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## ABSTRACT

Chemical Solidification and Stabilization of toxic metal-containing sludges is one of the most important problems for environmental protection. Although Chemical Solidification and Stabilization of hazardous wastes prior to disposal is increasing in importance, very little work has been done concerning the leaching mechanisms and kinetic models.

In this study, we apply Freundlich & Langmuir isotherms on Chemical Solidification and Stabilization process, and the theoretical results match with experimental data very well. In the same time, we develop a simple mathematical kinetic model which relates leaching concentration of heavy metal to curing time. In this study kinetic model, what you need to input are only leaching concentration,  $C$ , and curing time,  $t$ ; instead of cumulative contaminant loss, an, initial amount of contaminant,  $A_0$ , volume of specimen,  $V$ , surface area of specimen,  $S$ , time to the end of leaching period  $n$ ,  $t_n$ , and effective diffusion coefficient,  $D_e$ , which are used in Godbee's kinetic model.

**MATHEMATIC MODELS ON LEACHING BEHAVIOR OF CHEMICAL  
SOLIDIFICATION AND STABILIZATION PROCESS FOR HEAVY  
METAL SLUDGES**

By

Chen, Sz-Hung

Thesis submitted to the Faculty of the Graduate School of  
The New Jersey Institute of Technology  
in partial fulfillment of the requirements for the degree of  
Master of Science in Civil Engineering-Environmental Option

1992



APPROVAL SHEET

TITLE OF THESIS: MATHEMATIC MODELS ON LEACHING BEHAVIOR OF  
CHEMICAL SOLIDIFICATION AND STABILIZATION  
PROCESS FOR HEAVY METAL SLUDGES

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## ACRONYMS

BDAT	Best Demonstrated Available Technology.
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act.
CSS	Chemical Solidification and Stabilization.
EPA-EP	the U.S. EPA Extraction Procedure Toxicity Test.
HSWA	Hazardous and Solid Waste Amendments of 1984.
OPC	Ordinary Portland Cement.
RCRA	Resource Conservation and Recovery Act.
TCLP	the U.S. EPA Toxicity Characteristic Leaching Procedure

## NOMENCLATURE

- a= Langmuir isotherm constant
- a<sub>n</sub>= contaminant loss during leaching period n, mg
- A<sub>0</sub>= initial amount of a contaminant present in the specimen, mg
- b= Langmuir isotherm constant
- C= concentration of heavy metal leaching out, mg/L
- C<sub>min</sub>= concentration of heavy metal leaching out when time is infinite, mg/L
- D<sub>e</sub>= effective diffusion coefficient, cm<sup>2</sup>/sec.
- K= kinetic constant, (mg/L)\*(day)
- K<sub>d</sub>= decay constant, day
- K<sub>f</sub>= Freundlich isotherm constant
- M= amount of cementitious binder in the sample, mg/Kg
- M<sub>s</sub>= metal species in water
- n= Freundlich isotherm constant
- S= surface area of the specimen, cm<sup>2</sup>
- τ= curing time, day
- t<sub>n</sub>= time to the end of leaching period n, sec.
- V= volume of the specimen, cm<sup>3</sup>
- X= initial amount of heavy metal in the sample, mg/Kg

## I INTRODUCTION

### I-A The Reasons Using Chemical Solidification and Stabilization Process

One of the most difficult of the waste treatment processes in municipal operations is that of disposal of the solid fraction as sludge. This problem increases with the population growth.

Before many chemical wastes can be disposed of, especially in landfills, they must first be treated so that they will not release restricted materials into the environment - particularly into groundwater. One promising technology, the subject of this thesis, is chemical solidification and stabilization, CSS for short, process.

Much of the incentive for CSS of hazardous wastes has been provided by the Resource Conservation and Recovery Act (RCRA) of 1976, including the subsequent Hazardous and Solid Waste Amendments (HSWA) of 1984, and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), otherwise known as Superfund. Pushed by regulation that essentially mandates its use for many waste streams, CSS is becoming a standard unit process in liquid and hazardous waste treatment and disposal. The method has been designated as a Best Demonstrated Available Technology (BDAT) for some wastes and waste forms in the first-third landbans on the land disposal of hazardous wastes.

## I-B Description of Chemical Solidification and Stabilization process

Chemical solidification and stabilization process involves mixing a waste with one or more additives to convert the waste to a solid monolithic form. The most important additives include either ordinary Portland cement, OPC, alone, OPC-flyash, lime-flyash, or other pozzolanic materials. Ordinary Portland cement has probably been the most widely used inorganic ingredient.

CSS processes not only solidify the waste by chemical means but also insolubilize, immobilize or interact with waste components. It is also used to improve the handling and physical characteristics of aqueous wastes. The treatment also decreases waste leachability and has the potential to detoxify the hazardous constituents contained in the waste.

Cement-based CSS processes incorporate the waste as part of a rigid inorganic cement matrix. As the cement hydrates, a calcium-silicate-hydrate gel forms, followed by the hardening of the materials as thin, densely-packed, silicate fibrils grow and interlace. Studies have shown that heavy metal compounds interact in the hydration reactions of cementitious binders both during setting and later during the hardening process. Many of the heavy metals in the waste are converted to insoluble metal hydroxides in the highly alkaline environment of the cement paste and are trapped



with the pores of the cement paste matrix. The large amount of free alkalinity in the stabilized waste form is beneficial when it counters the effects of acids which may be present in leachants.

It is also possible that some of the metals may be physically bound to the paste lattice.

## I-C Leachability of Heavy Metal Bearing Waste

Before a waste is determined to be nonhazardous, it must be examined in terms of its leachability in a sanitary landfill under natural conditions.

Leaching is a rate phenomenon. In the rate, hazardous or other undesirable constituents are removed from the waste and passed into the environment via the leachate.

An idea leaching test should yield information regarding the equilibrium concentration of the important constituents of the leachate, the total amount of each constituent available for leaching from the waste, and the kinetics of the solubilization reactions, including the dynamic changes in leachate composition as various compounds are totally leached from the waste.

Unfortunately, no single existing leachate test fulfills all of above requirements and there is no standard method for extracting a leachate from a solid material. However, the most widely used leaching test for solidified and other waste materials have been two forms: the U.S. EPA Extraction Procedure Toxicity Test (EPA-EP) and the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP).

Table 1.1 lists the regulatory limits of heavy metals for EPA-EP and TCLP tests.

Table 1.1 The Regulatory Limits of Heavy Metals for EPA-EP and TCLP tests

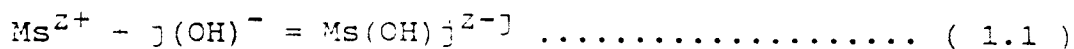
Contaminant	EPA-EP (ppm)	TCLP (ppm)
Arsenic	5.000	5.000
Barium	100.000	100.000
Cadmium	1.000	1.000
Chromium (+3)	5.000	5.000
Chromium (+6)	5.000	5.000
Lead	5.000	5.000
Mercury	0.200	0.200
Selenium	1.000	1.000
Silver	5.000	5.000

## I-D Aqueous Chemistry and Complex Formation of Heavy Metals

The theoretical aqueous chemistry and complex formation of heavy metals are often different from actual conditions in real waste-leachant systems. Nevertheless, as a starting point in choosing possible chemical reactions, it is useful to know the basic aqueous chemistry and complex formation of various species.

The sorption of metal ions with solid/aqueous solution interface is generally not only governed by the "free" metal ion, but also absorbed by much stronger hydroxo form, sulfato, carbonate, and other metal complex species [21]. Huang, et al. [11] have suggested that all metal hydrolysis species should be involved in the adsorption of metal ions. So, the metal species which occur in aquatic systems and the behavior of metal sorption onto solid/liquid interface is very important.

The metal species in water are primarily governed by PH. If hydrolysis equilibrium of metals can be described as:



At any specific PH value, the fraction of any metal species present in total metal species,  $\alpha$ , can be calculated by:

$$\alpha = \{Ms(OH)_j^{z-j}\} / \{[Ms^{z+}] + \sum [Ms(OH)_j^{z-j}]\} \dots ( 1.2 )$$

Five heavy metals are commonly found in sludge waste, namely, Pb(II), Cd(II), Cu(II), Zn(II), and Ni(II). The

speciation of each metal hydroxy species as a function of PH are shown in figure 1.1 to 1.5.

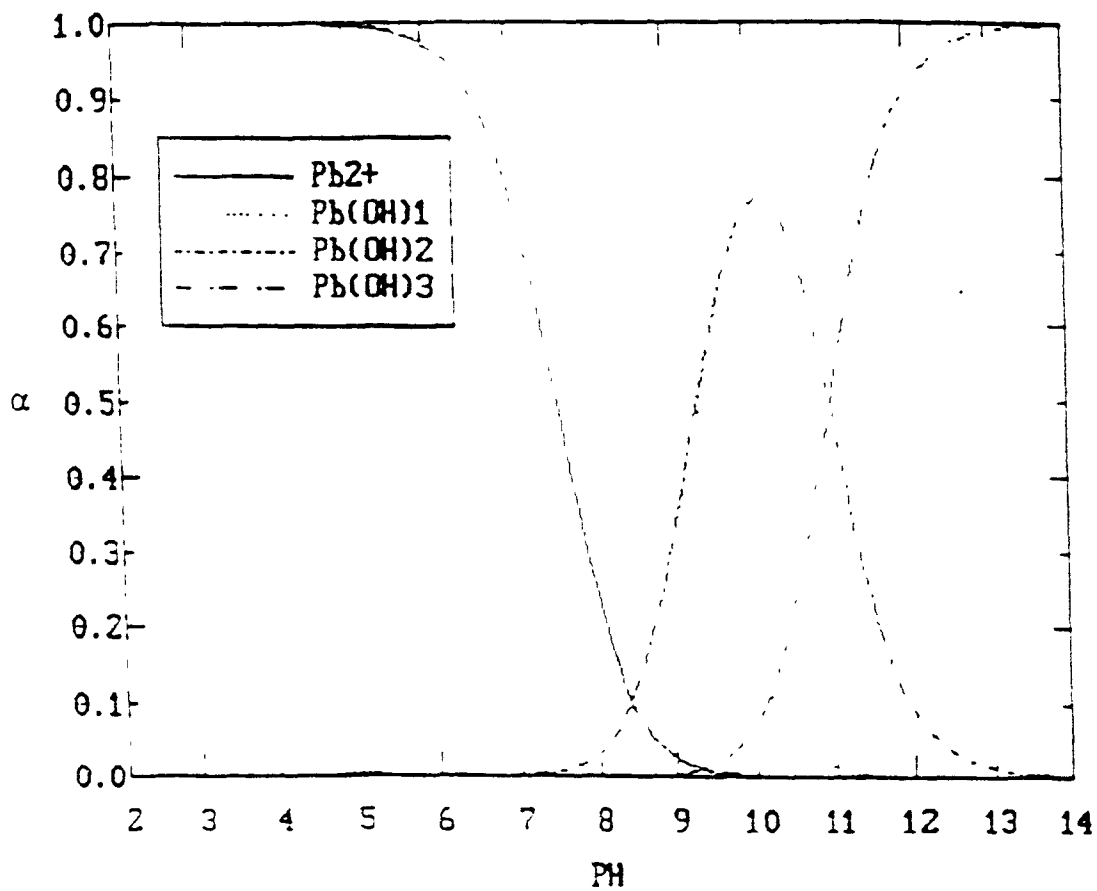


FIGURE 1.1 The speciation diagram of Pb(II). Conditions: 0.1 M NaClO<sub>4</sub>, 23°C.

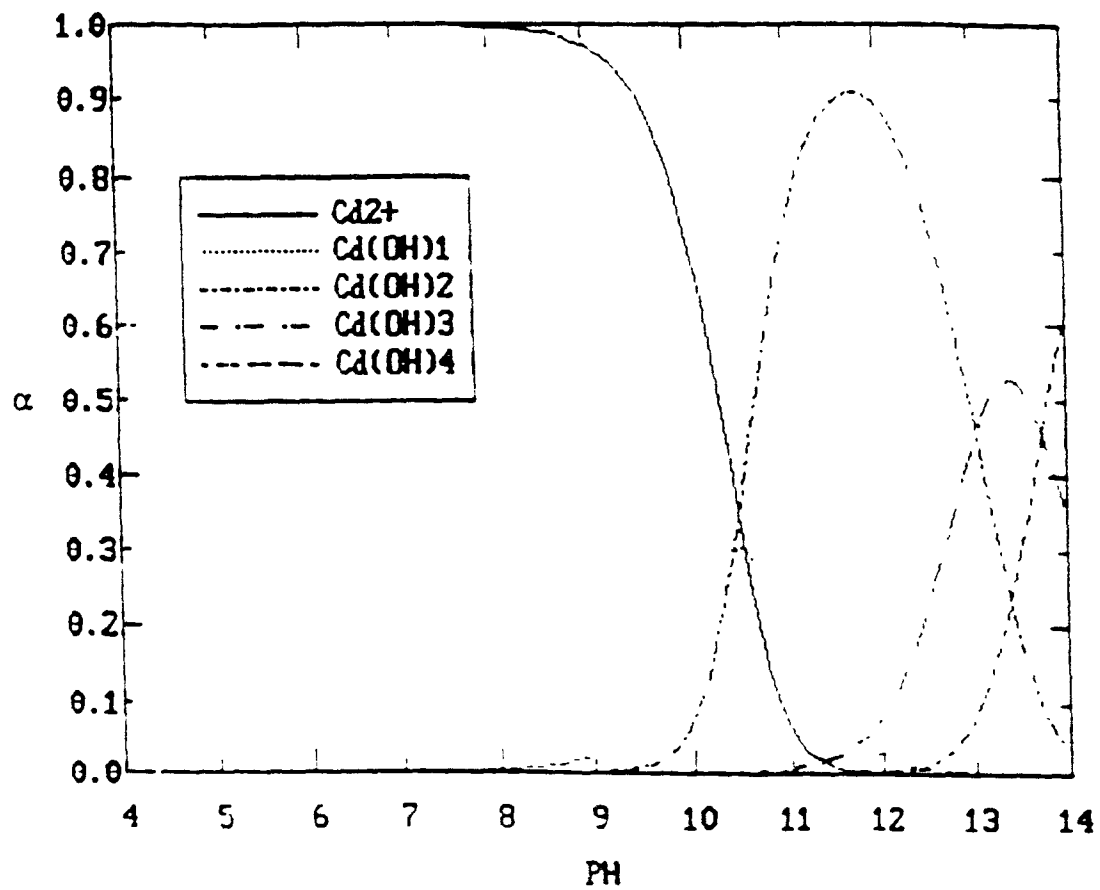


FIGURE 1.2 The speciation diagram of Cd(II). Conditions: 0.1 M NaClO<sub>4</sub>, 23°C.

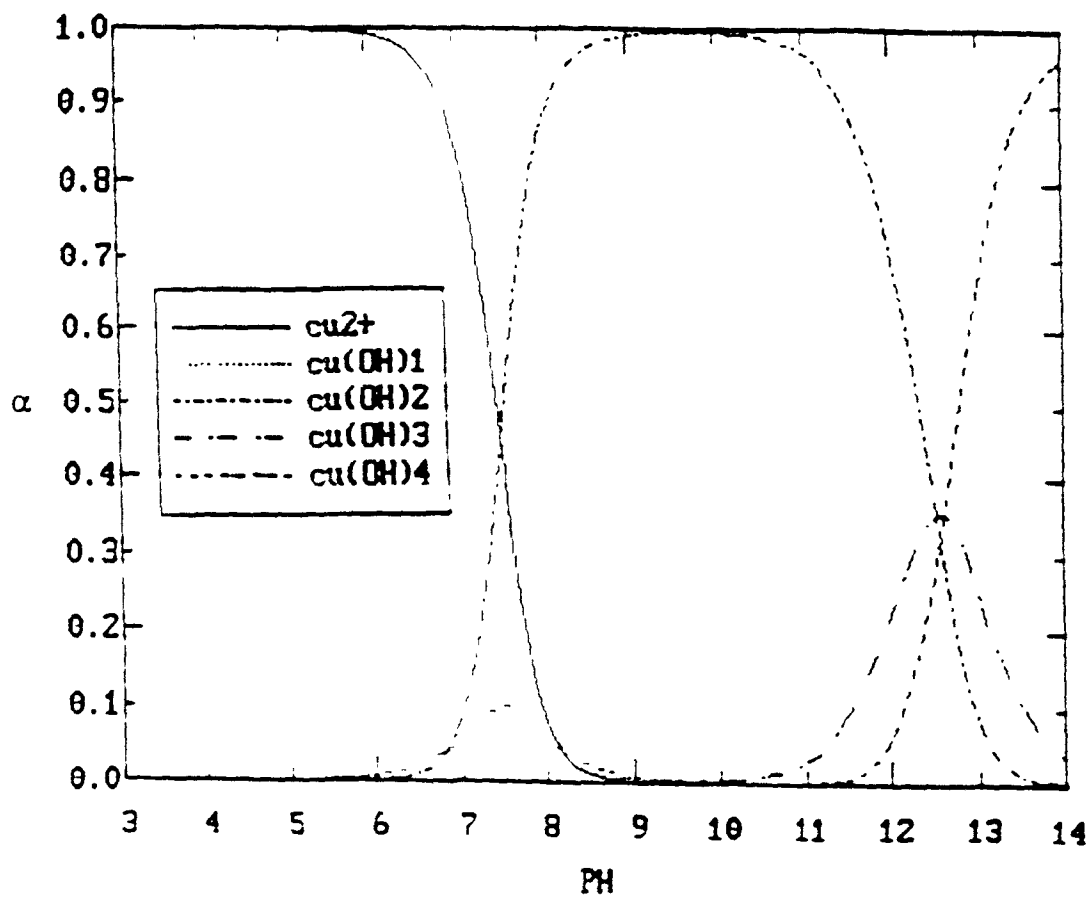


FIGURE 1.3 The speciation diagram of Cu(II). Conditions: 0.1 M  $\text{NaClO}_4$ , 23°C.



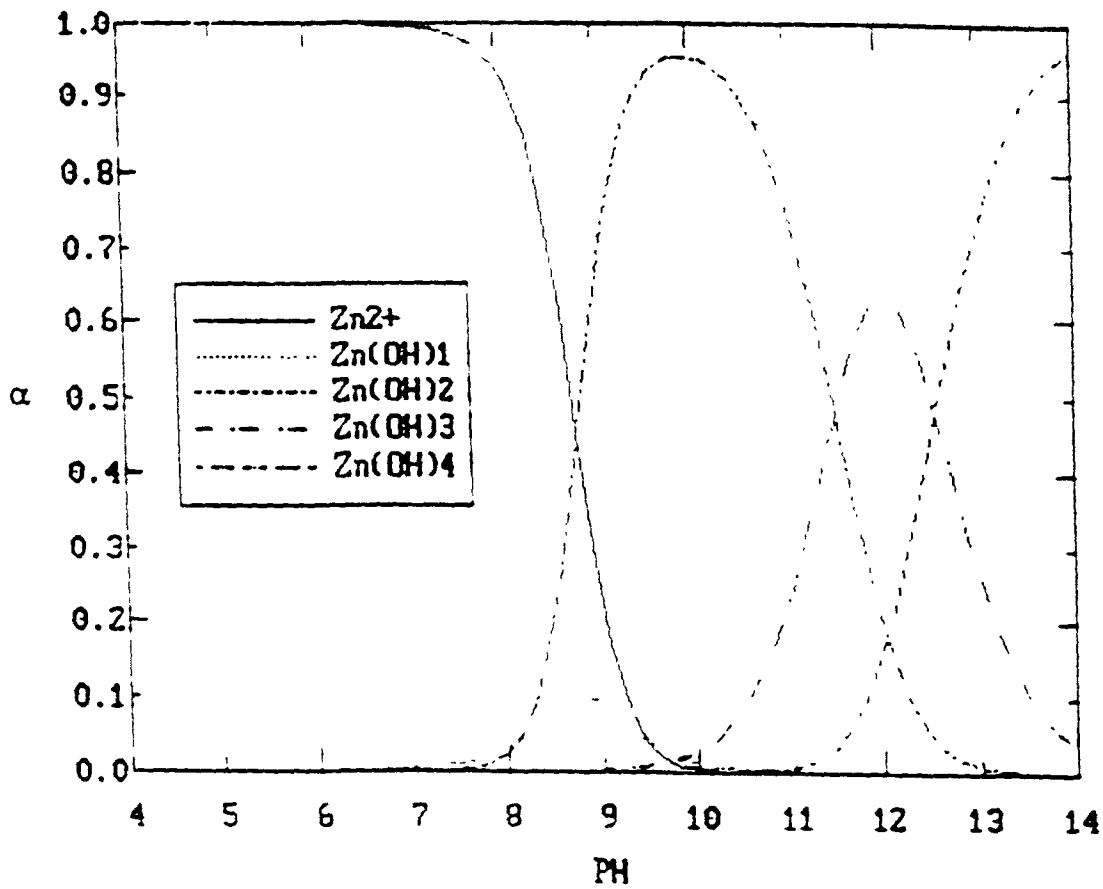


FIGURE 1.4 The speciation diagram of Zn(II). Conditions: 0.1 M NaClO<sub>4</sub>, 23°C.

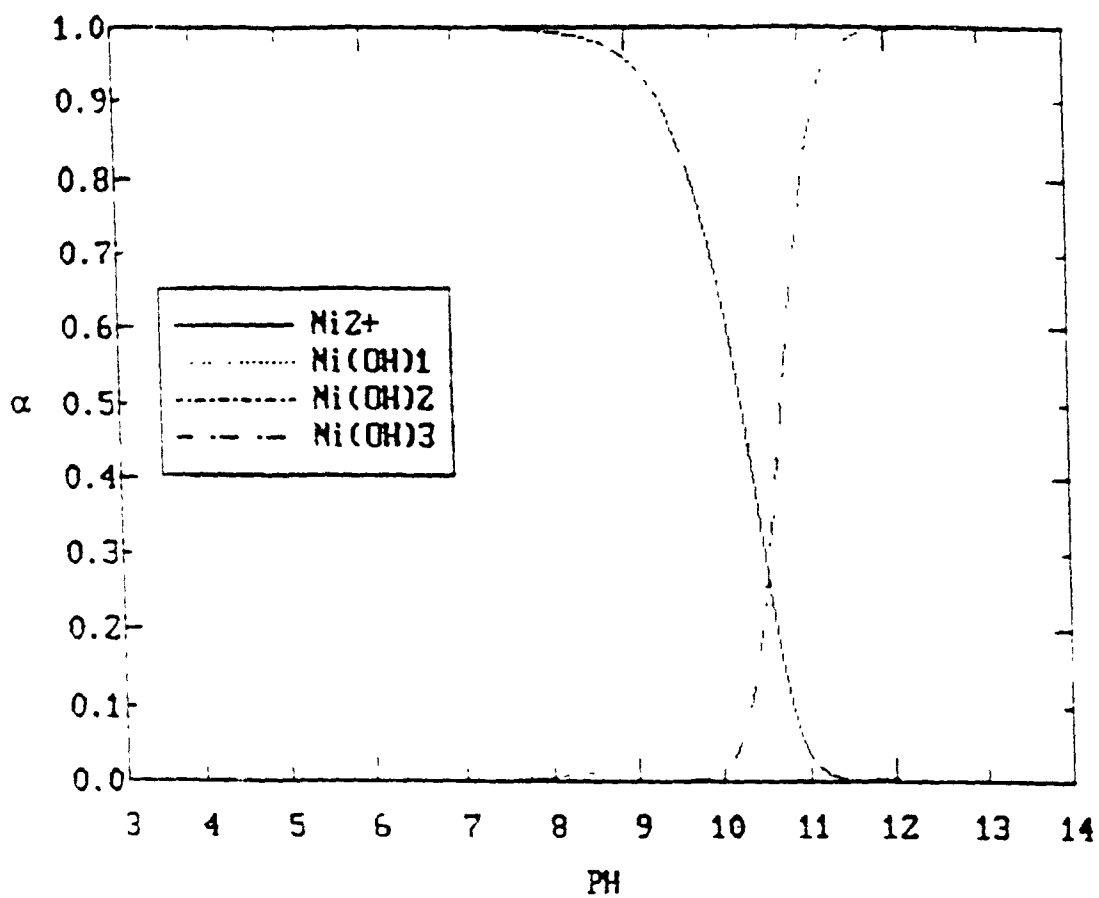


FIGURE 1.5 The speciation diagram of Ni(II). Conditions: 0.1 M  $\text{NaClO}_4$ , 23°C.

## II LITERATURE REVIEW

Bishop et al. [4] observed that heavy metal sludges stabilized with ordinary Portland cement produced a solid matrix that limit the metals' solubility and that it reduced the transport rate into the aquatic environment. Under acidic conditions ( $\text{PH} < 6$ ); leaching was limited by solubility and diffusion through the solid particles.

Poon et al. [17], [18] have reported that a CSS process can occur between waste sludges containing metallic cations and cement during the stabilization process. Cote & Bridle [8] have also reported on the leaching of metal ions from cement solidified wastes. Silicate addition is the basis of several proprietary CSS processes. [7]

It has been suggested [15] that the leaching of metals from the cement matrix could be divided into two distinct groups. Metals in the first group, comprising Zn, Pb and Cd, were effectively stabilized in both silicate-modified and cement-only samples, and results indicated that they formed insoluble metal hydroxides in the alkaline matrix. Metals in the second group, comprising Cu and Ni, were released more readily from stabilized sludge than from the unstabilized counterpart, suggesting that these metals exist as PH dependent metal complexes in the sludge itself.

Extensive studies of the hydration mechanism of cement [2], [13] indicate that the process of ordinary Portland cement

hydration involves an osmotic pressure gradient drawing water across an initially formed semipermeable membrane around the calcium silicate particle. Alternative mechanisms suggested for metal ion stabilized by cement involve absorption by cement hydrates, substitution and solid solution in hydrate structure, or formation of metal complexes. [22]

Malone & Jones [14] reported experiments on the solidification of anaerobic digester sludge containing high concentrations of Cu, Cd, Pb and Zn and sludge incinerator ash contaminated by Cr, Cu, Pb and Zn using processes based on OPC/silicate, lime and gypsum, respectively. The lime-based process produced the hardest, most durable material.

Bishop et al. [3] reported for the chromium samples, as the particle size decreased, the concentration of metals in the leachate increased, probably because of the increased exposed surface area of the smaller particles and the high solubility of the chromium. But, this was not the case with the lead and cadmium samples where the metals remained locked up in even the small particles. This may be due to the greater ion exchange capacity of the smaller particles which prevents significant leaching of the metals.

Brown et al. [5] indicated the difference in particle size is more important in determining availability of alkalinity than the availability of surface area. In the short time,

the largest amounts of alkalinity in the small particles is protective, preventing any metals from being released. Once the alkalinity is neutralized, however, the small particles release metals at a much higher rate than the larger particles that are still somewhat protected by the alkalinity inside the particle.

### III Mathematic Models on Leachability

#### III-A Sorption Isotherm

Sorption isotherms developed by Freundlich and Langmuir were applied to the variation of waste amount on leachability.

a) By Freundlich isotherm equation:

$$X/M = K_f \cdot C^{(1/n)} \dots\dots\dots ( 3-1 )$$

where: X = initial amount of heavy metal in the sample

M = amount of cementitious binder in the sample

C = concentration of heavy metal leaching out

K<sub>f</sub>, n = Freundlich isotherm constants

Converting equation (3-1) to the linear form, we got:

$$\log(X/M) = \log(K_f) + (1/n) \cdot \log(C) \dots\dots\dots ( 3-2 )$$

The observed n value varies with waste type, metal type, and cementitious binders.

Figure 3.1, 3.2, and 3.3 show Cr sludge stabilized with ordinary Portland cement, while samples were pulverized and sieved through a 3/8 in. (0.375 in. or 9.5 mm) sieve, a #20 (0.0331 in. or 0.8 mm) sieve, and a #200 (0.0029 in. or 0.07 mm) sieve. All particle sizes have same n = 0.66. Particle size 3/8 in. - #20 sieve has largest K<sub>f</sub> value, while particle size #200 sieve has smallest K<sub>f</sub> value.

Figure 3.4 shows Pb sludge and Figure 3.5 shows As sludge. The former got n = 0.33, while the latter got 0.84.

Figure 3.6, 3.7, and 3.8 show Cd sludges stabilized with CKD and OPC. Using CKD got smaller n, 0.78, while using OPC got larger n, 1.04,.

Table 3.1 lists Freundlich isotherm constants, Kf & n, using equation (3-2) for the leachability of Cr, Pb, As, and Cd sludges at Figure 3.1 to 3.8.

Fig. 3.1 Freundlich isotherm applied on Cr sludge stabilized with OPC at particle size: 3/8" - #20 sieve

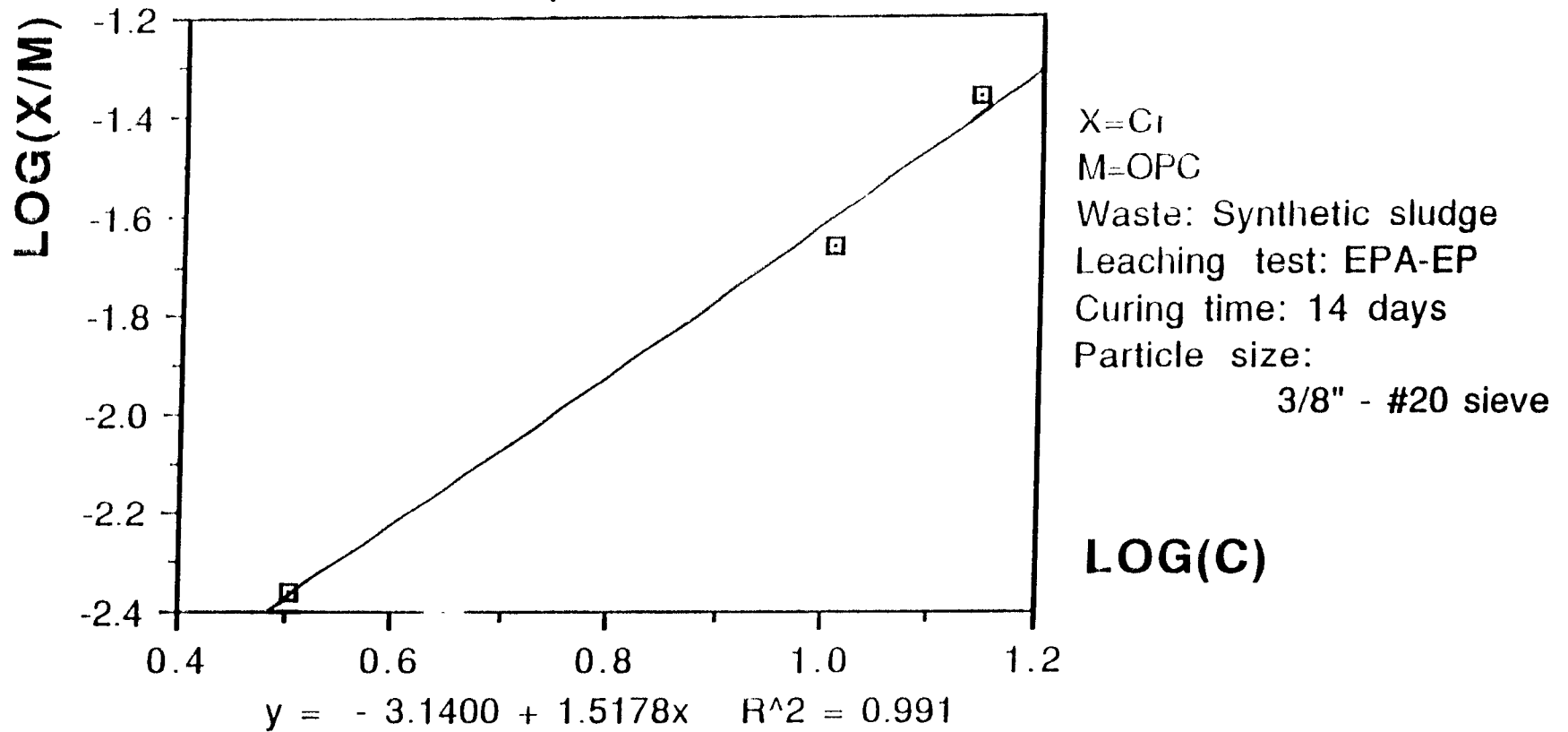




Fig. 3.2 Freundlich isotherm applied on Cr sludge stabilized with OPC at particle size: #20 - #200 sieve

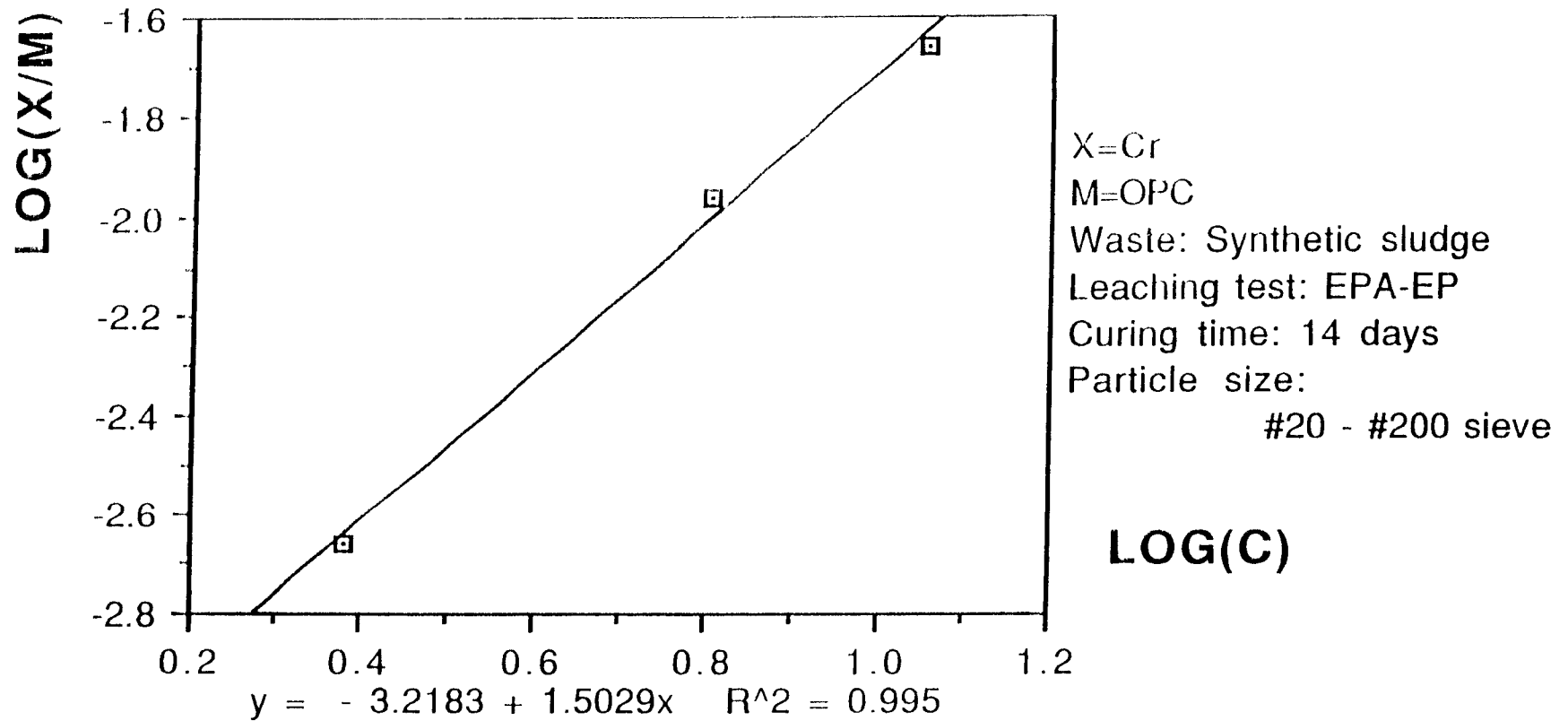


Fig. 3.3 Freundlich isotherm applied on Cr sludge stabilized with OPC at particle size: #200 sieve

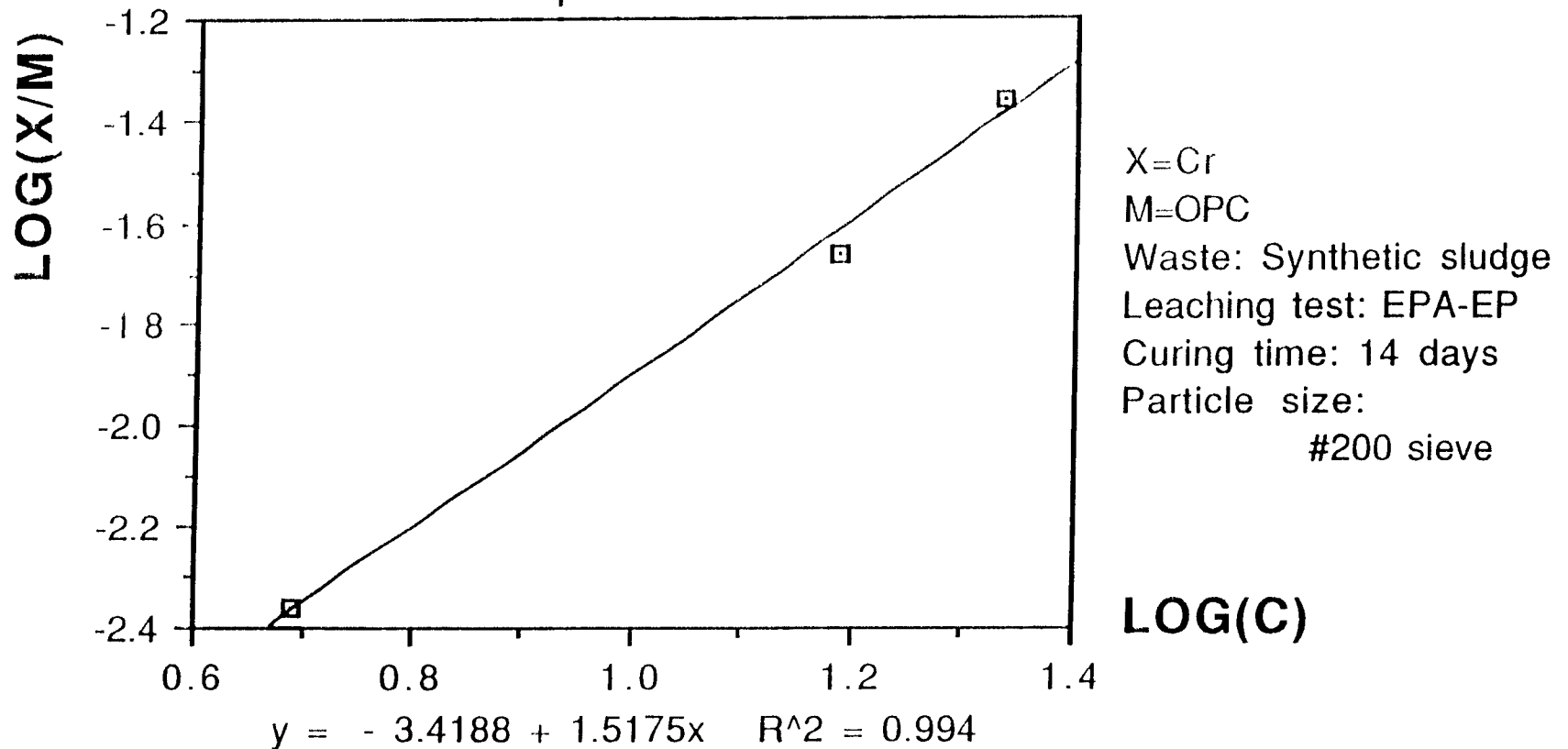


Fig. 3.4 Freundlich isotherm applied on Pb sludge stabilized with CKD

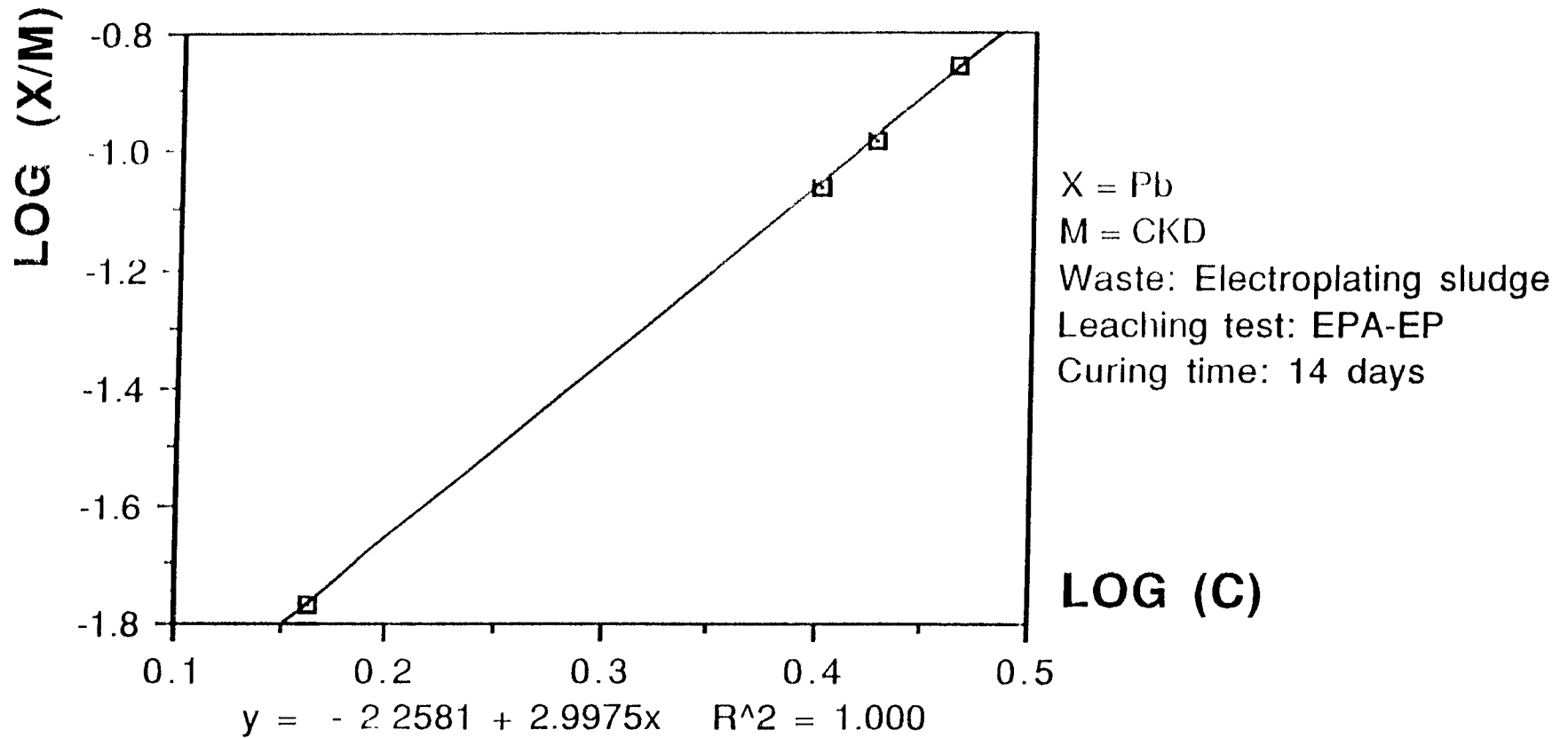


Fig. 3.5 Freundlich isotherm applied on As sludge stabilized with cement casting

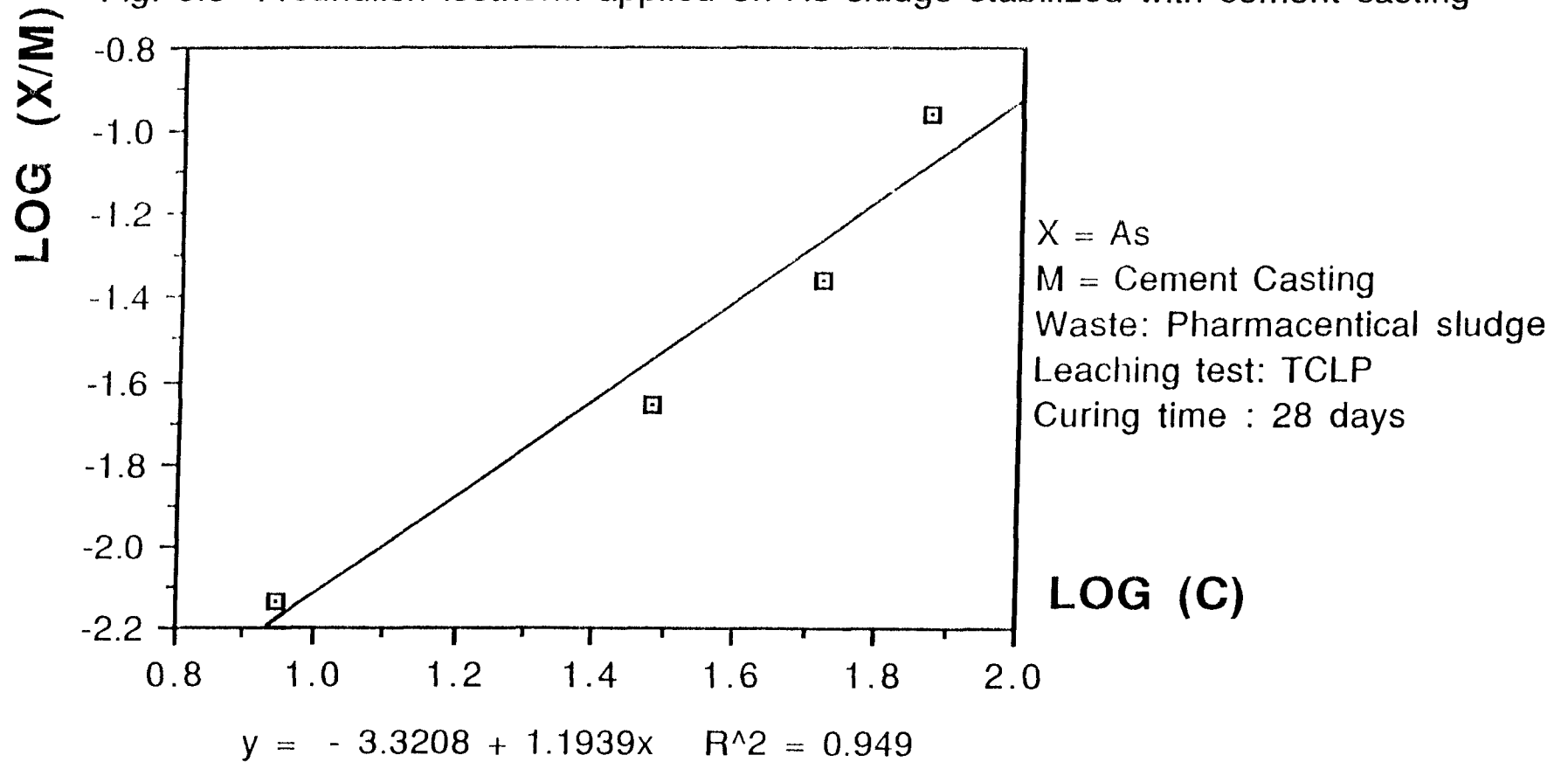


Fig. 3.6 Freundlich isotherm applied on Cd sludge stabilized with CKD

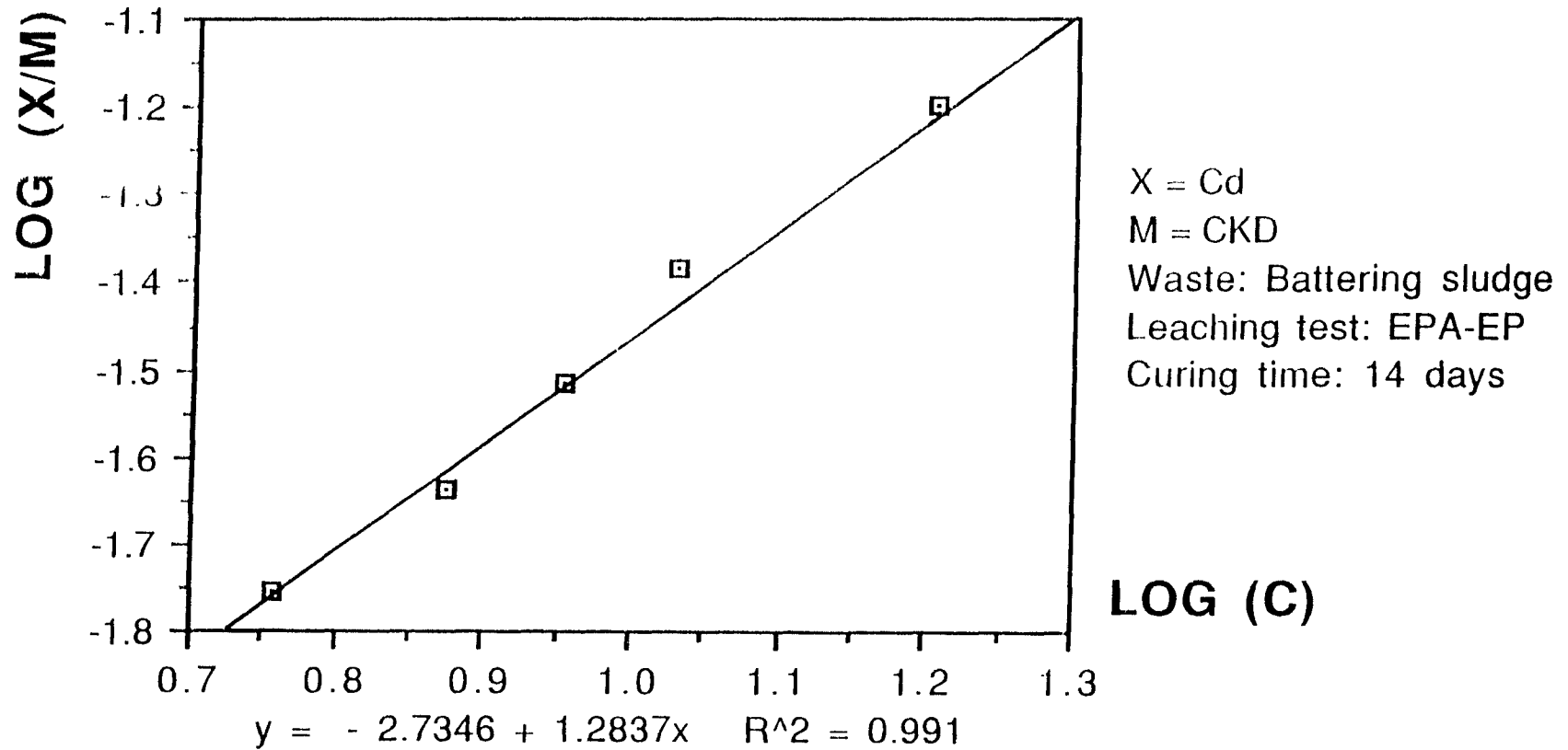
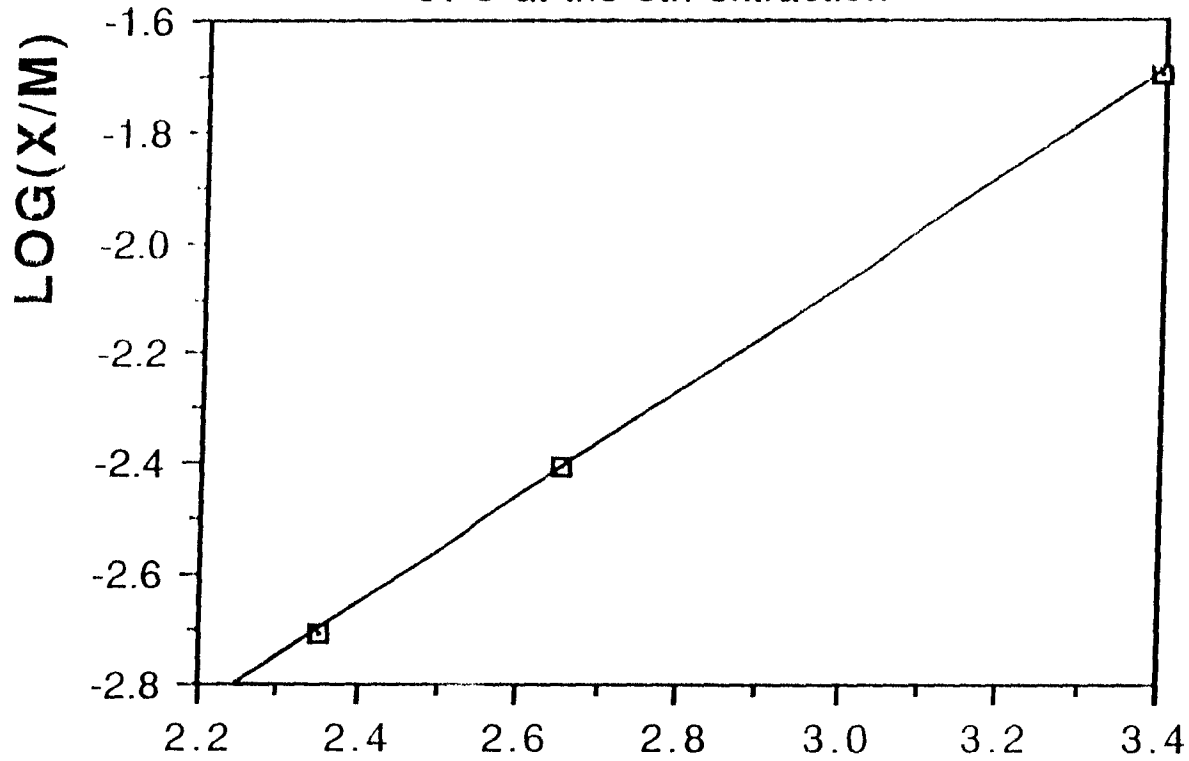


Fig. 3.7 Freundlich isotherm applied on Cd sludge stabilized with OPC at the 8th extraction



X=Cd  
M=OPC  
Waste: Synthetic sludge  
Leaching test: EPA-EP  
Curing time: 14 days  
At the 8th extraction

**LOG(C)**

$$y = -4.9638 + 0.96169x \quad R^2 = 1.000$$

Fig. 3.8 Freundlich isotherm applied on Cd sludge stabilized with OPC at the 10th extraction

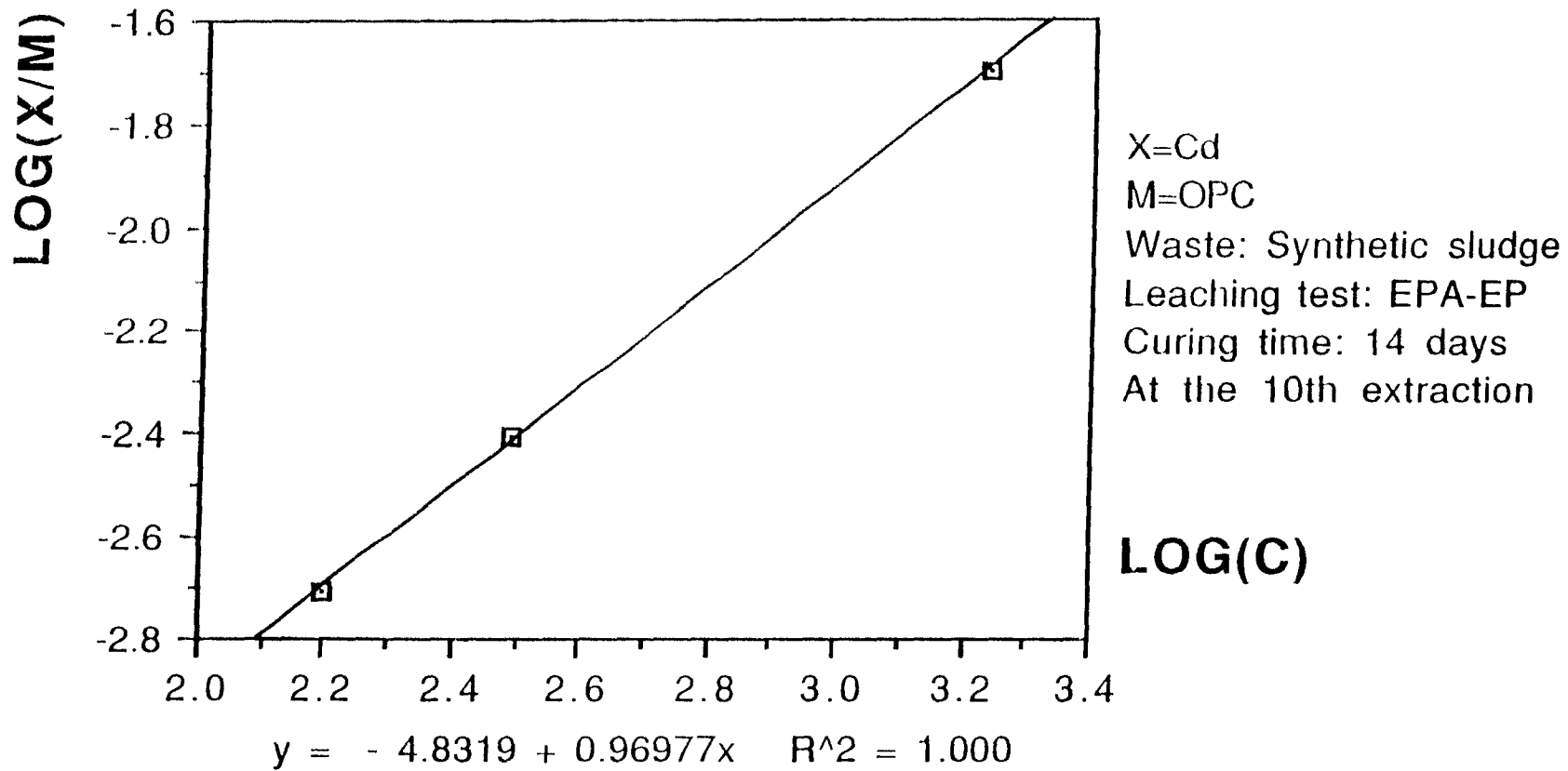


Table 3.1 Freundlich isotherm constants for the leachability of Cr, Pb, As, and Cd sludge

Figure	Sludge	Chemical	Freundlich Kf	constant n
3.1	Cr-I	OPC	0.000724	0.66
3.2	Cr-II	OPC	0.000605	0.67
3.3	Cr-III	OPC	0.000381	0.66
3.4	Pb	CKD	0.00552	0.33
3.5	As	Cement-Casting	0.000478	0.84
3.6	Cd-I	CKD	0.00184	0.78
3.7	Cd-II	OPC	0.000010	1.04
3.8	Cd-III	OPC	0.000015	1.03



b) By Langmuir isotherm equation:

$$X/M = (a*b*C)/(1+a*C) \dots\dots\dots ( 3-3 )$$

Where: X = initial amount of heavy metal in the sample

M = amount of cementitious binder in the sample

C = concentration of heavy metal leaching out

a & b = Langmuir isotherm constants

Converting equation (3-3) to the linear form, we got:

$$1/(X/M) = (1/b)+(1/a*b)*(1/C) \dots\dots\dots ( 3-4 )$$

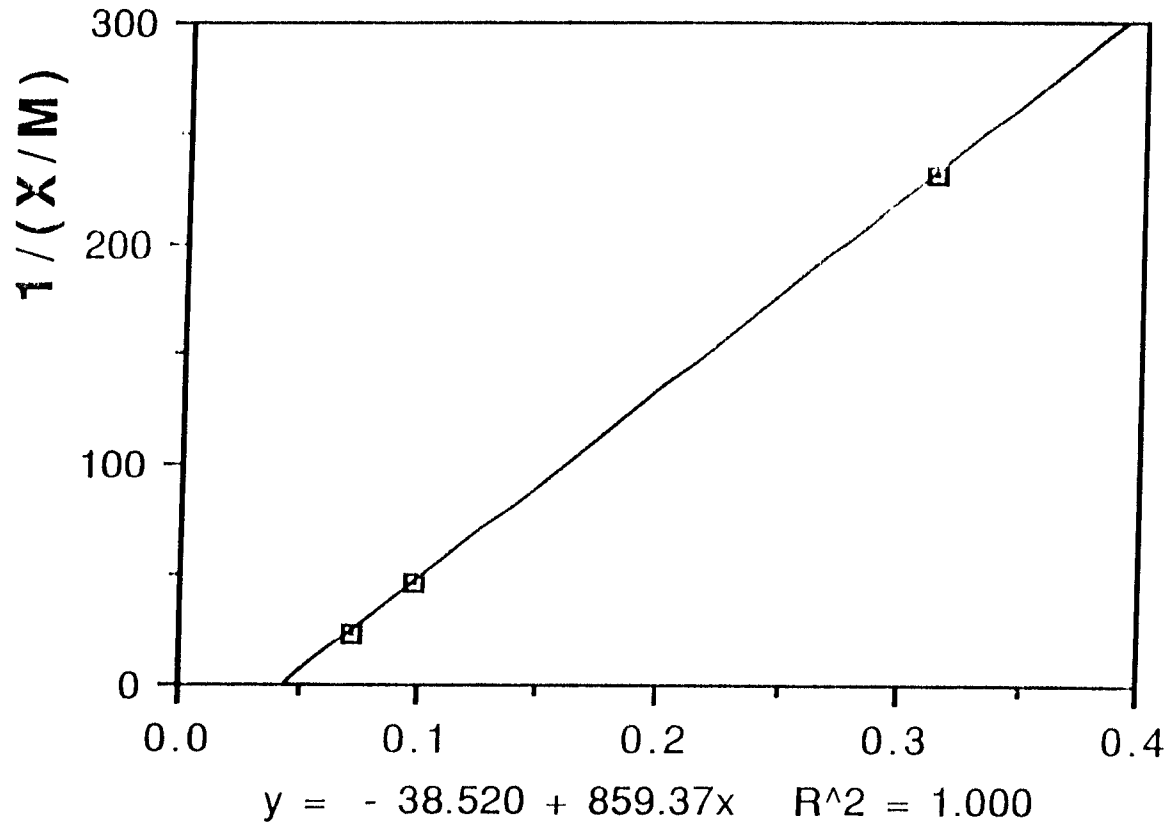
Figure 3.9, 3.10, and 3.11 show Cr sludge stabilized with ordinary Protland cement, while samples were pulverized and sieved through a 3/8 in. (0.375 in. or 9.5 mm) sieve, a #20 (0.0331 in. or 0.8 mm) sieve, and a #200 (0.0029 in. or 0.07 mm) sieve. Particle size 3/8" - #20 sieve and #200 sieve have same b value, -0.026, and particle size #20 -#200 sieve has smallest a value, -0.0674, as well as largest b value, -0.0114,.

Figure 3.12, 3.13, and 3.14 show leachability of Pb, As, and Cd sludges individually.

Table 3.2 lists Langmuir isotherm constants, a & b, using equation (3-4) for the leachability of Cr, Pb, As, and Cd sludges at Figure 3.9 to 3.14.

The corresponding data of each figure is shown in Appendix.

Fig. 3.9 Langmuir isotherm applied on Cr sludge stabilized with OPC at particle size: 3/8" - #20 sieve



X=Cr

M=OPC

Waste: Synthetic sludge

Leaching test: EPA-EP

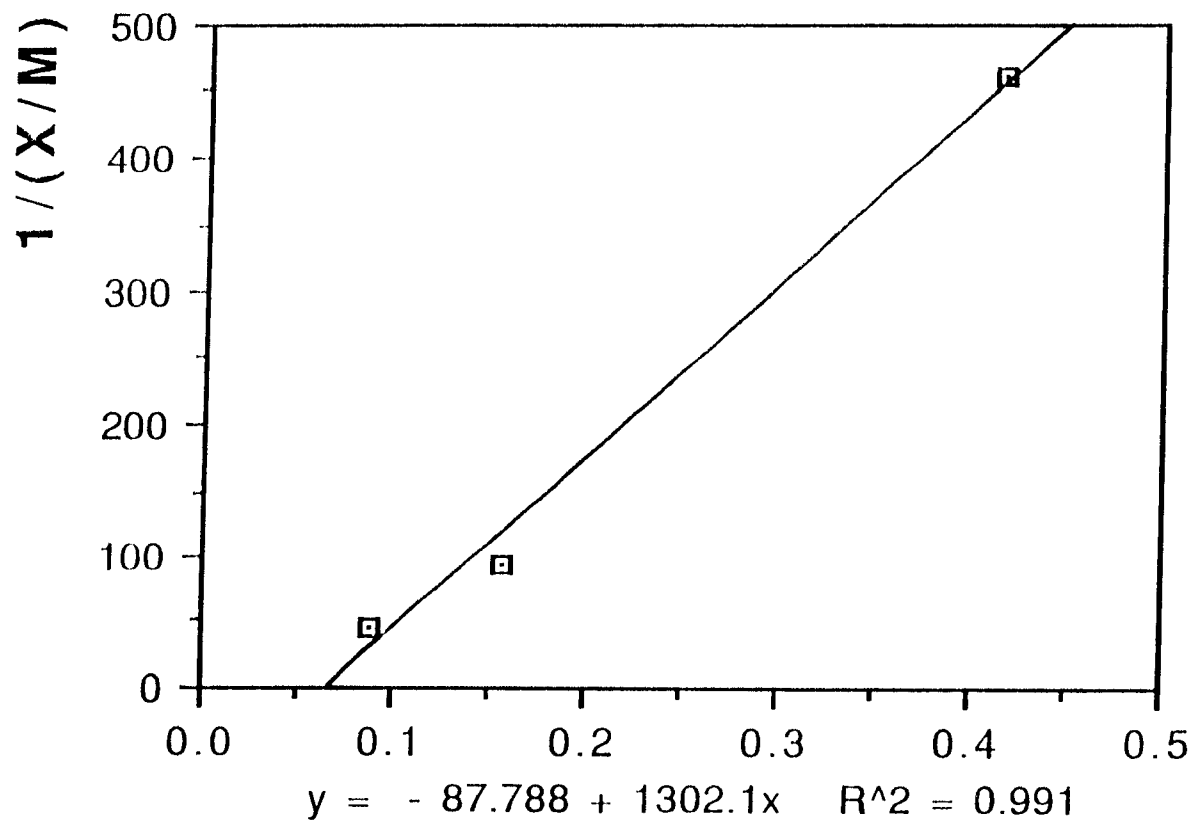
Curing time: 14 days

Particle size:

3/8" - #20 sieve

**1/Conc.**

Fig. 3.10 Langmuir isotherm applied on Cr sludge stabilized with OPC at particle size: #20 -#200 sieve



X=Cr

M=OPC

Waste: Synthetic sludge

Leaching test: EPA-EP

Curing time: 14 days

Particle size:

#20 - #200 sieve

**1/Conc.**

Fig. 3.11 Langmuir isotherm applied on Cr sludge stabilized with OPC at particle size: #200 sieve

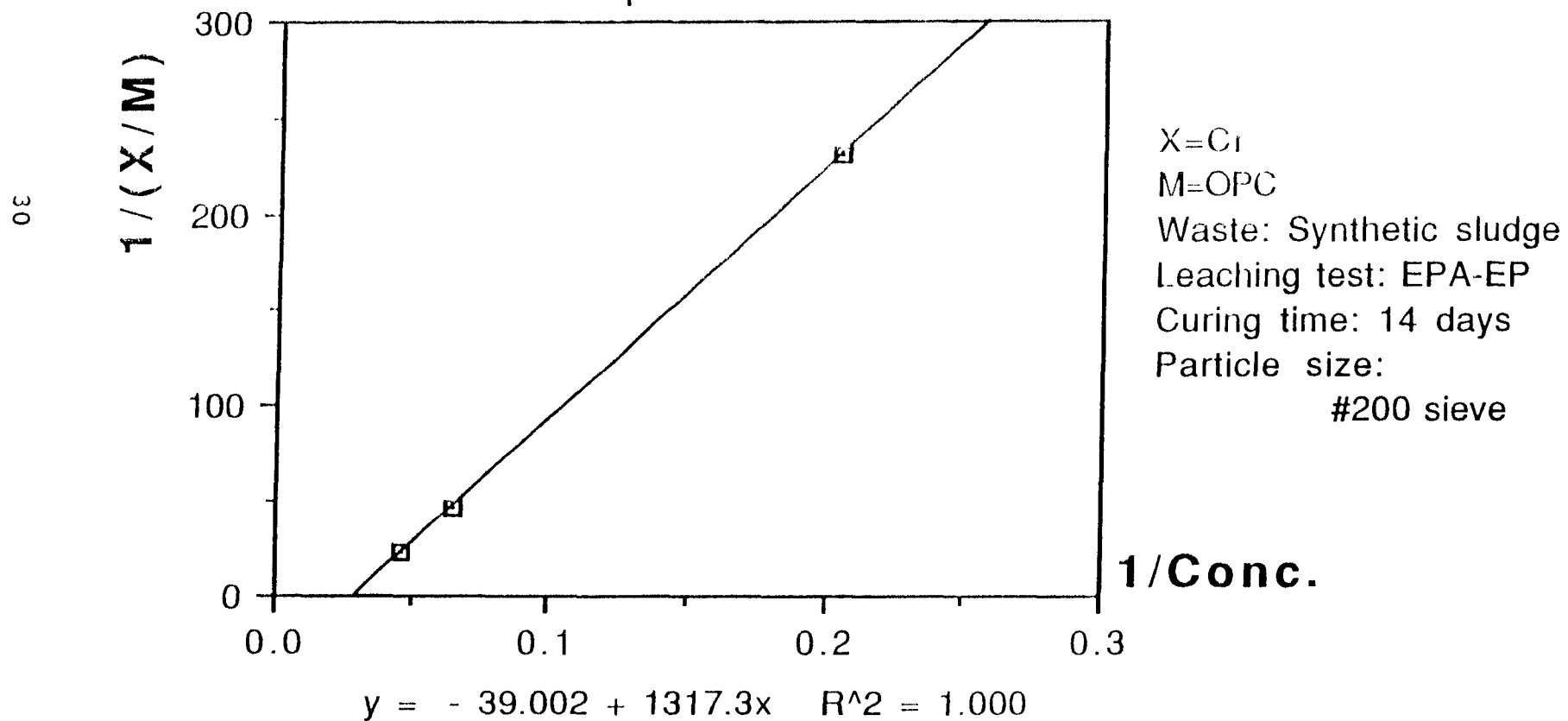


Fig. 3.12 Langmuir isotherm applied on Pb sludge stabilized with CKD

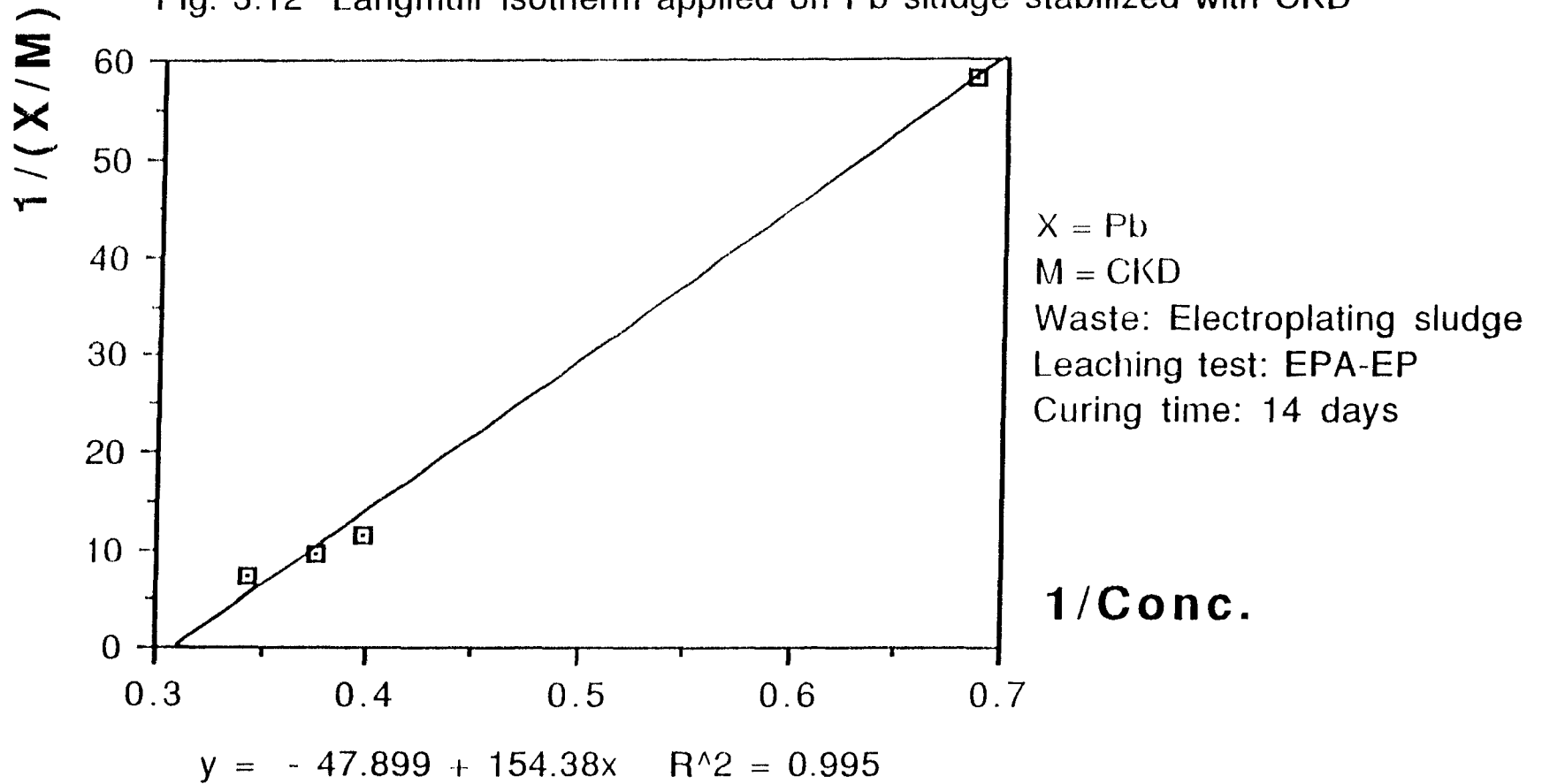


Fig. 3.13 Langmuir isotherm applied on As sludge stabilized with cement casting

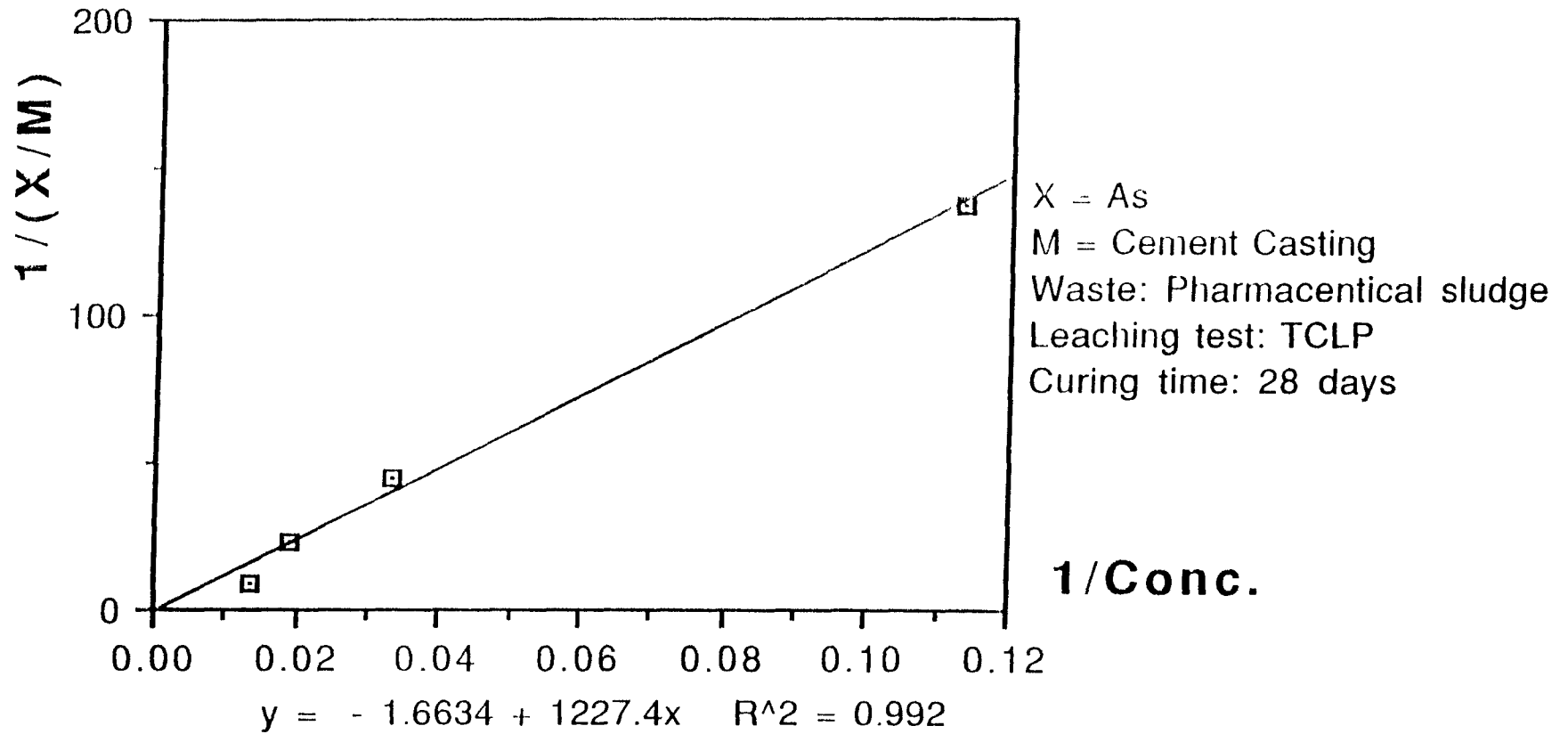


Fig. 3.14 Langmuir isotherm applied on Cd sludge stabilized with CKD

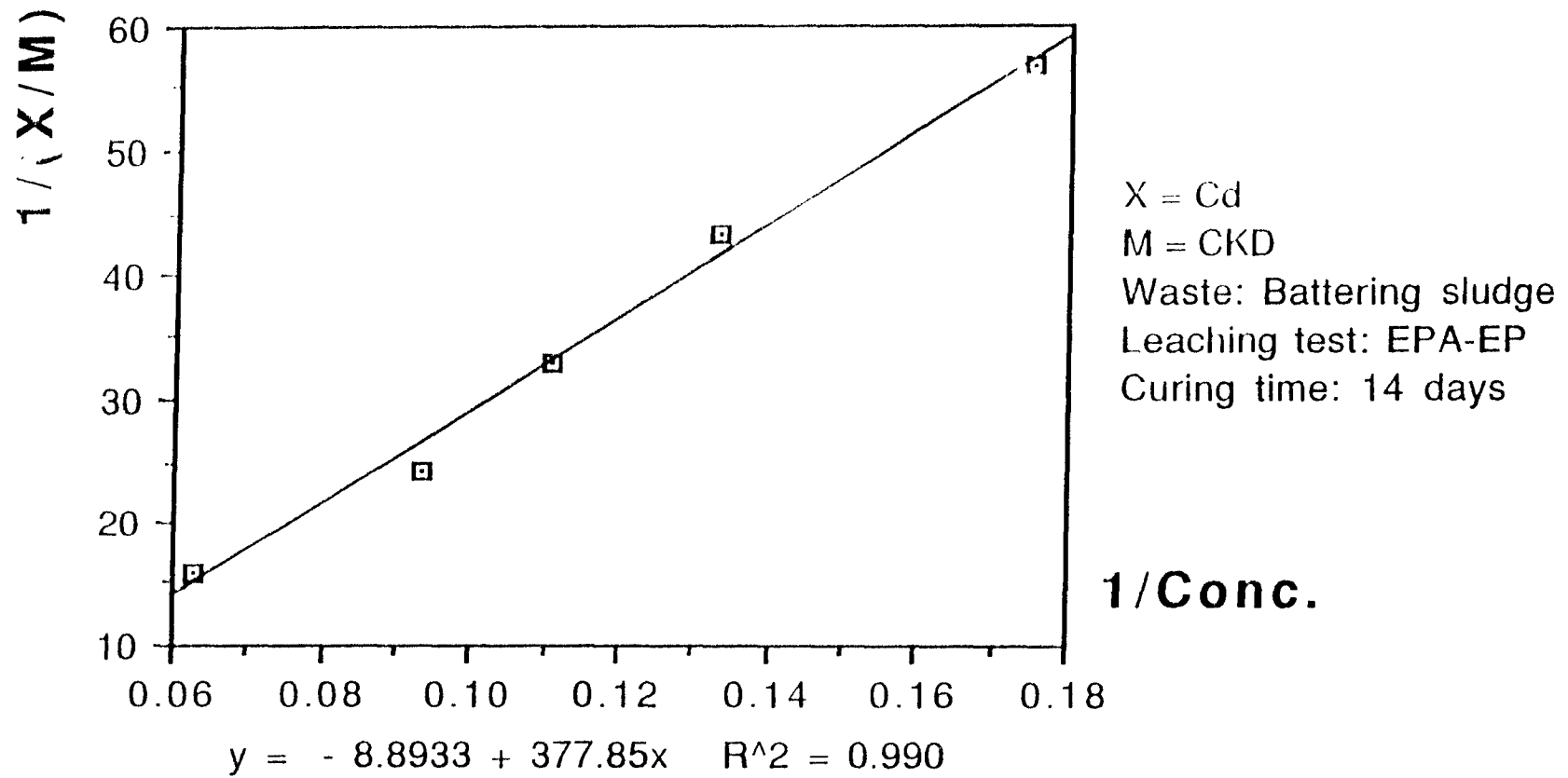


Table 3.2 Langmuir isotherm constants for the leachability of Cr, Pb, As, and Cd sludge

Figure	Sludge	Chemical	Langmuir constant	
			a	b
3.9	Cr-I	OPC	-0.0448	-0.026
3.10	Cr-II	OPC	-0.0674	-0.0114
3.11	Cr-III	OPC	-0.0296	-0.026
3.12	Pb	CKD	-0.31	-0.021
3.13	As	Cement-Casting	-0.0014	-0.601
3.14	Cd	CKD	-0.0235	-0.1124



### III-B Godbee's Model for Leaching Systems

In literature, the accepted model for leaching from chemical solidification and stabilization process is that proposed by Godbee et al.[9]. This model assumes that leaching is controlled by diffusion through the solid, a uniform initial contaminant concentration in the solid, and a zero surface concentration. The model takes the form:

$$\left[ \sum a_n/A_0 \right] [V/S] = 2[De/3.1416]^{0.5} t_n^{0.5} \dots (3-5)$$

where:  $a_n$  = contaminant loss during leaching period  $n$ , mg

$A_0$  = initial amount of a contaminant present in the specimen, mg

$V$  = volume of the specimen,  $\text{cm}^3$

$S$  = surface area of the specimen,  $\text{cm}^2$

$t_n$  = time to the end of leaching period  $n$ , sec.

$De$  = effective diffusion coefficient,  $\text{cm}^2/\text{sec}$ .

In literature, most experiments were run with the column leaching tests and multiple extraction batch leaching tests.

Figure 3.15 [16] shows cumulative fraction leached versus  $t^{0.5}$  for the  $\text{Zn}(\text{OH})_2$  system at an applied flow rate of 0.372 mL/min. Table 3.3 [16] lists the kinetic information using equation (3-5) for fig. 3.15.  $(V/S)$  estimated to be 0.001233 cm.

Figure 3.16 [16] shows cumulative fraction leached versus  $t^{0.5}$  for Zinc sludge at an applied flow rate of 0.588

mL/min. Table 3.4 [16] lists the kinetic information using equation (3-5) for fig. 3.16. (V/S) estimated to be 0.001233 cm.

FIGURE 3.15 Cumulative Fraction Leached ( $\sum a_n/A_0$ ) Versus  $t^{1/2}$  for the  $Zn(OH)_2$  System at an Applied Flow Rate of 0.372 mL/min.

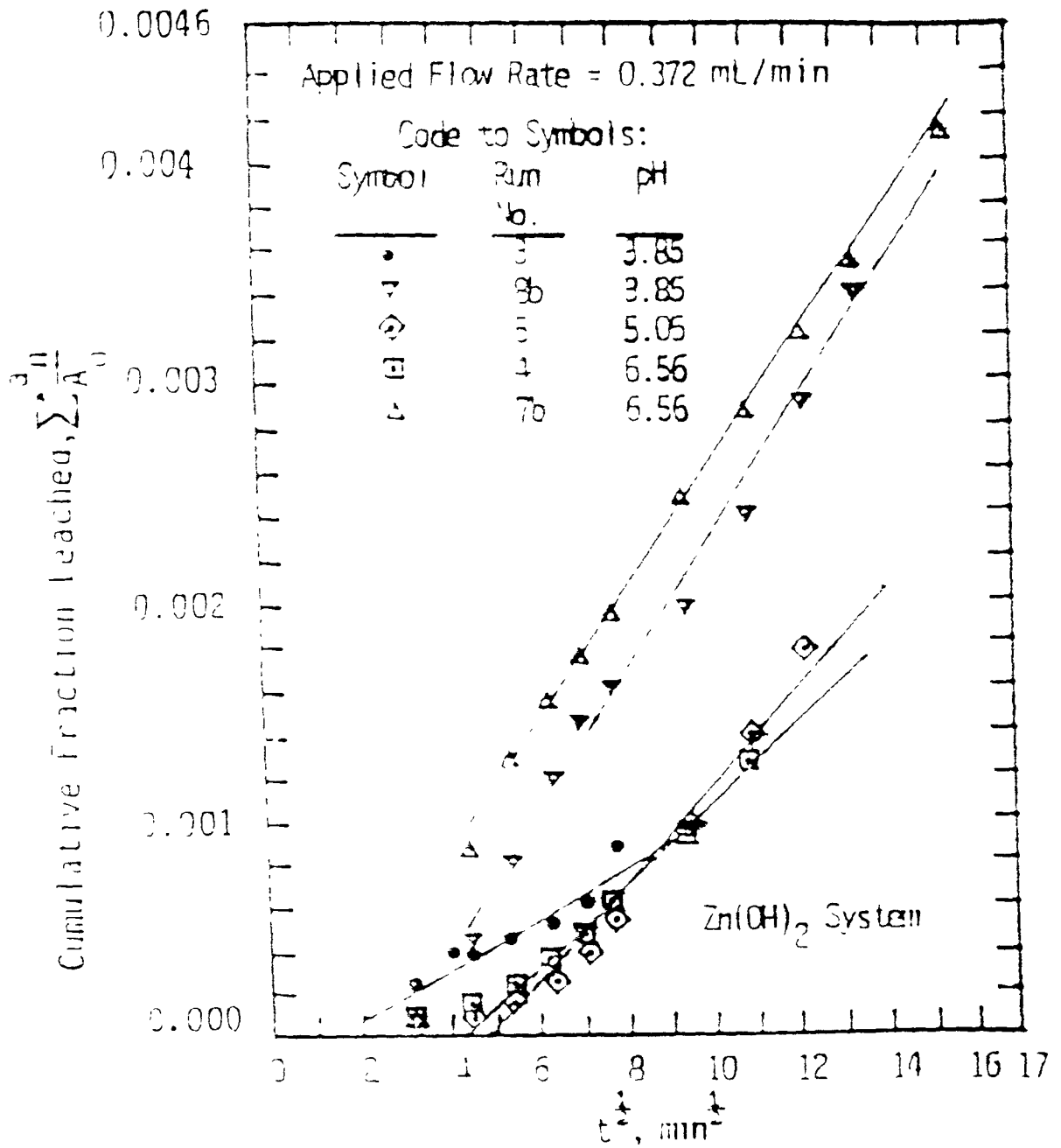


Table 3.3 The Kinetic Information Using Equation (3-5) for the Synthetic Plating Sludge (Fig. 3.15). (V/S) Estimated to be  $1.233 \times 10^{-3}$  cm

Sludge	Run No.	PH <sub>Applied</sub>	Slope, m	Intercept, b	r <sup>2</sup>	De, cm <sup>2</sup> /s
Zn	3	3.85	$1.24 \times 10^{-4}$	$-1.95 \times 10^{-4}$	0.95	$3.05 \times 10^{-16}$
Zn	4	6.56	$1.90 \times 10^{-4}$	$-8.28 \times 10^{-4}$	0.99	$7.15 \times 10^{-16}$
Zn	5	5.05	$2.24 \times 10^{-4}$	$-1.09 \times 10^{-3}$	0.99	$1.00 \times 10^{-15}$
Zn	7b	6.56	$2.89 \times 10^{-4}$	$-3.31 \times 10^{-4}$	0.99	$1.67 \times 10^{-15}$
Zn	8b	3.85	$3.09 \times 10^{-4}$	$-8.65 \times 10^{-4}$	0.99	$1.90 \times 10^{-15}$

FIGURE 3.16 Cumulative Fraction Leached ( $\sum a_n/A_0$ ) Versus  $\tau^{1/2}$  for Zinc sludge at an Applied Flow Rate of 0.588 mL/min.

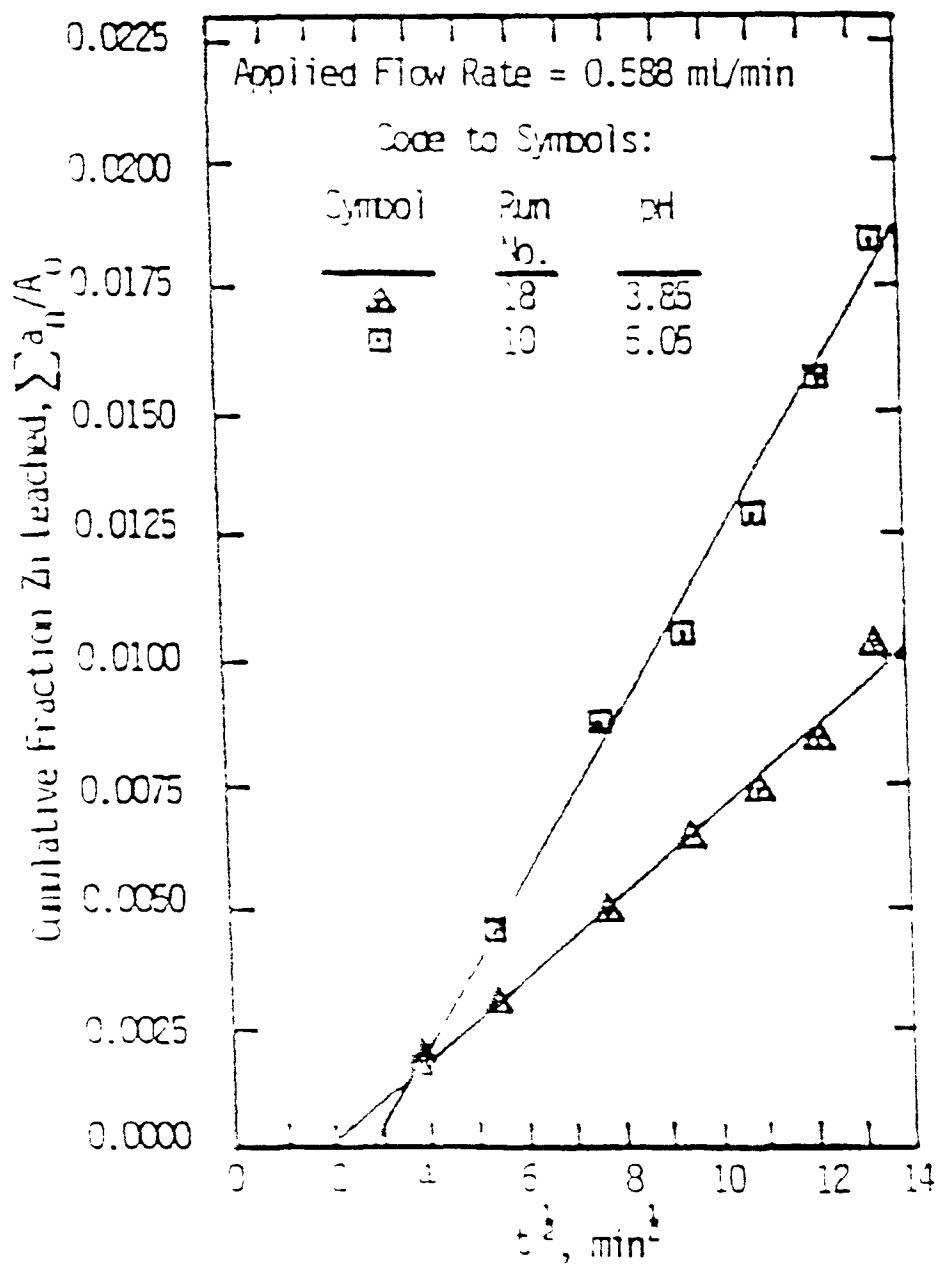


Table 3.4 The Kinetic Information Using Equation (3-5) for the Industrial Plating Sludge (Fig. 3.16). (V/S) Estimated to be  $1.233 \times 10^{-3}$  cm

Sludge	Run No.	PH <sub>applied</sub>	Slope, m	Intercept, b	r <sup>2</sup>	De, cm <sup>2</sup> /s
Zn	10	5.05	$1.67 \times 10^{-3}$	$-4.77 \times 10^{-3}$	0.99	$3.35 \times 10^{-12}$
Zn	18	3.85	$8.40 \times 10^{-4}$	$-1.55 \times 10^{-3}$	0.99	$8.43 \times 10^{-13}$

### III-C This Study Model for Leaching Systems

Here we suggest a model to study leaching rate. The rate is independent of the composition of the groundwater since the contaminant is already mobile. The observed leaching rate decreases with time. By developed linear regression technology, we found out the leaching rate decreases with time proportionally to the term  $[t^{(-2)}]$ , i.e.,

$$-(dC/dt) = K*t^{(-2)} \dots\dots\dots ( 3-6 )$$

$$dC = -K*t^{(-2)}dt \dots\dots\dots ( 3-7 )$$

$$\int dC = -K \int t^{(-2)}dt \dots\dots\dots ( 3-8 )$$

$$C-C_{min} = K*(1/t) \dots\dots\dots ( 3-9 )$$

where: C = concentration of heavy metal leaching out at  
time t, mg/L

C<sub>min</sub> = concentration of heavy metal leaching out when  
time is infinite, mg/L

K = kinetic constant, (mg/L)\*(day)

t = curing time, day

By equation (3-9), we got:

$$C = C_{min}+K*(1/t) \dots\dots\dots ( 3-10 )$$

$$C = (C_{min}*t+K)/t \dots\dots\dots ( 3-11 )$$

$$C = C_{min}*(t+K/C_{min})/t \dots\dots\dots ( 3-12 )$$

We define a new constant  $K_d$ :

$$K_d = K/C_{min} \dots\dots\dots ( 3-13 )$$

where:  $K_d$  = decay constant, day

So we got:

$$C = C_{min} \cdot (t + K_d) / t \dots\dots\dots ( 3-14 )$$

When  $C=2 \cdot C_{min}$ ,  $t=K_d$ . The decay constant,  $K_d$ , specifies the quantitative relationship between time and leaching concentration for different heavy metals, wastes, and cementitious binders. Each heavy metal, waste, and cementitious binder combination has its own characteristic  $K_d$ .

Converting equation (3-14) to the linear form, we have:

$$C \cdot t = C_{min} \cdot K_d + C_{min} \cdot t \dots\dots\dots ( 3-15 )$$

Figure 3.17, 3.18, 3.19, and 3.20 show concentration\*time versus time for Pb, Zn, Cu, and Ni sludges individually.

Table 3.5 shows the kinetic constants,  $C_{min}$  &  $K_d$ , using equation (3-15) for figure 3.17 to 3.20.



Fig. 3.17 This study model applied on Pb sludge

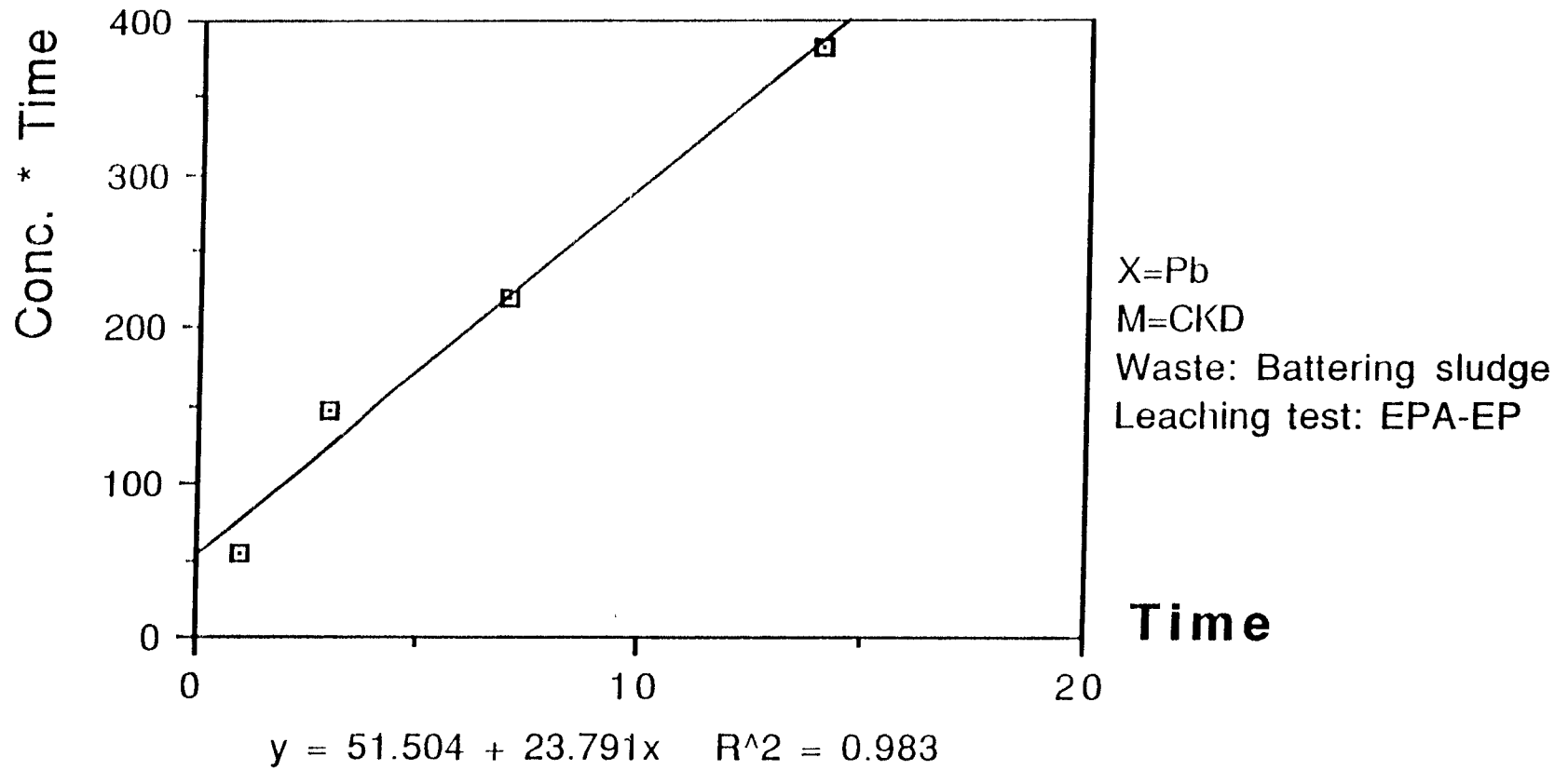


Fig. 3.18 This study model applied on Zn sludge

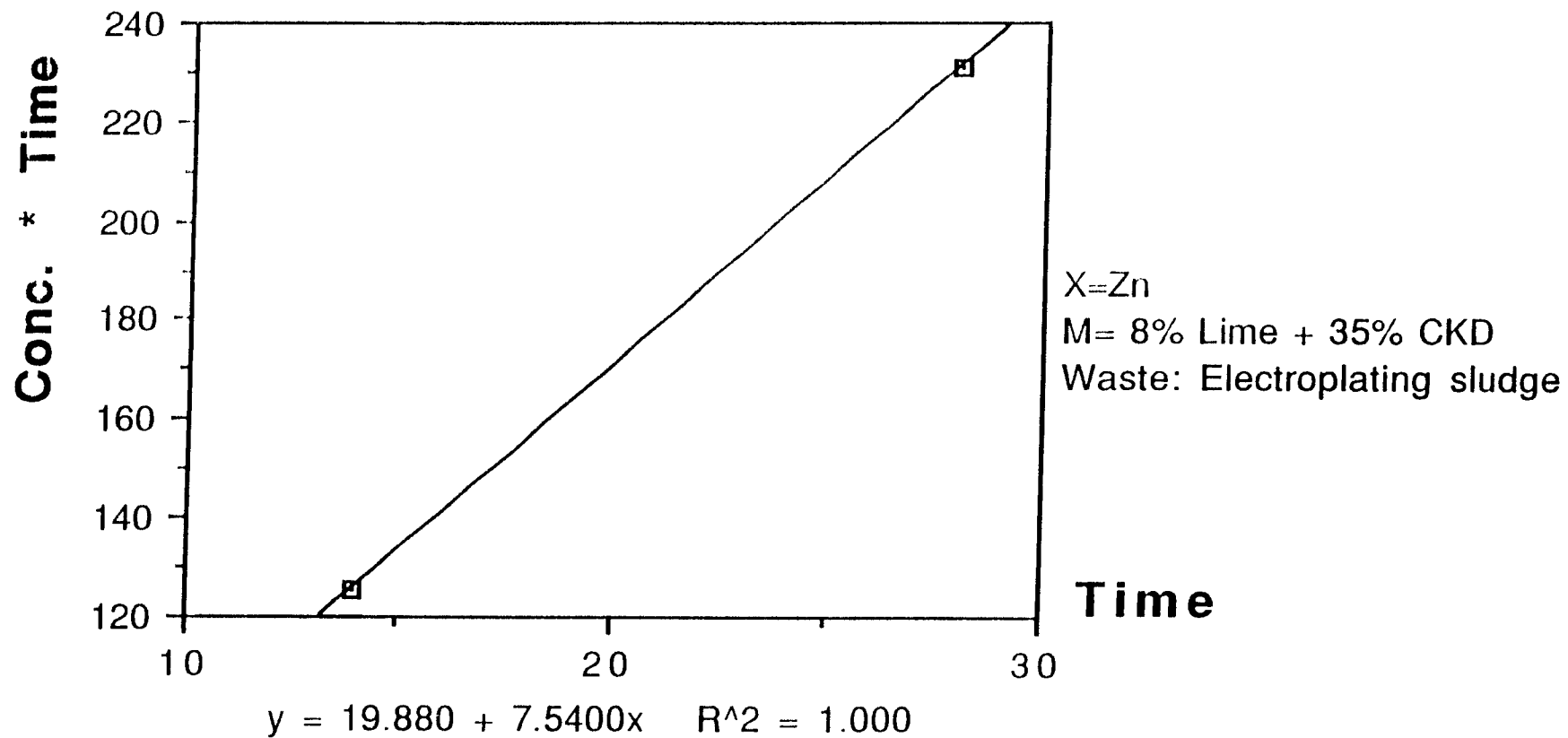


Fig. 3.19 This study model applied on Cu sludge

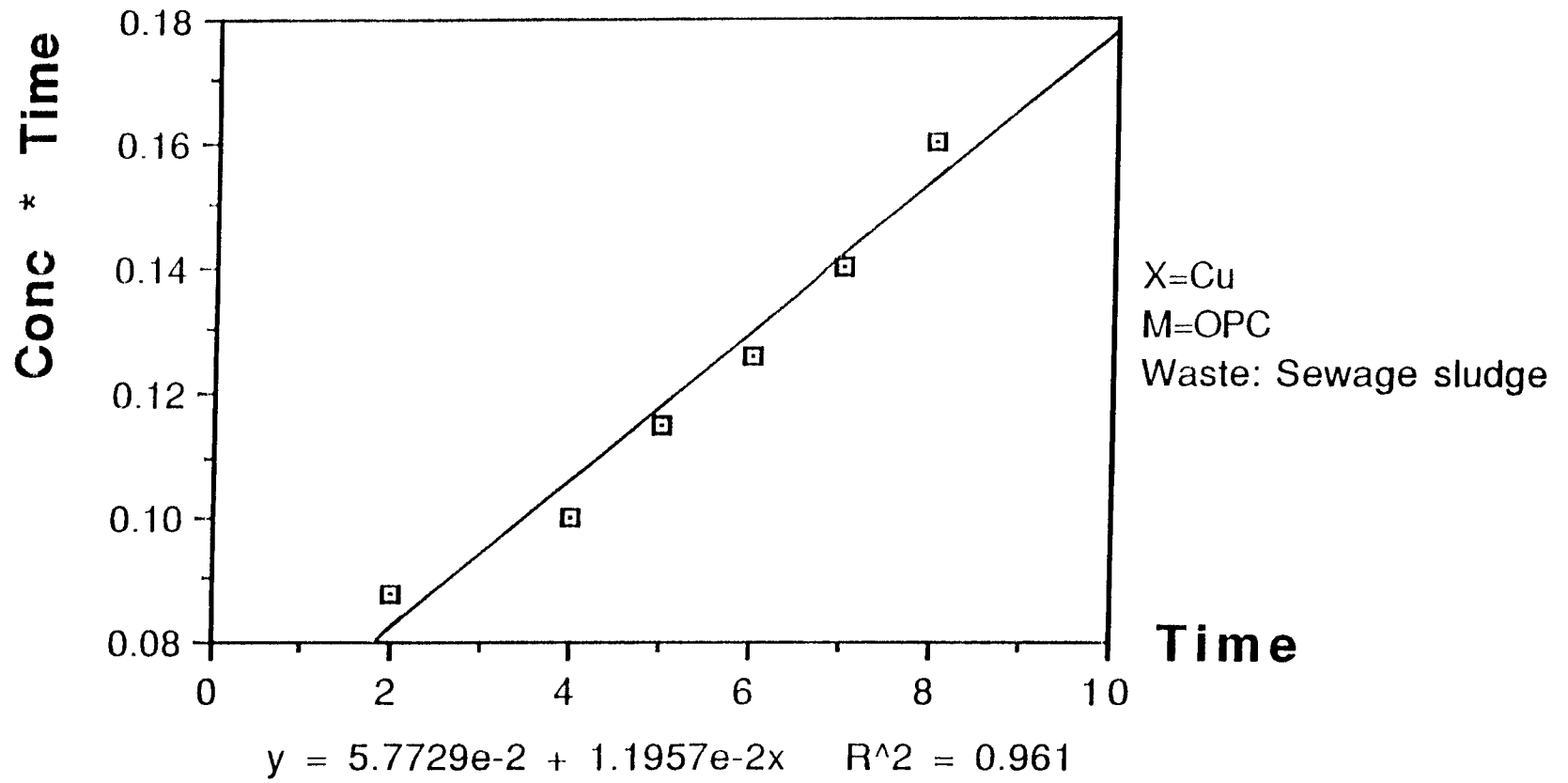


Fig. 3.20 This study model applied on Ni sludge

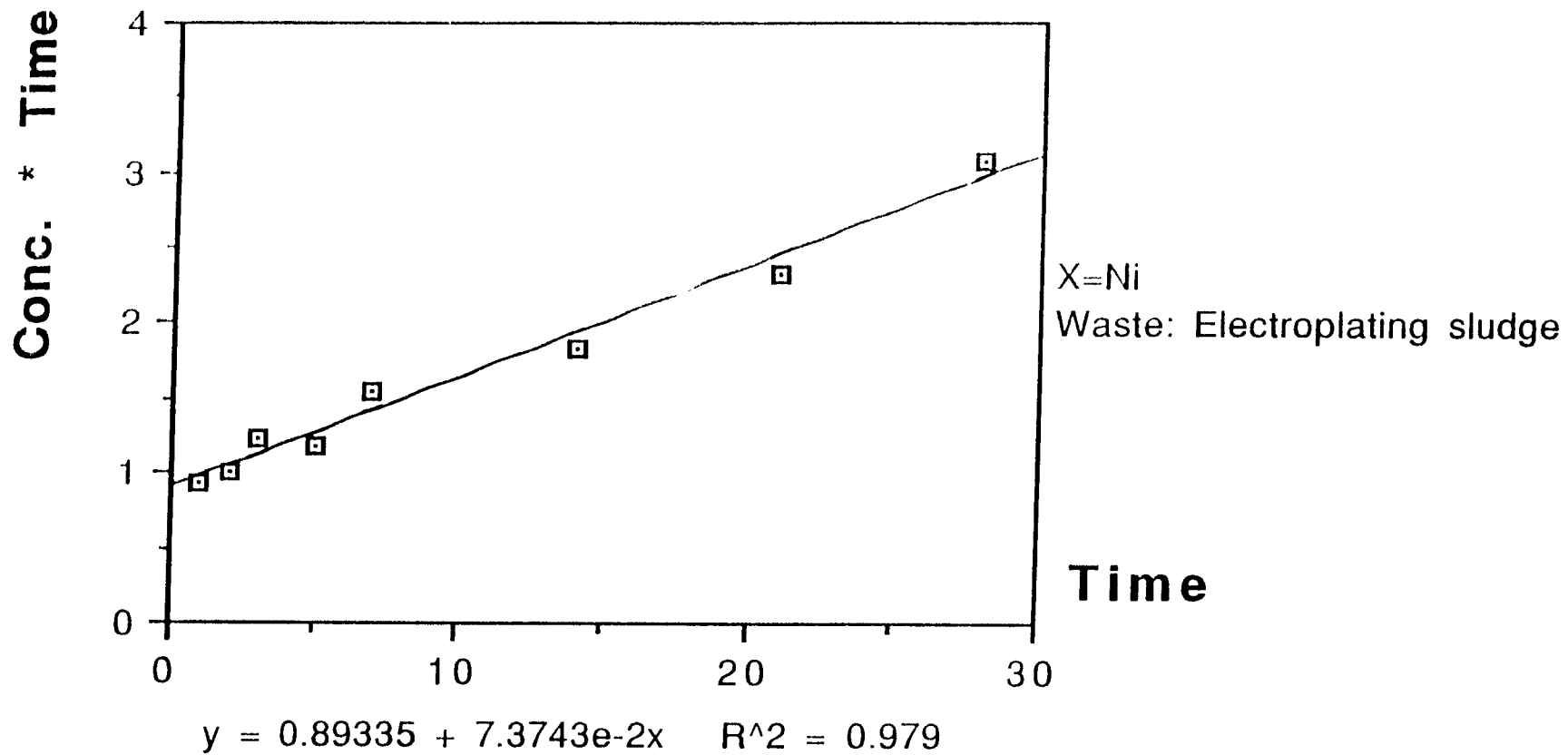


Table 3.5 This study kinetic constants, C<sub>min</sub> & K<sub>d</sub>, for Pb, Zn, Cu, and Ni sludges

Figure	Sludge	Kinetic constant	
		C <sub>min</sub>	K <sub>d</sub>
3.17	Pb	23.8	2.165
3.18	Zn	7.54	2.64
3.19	Cu	0.012	4.83
3.20	Ni	0.074	12.11

#### IV Discussion

1. This study has shown that a very simple mathematical model, equation (3.14), can be used to estimate the leaching rate, and Freundlich & Langmuir isotherms, equation (3-1) & (3-3), can also be applied on CSS process.

2. It has been suggested [15] that the release of metals from cement matrix could be divided into two distinct groups. The first group, comprising Zinc, Lead, and Cadmium, gave PH-dependent releases under equilibrium test conditions, suggesting that the metals are bound up in the cement matrix as the insoluble hydroxides at high PH. The second group, consisting of Copper and Nickel, were released throughout the test, suggesting that the metals were complexed by ligands present in the sludge. In this study model using equation (3-15), we got  $K_d$  of Pb and Zn are 2.165 and 2.64 individually, while  $K_d$  of Cu and Ni are 4.83 and 12.11. The result suggests that if  $K_d < 3.5$ , the metal is supposed to be of the first group, which is bound up as the insoluble hydroxides, and if  $K_d > 3.5$ , the metal could be of the second group, which is complexed by ligands.

3. Using Godbee's model, first you must measure or assume (V/S) value. Second, effective diffusion coefficient,  $D_e$ , varies with extraction time at multiple extraction batch leaching tests [5]. Third, an engineer point of view, those data like  $\sum \frac{a_n}{A_0}$  is not so useful. However, using this

study model, equation (3-14), is much easier and more clear than Godbee's model.

4. Coagulant chemicals such as alum, iron salts, and lime may also be used to treat sediments to stabilize heavy metals in the sediment matrix. Figure 4.1 and 4.2 apply Freundlich isotherm, equation (3-2), on As sludge stabilized with  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Al}_2(\text{SO}_4)_3$  individually, and figure 4.3 and 4.4 apply Langmuir isotherm, equation (3-4), on same sludge. Table 4.1 lists Freundlich and Langmuir isotherm constants for figure 4.1 to 4.4.

5. Metal leaching from solidified hazardous wastes is controlled by many complex factors, including waste type, cementitious binder paste formulation, heavy metal type, particle size, leachant type & PH, curing time, and time of leachant contacts with the waste. Using Freundlich & Langmuir isotherm constants,  $K_f$  &  $n$  &  $a$  &  $b$ , obtained by equation (3-2) & (3-4) and using kinetic constants of this study model,  $C_{\text{min}}$  &  $K_d$ , obtained by equation (3-15) must be careful to make sure all factors are matched. For example, Figure 3.4 and Figure 3.17 both use CKD to stabilize Pb sludge. The former waste is electroplating sludge, however the latter is battering sludge. When data  $(M, L, t) = (45.36, 5.0, 14)$  is used on figure 3.17, we got leaching concentration,  $C$ , is 27.5, but used on figure 3.4, we got 2.72.

Fig. 4 1 Freundlich isotherm applied on As sludge stabilized with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

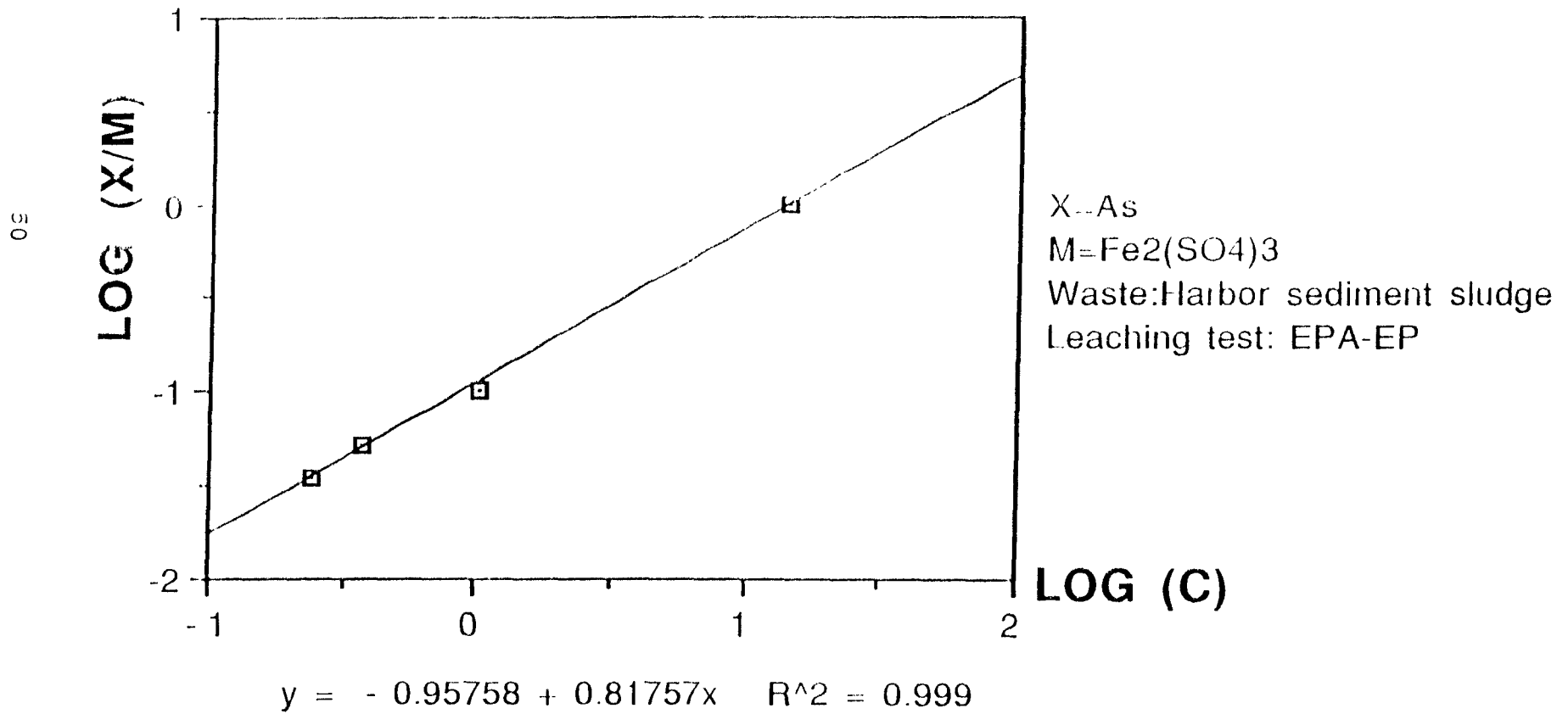




Fig. 4.2 Freundlich isotherm applied on As sludge stabilized with  $\text{Al}_2(\text{SO}_4)_3$

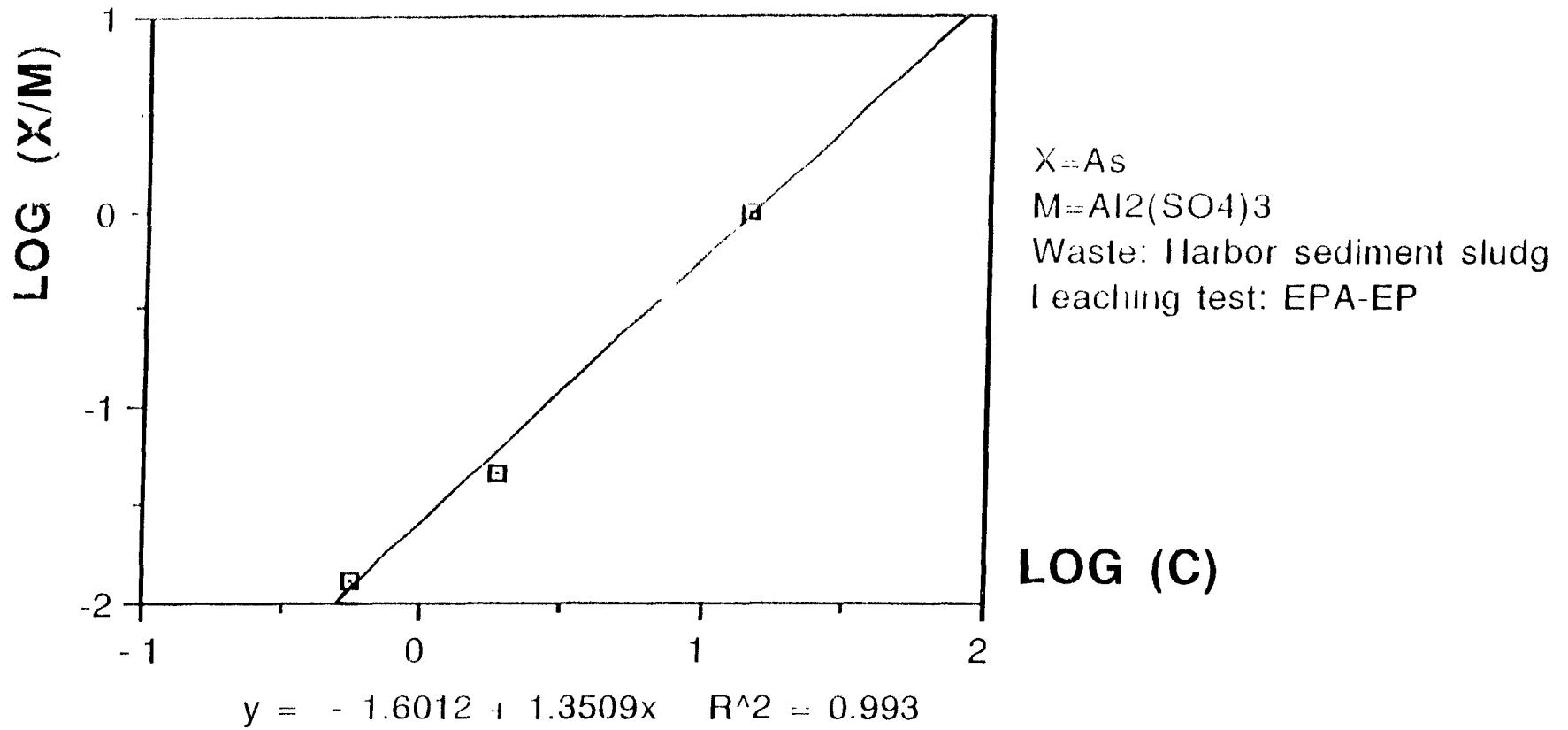


Fig. 4.3 Langmuir isotherm applied on As sludge stabilized with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

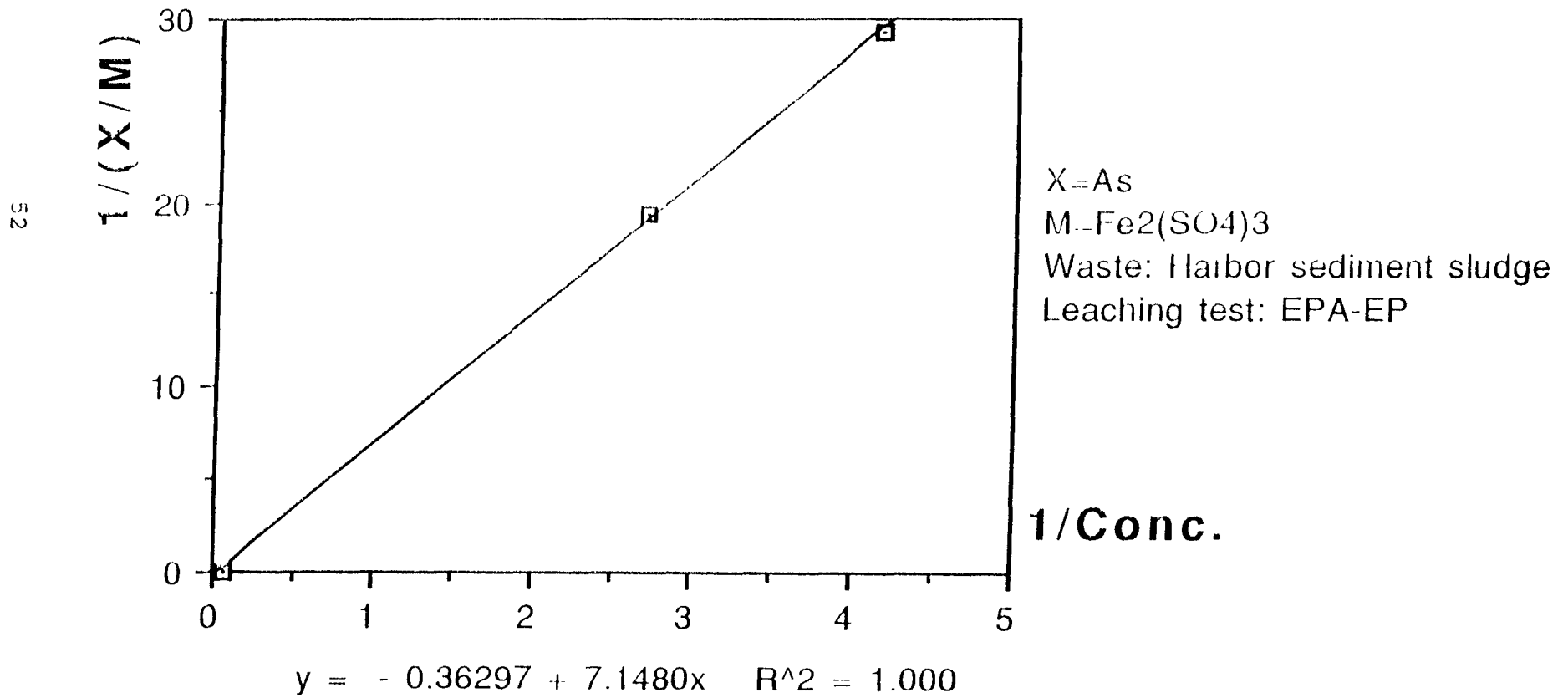


Fig. 4.4 Langmuir isotherm applied on As sludge stabilized with  $\text{Al}_2(\text{SO}_4)_3$

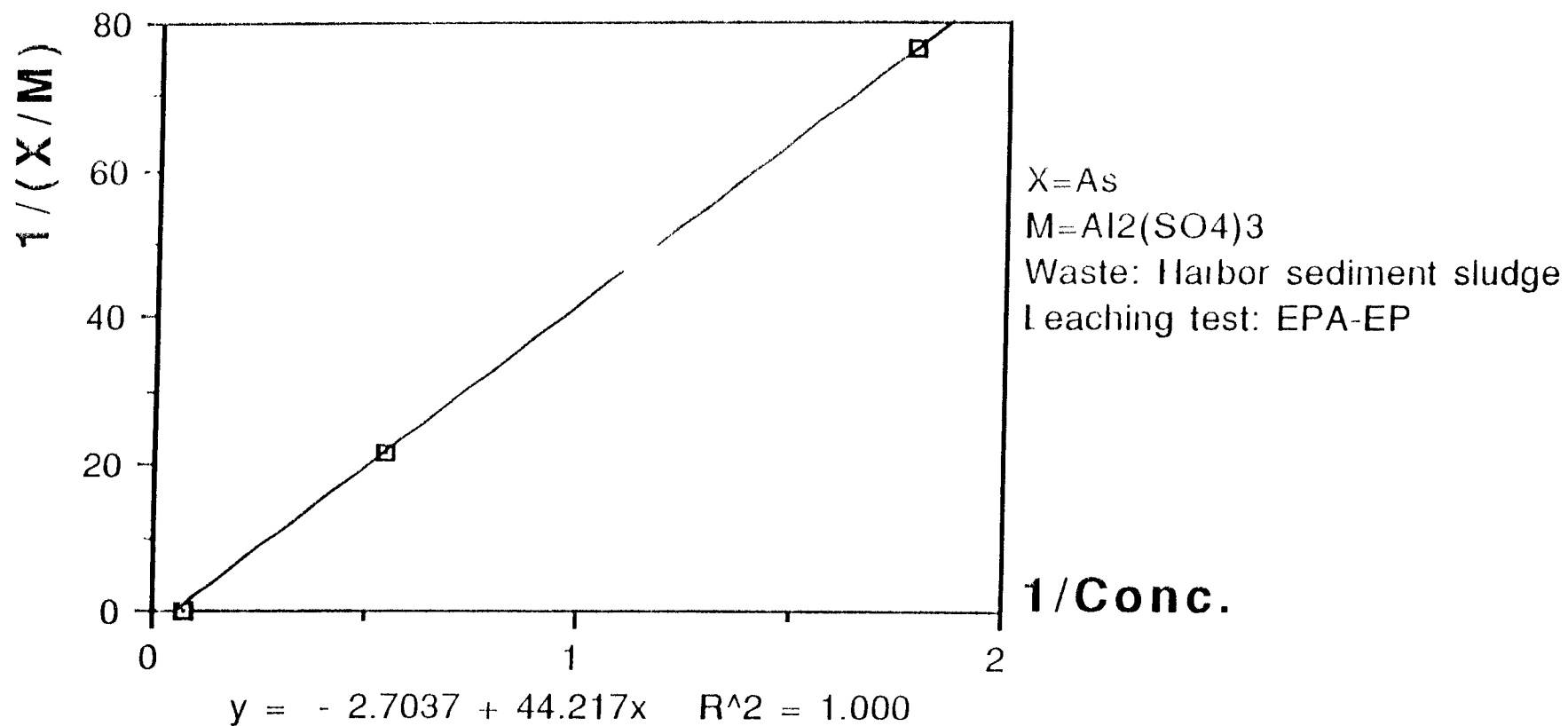


Table 4.1 Freundlich and Langmuir isotherm constants for As sludge

Figure	Sludge	Chemical	Freundlich constant	
			Kf	n
4.1	As	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.11	1.22
4.2	As	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.025	0.74

Figure	Sludge	Chemical	Langmuir constant	
			a	b
4.3	As	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-0.051	-2.755
4.4	As	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-0.061	-0.370

APPENDIX

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
3.1	5.0	1150	3.2	0.0044	-2.36	0.51	[3]
	25.0	1150	10.2	0.0217	-1.66	1.01	
	50.0	1150	13.9	0.0435	-1.36	1.14	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
3.2	5.0	2300	2.4	0.0022	-2.66	0.38	[3]
	25.0	2300	5.4	0.0109	-1.96	0.81	
	50.0	2300	11.3	0.0217	-1.66	1.05	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
3.3	5.0	1150	4.9	0.0044	-2.36	0.69	[3]
	25.0	1150	15.3	0.0217	-1.66	1.18	
	50.0	1150	21.6	0.0435	-1.36	1.33	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
3.4	0.78	45.4	1.46	0.0172	-1.76	0.16	[12]
	3.91	45.4	2.51	0.0861	-1.06	0.40	
	4.69	45.4	2.66	0.1033	-0.99	0.42	
	6.25	45.4	2.91	0.1377	-0.86	0.46	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
3.5	22.0	3000	8.81	0.0073	-2.13	0.94	[23]
	22.0	1000	30.10	0.0220	-1.66	1.48	
	22.0	500	51.90	0.0440	-1.36	1.72	
	22.0	200	74.20	0.1100	-0.96	1.87	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
3.6	0.80	45.4	5.7	0.018	-1.75	0.76	[12]
	1.05	45.4	7.5	0.023	-1.64	0.88	
	1.38	45.4	9.0	0.030	-1.52	0.95	
	1.88	45.4	10.7	0.041	-1.38	1.03	
	2.88	45.4	16.0	0.063	-1.20	1.20	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
3.7	23.0	1150	2492	0.020	-1.70	3.40	[20]
	4.5	1150	447	0.004	-2.41	2.65	
	4.5	2300	223	0.002	-2.71	2.35	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
3.8	23.0	1150	1716	0.020	-1.70	3.23	[20]
	4.5	1150	308	0.004	-2.41	2.49	
	4.5	2300	158	0.002	-2.71	2.20	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	1/(X/M)	1/C	Ref.
3.9	5.0	1150	3.2	0.0044	227	0.313	[3]
	25.0	1150	10.2	0.0217	46	0.098	
	50.0	1150	13.9	0.0435	23	0.072	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	1/(X/M)	1/C	Ref.
3.10	5.0	2300	2.4	0.0022	455	0.417	[3]
	25.0	2300	6.4	0.0109	92	0.156	
	50.0	2300	11.0	0.0217	46	0.088	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	1/(X/M)	1/C	Ref.
3.11	5.0	1150	4.9	0.0044	227	0.204	[3]
	25.0	1150	15.3	0.0217	46	0.065	
	50.0	1150	21.6	0.0435	23	0.046	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	1/(X/M)	1/C	Ref.
3.12	0.78	45.4	1.46	0.017	58.2	0.68	[12]
	3.91	45.4	2.51	0.086	11.6	0.40	
	4.69	45.4	2.66	0.103	9.7	0.38	
	6.25	45.4	2.91	0.138	7.3	0.34	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	1/(X/M)	1/C	Ref.
3.13	22.0	3000	3.81	0.0073	136.4	0.114	[23]
	22.0	1000	30.10	0.0220	45.4	0.033	
	22.0	500	51.90	0.0440	22.7	0.019	
	22.0	200	74.20	0.1100	9.1	0.013	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	1/(X/M)	1/C	Ref.
3.14	0.80	45.4	5.7	0.013	56.8	0.18	[12]
	1.05	45.4	7.5	0.023	43.2	0.13	
	1.38	45.4	9.0	0.030	32.9	0.11	
	1.38	45.4	10.7	0.041	24.1	0.09	
	2.88	45.4	16.0	0.063	15.8	0.06	

FIGURE	C, (ppm)	t, (day)	C*t	Reference
3.17	55.2	1	55.2	[12]
	48.8	3	146.4	
	31.2	7	218.4	
	27.2	14	380.8	

FIGURE	C, (ppm)	t, (day)	C*t	Reference
3.18	8.96	14	125.44	[6]
	8.25	28	231.00	

FIGURE	C, (ppm)	t, (day)	C*t	Reference
3.19	0.044	2	0.088	[15]
	0.025	4	0.100	
	0.023	5	0.115	
	0.021	6	0.126	
	0.020	7	0.140	
	0.020	8	0.016	

FIGURE	C, (ppm)	t, (day)	C*t	Reference
3.20	0.94	1	0.94	[16]
	0.50	2	1.00	
	0.41	3	1.23	
	0.24	5	1.20	
	0.22	7	1.54	
	0.13	14	1.82	
	0.11	21	2.31	
	0.11	28	3.08	



FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
4.1	0.771	0	14.44	N.A.	0	1.160	[24]
	0.771	7.43	1.02	0.104	-0.98	0.009	
	0.771	14.90	0.37	0.052	-1.29	-0.432	
	0.771	22.50	0.24	0.034	-1.47	-0.620	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	LOG(X/M)	LOG(C)	Ref.
4.2	0.771	0	14.44	N.A.	0	1.16	[24]
	0.771	16.9	1.83	0.046	-1.34	0.26	
	0.771	58.7	0.56	0.013	-1.88	-0.25	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	1/(X/M)	1/C	Ref.
4.3	0.771	0	14.44	N.A.	0	0.069	[24]
	0.771	14.9	0.37	0.052	19.33	2.703	
	0.771	22.5	0.24	0.034	29.18	4.167	

FIGURE	X, (g)	M, (g)	C, (ppm)	X/M	1/(X/M)	1/C	Ref.
4.4	0.771	0	14.44	N.A.	0	0.069	[24]
	0.771	16.9	1.83	0.046	21.9	0.546	
	0.771	58.7	0.56	0.013	76.1	1.786	

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