-	-	.28	51.7	.040	91.1	.045	91
50.0	~.03	>95	<.02	>96	.14	73	.165	72.5	.29	56.7	.32	44.8	-	-	.040	92
Initial Conc.	.52		.55		.52		.60		.67		.58		.45		.50	
Avg pH	11.25		11.13		11.39		11.13		11.40		11.13		11.36		11.13	

TABLE 15

Percent Removals for Filtered and Unfiltered Samples
of Combinations of Heavy Metals in Prechlorinated
Primary Effluent

pH 10.0

Mg ²⁺ Dose (mg/l)	Chromium		Copper		Nickel		Zinc	
	Filtered	Unfiltered	F	Unf	F	Unf	F	Unf
0	75	73.1	31.0	34.5	16.1	16.1	-	-
8.33	82.7	82.7	37.9	41.4	17.9	16.1	-	-
16.66	84.6	82.7	34.5	41.4	17.9	16.1	-	-
33.33	88.5	86.5	41.4	44.8	-	16.1	-	-
50.0	88.5	86.5	-	41.4	-	-	-	-

pH 10.6

0	-	92.7	54.7	56.1	31	15.5	80.0	61.4
8.33	>94.5	90.9	58.3	60.0	31	20.7	81.4	80.0
16.66	>94.5	94.5	60.0	61.7	36.2	31.0	86.0	84.0
33.33	>94.5	94.5	58.3	59.0	37.9	31.0	82.0	82.0
50.0	>94.5	94.5	55.0	61.7	37.9	34.5	82.0	86.0

pH 11.4

0	>96.3	>96.3	64.2	66.7	46.6	48.3	-	-
8.33	>96.3	>96.3	65.0	68.3	46.6	44.8	-	-
16.66	>96.3	>96.3	-	70.8	53.4	53.4	-	-
33.33	>96.3	>96.3	68.3	71.1	53.4	51.7	-	-
50.0	>96.3	>96.3	70.0	72.5	44.8	44.8	-	-

6.4 The removal efficiency of mixed metals from Raw Sewage - Unfiltered and Filtered Results

A set of experiments were performed on raw sewage that had been spiked to approximately .50 mg/l M^{n+} with each of the five heavy metals. The results of these experiments were then compared to the mixed metal results performed on PPE. Comparisons of the residuals and the removal efficiencies are shown in Tables 16, 17 and 18. Since no mixed metal PPE results were obtained for Pb^{2+} , the individual Pb^{2+} results were substituted.

The comparisons for the experiments done at pH 10.6 and 11.4 (Tables 17 and 18) indicate that the two sets of results are comparable in 8 out of the 10 cases. The two sets of data that were not comparable were inconsistent in opposite direction. (Table 17 - Pb^{2+} at pH 10.6 and Table 18 - Zn^{2+} at pH 11.4).

The comparison of the experiments done at pH 10.00 (Table 16) indicates a substantial improvement in metal removal when using raw sewage. All metals except Ni^{2+} showed an increase in removal efficiency. The raw sewage sample used for the pH 10 experiment was a different sample than that used for the pH 10.6 and 11.4 experiments (which were both done on the same sample). The pH 10 raw sewage may have been chemically different, although the reaction pH and required lime dosage were not abnormal.

Table 19 compares the unfiltered and filtered removal efficiencies for the raw sewage experiments. The small increase in removal efficiency caused by filtration is approximately as found for mixed samples of PPE (1-2%).

6.5 The Effect of Alkalinity on Heavy Metal Removal

A set of experiments was performed to determine the effects of increased alkalinity on the removal of heavy metals from PPE. It was felt

TABLE 16

Comparison of the Removal Efficiencies of Combinations of Metals
in Prechlorinated Primary Effluent (PPE) and Raw Sewage (RS) at pH 10.0.

Mg ²⁺ Dose (mg/l)	Chromium				Copper				Lead*				Nickel				Zinc			
	PPE		RS		PPE		RS		Individual		RS		PPE		RS		PPE		RS	
	Residual	Removal	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem
0	.14	73.1	.04	93.1	.38	34.5	.19	69.8	1.15	43.6	.28	86.9	.47	16.1	.43	17.3	.26	61.9	.08	82.4
8.33	.09	82.7	-	-	.34	41.4	-	-	.75	63.2	-	-	.47	16.1	-	-	.20	63.0	-	-
16.66	.09	82.7	.04	93.1	.34	41.4	.18	71.4	.60	70.6	.28	86.9	-	-	.43	17.3	.18	66.7	.07	84.6
33.33	.07	86.5	.03	94.8	.32	44.8	.165	73.8	.54	73.5	.24	88.8	-	-	.42.5	18.3	.10	81.5	.07	84.6
50.0	.07	86.5	.03	94.8	.34	41.4	.17	73.0	.45	77.9	.20	90.7	.47	16.1	.45	13.5	.12	77.8	.07	84.6
Initial Conc.	152		.58		.58		.63		2.04		2.14		.56		.52		.54		.46	
Avg pH	9.94		9.92		9.94		9.92		9.88		9.92		9.94		9.92		9.94		9.92	

* Individual Lead data used in place of combination PPE Lead data.
Lead results were concentrated 4x.

TABLE 17

Comparison of the Removal Efficiencies of Combinations of
Metals in Prechlorinated Primary Effluent (PPE) and Raw Sewage (RS) at pH 10.60.

Mg ²⁺ Dose (mg/l)	Chromium				Copper				Lead*				Nickel				Zinc			
	PPE		RS		PPE		RS		Individual		RS		PPE		RS		PPE		RS	
	Residual	Removal	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem
0	.04	92.7	.02	96.6	.26	56.1	.30	62.9	.45	77.9	.18	92.1	.49	15.5	.47	9.6	.19	61.4	.11	76.6
8.33	.05	90.9	<.02	>96.6	.24	60	.28	64.5	.37	81.8	.14	93.9	.46	20.7	.47	9.6	.10	80	.10	78.7
16.66	<.03	>95	<.02	>96.6	.23	61.7	.29	63.3	.35	82.8	.14	93.9	.40	31	.47	9.6	.08	84	-	-
33.33	<.03	>95	<.02	>96.6	.25	58.3	.27	65.8	.33	83.8	.12	94.7	.40	31	.43	17.3	.09	82	.095	79.8
50.0	<.03	>95	<.02	>96.6	.23	61.7	.25	68.4	.28	86.3	.16	93.0	.38	34.5	.45	13.5	.07	86	.08	83
Initial Conc.	.55		.57		.60		.79		2.04		2.28		.58		.52		.50		.47	
Avg pH	10.56		10.67		10.56		10.67		10.56		10.67		10.56		10.67		10.56		10.67	

* Individual Lead data used in place of combination PPE Lead data.
Lead results concentrated 4x.

TABLE 18

Comparison of the Removal Efficiencies of Combinations of Metals
in Prechlorinated Primary Effluent (PPE) and Raw Sewage (RS) at pH 11.40.

Mg ²⁺ Dose (mg/l)	Chromium				Copper				Lead [*]				Nickel				Zinc			
	PPE		RS		PPE		RS		Individual		RS		PPE		RS		PPE		RS	
	Residual	Removal	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem	Res	Rem
0	<.02	>96	<.02	>96	.20	66.7	.21	73.4	.40	80.4	.195	91.4	.30	48.3	.35	32.7	.045	91	.08	83
8.33	<.02	>96	<.02	>96	.19	68.3	.195	75.3	.35	82.8	.16	93	.32	44.8	.30	42.3	.045	91	.07	85.1
16.66	<.02	>96	<.02	>96	.175	70.8	.18	77.2	.13	93.6	.16	93	.27	53.4	.25	51.9	.045	91	.07	85.1
33.33	<.02	>96	<.02	>96	.17	71.7	.21	73.4	.15	92.6	.085	96.3	.28	51.7	.30	42.3	.045	91	.09	80.9
50.0	<.02	>96	<.02	>96	.165	72.5	.16	79.7	.10	95.1	.085	96.3	.32	44.8	.30	42.3	.040	92	.07	85.1
Initial Conc.	.55		.57		.60		.79		2.04		2.28		.58		.52		.50		.47	
Avg pH	11.13		11.16		11.13		11.16		11.18		11.16		11.13		11.16		11.13		11.16	

* Individual Lead data used in place of combination PPE Lead data
Lead results concentrated 4x.

TABLE 19

Percent Removals for Filtered and Unfiltered
Samples of Combinations of Heavy Metals in Raw
Sewage

pH 10.0

Mg ²⁺ Dose (mg/l)	Chromium		Copper		Nickel		Zinc	
	Filtered	Unfiltered	F	Unf	F	Unf	F	Unf
0	93.1	93.1	68.3	69.8	13.5	17.3	80.2	82.4
8.33	-	-	-	-	-	-	-	-
16.66	93.1	93.1	69.8	71.4	17.3	17.3	80.2	84.6
33.33	94.8	94.8	74.6	73.8	13.5	18.3	80.2	84.6
50.0	94.8	94.8	-	73.0	17.3	13.5	-	84.6

pH 10.6

0	96.6	96.6	65.8	62.9	13.5	9.6	80.9	76.6
8.33	≥96.6	>96.6	70.9	64.5	17.3	9.6	78.7	78.7
16.66	>96.6	>96.6	70.9	63.3	17.3	9.6	80.9	-
33.33	>96.6	>96.6	70.9	65.8	17.3	17.3	78.7	79.8
50.0	>96.6	>96.6	68.4	68.4	17.3	13.5	79.8	83.0

pH 11.4

0	>96.6	>96.6	71.5	73.4	46.1	32.7	75.5	83.0
8.33	>96.6	>96.6	75.9	75.3	49.0	42.3	80.9	85.1
16.66	>96.6	>96.6	79.7	77.2	59.6	51.9	81.9	85.1
33.33	>96.6	>96.6	81	78.4	51.9	42.3	81.9	80.9
50.0	>96.6	>96.6	78.5	79.7	50	42.3	81.9	85.1

that such addition could be beneficial to the metal removal process because there is stoichiometrically insufficient alkalinity to precipitate all the Ca^{2+} as CaCO_3 for the three average lime dosages. The stoichiometric ratio of alkalinity to lime is 1:1 whereas the ratios for the three averaged lime dosages were: 1:1.6, 1:2.4 and 1:4.2.

The experiments on the individual heavy metals ($[\text{M}^{n+}]_i = 2.5 \text{ mg/l}$), performed at the natural PPE alkalinity of 120-130 mg/l as CaCO_3 , were duplicated with the alkalinity spiked to levels of 180-200 mg/l using sodium bicarbonate. The experiments were performed at the intermediate lime dosage rather than the high lime dosage because the removals were so high (+90%) at the high lime dosage (except Ni^{2+}) that it was felt that it would be difficult to distinguish significant differences in removal efficiency. The results of the experiments are plotted on Figures 19, 20 and 21. There does not appear to be any significant difference in removal efficiency, at least up to the intermediate lime dosage.

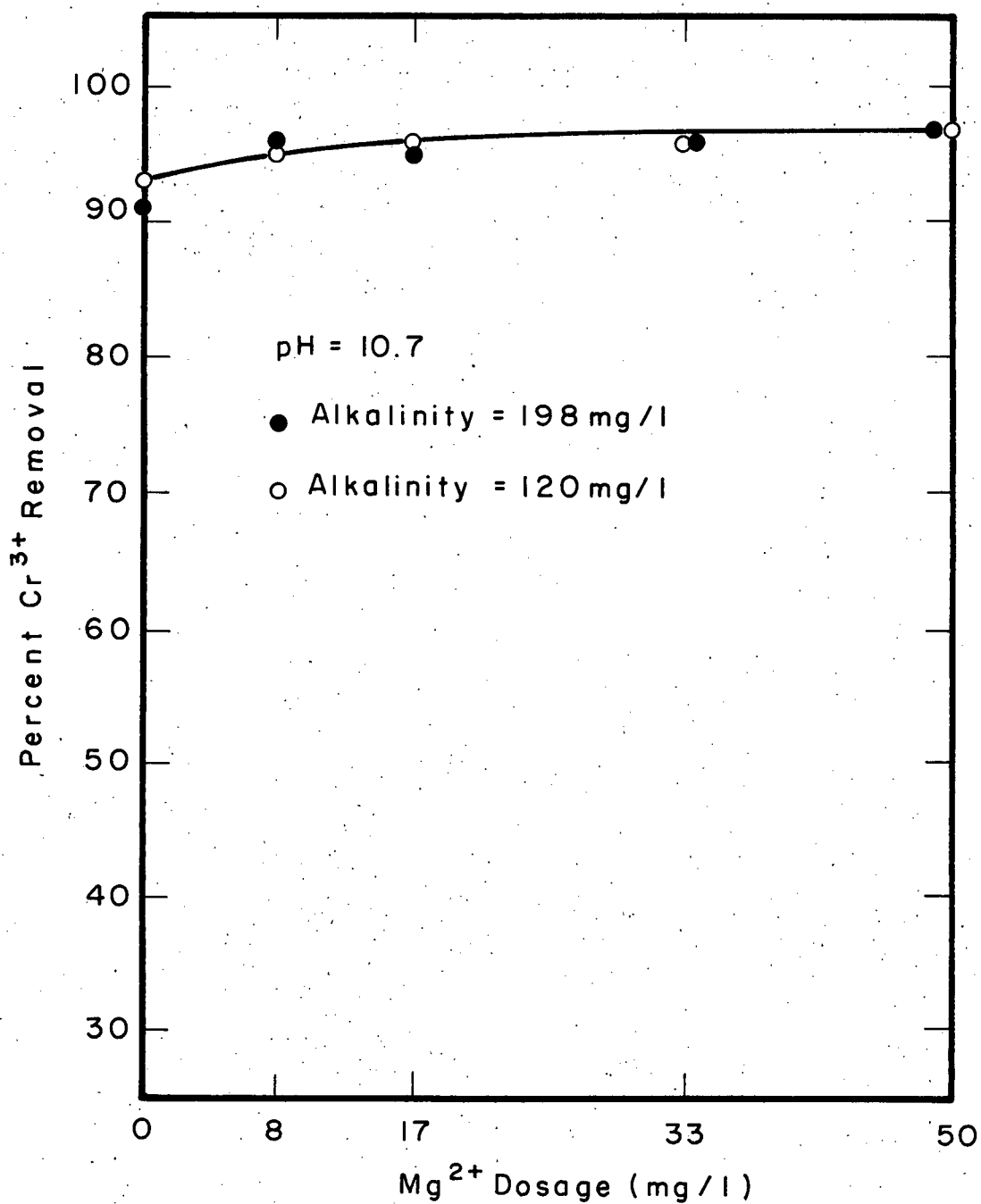


FIGURE 19 PERCENT Cr³⁺ REMOVAL Vs. Mg²⁺ DOSAGE FOR DIFFERENT ALKALINITIES.

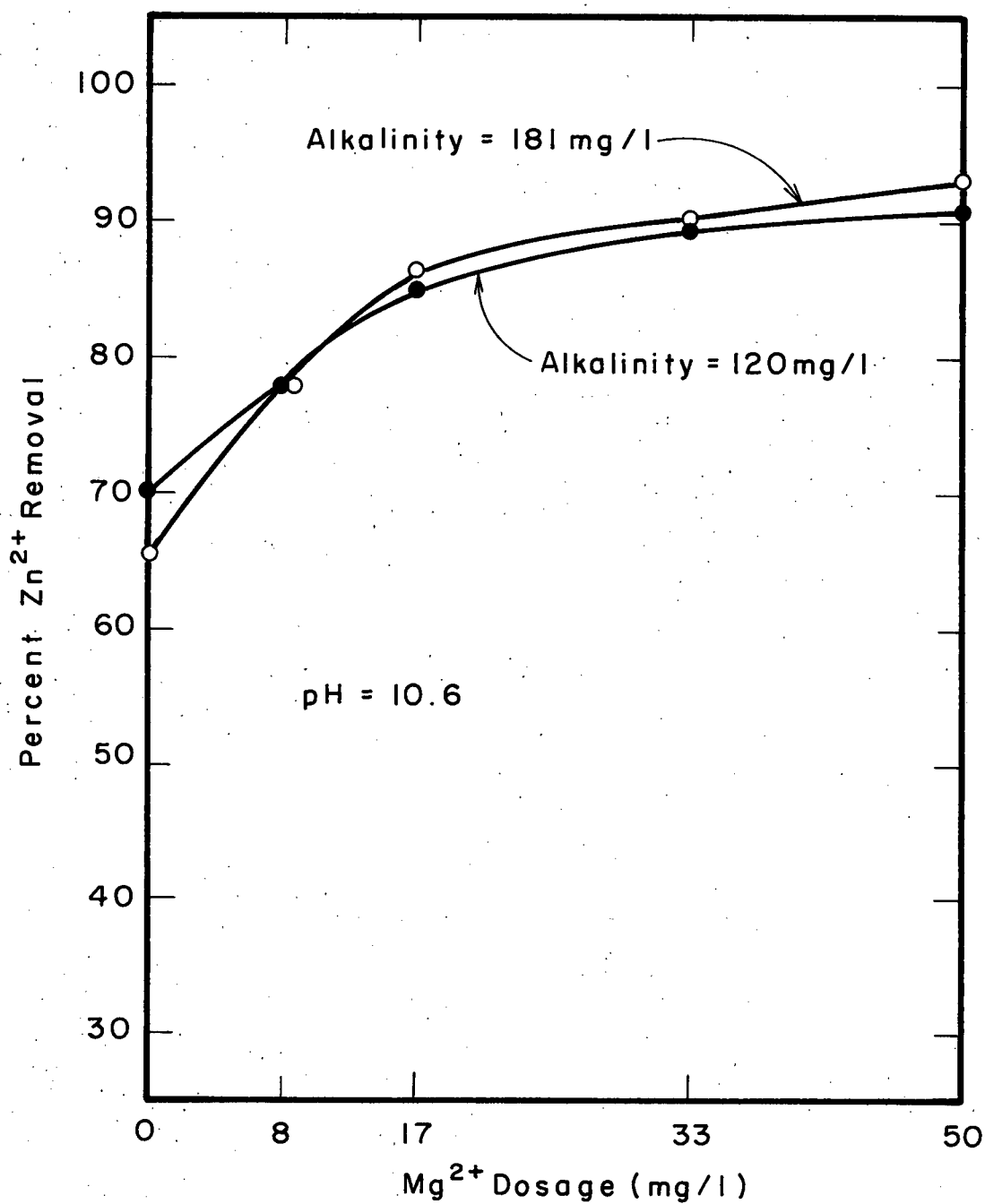


FIGURE 20 PERCENT Zn^{2+} REMOVAL Vs. Mg^{2+} DOSAGE FOR DIFFERENT ALKALINITIES.

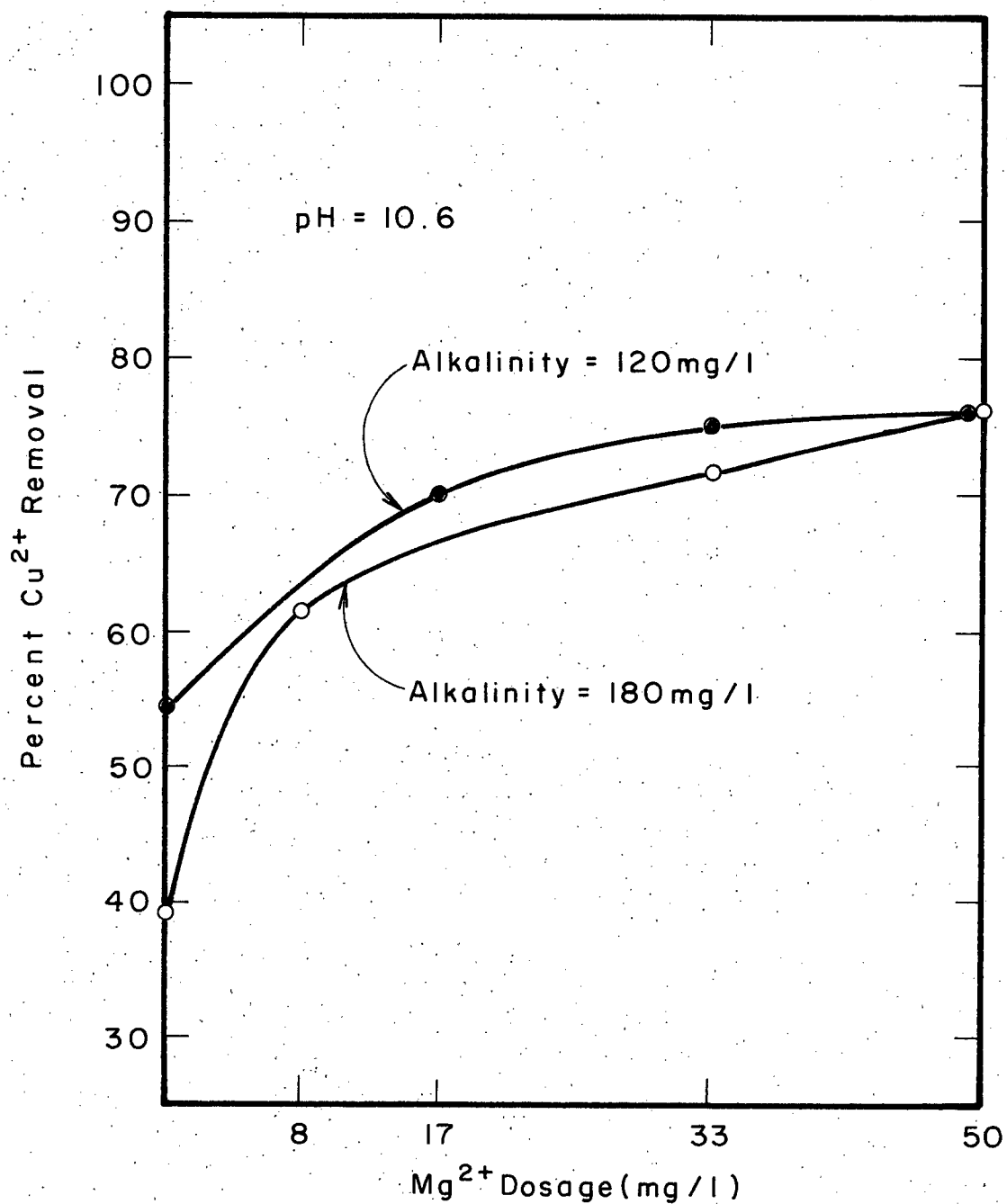


FIGURE 21 PERCENT Cu^{2+} REMOVAL Vs. Mg^{2+} DOSAGE FOR DIFFERENT ALKALINITIES.

CHAPTER 7

CONCLUSIONS

7.1 The Effectiveness of Mg^{2+} at Various pH's7.1.1 General

a) The effect of Mg^{2+} on the removal of heavy metals is most significant when used in conjunction with low lime treatment (pH 10.0).

b) The greatest removals were found at high lime treatment (pH 11.4). At this pH the effect of Mg^{2+} was significant for Cu^{2+} and Zn^{2+} only.

7.1.2 Individual Metals in PPE

a) The effect of Mg^{2+} was most significant for Zn^{2+} with major influence on Cu^{2+} and Pb^{2+} removal also being noted.

b) There was very good removal for Cr^{3+} in the absence of Mg^{2+} due to its low solubility product ($k_{sp} = 10^{-30}$).

c) The removal of Ni^{2+} was poor and the effect of Mg^{2+} was insignificant.

7.1.3 Mixed Metals in PPE

a) The removal of metals does not appear to be affected by the presence of other metal ions in solution at the same initial concentration. The removal efficiency of each metal in the mixture was comparable to the removal efficiency of that metal when treated by itself.

7.1.4 Mixed Metals in Raw Sewage

a) The removal of mixed metals from raw sewage was comparable to that from PPE. There was, however, an increase in required lime dosage of 10-15% to get to the same reaction pH.

7.2 Residual Metals in the Settled Supernatant

a) Filtration of the supernatant increased the removal efficiency

by only 1-2 percentage points.

b) Since the supernatant samples were carefully pipetted from beakers that had been settled for 30 minutes, these removals do not simulate an actual flow through process. Further work is required to establish the need for filtration in this process.

7.3 The Effect of Alkalinity on Heavy Metal Removal

a) There is sufficient alkalinity in the wastewater so as to not inhibit heavy metal removal up to at least the intermediate pH.

b) The effect of alkalinity at the high pH could not be researched due to a lack of analytical sensitivity.

7.4 The Potential of Mg^{2+} for Full Scale Treatment

a) A rough comparison of high lime treatment vs intermediate lime plus Mg^{2+} treatment is presented in Appendix B. Although further research is required, the comparison indicates that the combined treatment might be cheaper.

b) This type of process might be applicable in the following areas:

i. For the reduction of heavy metal concentrations of industrial waste streams prior to their dilution in municipal sewers;

ii. Incorporation within the primary treatment process. Grit removal and rapid mixing might be achieved simultaneously, so that the only major additions to a primary treatment flow stream would be flocculation and recarbonation.

BIBLIOGRAPHY

1. APHA, AWWA, WPCF. "Standard Methods for the Examination of Water and Wastewater", 14th Edition (1976).
2. Argo, D.G. and Culp, G.L. "Heavy Metal Removal in Wastewater Treatment Processes: Part I", Water and Sewage Works, Vol. 119:2, p. 62, (August 1972).
3. Argo, D.G. and Culp, G.L. "Heavy Metal Removal in Wastewater Treatment Processes: Part II", Water and Sewage Works, Vol. 119:2, p. 128, (September 1972).
4. B.C. Research. "Water Quality Studies in the Lower Fraser River", Prepared for the Greater Vancouver Sewerage and Drainage District, (May 1973).
5. Benedict, A.H. Hall, K.J. and Koch, F.A. "A Preliminary Water Quality Survey of the Lower Fraser River System", Wastewater Research Centre, University of British Columbia, Technical Report No. 2, (April 1973).
6. Barth, E.F. and others. "Summary Report on the Effects of Heavy Metals on the Biological Treatment Processes", Journ. WPCF, Vol. 37, p. 90 (1965).
7. Barth, E.F. and others. "Field Survey of Four Municipal Wastewater Treatment Plants Receiving Metallic Wastes", Journ. WPCF, Vol. 37, p. 1101 (1965).
8. Black, A.P., DuBose, A.T. and Vogh, R.P. "Physical-Chemical Treatment of Municipal Wastes by Recycled Magnesium Carbonate", EPA-660/2-74-055 (June 1974).
9. Black, A.P. and Thompson, C.G. "Plant Scale Studies of the Magnesium Carbonate Water Treatment Process", EPA-660/2-75-006 (May 1975).
10. Brouzes, R.J.P. "The Use of Lime in the Treatment of Municipal Wastewaters", Research Report No. 21, Environment Canada.
11. Culp, R.L. and Culp, G.L. "Advanced Wastewater Treatment", Van Nostrand Reinhold Company (1971).
12. Grieve, D. and Fletcher, K. "Trace Metals in Fraser Delta Sediments", Geological Survey of Canada, Project 740062.
13. Hall, K.J., Yesaki, J. and Chan, J. "Trace Metals and Chlorinated Hydrocarbons in the Sediments of a Metropolitan Watershed", Wastewater Research Centre, University of British Columbia, Technical Report No. 10 (May 1976).

14. Hall, K.J. Assistant Professor, Department of Civil Engineering, University of British Columbia, Personal Communication (December 1976).
15. Langier, W.F. "Effects of Temperature on the pH of Natural Waters", J. AWWA, Vol. 38, p. 179 (February 1946).
16. Larson, T.E., Lane, R.W. and Neff, C.H. "Stabilization of Magnesium in Hydroxide in the Solids Contact Process", J. AWWA, 51: 1551 (December 1959).
17. Lecompte, A.R. "Water Reclamation by Excess Lime Treatment of Effluent", Tappi, Vol. 49, No. 12, p. 121-124, (December 1966).
18. Lindstedt, JWPCF, Vol. 43, p. 1507.
19. McKee, M.E. and Wolf, H.W. "Water Quality Criteria", Second Edition, Publication 3-A, California State Water Resources Control Board.
20. Riaz, M. "Removal of Heavy Metals Using Granular Coal", M.A.Sc. Dissertation, University of British Columbia (August, 1974).
21. Rush, R.J. "Magnesium-Lime Process for Decolourization of Kraft Mill Effluents", M.A.Sc. Dissertation, University of British Columbia (April, 1976).
22. Sabadell, J.E. (Editor). "Traces of Heavy Metals in Water-Removal Processes and Monitoring", EPA-902/9-74-001, p. 57.
23. Sartor, J.D. and Boyd, G.B. "Water Pollution Aspects of Street Surface Contaminants", E.P. Technology Series, EPA-R2-70-081 (November 1972).
24. Stumm, W. and Morgan, J.J. "Aquatic Chemistry", Wiley-Interscience, N.Y., N.Y. (1970).
25. Tanner, G., Trasolini, G. and Nemeth, L. "A Study on Wastewater Characteristics of Greater Vancouver Sewage Treatment Plants and Major Sewers", Report EPS 5-PR-73-11 (December 1973).
26. Thompson, C.G., Singley, J.E. and Black, A.P. "Magnesium Carbonate A Recycled Coagulant", Journ. AWWA Part I, p. 11-19 (January 1972).
27. Travers, A. and Nouvel. "On the Solubility of Magnesium Hydroxide at High Temperatures", Compt. Rend (Fr.) 188: 499 (1929).

APPENDIX A

TEST PROCEDURE DEVELOPMENT1. Introduction

Due to the limited amount of work that has been done using the lime-magnesium process, a test procedure had to be first developed that would give reproducible results. The test procedure developed by Rush (21) for colour removal from kraft mill effluents was used as a base from which a satisfactory procedure was developed.

An outline of the test procedure development is presented in the following section to give some insight into the practical problems that may concern future researchers.

2. Development of the Jar Test Procedure

The main factors that were expected to affect trace metal removal included

- i) time (of rapid mixing, flocculation and settling)
- ii) mixing speed
- iii) pH stabilization
- iv) the alkalinity of the sewage
- v) the dosage and method of Mg^{2+} addition
- vi) the dosage and method of lime addition

Initial jar tests were carried out on 600 ml samples of PPE to see i) the effect of the alkalinity of the sewage on pH stabilization, ii) if the rapid mix times recommended by Rush (21) would be satisfactory for heavy metal removal (it was felt that pH stabilization was important in that it indicated the practical completion of the precipitation reactions and thus the completion of the rapid mix time). The initial jar tests were done as follows:

i) A 600 ml sample of PPE was limed to the pH range 10.8 to 11.3 by a predetermined slug dose.

ii) The pH was monitored continuously.

iii) A rapid mix (100 rpm) was maintained until the pH had stabilized.

iv) The samples were then allowed to flocculate at 15-20 rpm until an adequate floc formed from a visual point of view.

v) The samples were then settled (0 rpm) and the settling time was measured.

The procedure outlined above was repeated for samples spiked to an alkalinity of 200 mg/l as CaCO_3 and for Mg^{2+} dosages from 0 to 50 mg/l. The pH stabilization curves are plotted on Figure 22, 23 and 24. The conclusions of this series of tests are as follows:

i) At the normal alkalinity of the PPE, an increase in Mg^{2+} dosage does not appear to affect the pH stabilization time (see Figure 22).

ii) At the elevated alkalinity, an increase in Mg^{2+} dosage increases the pH stabilization time (see Figures 23 and 24).

iii) Increased alkalinity at a constant Mg^{2+} dosage does not increase the pH stabilization time (see Figures 22 and 23).

iv) A rapid mix time of 15 minutes would stabilize the pH under all conditions except the case of high Mg^{2+} (50 mg/l) and high alkalinity (192 mg/l as CaCO_3).

v) A flocculation time of 3 minutes was adequate from a visual point of view.

vi) The sample settled in 10-15 minutes.

The next series of tests were performed to establish the flocculation time. It was felt that although the pH had stabilized after 15 minutes

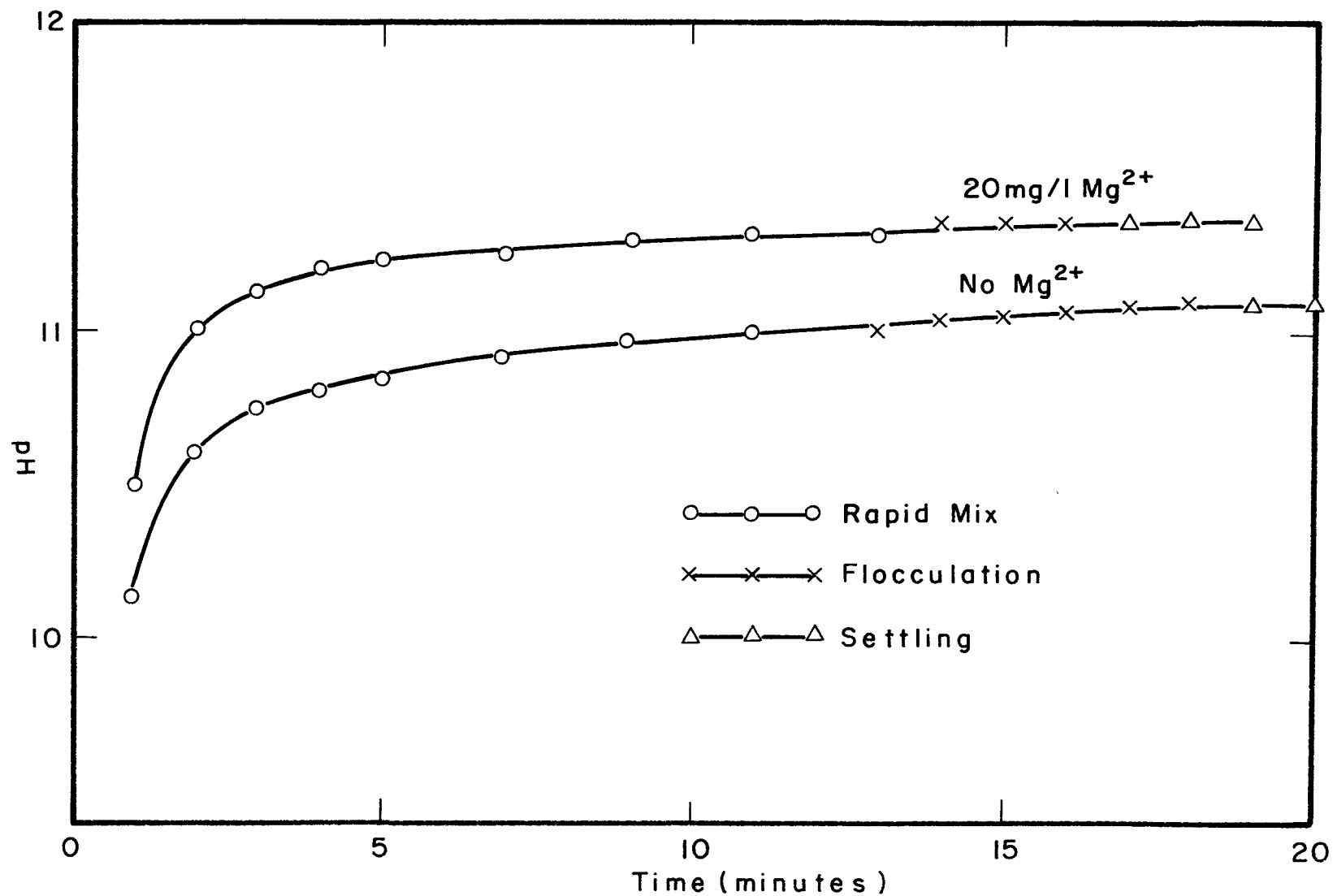


FIGURE 22 pH Vs. TIME FOR PPE AT NATURAL ALKALINITY (130mg/l CaCO_3).

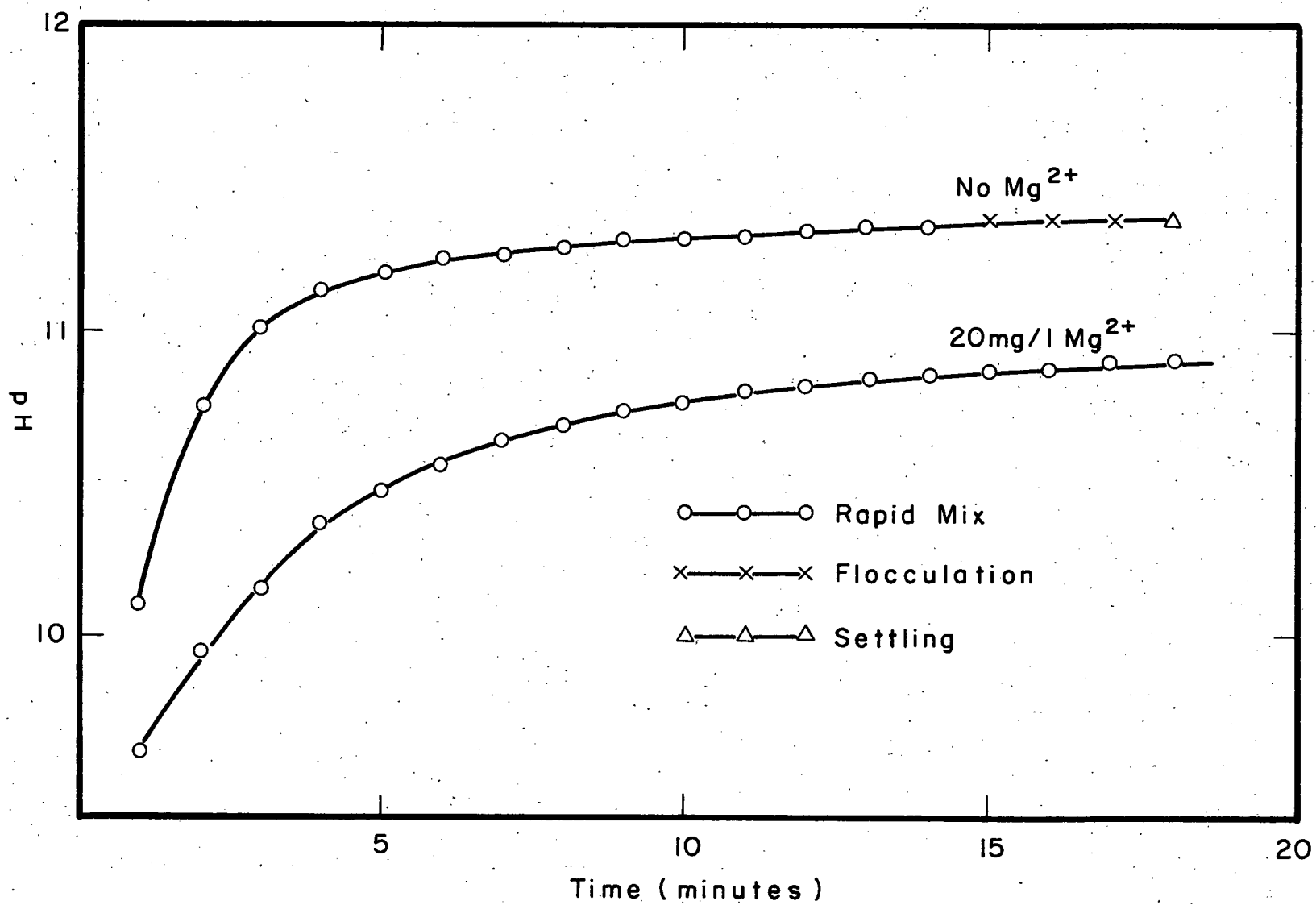


FIGURE 23 pH Vs. TIME FOR PPE AT ELEVATED ALKALINITY (200mg/l CaCO₃).

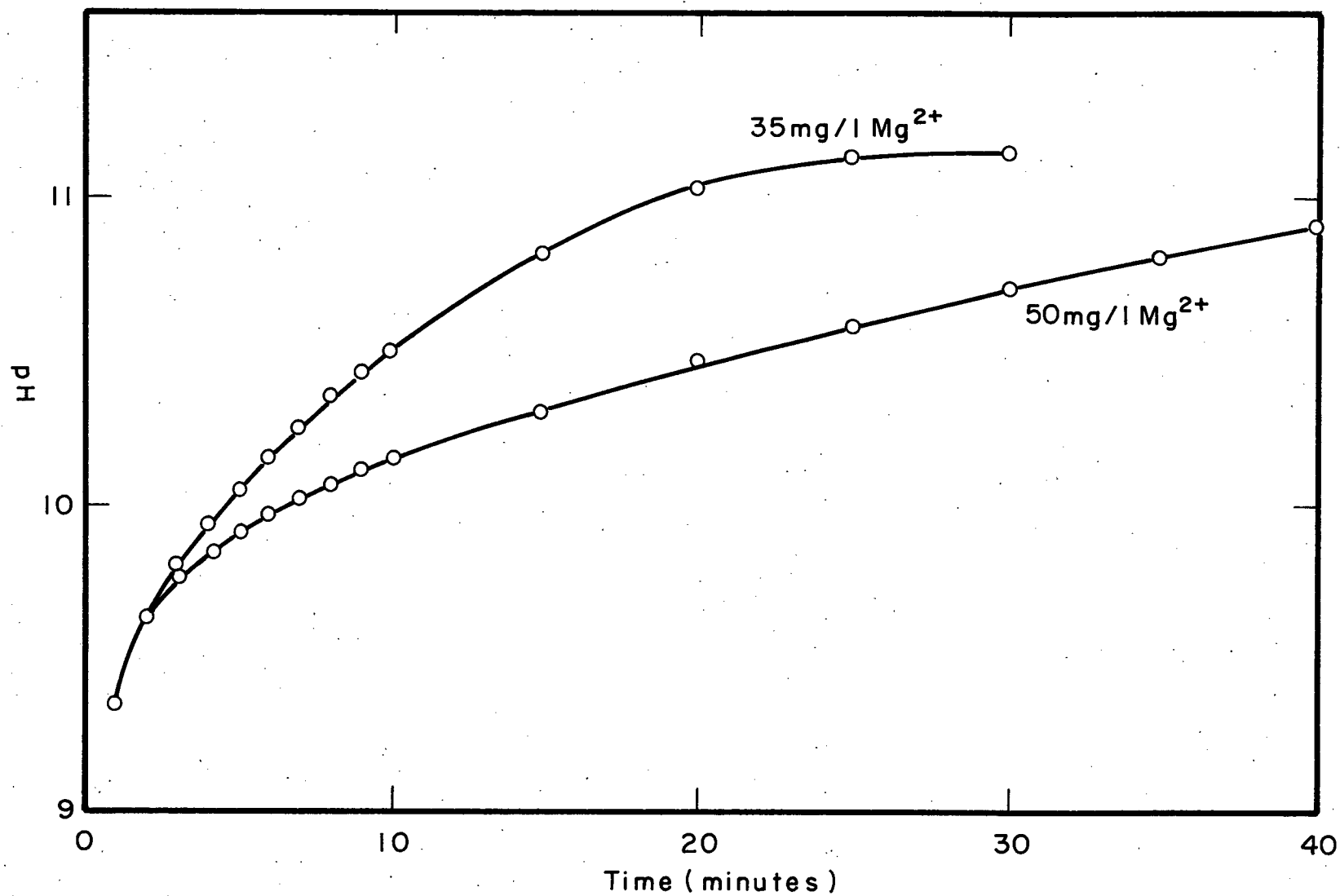


FIGURE 24 pH Vs. TIME FOR PPE AT ELEVATED ALKALINITY(192 mg/l as CaCO₃).

other trace metal removal mechanisms (i.e. entrapment, complexation) may require further reaction time. To test this theory, a series of Zn^{2+} removal tests were performed in which the overall reaction time (rapid mix plus flocculation) were varied between 15 and 60 minutes. Zinc at 5.0 mg/l was arbitrarily chosen as the heavy metal for the tests. The test was performed at the middle of the pH range (10.6) and Mg^{2+} dosage of 17 mg/l was chosen from previous test work. The results of the tests are plotted in Figure 25. The minimum time required to reduce the Zn^{2+} residual to its minimum range appeared to be 25 minutes. A 15 minute rapid mix time and a 10 minute flocculation time was therefore adopted for all future test work.

As previously mentioned, settling was completed from a visual point of view within 15 minutes therefore a settling time of 30 minutes was arbitrarily chosen.

In the initial test work a rapid mix time of 100 ± 5 rpm was used and due to the long pH stabilization times that were discovered it was felt that this speed would be suitable for future testing. A flocculation speed of 15-20 rpm was adopted on the recommendation of Rush (21). Settling was done at 0 rpm.

3. Dosage and Method of Mg^{2+} Addition

The generally accepted theory that magnesium must be added in its ionic form so that it precipitates "in situ" for optimum removal was tested. A series of experiments were performed using lime and magnesium in the form of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$. The results are shown in Table 20. The best removal is obtained when the coagulation is performed using lime and Mg^{2+} rather than lime and $\text{Mg}(\text{OH})_2$.

The magnesium was therefore added in the form of a 10^4 mg/l Mg^{2+} .

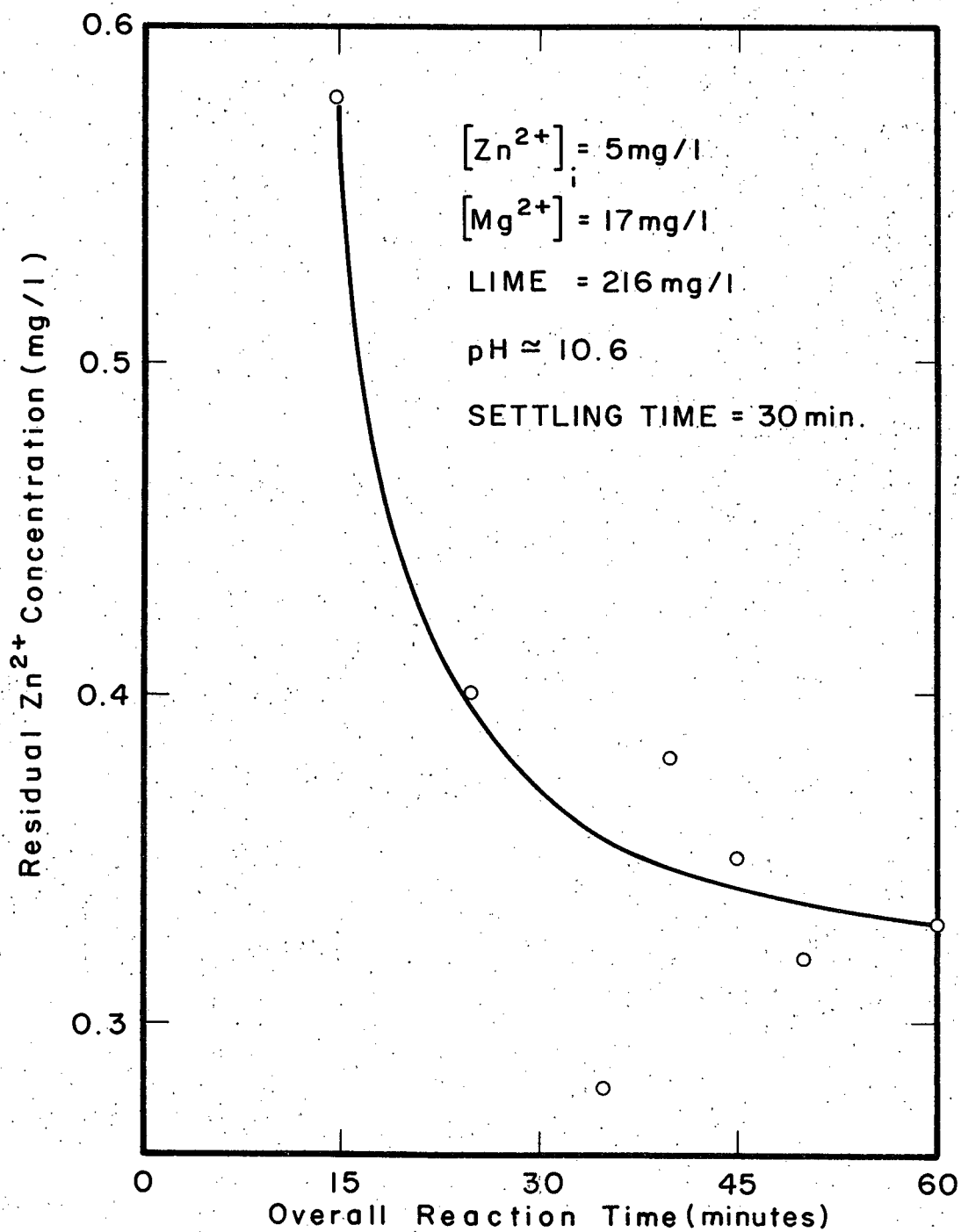


FIGURE 25 RESIDUAL Zn^{2+} CONCENTRATION Vs. OVERALL REACTION TIME (RAPID MIX+FLOCCULATION).

TABLE 20

A comparison of Heavy Metal Removals Using
Lime and $\text{Mg}(\text{OH})_2$ and Lime and Mg^{2+}

Trace Metal	% Removal (Unfiltered Data)		
	Lime Only	Lime and $\text{Mg}(\text{OH})_2$	Lime and Mg^{2+}
Cr	92.7	95.6	96.6
Cu	54	57.1	70
Ni	56	56.3	57
Zn	79	86.2	90

Initial Conditions

Initial metal concentration 2.6 mg/l (approx)

Lime Dosage 186 mg/l (average)

Mg^{2+} Dosage 17 mg/l

solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. On the recommendations of Rush (21), the Mg^{2+} addition was given a 1 minute rapid mix time in order to achieve dispersal, prior to the lime addition.

4. Dosage and Method of the Lime Addition

Initially, the lime addition was made using a 10 weight percent slurry of high purity reagent grade $\text{Ca}(\text{OH})_2$ in distilled water. This procedure gave poor reproducibility, presumably due to slurry settling, and was replaced by a dry reagent grade $\text{Ca}(\text{OH})_2$ addition. With the dry reagent grade $\text{Ca}(\text{OH})_2$ addition it was necessary to stir the test beaker for about 3 seconds with a glass rod immediately after the addition to prevent the $\text{Ca}(\text{OH})_2$ from floating on the surface.

5. Lime-Magnesium Coagulation Test Sequence

The preliminary test work was carried out to develop a coagulation procedure that would produce comparable results for the removal of five different heavy metals from municipal wastewater. The detailed test procedure consisted of the following procedure:

- 1) Every Monday morning during the test period, a sample of PPE was obtained from Annacis Island Sewage Treatment Plant and stored in the 3°C incubator.

- 2) For each run a set of 7 - 600 ml samples were measured out into 1 litre beakers using a 1 litre graduated cylinder. The samples were then warmed to $20-21^\circ\text{C}$ by placing them in the 35°C incubator for about $1\frac{1}{2}$ hours.

- 3) The samples were then spiked to the required initial metal ion concentrations using the heavy metal spike solutions.

- 4) For runs done at elevated alkalinity, the samples were then spiked with the alkalinity spike solution.

5) One of the samples was set aside for initial metal ion concentration(s) analysis.

6) One of the samples was then used to calculate the lime dosage. The sample was mixed at 100 rpm on a Phipps and Bird Laboratory stirrer and the pH was constantly monitored to 10.0, 10.7 or 11.4. The Ca(OH)_2 requirement was calculated and five doses were measured out.

7) The five remaining samples were stirred on the laboratory stirrer at 100 rpm for 1 minute to disperse the metal ion and the alkalinity spike.

8) With the stirrer off, the following additions of the Mg^{2+} solution were pipetted into the samples: 0.5 ml, 1 ml, 2 ml and 3 ml. These additions corresponded to 0, 8, 17, 33 and 50 mg/l Mg^{2+} respectively.

9) The samples were stirred for 1 minute at 100 rpm and then the Ca(OH)_2 addition was made.

10) The samples were then given a 15 minute rapid mix, a 10 minute flocculation and a 30 minute settle as previously discussed.

11) Since the final pH measurement and supernatant sampling took about 10 minutes, they were begun after 25 minutes settling. For all runs except those using Pb^{2+} , two 50 ml samples were pipetted from each beaker. To reduce contamination problems, the supernatant samples were taken in order of decreasing Mg^{2+} dosage. For the Pb^{2+} runs, two 100 ml samples were required as it was necessary to concentrate them four times by boiling.

12) One of the two supernatant samples was filtered through #2 Whatman filter paper.

13) The metal analysis was then performed by Atomic Absorption Spectroscopy as described in Section 5.2.2.

14) The heavy metal percent removals were then calculated using

the following formula:

$$\frac{[M^{n+}]_i - [M^{n+}]_f}{[M^{n+}]_i} \times 100$$

15) A completed data sheet is shown in Figure 26.

Object: Cu @ 5.0 mg/l; pH 10.7

Date: 20 July 1976

Run #: 1 Cu²⁺

Floc test:

Beaker	pH	Mg ⁺⁺
1	10.70	0
2	10.70	8
3	10.65	17
4	10.60	33
5	10.54	50

Start: 1:14

A-A Analysis: (810)

Sample	ABS	Conc	Removal
1 f		1.85	63
2		1.35	73
3		1.25	75
4		1.90	82
5		.85	83
1 unf		1.70	66
2		1.30	74
3		1.10	78
4		.85	83
5		.80	84
#6			5.0
#12			~0

Lime Dosage:

Initial wt	-	1.0376
Final wt	-	.9094
Addition	-	.1282

Remarks:

Cu²⁺ spike - 2.9 mlSample #12 - Acids only
in distilled waterSample #6 - Initial Cu²⁺

Alkalinity - 120-130 mg/l

Figure 26: Completed Data Sheet

APPENDIX B

COMPARISON OF EFFECTIVENESS AND COSTS OF

HIGH LIME TREATMENT (H.L.) vs

INTERMEDIATE LIME/Mg²⁺ TREATMENT (I.L./Mg²⁺)

Basis:

- (1) Comparison based on a 10 mgd plant with wastewater containing 2.5 mg/l of Cr³⁺, Cu²⁺, Pb²⁺ and Zn²⁺. Nickel has been eliminated because I.L./Mg²⁺ would not be considered as a possible treatment process for this metal.
- (2) Supernatants of the following quality would be obtained for the chemical dosages shown. The A-A and B-B Pollution Control objectives for municipal type wastewaters in B.C. have been shown for comparison.

	H.L. treatment (400 mg/l Ca(OH) ₂)	I.L./Mg ²⁺ treatment 220 mg/l Ca(OH) ₂ 33 mg/l Mg ²⁺	A-A	B-B
Cr ³⁺	.06	.10	.1	.3
Cu ²⁺	.38	.59	.2	.5
Pb ²⁺	.21	.14	.05	.10
Zn ²⁺	.26	.19	.5	5.0

- (3) Assume 90% Mg²⁺ recovery and recycle (Rush) and zero recycle of the lime due to heavy metal contamination.
- (4) Assume that if filtration is required (and this is very likely), that it will be required for both processes.

Treatment Comparison:

Process Parameters	H.L.	I.L./Mg ²⁺
Reaction pH	11.4	10.6
Sludge Volume (minus impurities)	400 mg/l	223 mg/l
Chlorination requirement	possibly not	yes
Chemical costs* (per day)	\$1200 (lime)	\$675 (lime) + \$100 (Mg ²⁺) = \$775
Costs not estimated	a) excess recarbonation costs for H.L. treatment. b) excess sludge handling costs for H.L. treatment.	
Miscellaneous	sludge settling for I.L./Mg ²⁺ may be a problem	

* Dow Chemical - MgCl₂ @ \$8.20/cwt (bulk)

Domtar - Lime @ \$62.50/ton (22 ton lots)

The above comparison indicates that I.L./Mg²⁺ treatment might be cheaper when treating identical waste streams to similar supernatant quality.