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ABSTRACT

I. REMOVAL OF CHROMIUM FROM A HIGHLY CONTAMINATED
SOIL/SLAG MATRIX BY SOIL WASHING AT LOW pH

II. REMOVAL OF CHROMIUM FROM IMPREGNATED CLAY
MATRICES BY SOIL WASHING AT LOW pH

by

Erez Gotlieb

Section I. Chromium is a major soil contaminant of industrial sites in New Jersey, as well as in many of the Superfund sites throughout the United States. Removal of chromium by soil/slag washing with low pH sulfuric acid solutions is described. The extraction parameters are acid concentration, contact time, temperature, solvent/soil ratio, and acid type. The effect of two-stage extraction is discussed.

Soil/slag washing with sulfuric acid concentrations of 2% weight:volume (units are g/ml. This concentration is approximately equal to 0.4 N) at 75:1 v:w solvent/soil ratios yielded chromium extraction efficiencies of 95%, but 50% of the soil matrix was dissolved. Residual chromium concentrations up to 4000 ppm were observed from soil/slag originally containing 21,000 ppm Cr. Residual chromium is postulated to consist of immobilized chromium fixed to the soil/slag matrix, whereas all surface adsorbed and free

chromium is removed.

A study of kinetics revealed that extraction at 95°C is completed within five minutes. The effect of temperature is such that chromium removal is improved by a factor of almost two when extraction is carried out at boiling temperature rather than at room temperature. At a 75:1 v:w solvent/soil ratio, peak extraction is achieved at a lower concentration than at 25:1 and matrix weight loss is greater. In addition, at 75:1, 95% chromium extraction is achievable, but at 25:1, the maximum chromium removal levels off at 80%. No significant difference is detected in the extractive capabilities of the different mineral acids tested: sulfuric, hydrochloric, and nitric acids. Sulfuric acid is a suitable choice as extractant because of its lower cost and other advantages, such as its reduced corrosivity.

Section II. Chromium is a major soil contaminant of industrial sites in New Jersey, as well as in many of the Superfund sites throughout the United States. Removal of chromium by soil washing of chromium(III) impregnated Kaolin, Montmorillonite, and Bentonite clays with low pH acid solutions is described. The extraction parameters studied are acid concentration and kinetics.

Soil washing with sulfuric acid concentrations as high as 3.3% weight:volume (0.67 N) at 75:1 v:w solvent/soil ratios yielded chromium extraction efficiencies between 87 -

99% for the three clay types when extracted for one hour at 95°C. Residual chromium concentrations were 80 ppm for Kaolin, 40 ppm for Montmorillonite, and 500 ppm for Bentonite. Initial chromium concentrations were 650 ppm for Kaolin, 4800 ppm for Montmorillonite, and 17,000 ppm for Bentonite. A study of extraction kinetics showed that the bulk of the chromium extraction at 2% w:v sulfuric acid concentration at 95°C was completed within 20 minutes.

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CHAPTER 1: INTRODUCTION

The adverse effects of chromium on human health have been well documented. In 1827, Cumin identified skin ulcerations and dermatitis in British dye workers handling potassium dichromate. Later, MacKenzie noted perforations along the nasal septa of workers exposed to potassium dichromate. During World War II, a linkage between inhalation of chromium dust and lung cancer was made.¹

Most adverse health effects due to exposure to chromium are associated with Cr(VI), or hexavalent chromium. Cr(VI) has been identified as being mutagenic and is a suspected carcinogen. Its harmfulness has been attributed to its potential as an oxidant. The EPA has designated chromium a priority toxic pollutant and a hazardous waste constituent. Cr(III), or trivalent chromium, can be metabolized in the human body and, therefore, poses less of a risk than does Cr(VI).^{1,2}

Routes of entry are by ingestion, inhalation, or through the skin.² The maximum concentration limit (MCL) set for total chromium in drinking water by the Safe Drinking Water Act (40 CFR 141.11) is 50 ppb.³

Chromium contamination of soil poses a risk to the general welfare by its potential for leaching into groundwater supplies. The various remediation options available include stabilization and land application, and biological

and chemical treatments.

Rinaldo-Lee et al.⁴ report the successful landfilling of waste containing water soluble Cr(VI) on an existing soda ash (Na_2CO_3) wastebed. The majority of water soluble chromium is adsorbed within the top few meters of the total depth of the bed. The remainder of mobile chromium reduces to Cr(III) and is then precipitated and stabilized in the bottom layers of the bed.

Cr(VI) can be reduced to the less harmful Cr(III) in-situ in the presence of a ferrous ion (Fe^{2+}) reductant such as ferrous sulfate. The resultant Cr(III) concentrations are stabilized using physical methods for prevention of leaching.⁵

The land application of chromium-laden tannery wastes has been investigated by Dreiss.⁶ Sludges containing 21,000 to 55,000 ppm of chromium were applied to an experimental test site in California. Less than 0.1% of the total applied chromium migrated beyond the most heavily loaded plot of land over the course of an entire field season. The small amounts of chromium which traveled beneath the top 45 cm of soil were taken up by the soil and, thus, removed from solution.

Although stabilization and land application methods have shown effectiveness in controlling the leaching of chromium, they are only temporary measures and not solutions. Unless the contaminant is removed, its migration is

always a concern.

Biological treatments of chromium contamination are available. Removal rates of 70 - 90% for Cr(III) and 20% for Cr(VI) have been achieved using modified Hussman's activated sludge units. Chromium removal at various sites ranged between 5% to 88%.⁷ The weakness of biological treatment in removing hexavalent chromium, however, limits its applicability. Detoxification of chromium contamination by biological methods requires chemical reduction of Cr(VI) to Cr(III) as a preliminary step. Biological treatments are also limited by the sensitive requirements of microorganisms.

The most promising technologies for chromium decontamination are chemical treatments. Bartlett and Kimble⁸ experimented with $\text{Na}_4\text{P}_2\text{O}_7$, pH 4.8 NH_4OAc , 0.1 M NaF, and 1 M HCl by adding them to soils with varying (up to 10%) organic content that were previously impregnated with trivalent chromium. At solvent/soil ratios of 5:1 and contact times of 15 minutes each, only $\text{Na}_4\text{P}_2\text{O}_7$ and HCl remove significant amounts of Cr(III). HCl was shown to be capable of removing both inorganic and organic complexes of chromium, while $\text{Na}_4\text{P}_2\text{O}_7$ is only effective at removal of organic complexes. Extraction efficiencies of 1 - 4.5% for the NH_4OAc and 0.3 - 4.1% of the original chromium content for NaF were reported while removal between 3 and 65% was achieved for $\text{Na}_4\text{P}_2\text{O}_7$. The most successful attempt at chromium removal, however, was produced by extraction with 1 M HCl, in which 10 - 75%

was successfully extracted.

Grove and Ellis⁹ added Cr(III), Cr(VI), and sludge Cr to Rubicon sand, Morley clay loam, and limed (for pH adjustent) Morley clay loam. They attempted extraction with consecutive applications of H₂O, 1 M NH₄Cl, 0.1 M CuSO₄, 0.3 M (NH₄)₂C₂O₄, and citrate-dithionite-bicarbonate. Water soluble chromium was removed in the initial water wash step. The majority of subsequent chromium removal was accomplished in the oxalate ((NH₄)₂C₂O₄) and dithionite-citrate stages.

Hsieh, Raghu, Liskowitz, and Grow¹⁰ studied the efficiency of chromium extraction by soil washing with sodium hypochlorite and EDTA. Ten successive cycles of washing with sodium hypochlorite yielded 46% removal, while an extraction of 58% chromium was achieved by washing with nine cycles of EDTA solution. R. Peters and H. Elliott¹¹ reported removal efficiencies between 40 - 60% for heavy metals such as chromium and lead using EDTA as a complexing agent.

Kilau and Shah¹² reported the possibility of chromium leaching from land secured industrial waste slags under acidic conditions. Chromium that is stabilized is likely to leach under acidic conditions when the CaO/SiO₂ ratio is greater than 2.0 depending upon Mg content. Since industrial effluents from operations involving chromium are often limed, the likelihood of such circumstances occuring is high.

The conditions described by Kilau and Shah that produce

the undesirable effects of chromium leaching may, however, be utilized to achieve chromium removal by acid extraction. Tan¹³ treated a range of clay and sand media impregnated with chromium with acid solutions and achieved mixed results. The strongest acid concentrations used had pH 1.5.

The conclusions drawn from literature are that stabilization and land application approaches may be successful in containing chromium contaminated waste. They do not, however, remove the contamination. Biological methods of decontamination are limited because hexavalent chromium is toxic to microorganisms. Biological treatments are limited in their range of applications. Chemical treatment of chromium contaminated waste shows great potential. A number of different chemical treatments have been studied, but an effective method for chromium removal has not been found. Promising results have been achieved with acid extraction, thus warranting further study. The difficulties encountered in the removal of chromium from soil may be overcome by high concentration acid extraction.

The objectives of the study were to evaluate several different extraction parameters associated with the removal of chromium from soil by soil washing at low pH. The extraction parameters are acid concentration, contact time, temperature, solvent/soil ratio, acid type, and the effects of two-stage extraction.

All the tests were preceded by a water wash step to

remove water soluble hexavalent chromium. Water washed samples were oven dried overnight at 85°C. A series of tests were run to examine the various parameters. For each test, the parameter being studied was varied as all the others were kept constant. A set of standard operating conditions was developed to ensure that maximum extraction was taking place. These standard conditions were applicable for parameters held constant. The standard conditions were: a contact time of one hour, solvent/soil ratio of 75:1 v:w (ml/g), temperature at 95°C, and a sulfuric acid concentration of 2% w:v (0.4 N).

After each extraction run was completed, both the extract and the residue were analyzed for total chromium by atomic absorption spectroscopy. Extraction efficiencies were calculated as the fraction of chromium extracted from total chromium. Total chromium was determined by material balance.

We found that chromium extraction efficiencies in excess of 95% are obtainable from highly contaminated (21,000 ppm of chromium) soil/slag samples using sulfuric acid concentrations of 2% w:v (0.4 N) and higher at the standard operating conditions of one hour, 95°C, and 75:1 solvent/soil ratio.

CHAPTER 2: SOIL/SLAG HANDLING

A sample containing approximately 9.5 kg of chromium-laden industrial slag mixed with soil was received via the New Jersey Department of Environmental Protection from a contaminated site in Kearny, New Jersey as a representative soil material. This material will be referred to as "soil/slag" because it has the unique properties of industrial slag and cannot be properly termed soil.

Upon receipt from the NJDEP, the soil/slag was dry-screened through a 1/8" pore stainless steel screen to remove oversize particles. Undersize material was placed in a 5 gallon polyethylene pail and mixed to achieve homogeneity. Oversize particles constituted 1.15 kg of the total received sample. Typical total chromium concentration in the slag was 21,000 ppm, or 2.1%, by weight, as determined by atomic absorption analysis following acid digestion and dilution.

CHAPTER 3: SOIL/SLAG CHARACTERISTICS

Total organic extractables were determined by soxhlet extraction analysis using dichloromethane as a solvent. Particle size analysis was done on a dried 200 g sample in an analytical sieve shaker with standard Tyler wiremesh screen Nos. 12, 20, 60, 100, 200, 325.

Bulk density was determined by measuring the volume of a given dried sample in a graduated cylinder and weighing the contents of the cylinder. Void density represents the actual density of the slag/soil. The void density was arrived at by filling the graduated cylinder containing the sample to a certain volume with water and weighing the sample in water. The water fills the air pockets within the soil/slag and, since the density of water is known to be 1.0, the real density of the soil/slag is obtainable.

The H₂O fraction was determined by placing a sample of material in an oven to dry overnight at 85°C. The weight loss due to drying was used to calculate the H₂O fraction. The characteristics of the soil/slag sample studied are shown in Table 1.

Tests were run to determine the various extraction efficiencies under different conditions. Initial determinations were selection of mineral acid, total organic extractables and particle size analysis.

TABLE 1 - Soil/slag Characteristics

Particle Size Analysis

Sieve #	>12	12	20	60	100	200	325
Wt. Percent	0.02	1.4	18.7	12.3	20.0	13.0	34.5

Bulk density	1.12 g/ml (dry)
Real density	2.24 g/ml (dry)
H ₂ O fraction	30.6 %
Silicates and Al ₂ O ₃	n.a.
Chromium concentration	21,000 ppm
Total organic extractables	0.1%

The chromium extraction efficiencies of three mineral acids (sulfuric, hydrochloric, and nitric) were studied. The results indicated that extraction efficiency is not dependent upon which of the three acid types is used. The selection of sulfuric acid as the extractant was based upon several considerations discussed below.

After the selection of sulfuric acid as the extractant, the following parameters were analyzed: acid concentration, extraction kinetics, the effect of temperature, solvent/soil ratio, and two-stage extraction. In each case, the effect upon extraction efficiency and matrix dissolution was assessed.

CHAPTER 4: EXPERIMENTAL PROCEDURE

Prior to acid extraction, soil/slag samples of 20 g each were water washed at a 75:1 v:w water/soil ratio at 95°C for one hour as a preliminary step to remove hexavalent chromium and then dried overnight in an oven at 75°C. Acid solutions were prepared from stock solutions of 0.5% and 10% sulfuric acid:water (weight:volume), which were diluted from an original 40% w:v concentrated (95.0 - 98.0%) sulfuric acid stock solution in which the sulfuric acid was weighed on a semi-analytical scale.

Acid concentrations were measured as weight:volume ratios because the pH range at which analysis was done is very low and no accurate method of pH measurement at that range was available. Even estimation of pH is uncertain due to the unknown extent of H^+ dissociation from H_2SO_4 at high acid concentration. Sulfuric acid has a pK_1 of approximately -3 and a pK_2 of 1.96.¹⁴ Consequently, dissociation of H^+ from H_2SO_4 is incomplete. Concentrated sulfuric acid has a normality of approximately 36. At 10% w:v, sulfuric acid has a calculated normality of 1.95 - 2.0 N, depending upon the sulfuric acid:water purity.

Solutions containing soil/slag samples of 1 - 3 g (dry basis) each were heated to 95°C for one hour and filtered under vacuum. The residue cake was rinsed with an equal volume of extracting solution to remove residual acid and

chromium. Unless otherwise noted, solvent/soil ratios were 75:1 v:w (ml/g). When acid concentration was not used as a variable, it was maintained at 2% weight to volume (0.4 N) extracting solution. The sample residue was digested after overnight drying at 85°C and both the filter extract and digestate were analyzed for total chromium.

Digestion was done alternately by EPA Method 3050 for heavy metal digestion¹⁵ and by microwave digestion. Tests indicated that the two approaches produced results which were within $\pm 1\%$ of each other. Microwave digestion of samples weighing 1 g or less was carried out in vessels containing 20 ml of 50% Fisher Scientific trace metal grade concentrated (70.1%) nitric acid/water v:v for 30 minutes at 100 psi pressure. Digestion residue and digestate were separated by gravity filtration. The residue cake was rinsed with approximately 100 ml of fresh 50% nitric acid to remove residual chromium. Additional tests were run to determine the extent to which digestion is complete by double and triple digestions.

Samples were analyzed for total chromium using a Thermal Jarrel Ash model 1200 atomic absorption flame spectrometer at a wavelength of 357.9 nm with an acetylene/air flame and Smith-Hieftje background correction. Hexavalent chromium standards at 1, 3, 5, and 10 ppm were used to construct calibration curves for quantitative chromium concentration determinations. Standards were prepared by volumetrically

diluting a purchased (from J.T. Baker) 1000 ppm ammonium dichromate standard solution.

Extraction efficiencies were calculated by mass balance; chromium content was determined as the sum of chromium removed by extraction and chromium removed in digestion. Extraction efficiency is the mass of chromium removed by digestion divided by total chromium removed.

No differentiation was made between hexavalent chromium and trivalent chromium in the study. Hexavalent chromium has a high water solubility and is, therefore, less likely than trivalent chromium to be found in soil media after water extraction. It was assumed that the majority of hexavalent chromium was removed in the water wash and the acid extraction step was devoted to removal of trivalent chromium.

The initial study on the effect of acid concentration on extraction efficiency was repeated to ensure the reliability of the results. Otherwise, reported results are based on a single run, unless spillage occurred or inconsistent data was generated, in which case, the run was also repeated.

CHAPTER 5: RESULTS AND DISCUSSION

5.1 Acid Strength

Chromium extraction as a function of sulfuric acid concentration is shown in Figure 1. The extraction parameters of time, temperature, and solvent/soil ratio are held constant at one hour, 95°C, and 75:1 v:w, respectively. There is a steep increase in extraction efficiency between 0.5% (0.1 N) and 2% (0.4 N) acid concentration and efficiency levels out at 95% removal at concentrations higher than 2%. No appreciable improvement in extraction occurs at acid concentrations higher than 2.0% at a 75:1 solvent/soil ratio.

5.2 Matrix Solubility

There is considerable dissolution of sample matrix as a result of acid extraction. Figure 2 illustrates that matrix weight loss is nearly linear as a function of acid concentration. This phenomenon is a result of the unique character of the soil/slag matrix analyzed. The slag matrix is typical of chromium refining waste streams in which lime and other basic salts are commonly used. Lime is used to modify physical characteristics during processing and to enhance oxidation.¹⁶ During acid extraction, there is an evolution of CO₂ gases that accounts in part for the weight loss. Preliminary results show that there is no significant weight loss

FIGURE 1: EFFECT OF ACID CONCENTRATION ON EXTRACTION EFFICIENCY

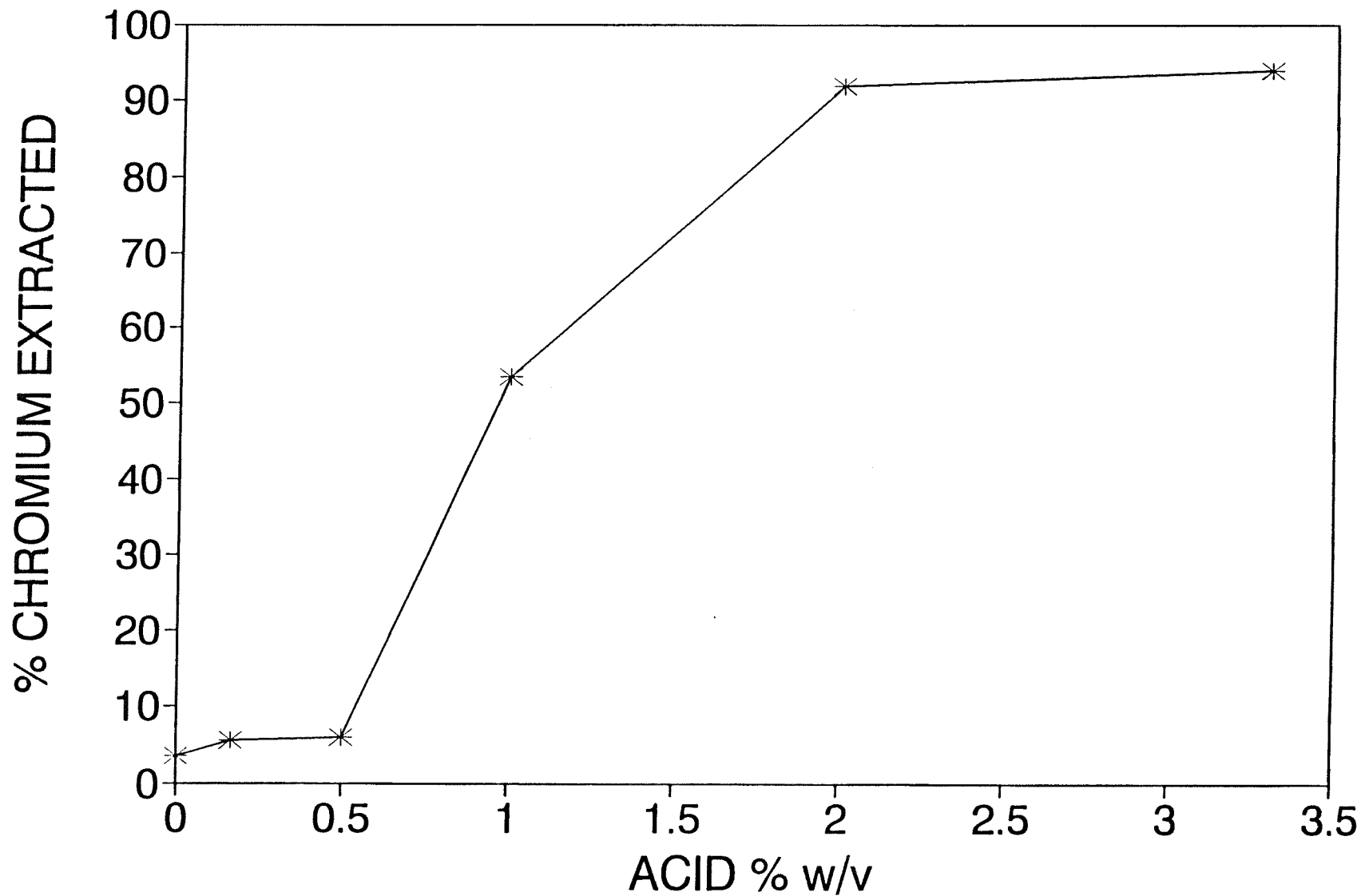
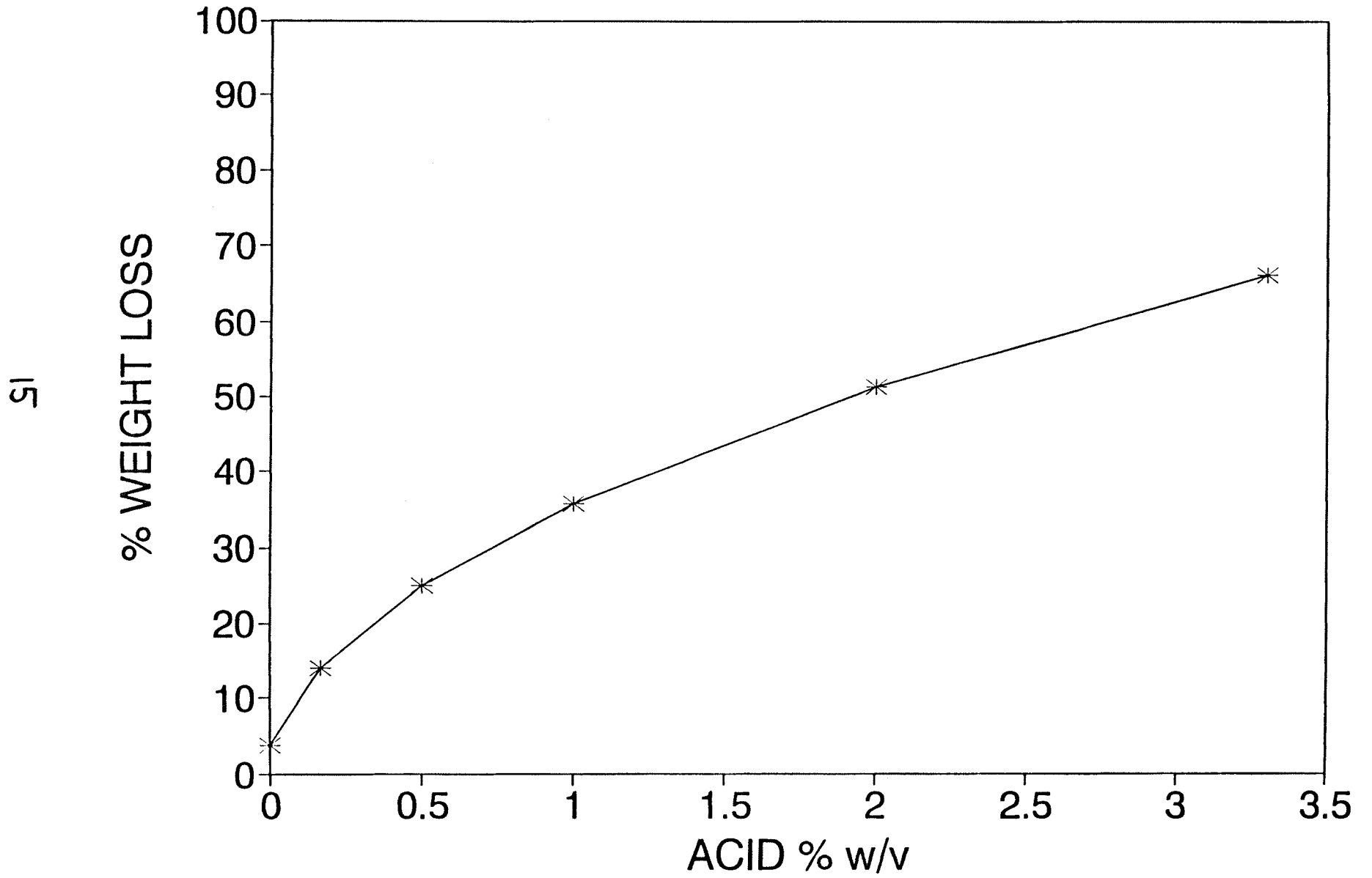


FIGURE 2: MATRIX WEIGHT LOSS



present when extraction is carried out on more common or normal soil samples.

5.3 Kinetics

A study of extraction kinetics indicates that extraction with 2% sulfuric acid concentration at 95°C is complete within 5 minutes, as seen in Figure 3. No analysis was done for durations less than 5 minutes and, thus, it seems that extraction proceeds to completion upon mixing and that contact time is a limitation only as a function of mixing.

5.4 Temperature

The effect of temperature on extraction efficiency was assessed. The results are shown in Figure 4. The curve shown in Figure 4 is meant to be illustrative only and does not represent a speculation of the true form of the curve. A comparison of efficiencies at three different sulfuric acid concentrations (extracted for one hour) at boiling temperature (100°C) vs. room temperature (20°C) shows that extraction increases by a factor of 1.8 when it is carried out at boiling temperature over room temperature. Thus, it is evident that thermodynamics plays a role in acid extraction.

FIGURE 3: CHROMIUM
EXTRACTION KINETICS

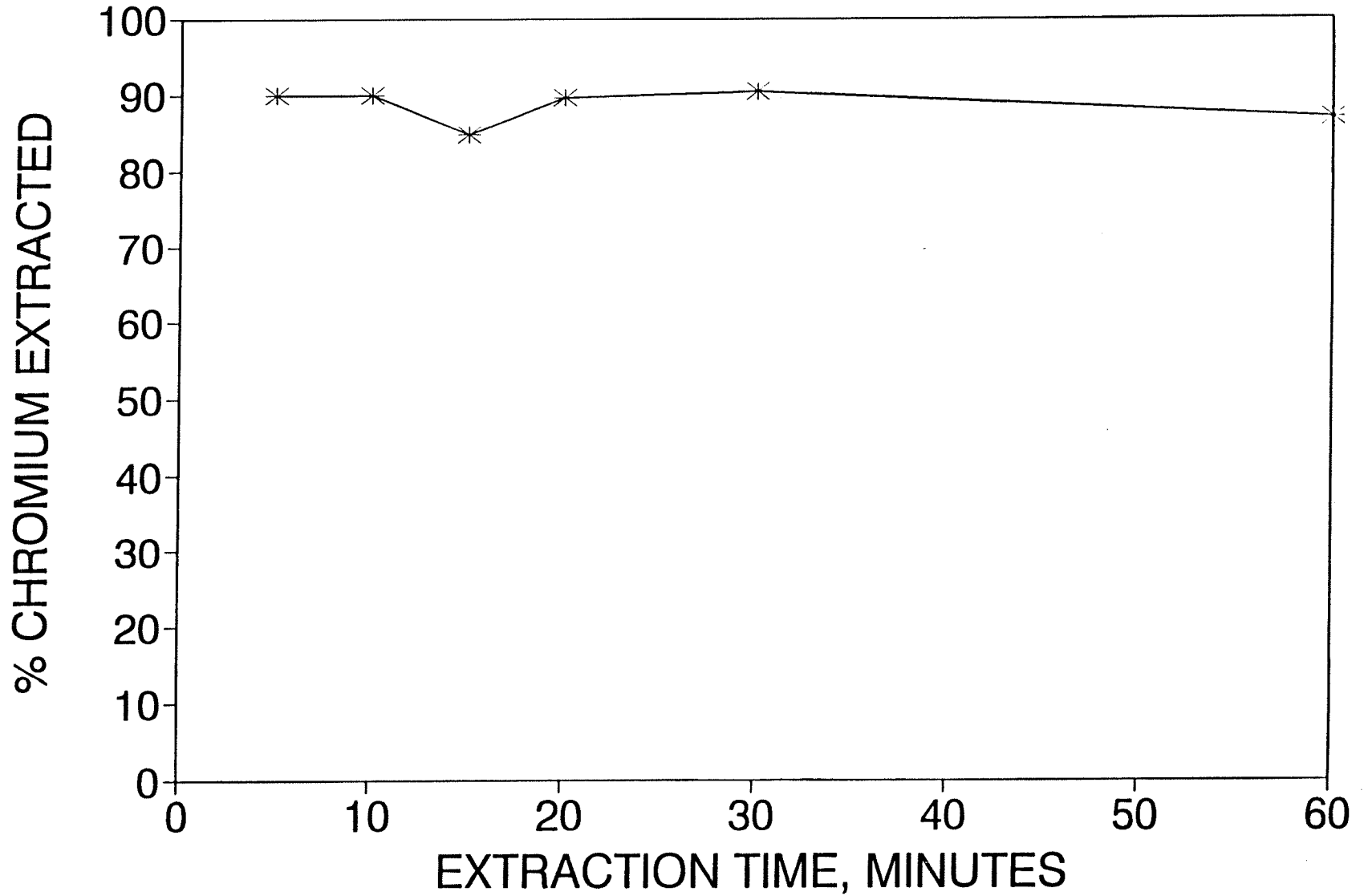
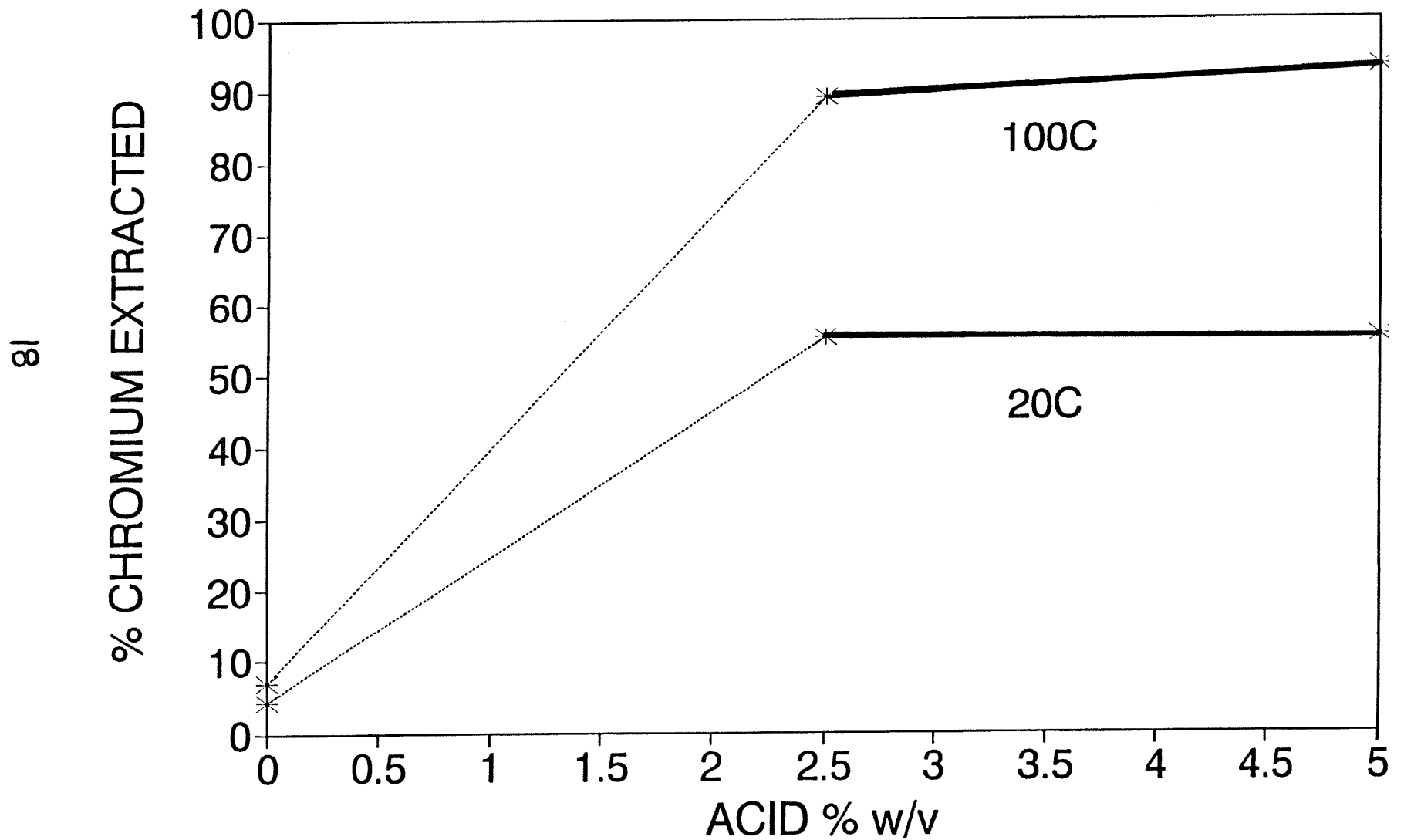


FIGURE 4: EFFECT OF TEMPERATURE
ON EXTRACTION EFFICIENCY



5.5 Solvent/soil Ratio

The results of a study detailing the effects of solvent/soil ratio on extraction efficiency and matrix weight loss are presented in Figures 5 and 6. At a 75:1 solvent/soil ratio, peak extraction is achieved at a lower concentration than at 25:1 and matrix weight loss is greater, as expected. Tests indicate, however, that at 75:1, 95% extraction is achievable, but at 25:1, the maximum chromium removal levels off at 80%.

5.6 Acid Type

Selection of sulfuric acid as the extractant is based upon its lower cost relative to other mineral acids along with other advantages. Market prices for industrial grade mineral acids as of December 9, 1991, are \$75/ton for concentrated sulfuric acid and \$55-110/ton and \$175-185/ton, respectively, for hydrochloric acid and nitric acid.¹⁷ Since the sulfuric acid is approximately three times more concentrated than hydrochloric acid and 50% more concentrated than nitric acid, sulfuric acid has less than one-third the cost of the other two mineral acids. Other mineral acids, such as phosphoric acid, are even more expensive.

Hydrochloric and nitric acids also present the problems of noxious vapor emissions and corrosion. Extraction with nitric acid is further complicated by the explosive potential of organic nitrate byproducts. Sulfuric acid does not

FIGURE 5: EFFECT OF SOLVENT/SOIL RATIO ON EXTRACTION EFFICIENCY

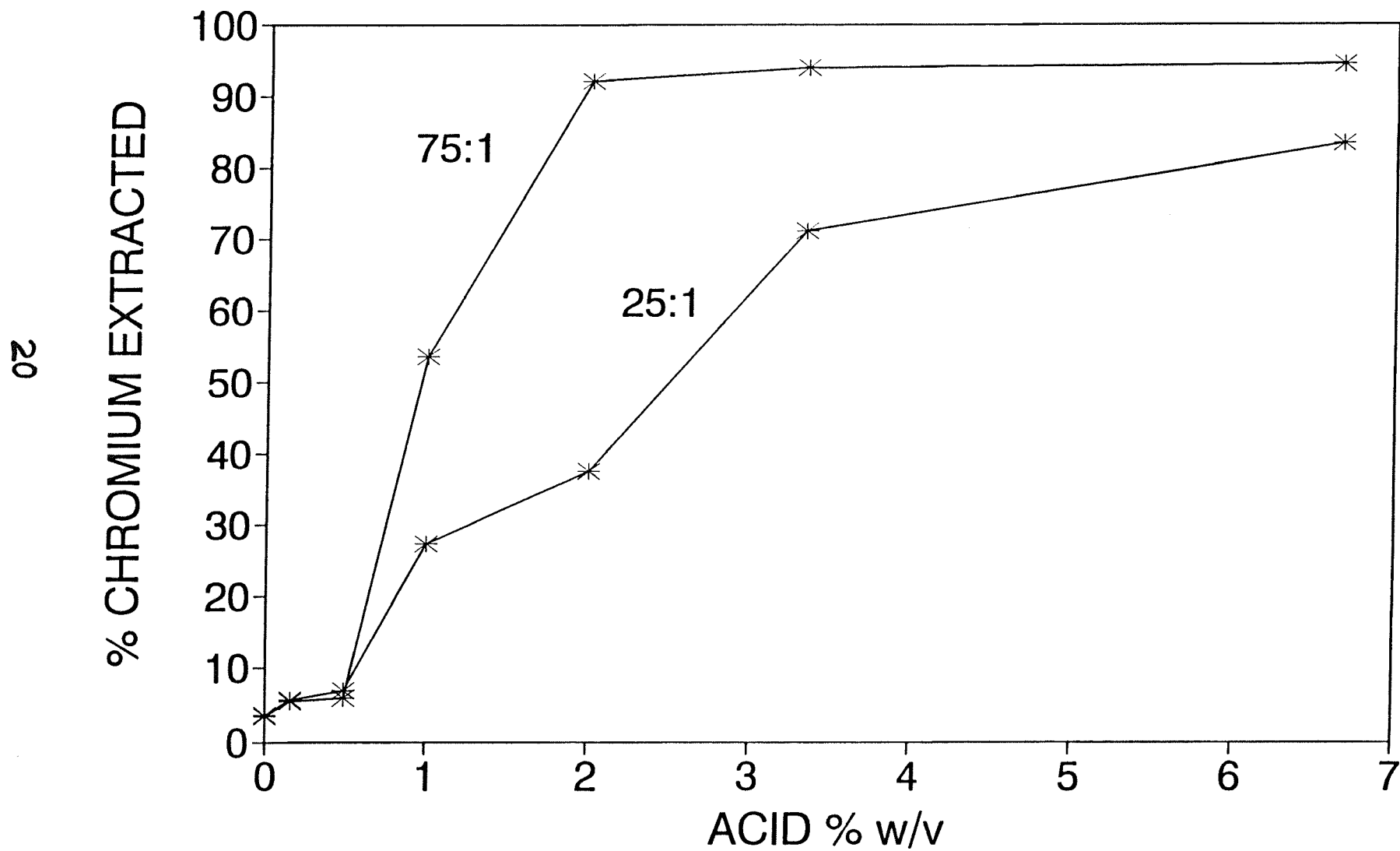
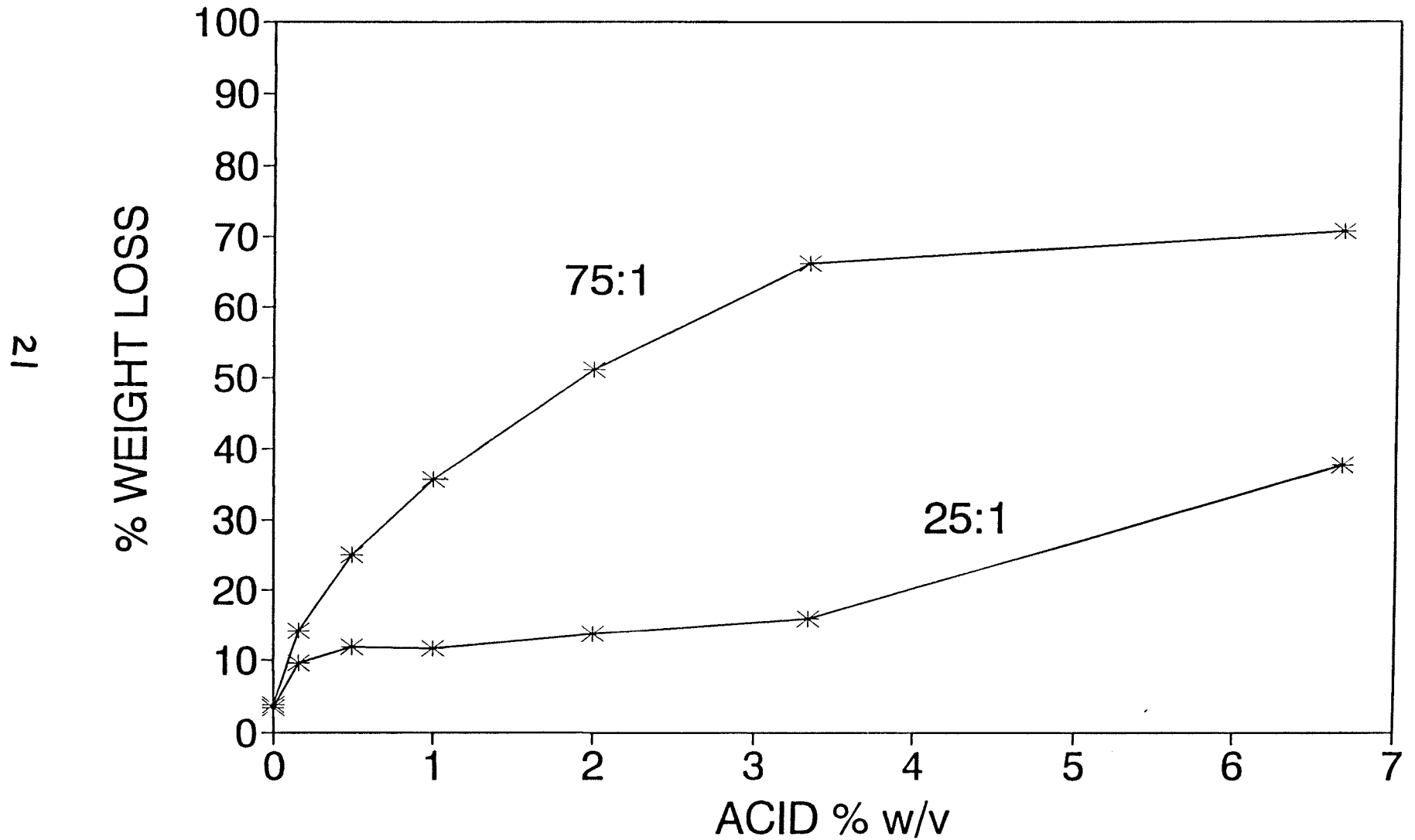


FIGURE 6: EFFECT OF SOLVENT/SOIL RATIO ON MATRIX WEIGHT LOSS



produce fumes, is better for handling and is less corrosive, and can be neutralized by precipitation with lime. A comparison of the effects of three mineral acid types on acid extraction indicated that differences are negligible. These results are shown in Figure 7. In a large scale decontamination of chromium in soil, material costs are likely to be significant and, therefore, the usage of sulfuric acid constitutes a considerable savings in cost.

5.7 Residual Chromium

Although 95% extraction is achieved, a residual concentration of 4000 ppm remains in the slag after extraction. The initial chromium contamination is 21,000 ppm and matrix weight loss can be as high as 65%. Analysis of two-stage extraction (Figure 8) shows that a second extraction following acid washes of 2% sulfuric acid concentration or higher yields little additional chromium removal.

Dragun¹⁸ distinguishes between trace metals adsorbed to soil and metals fixed to soil. The residual 4000 ppm of chromium in this soil/slag matrix appears to be fixed to the soil, meaning that the chromium is incorporated into the soil structure. As such, it is possible to remove the chromium only through complete dissolution of the soil medium. Dragun reports that the native soil concentration of chromium ranges between 5.0 - 3000 ppm, with extreme limits of 0.5 - 10,000 ppm. Because the samples analyzed in this

FIGURE 7: EFFECT OF ACID TYPE ON EXTRACTION EFFICIENCY

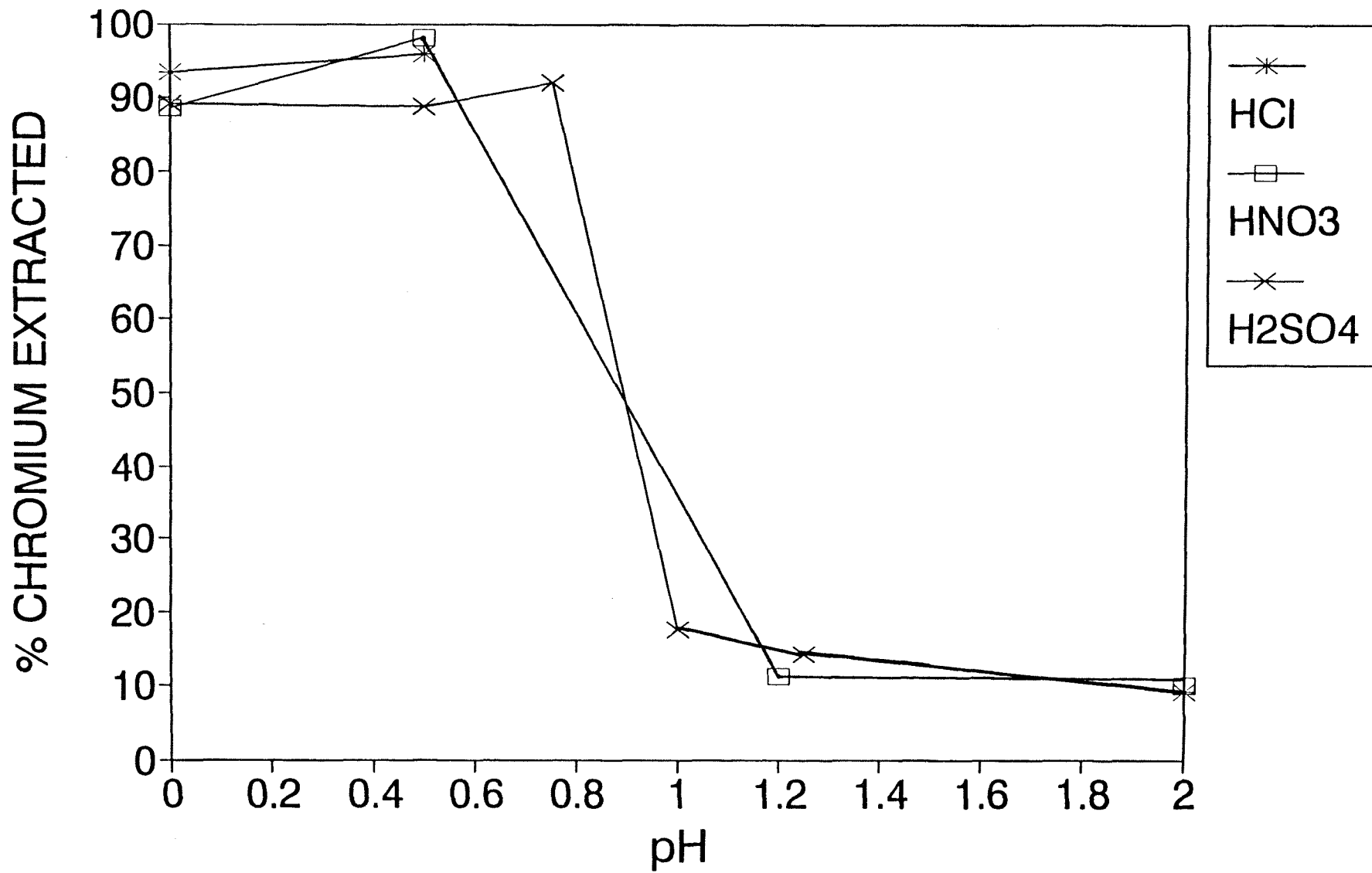
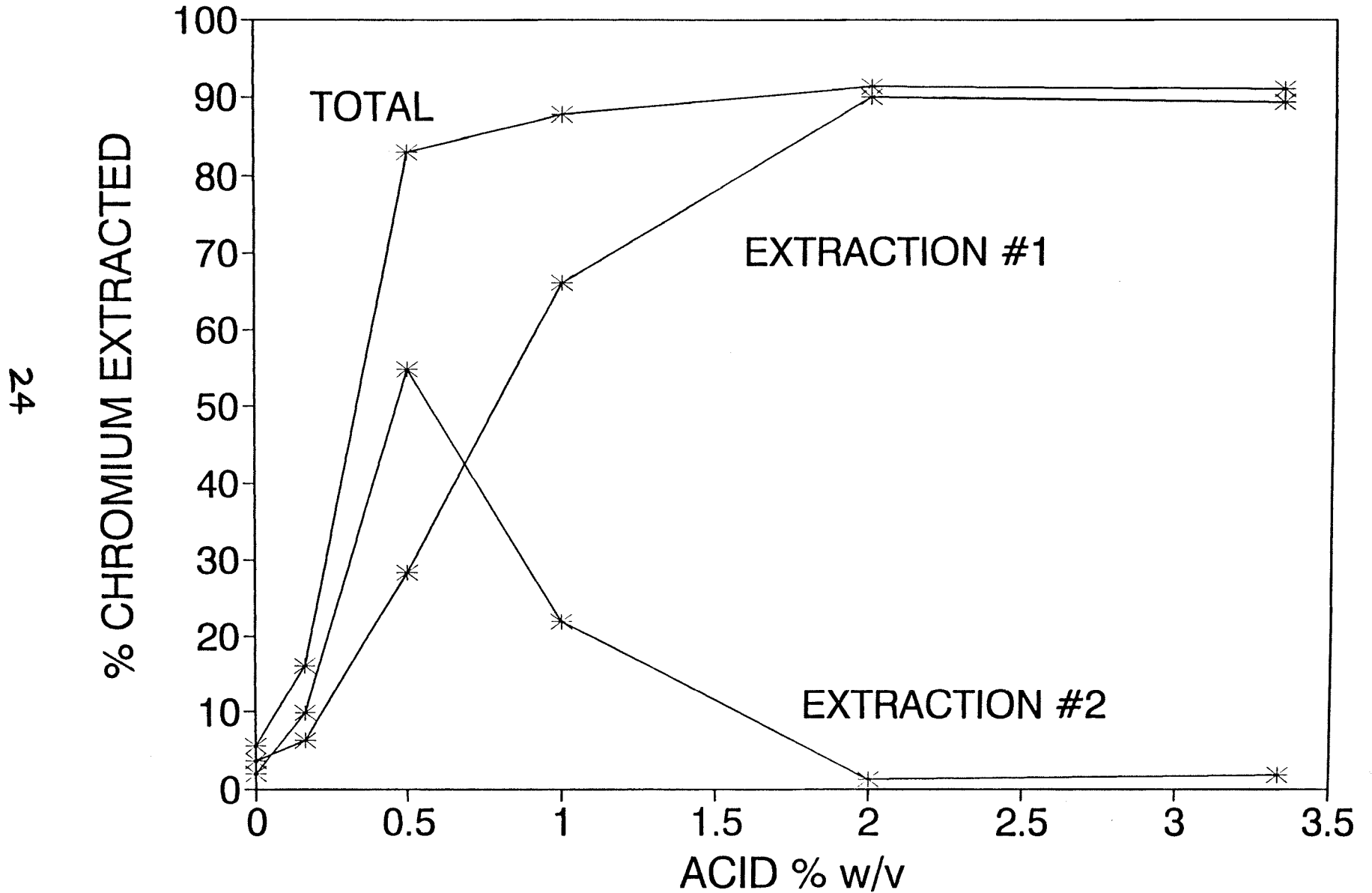


FIGURE 8: SECOND STAGE EXTRACTION



study contained actual industrial chromium waste slag mixed with soil, the native chromium concentration of this soil/slag matrix is likely to be very high, perhaps approaching the extreme limit of 10,000 ppm.

Acid digestion for analysis (EPA Method 3050) is supposed to remove all traces of soil chromium, yet residual concentrations of chromium were detected even after multiple digestions. The results of this study are shown in Table 2. Four consecutive digestions were carried out on two 5 g samples. Each digestion revealed removal of chromium accompanied by matrix weight loss, indicating the liberation of fixed chromium simultaneous with dissolution of the slag matrix.

One might expect that the ratio of chromium removed to mass decrease of the soil/slag matrix upon digestion would indicate the concentration of fixed chromium in the sample matrix. The lack of consistency in the results shown in Table 2 points to the nonuniformity of fixed chromium in the sample matrix. It is noted that the small sample size (5 grams starting material) yields little matrix dissolution by the third and fourth digestions so accuracy is compromised. These results show that the chromium content that is fixed to the soil/slag matrix ranges between 1,000 to 15,000 ppm.

It seems clear that adsorbed chromium is almost completely removed by 2% acid extraction at 95°C for five minutes and any chromium remaining on the soil/slag is fixed

TABLE 2: Multiple Acid Digestion of Two Samples for Analysis

Sample A Run #	Chromium Detected,mg	Sample Dissolution,mg	<u>mg (Cr removed)</u> mg(mass decreased)
1	74.875	3406	2.20%
2	1.243	411	0.302%
3	1.056	76	1.39%
4	0.534	61	0.875%
Avg. 2-4			0.9%

Sample B Run #	Chromium Detected,mg	Sample Dissolution,mg	<u>mg (Cr removed)</u> mg(mass decreased)
1	71.250	2825	2.52%
2	0.940	723	0.130%
3	0.446	374	0.119%
4	0.427	75	0.570%
Avg. 2-4			0.26%

chromium that is not likely to leach out into a natural aqueous medium. Thus, chromium removal by 2% acid concentration significantly reduces the risks associated with chromium contamination to aquifers or other streams.

CHAPTER 6: CONCLUSIONS

Acid extraction of the soil/slag samples yielded 95% chromium extraction efficiency, but 50% matrix weight loss. All leachable chromium is believed to be removed. The matrix weight loss is accounted for by the unique medium of the slag samples analyzed which contain abnormally high concentrations of lime and other basic salts that react with the acid and form carbon dioxide which is released to the atmosphere. We have studied the extraction parameters of acid concentration, contact time, temperature, solvent/soil ratio, acid type, and the effects of two-stage extraction.

We have found that there is a steep increase in chromium extraction efficiency between 0.5% (0.1 N) and 2% (0.4 N) sulfuric acid concentration and efficiency levels out at 95% removal at concentrations higher than 2%. Extraction is completed within five minutes and extraction is almost twice as efficient when carried out at boiling temperature rather than at room temperature. At a 75:1 v:w solvent/soil ratio, peak extraction is achieved at a lower concentration than at 25:1 and matrix weight loss is greater. Additionally, at 75:1, 95% chromium extraction is achievable, but at 25:1, the maximum chromium removal levels off at 80%. No significant difference is detected in the extractive capabilities of the different mineral acids tested, sulfuric, hydrochloric, and nitric acids. Sulfuric acid is a suitable choice as extractant because of its reduced cost and other advantages.

WORKS CITED

1. W. Rinehart, S. Gad, "Current Concepts in Occupational Health: Metals - Chromium" Am. Ind. Hyg. Assoc. J., 47(11):696-699(1986).
2. M. Sittig, Handbook of Toxic and Hazardous Chemicals and Carcinogens, Noyes Publ., Park Ridge, NJ, 2nd Ed., 1985, pp. 243-247.
3. "Environmental Reporter" The Bureau of National Affairs, 7/19/91, p. 132:0105.
4. M. Rinaldo-Lee, J. Hagarman, A. Diefendorf, "Siting of a Metals Industry Landfill on Abandoned Soda Ash Waste Beds" Hazardous and Industrial Waste Management and Testing: Third Symposium, ASTM STP 851, 1984, pp 171-192.
5. D. Arnold, et al., "Remediation of Subsurface Chromium Contamination Utilizing Above Ground and In-situ Methods" presented at Technology Transfer Conference on Environmental Cleanup, The Society of American Military Engineers, 13-15 Nov 1991, Denver, CO.
6. S. Dreiss, "Chromium Migration Through Sludge-Treated Soils" Ground Water, v.24, No.3, pp. 312-321.
7. J. Lester, "Biological Treatment" Heavy Metals in Wastewater and Sludge Treatment Processes, Volume II, CRC Press, Boca Raton, 1987, pp. 21-23.
8. R. Bartlett, J. Kimble, "Behavior of Chromium in Soils: I. Trivalent Forms" J. Environ. Qual., v.5, 1976, pp. 379-386.
9. J. Grove, B. Ellis, "Extractable Chromium as Related to Soil pH and Applied Chromium" Soil Sci. Soc. Am. J., v.44, 1980, pp. 238-242.
10. H. Hsieh, D. Raghu, J. Liskowitz, J. Grow, "Soil Washing Techniques for Removal of Chromium Contaminants from Soil" Proceedings of the Twenty-first Mid-Atlantic Industrial Waste Conference, ed. C. Cole, D. Long, pp. 651-660.
11. R. Peters, H. Elliott, American Institute of Chemical Engineers, 1991 Annual Meeting, Nov. 17-22, 1991, Los Angeles, CA.

12. H. Kilau, I. Shah, "Chromium-bearing Waste Slag: Evaluation of Leachability When Exposed to Simulated Acid Precipitation" Hazardous and Industrial Waste Management and Testing: Third Symposium, ASTM STP 851, 1984, pp. 61-80.
13. K.Tan, "Adsorption and Desorption of Chromium on Clayey Soils" New Jersey Inst. of Tech., MSc. Thesis, 1989.
14. Lange's Handbook of Chemistry, ed. J. Dean, 12th Edition, McGraw-Hill, New York, 1979.
15. "Test Methods for Evaluating Solid Waste" United States Environmental Protection Agency, SW-846, Nov. 1986, 3rd Edition.
16. M. Udy, Chromium: Chemistry of Chromium and its Compounds, v.1, Reinhold, New York, 1956, p.266.
17. "Chemical Marketing Reporter" December 9, 1991.
18. J. Dragun, The Soil Chemistry of Hazardous Materials, Hazardous Materials Control Research Institute, Silver Spring, Maryland, 1988, pp. 75-76.

II. REMOVAL OF CHROMIUM FROM IMPREGNATED CLAY
MATRICES BY SOIL WASHING AT LOW pH

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SECTION II. REMOVAL OF CHROMIUM FROM IMPREGNATED CLAY
MATRICES BY SOIL WASHING AT LOW pH

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CHAPTER 1: INTRODUCTION

The adverse effects of chromium on human health have been well documented. In 1827, Cumin identified skin ulcerations and dermatitis in British dye workers handling potassium dichromate. Later, MacKenzie noted perforations along the nasal septa of workers exposed to potassium dichromate. During World War II, a linkage between inhalation of chromium dust and lung cancer was made.¹

Most adverse health effects due to exposure to chromium are associated with Cr(VI), or hexavalent chromium. Cr(VI) has been identified as being mutagenic and is a suspected carcinogen. Its harmfulness has been attributed to its potential as an oxidant. The EPA has designated chromium a priority toxic pollutant and a hazardous waste constituent. Cr(III), or trivalent chromium, can be metabolized in the human body and, therefore, poses less of a risk than does Cr(VI).^{1,2}

Routes of entry are by ingestion, inhalation, or through the skin.² The maximum concentration limit (MCL) set for total chromium in drinking water by the Safe Drinking Water Act (40 CFR 141.11) is 50 ppb.³

Chromium contamination of soil poses a risk to the general welfare by its potential for leaching into groundwater supplies. The various remediation options available include stabilization and land application, and biological

and chemical treatments.

Rinaldo-Lee et al.⁴ report the successful landfilling of waste containing water soluble Cr(VI) on an existing soda ash (Na_2CO_3) wastebed. The majority of water soluble chromium is adsorbed within the top few meters of the total depth of the bed. The remainder of mobile chromium reduces to Cr(III) and is then precipitated and stabilized in the bottom layers of the bed.

Cr(VI) can be reduced to the less harmful Cr(III) in-situ in the presence of a ferrous ion (Fe^{2+}) reductant such as ferrous sulfate. The resultant Cr(III) concentrations are stabilized using physical methods for prevention of leaching.⁵

The land application of chromium-laden tannery wastes has been investigated by Dreiss.⁶ Sludges containing 21,000 to 55,000 ppm of chromium were applied to an experimental test site in California. Less than 0.1% of the total applied chromium migrated beyond the most heavily loaded plot of land over the course of an entire field season. The small amounts of chromium which traveled beneath the top 45 cm of soil were taken up by the soil and, thus, removed from solution.

Although stabilization and land application methods have shown effectiveness in controlling the leaching of chromium, they are only temporary measures and not solutions. Unless the contaminant is removed, its migration is

always a concern.

Biological treatments of chromium contamination are available. Removal rates of 70 - 90% for Cr(III) and 20% for Cr(VI) have been achieved using modified Hussman's activated sludge units. Chromium removal at various sites ranged between 5% to 88%.⁷ The weakness of biological treatment in removing hexavalent chromium, however, limits its applicability. Detoxification of chromium contamination by biological methods requires chemical reduction of Cr(VI) to Cr(III) as a preliminary step. Biological treatments are also limited by the sensitive requirements of microorganisms.

The most promising technologies for chromium decontamination are chemical treatments. Bartlett and Kimble⁸ experimented with $\text{Na}_4\text{P}_2\text{O}_7$, pH 4.8 NH_4OAc , 0.1 M NaF, and 1 M HCl by adding them to soils with varying (up to 10%) organic content that were previously impregnated with trivalent chromium. At solvent/soil ratios of 5:1 and contact times of 15 minutes each, only $\text{Na}_4\text{P}_2\text{O}_7$ and HCl remove significant amounts of Cr(III). HCl was shown to be capable of removing both inorganic and organic complexes of chromium, while $\text{Na}_4\text{P}_2\text{O}_7$ is only effective at removal of organic complexes. Extraction efficiencies of 1 - 4.5% for the NH_4OAc and 0.3 - 4.1% of the original chromium content for NaF were reported while removal between 3 and 65% was achieved for $\text{Na}_4\text{P}_2\text{O}_7$. The most successful attempt at chromium removal, however, was produced by extraction with 1 M HCl, in which 10 - 75%

was successfully extracted.

Grove and Ellis⁹ added Cr(III), Cr(VI), and sludge Cr to Rubicon sand, Morley clay loam, and limed (for pH adjustment) Morley clay loam. They attempted extraction with consecutive applications of H₂O, 1 M NH₄Cl, 0.1 M CuSO₄, 0.3 M (NH₄)₂C₂O₄, and citrate-dithionite-bicarbonate. Water soluble chromium was removed in the initial water wash step. The majority of subsequent chromium removal was accomplished in the oxalate ((NH₄)₂C₂O₄) and dithionite-citrate stages.

Hsieh, Raghu, Liskowitz, and Grow¹⁰ studied the efficiency of chromium extraction by soil washing with sodium hypochlorite and EDTA. Ten successive cycles of washing with sodium hypochlorite yielded 46% removal, while an extraction of 58% chromium was achieved by washing with nine cycles of EDTA solution. R. Peters and H. Elliott¹¹ reported removal efficiencies between 40 - 60% for heavy metals such as chromium and lead using EDTA as a complexing agent.

Kilau and Shah¹² reported the possibility of chromium leaching from land secured industrial waste slags under acidic conditions. Chromium that is stabilized is likely to leach under acidic conditions when the CaO/SiO₂ ratio is greater than 2.0 depending upon Mg content. Since industrial effluents from operations involving chromium are often limed, the likelihood of such circumstances occurring is high.

The conditions described by Kilau and Shah that produce

the undesirable effects of chromium leaching may, however, be utilized to achieve chromium removal by acid extraction. Tan¹³ treated a range of clay and sand media impregnated with chromium with acid solutions and achieved mixed results. The strongest acid concentrations used had pH 1.5.

The conclusions drawn from literature are that stabilization and land application approaches may be successful in containing chromium contaminated waste. They do not, however, remove the contamination. Biological methods of decontamination are limited because hexavalent chromium is toxic to microorganisms. Biological treatments are limited in their range of applications. Chemical treatment of chromium contaminated waste shows great potential. A number of different chemical treatments have been studied, but an effective method for chromium removal has not been found. Promising results have been achieved with acid extraction, thus warranting further study. The difficulties encountered in the removal of chromium from soil may be overcome by high concentration acid extraction.

The objectives of the study were to evaluate the effects of sulfuric acid concentration and kinetics on chromium extraction efficiency in removing previously impregnated Cr(III) from Kaolin, Montmorillonite, and Bentonite clay samples. The range of sulfuric acid concentrations studied was 0.17 - 3.3% w:v (0.03 N - 0.67 N) and the results compared with extraction by a deionized water wash. Extraction

parameters maintained constant throughout the study were contact time (one hour), temperature (95°C), and solvent/soil ratio (75:1 v:w). The effect of kinetics was studied by measuring extraction efficiencies and residual chromium concentrations of 2% w:v (0.4 N) sulfuric acid concentrations at 95°C for contact times ranging between 10 and 60 minutes.

After each extraction run was completed, both the extract and the residue were analyzed for total chromium by atomic absorption spectroscopy. Extraction efficiencies were calculated as the fraction of chromium extracted from total chromium. Total chromium was determined by material balance.

Sulfuric acid extraction at 75:1 v:w solvent/soil ratios yielded chromium extraction efficiencies between 87 - 99% for the three clay types. Residual chromium concentrations were 80 ppm for Kaolin, 40 ppm for Montmorillonite, and 500 ppm for Bentonite. Initial chromium concentrations were 650 ppm for Kaolin, 4800 ppm for Montmorillonite, and 17,000 ppm for Bentonite. The majority of the extraction was completed within 20 minutes.

CHAPTER 2: EXPERIMENTAL PROCEDURE

Acid solutions of 0.17, 0.5, 1.0, 2.0, and 3.3% w:v were prepared from a stock solution of 10% sulfuric acid:water (weight:volume, in g/ml), which was prepared by dissolving 100.022 g of concentrated (95.0 - 98.0%) sulfuric acid in 1 L of deionized water. The sulfuric acid was weighed on a semi-analytical scale.

Acid concentrations were measured as weight:volume ratios because the pH range at which analysis was done is very low and no accurate method of pH measurement at that range was available. Even estimation of pH is uncertain due to the unknown extent of H^+ dissociation from H_2SO_4 at high acid concentration. Sulfuric acid has a pK_1 of approximately -3 and a pK_2 of 1.96.¹⁴ Consequently, dissociation of H^+ from H_2SO_4 is incomplete. Concentrated sulfuric acid has a normality of approximately 36. At 10% w:v, sulfuric acid has a calculated normality of 1.95 - 2.0 N, depending upon the sulfuric acid:water purity.

For the determination of extraction as a function of acid concentration, solutions containing impregnated clay samples of 1 g (dry basis) each with an acid solvent/soil ratio of 75:1 v:w were heated to 95°C for one hour with magnetic stirring at 300 rpm. Solid-liquid separation following extraction presented a challenge because the clays form suspensions in water. Bentonite was most difficult to

separate. Separation was accomplished by using a combination of gravity filtration, settling and decantation, and centrifugation. Centrifugation was carried out in 10 ml tubes at 4000 rpm for 7.5 minutes. Samples were rinsed with 25 ml of fresh solution and deionized water to remove extracted chromium left on the residue cake. The sample residue was digested after overnight drying and the filter extract and digestate were analyzed for total chromium.

The role of kinetics in extraction was studied under similar conditions. The extractant used throughout the kinetics studies was 2% w:v (0.4 N) sulfuric acid. Different samples having contact times of 10, 20, 30, and 60 minutes were extracted.

Digestion of extraction residue for analysis was done by microwave digestion. Previous tests indicated that microwave digestion produces results similar to those achieved using EPA Method 3050¹⁵ for heavy metal digestion (within $\pm 1\%$). Microwave digestion of samples weighing 1 g or less was carried out in vessels containing 20 ml of 50% Fisher Scientific trace metal grade concentrated (70.1%) nitric acid/water v:v for 30 minutes at 100 psi pressure. Digestion residue and digestate were separated by gravity filtration. The residue cake was rinsed with approximately 100 ml of fresh 50% nitric acid to remove residual chromium.

Samples were analyzed for total chromium using a Thermal Jarrel Ash model 1200 atomic absorption flame spectrome-

ter at a wavelength of 357.9 nm with an acetylene/air flame and Smith-Hieftje background correction. Hexavalent chromium standards at 1, 3, 5, and 10 ppm were used to construct calibration curves for quantitative chromium concentration determinations. Standards were prepared by volumetrically diluting a purchased (from J.T. Baker) 1000 ppm ammonium dichromate standard solution.

Extraction efficiencies were calculated by mass balance; chromium content was determined as the sum of chromium removed by extraction and chromium removed in digestion. Extraction efficiency is the mass of chromium removed by washing divided by total chromium removed.

CHAPTER 3: IMPREGNATION

The Kaolin [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$], Montmorillonite, and Bentonite clay types were purchased from the Aldrich Chemical Co. and impregnated with chromium by rinsing with chromium(III) nitrate solution, followed by filtration and oven drying. The Montmorillonite is of the K-10 type and has a surface area of 220-270 m^2/g and a bulk density of 300-370 g/l .

20 g samples of the three types of clay were mixed with 500 ppm Cr(III) solution at a solution/soil ratio of 100:1 for 18 hours for chromium impregnation. Samples were oven dried overnight. The chromium solution was prepared using $\text{Cr}(\text{NO}_3)_3$ dissolved in deionized water. Impregnation was aided by magnetic stirring at 600 rpm. The Kaolin sample was separated from the chromium solution by vacuum filtration, while the Bentonite and Montmorillonite samples were separated by settling and decantation. Each sample was given two water rinses to remove excess chromium solution from the cake. Bentonite has a strong affinity for water and also adsorbs the most chromium, while Kaolin adsorbs the least chromium. The extent of chromium adsorption is summarized in Table 1.

Table 1: Adsorption of Cr(III) on clay types

Clay Type	Cr(III) Adsorption, ppm
Kaolin	650
Montmorillonite	4800
Bentonite	17000

CHAPTER 4: DISCUSSION

4.1 Acid Strength

Chromium extraction as a function of acid concentration for the three clay types studied are shown in Figures 1, 2, and 3. Less than 0.1% of total adsorbed chromium is extracted by deionized water wash. When acid solutions are used, a steep increase in extraction efficiency is observed. Beyond a certain acid concentration, extraction efficiency is not appreciably improved by increasing acid concentration.

A maximum of 88% extraction was achieved by acid washing of chromium impregnated Kaolin. Because Kaolin adsorption of chromium is limited, acid extraction is successful in reducing residual chromium in the clay to 80 ppm, which is very low. Peak extraction is reached at 1% w:v acid concentration, while an extraction efficiency of 73% is achievable at 0.17% acid concentration.

Cr(III) may be extracted from Montmorillonite to a residual concentration of 40 ppm by washing with 3.3% w:v sulfuric acid. Removal at this concentration is in excess of 99% of the initial chromium level. Removal efficiencies in excess of 90%, however, are attainable at a concentration of 0.5% sulfuric acid.

Bentonite clay adsorbs Cr(III) to a greater extent than the other clay types studied. Acid extraction is successful in reducing the residual chromium concentration to only 500

Figure 1: Extraction as function of concentration for Kaolin

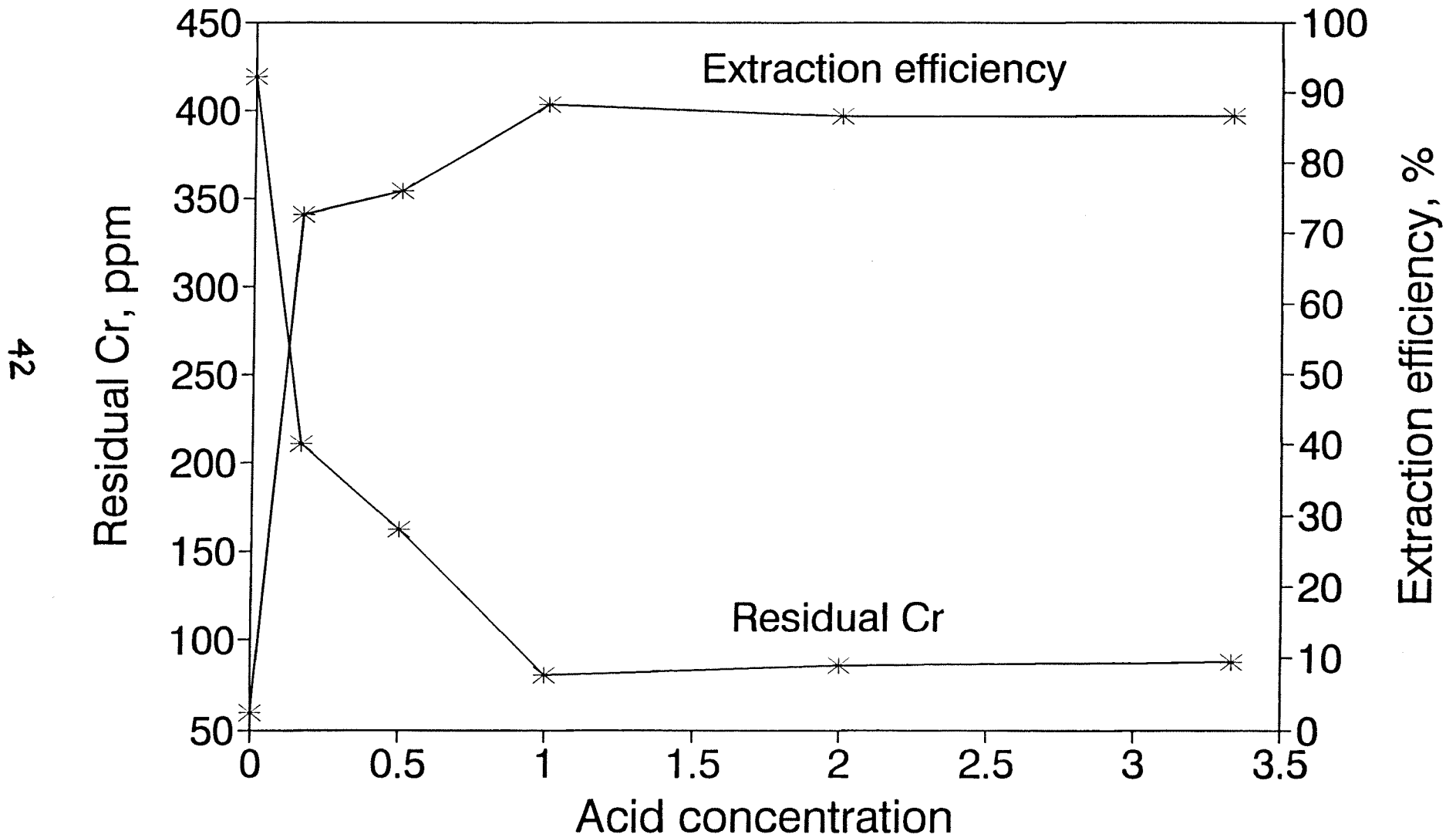


Figure 2: Extraction as function of concentration for Montmorillonite

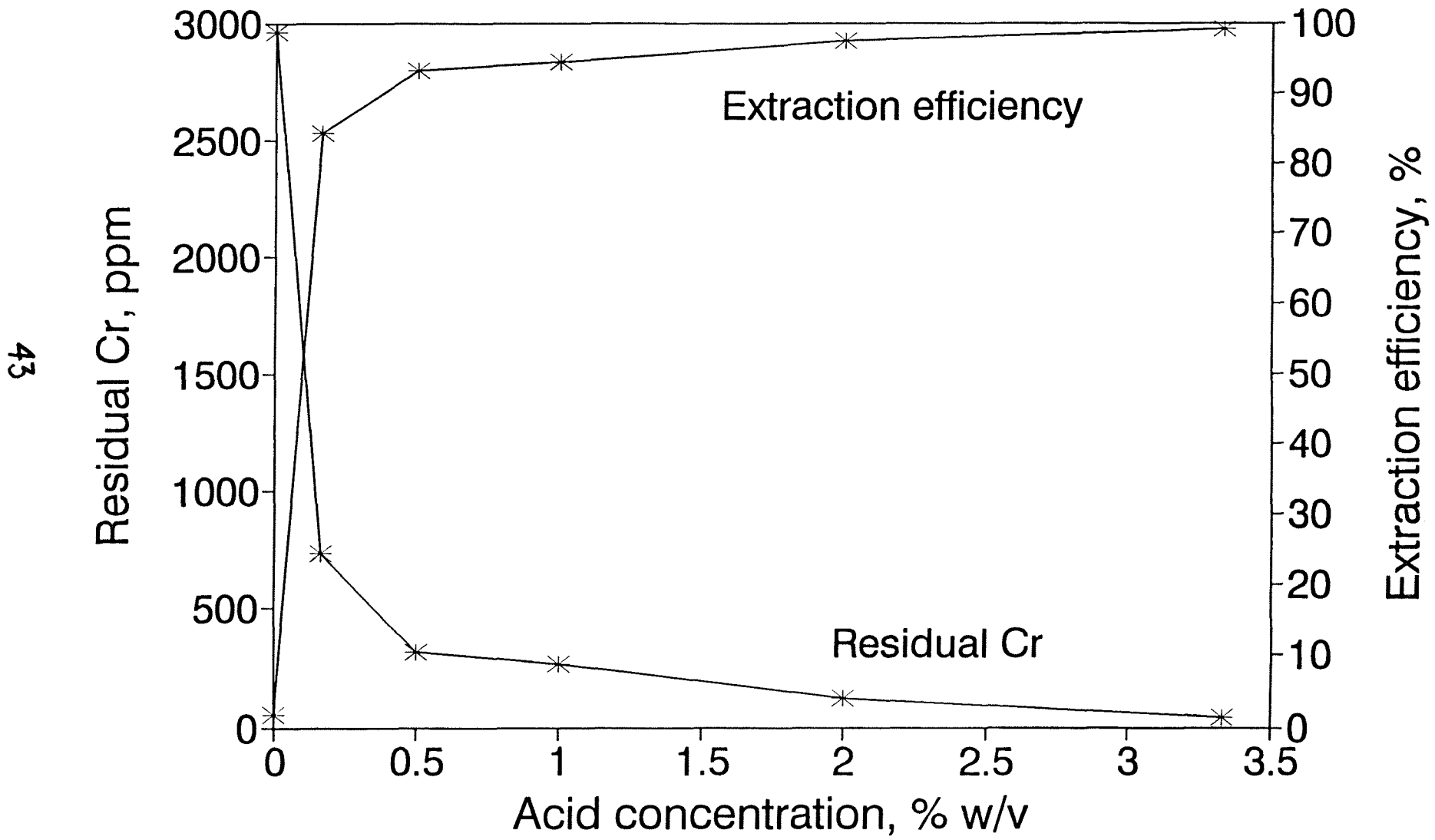
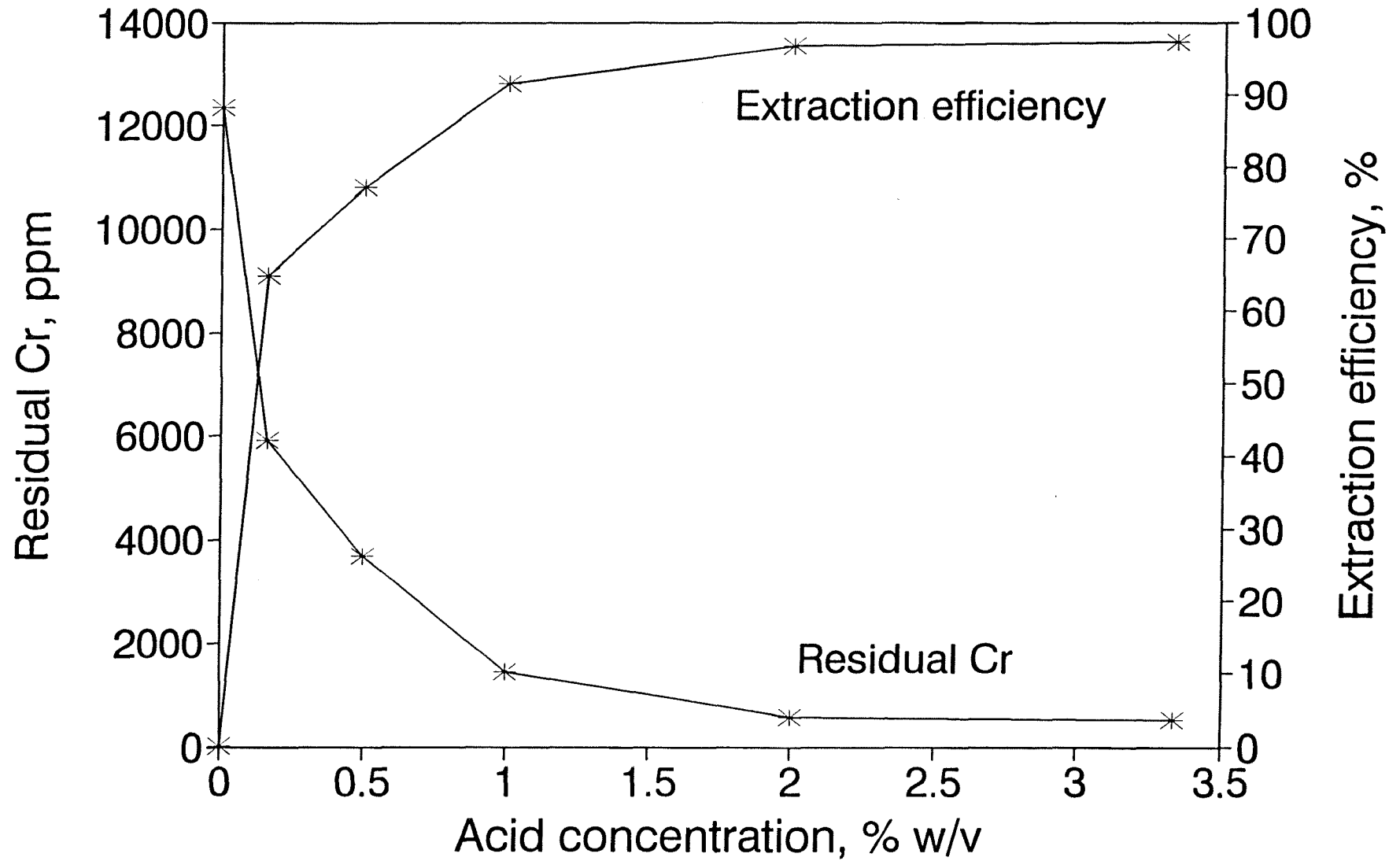


Figure 3: Extraction as function of concentration for Bentonite

44



ppm. This removal represents an extraction efficiency exceeding 97%. The rapid increase in extraction efficiency with respect to acid concentration that is observed for Kaolin and Montmorillonite is not as pronounced for Bentonite. 90% extraction requires soil washing with 2% sulfuric acid for Bentonite, while peak extractions are achieved with 0.5% sulfuric acid solutions with Kaolin and Montmorillonite.

4.2 Kinetics

A study of extraction kinetics indicates that extraction is essentially complete within 20 minutes for the three clay types, as seen in Figures 4, 5, and 6. A large part of the extraction (66.2% for Kaolin, 87.1% for Montmorillonite, and 85.4% for Bentonite) is accomplished within 10 minutes, as well. Extraction is delayed in the kinetic study for Kaolin, but this may be attributed to the fact that boiling may not have commenced within the first 10 minutes.

Results from the kinetics study are consistent with the predictions of Tuin and Tels¹⁶ concerning the extraction of several heavy metals (Cu, Ni, Pb, Zn) from clay soils with 0.1 N HCl. They concluded that the kinetics are governed by a two-fold mechanism: a fast, irreversible reaction, first order in metal concentration, and a slow, reversible, first order reaction.

The results shown in Figures 4-6 seem to substantiate

Figure 4: Extraction kinetics for Kaolin

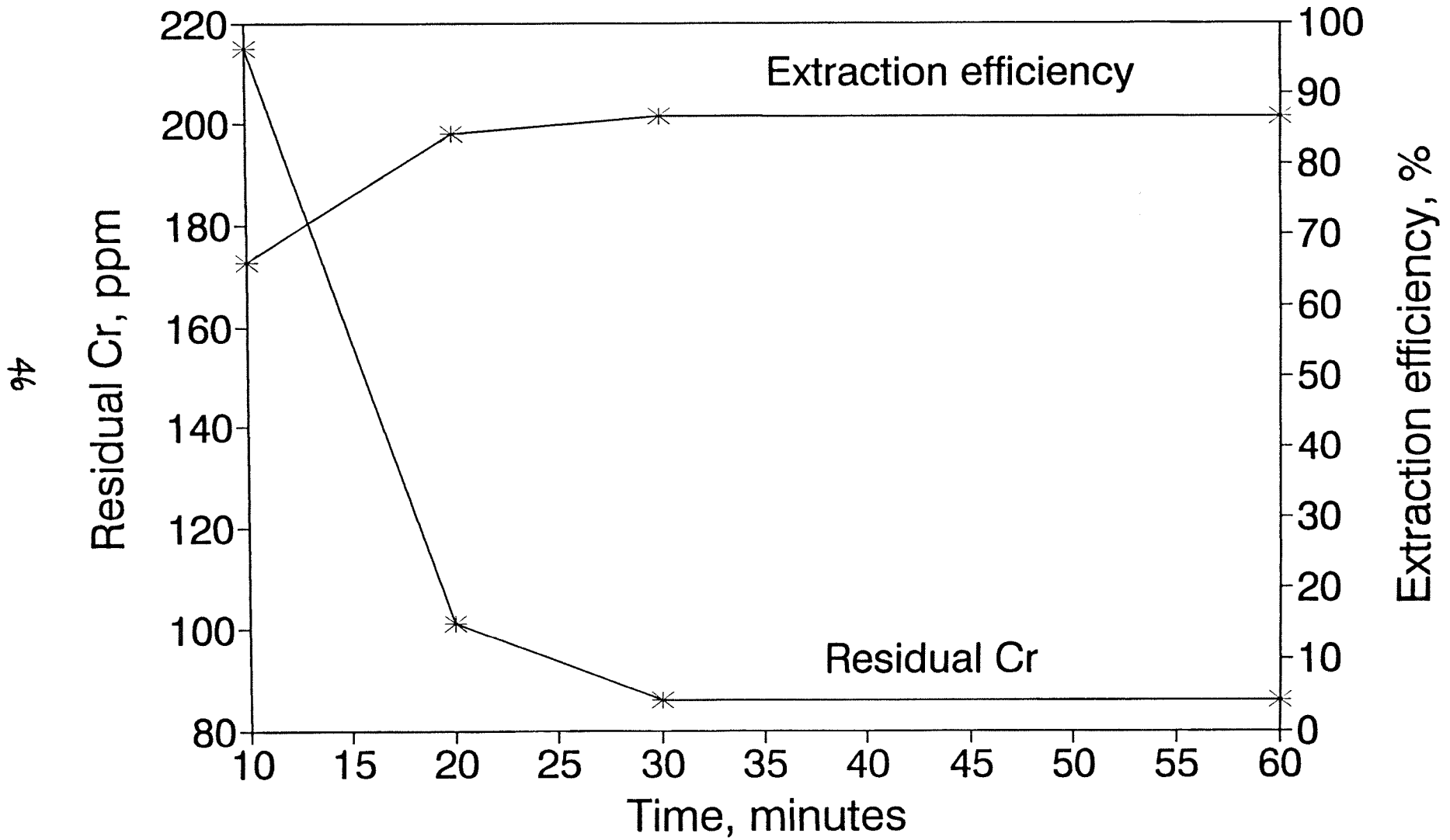


Figure 5: Extraction kinetics for Montmorillonite

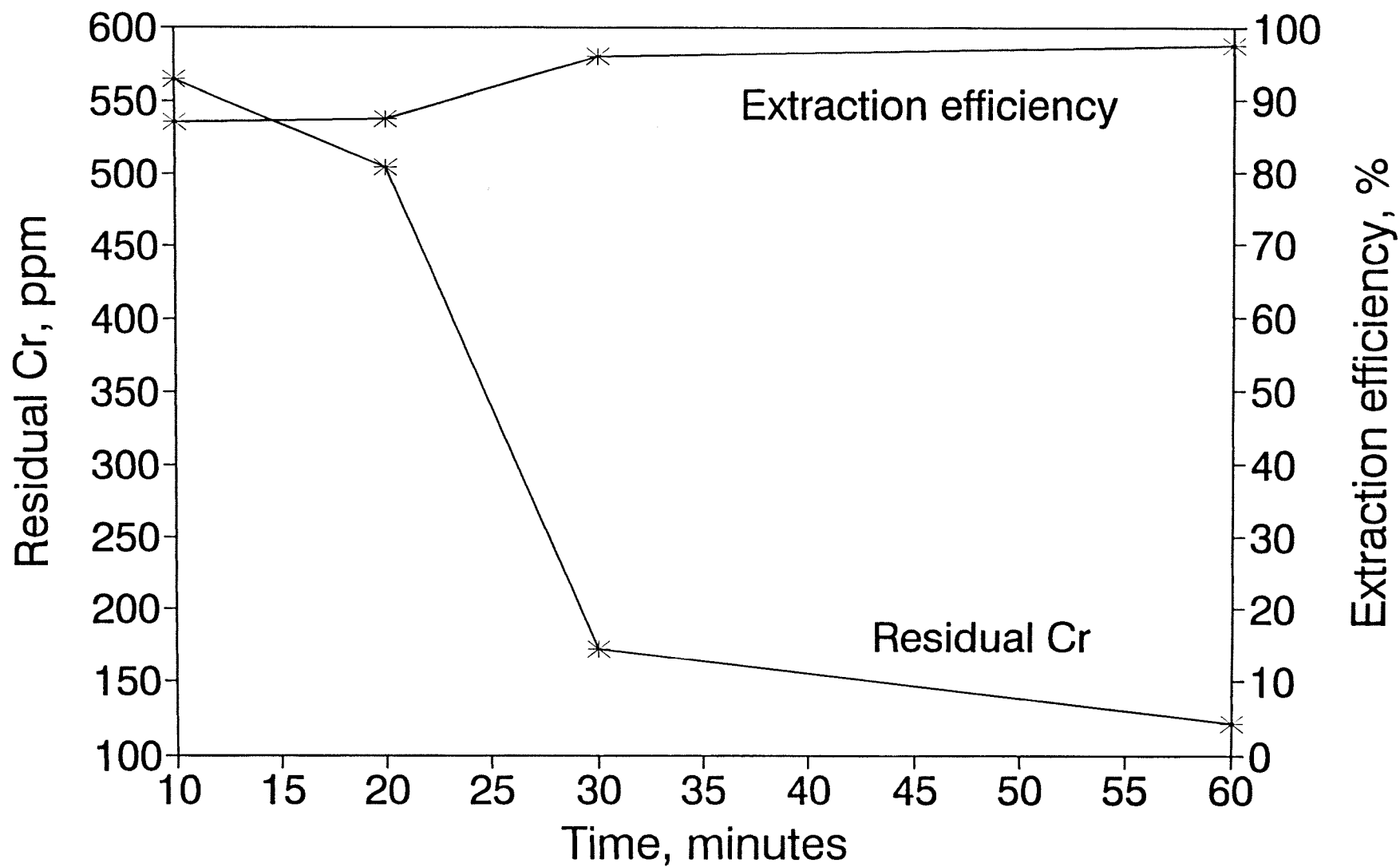
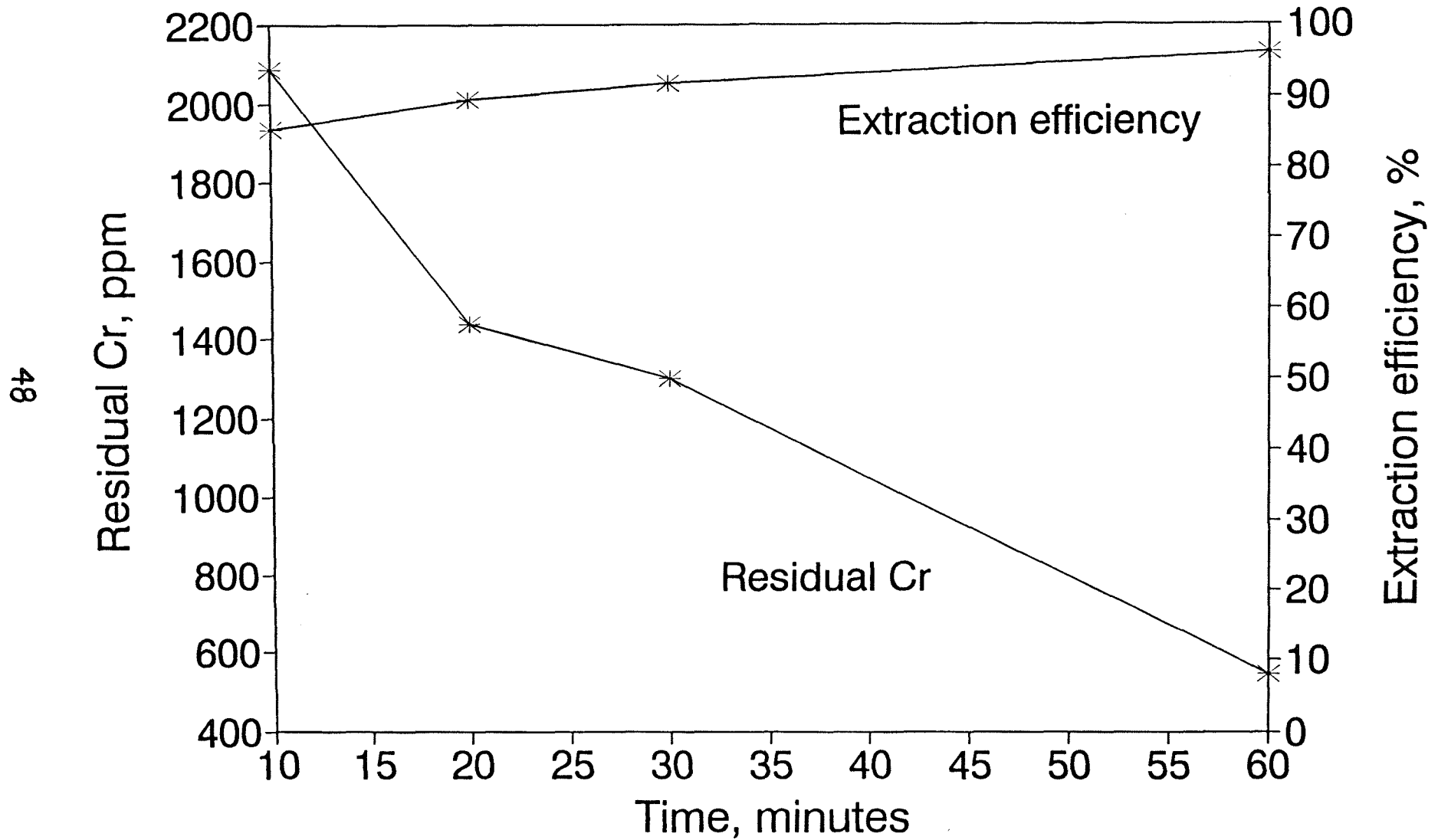


Figure 6: Extraction kinetics for Bentonite



this hypothesis. The majority of extraction occurs very quickly, while additional contact time improves removal efficiency slightly. The range of contact times used in the Tuin and Tels study extend to 1500 minutes (as opposed to 60 minutes), so the basis for comparison may be limited. Since, the acid concentrations used by Tuin and Tels were lower than the ones used in the present study (0.1 N HCl vs. 0.4 N H₂SO₄), the effect of contact time might be delayed. Also, Tuin and Tels studied the extraction kinetics of heavy metals other than chromium. The kinetics in the present study, though, seem to be governed by the same mechanism as that studied by Tuin and Tels.

CHAPTER 5: CONCLUSIONS

Acid extraction for one hour at 95°C of the Cr(III) impregnated samples of Kaolin, Montmorillonite, and Bentonite clays yielded high extraction efficiencies. Residual chromium concentrations were reduced to below 50 ppm for Montmorillonite, below 100 ppm for Kaolin, and approximately 500 ppm for Bentonite. The affinity for chromium was highest for Bentonite and lowest for Kaolin, as shown by the extent to which chromium was adsorbed to the clays in the impregnation process. Extraction efficiencies of 88%, 99%, and 97% (corresponding to residual chromium levels of 80, 40, and 500 ppm) were achieved for Kaolin, Montmorillonite, and Bentonite, respectively. Deionized water wash at 95°C for one hour removed less than 0.1% of the total adsorbed chromium. The increase in chromium extraction with increasing acid concentration was steep until a maximum was approached, at which point extraction efficiency leveled. High extraction is achieved with 0.5% sulfuric acid for Kaolin and Montmorillonite, while Bentonite approaches a peak extraction at 2% sulfuric acid.

A study of the kinetics involved in acid extraction showed that the majority of extraction is completed within 20 minutes, with a slow increase in extraction with further contact time. A large degree of extraction occurs within the first 10 minutes.

WORKS CITED

1. W. Rinehart, S. Gad, "Current Concepts in Occupational Health: Metals - Chromium" Am. Ind. Hyg. Assoc. J., 47(11):696-699(1986).
2. M. Sittig, Handbook of Toxic and Hazardous Chemicals and Carcinogens, Noyes Publ., Park Ridge, NJ, 2nd Ed., 1985, pp. 243-247.
3. "Environmental Reporter" The Bureau of National Affairs, 7/19/91, p. 132:0105.
4. M. Rinaldo-Lee, J. Hagarman, A. Diefendorf, "Siting of a Metals Industry Landfill on Abandoned Soda Ash Waste Beds" Hazardous and Industrial Waste Management and Testing: Third Symposium, ASTM STP 851, 1984, pp 171-192.
5. D. Arnold, et al., "Remediation of Subsurface Chromium Contamination Utilizing Above Ground and In-situ Methods" presented at Technology Transfer Conference on Environmental Cleanup, The Society of American Military Engineers, 13-15 Nov 1991, Denver, CO.
6. S. Dreiss, "Chromium Migration Through Sludge-Treated Soils" Ground Water, v.24, No.3, pp. 312-321.
7. J. Lester, "Biological Treatment" Heavy Metals in Wastewater and Sludge Treatment Processes, Volume II, CRC Press, Boca Raton, 1987, pp. 21-23.
8. R. Bartlett, J. Kimble, "Behavior of Chromium in Soils: I. Trivalent Forms" J. Environ. Qual., v.5, 1976, pp. 379-386.
9. J. Grove, B. Ellis, "Extractable Chromium as Related to Soil pH and Applied Chromium" Soil Sci. Soc. Am. J., v.44, 1980, pp. 238-242.
10. H. Hsieh, D. Raghu, J. Liskowitz, J. Grow, "Soil Washing Techniques for Removal of Chromium Contaminants from Soil" Proceedings of the Twenty-first Mid-Atlantic Industrial Waste Conference, ed. C. Cole, D. Long, pp. 651-660.
11. R. Peters, H. Elliott, American Institute of Chemical Engineers, 1991 Annual Meeting, Nov. 17-22, 1991, Los Angeles, CA.

12. H. Kilau, I. Shah, "Chromium-bearing Waste Slag: Evaluation of Leachability When Exposed to Simulated Acid Precipitation" Hazardous and Industrial Waste Management and Testing: Third Symposium, ASTM STP 851, 1984, pp. 61-80.
13. K.Tan, "Adsorption and Desorption of Chromium on Clayey Soils" New Jersey Inst. of Tech., MSc. Thesis, 1989.
14. Lange's Handbook of Chemistry, ed. J. Dean, 12th Edition, McGraw-Hill, New York, 1979.
15. "Test Methods for Evaluating Solid Waste" United States Environmental Protection Agency, SW-846, Nov. 1986, 3rd Edition.
16. B. Tuin, M. Tels, "Extraction Kinetics of Six Heavy Metals from Contaminated Clay Soils" Environmental Technology, v.11, pp. 541-554.