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DISSOLUTION AND PRECIPITATION OF GYPSUM

IN THE SOIL UNDER IRRIGATION

by

Badier J. Alawi

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soil Science

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Badier J. Alawi
Badier J. Alawi

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
NOTATIONS	vi
ABSTRACT	vii
Chapter	
I. INTRODUCTION	1
Objective	2
II. LITERATURE REVIEW	3
III. THEORY	20
a) Effluent in equilibrium with gypsum	22
b) Effluent in equilibrium with both gypsum and lime	24
c) Effluent in equilibrium with lime	28
IV. MATERIALS AND METHODS	33
Soil column studies	33
V. RESULTS AND DISCUSSION	37
VI. SUMMARY AND CONCLUSIONS	70
LITERATURE CITED	73
VITA	75

LIST OF TABLES

Table	Page
1. Characteristics of Vernal soil columns	35
2. Characteristics of Yolo soil columns. Saturated moisture studies	35
3. The flow rate and the moisture content under unsaturated moisture studies of Yolo and Vernal soils columns	36
4. Solubility of CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in waters used in this study	38
5. Solubility product data for Yolo loam soil column with 2% gypsum and 1% lime leached with Logan river water	46
6. Solubility product data for Yolo loam soil column with 2% gypsum and 1% lime leached with K_2SO_4	48
7. Solubility product data for Yolo loam soil column with 2% gypsum and 1% lime leached with KCl	50
8. Solubility product data for Yolo loam soil column with 1% gypsum and 1% lime leached with Logan river water (unsaturated flow)	52
9. Solubility product data for Yolo soil with 1% gypsum and 1% lime leached with Logan river water (unsaturated flow)	56
10. The solubility product data for Vernal soil leached with Logan river water (saturated flow).	60
11. The solubility product data for Vernal soil leached with Logan river water (unsaturated flow).	61
12. Calcium and sulfate removal from treated Yolo loam soil	67

LIST OF FIGURES

Figure	Page
1A. Electrical conductivity of the effluent of Yolo soil columns leached with Logan River water under saturated conditions	40
1B. pC_{Ca} of the effluent of Yolo soil columns leached with Logan River water under saturated conditions.	42
2A. Electrical conductivity of the effluent of Yolo soil (2% gypsum + 1% lime) columns leached under saturated conditions.	43
2B. pC_{Ca} of the effluent of Yolo soil (2% gypsum + 1% lime) columns leached under saturated conditions.	44
3A. Electrical conductivity of the effluent of Yolo soil (1% gypsum + 1% lime) columns leached with Logan River water.	54
3B. pC_{Ca} of the effluent of Yolo soil (1% gypsum + 1% lime) columns leached with Logan River water	55
4A. Electrical conductivity of the effluent of Vernal soil leached with Logan River water	58
4B. pC_{Ca} of the effluent of Vernal soil columns leached with Logan River water.	59
5A. Electrical conductivity of the effluent of soil columns leached under unsaturated conditions with Logan River water.	62
5B. pC_{Ca} of the effluent of soil columns leached under unsaturated conditions with Logan River water	63
6A. Calcium concentration of the effluent of a Yolo soil (2% gypsum + 1% lime) column leached with KCl solution under saturated conditions	65
6B. Sulfate concentration of the effluent of a Yolo soil (2% gypsum + 1% lime) column leached with KCl solution under saturated conditions	69

NOTATIONS

a_i	Activity of ionic specie i
[]	Concentration of ionic specie in the solution (moles/Liter)
K_h	Henry's Law constant
()	Activity of ionic specie in solution
I	Ionic strength (moles/Liter)
γ_i	Activity coefficient of specie i
[] _T	Total analytical concentration of ionic specie in solution
$K_d \text{HCO}_3$	Dissociation constant of Bicarbonate complex
$K_d \text{CO}_3$	Dissociation constant of carbonate complex
$K_d \text{SO}_4$	Dissociation constant of sulfate complex
$K_d \text{OH}$	Dissociation constant of hydroxyle complex
$K_{sp} \text{SO}_4$	Solubility product of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$K_{sp} \text{CO}_3$	Solubility product of CaCO_3
K_{A1}	First dissociation constant of H_2CO_3
K_{A2}	Second dissociation constant of H_2CO_3
P_{CO_2}	Partial pressure of CO_2 (atmosphere)
pC_{Ca}	$-\text{Log} [\text{Ca}]_T$

ABSTRACT

Dissolution and Precipitation of Gypsum
in the Soil Under Irrigation

by

Badier J. Alawi, Master of Science

Utah State University, 1974

Major Professor: Dr. J. J. Jurinak
Department: Soil Science and Biometrology

Two soils were used in this soil column study. Yolo loam soil a non-calcareous, non-gypsiferous soil from central California and Vernal soil a calcareous soil from eastern Utah.

Initial studies were conducted where the solubilities of pure CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were determined in the presence of Logan river water, a KCl solution (2.8 mmhos/cm) and a K_2SO_4 solution (2.7 mmhos/cm). Gypsum was more soluble in the KCl solution than in the K_2SO_4 solution. The solubility product of both gypsum and lime were determined from the analytical data. The formation of CaSO_4^0 and CaCO_3^0 ion pairs were considered to be the most important complex ions present. A reasonable agreement was observed between the theoretical values of K_{sp} and the calculated K_{sp} . Essentially the same results were obtained when these waters were used in leaching the columns of Yolo and Vernal soil columns.

The solubility of gypsum was greatest using the KCl leaching solution and least using the K_2SO_4 leaching solution. Logan river water gave intermediate values.

Calcium carbonate was most soluble in the K_2SO_4 leaching solution and less in the KCl solution. It was found that measuring the Ca^{2+} concentration in the effluent was a more reliable index to steady state condition than using an electrical conductivity measurement. Unsaturated flow removed more salt per unit volume of effluent than saturated flow. The relative area method was used to analyze the effluent under saturated moisture flow. It was found that a certain amount of Ca^{2+} derived from gypsum dissolution precipitated in the column as $CaCO_3$. This amount was greater than 15% of the Ca^{2+} dissolved from gypsum.

(83 pages)

CHAPTER I

INTRODUCTION

The quality of irrigation water is one of the most important factors which influence, directly or indirectly soil and water management practices, plant growth, and crop yields. Knowledge of irrigation water quality allows decisions to be made as to how best use this resource from maximum benefit. For example, consideration of the quality of available irrigation water together with soil and climate data help determine, to a large extent, what crops can be grown or cannot be grown in a given area. In addition, the method of irrigation and its frequency are also dependent on the quality of irrigation water available for given project. Water and its soluble components, applied during irrigation are subjected to numerous chemical reactions as it percolates through the soil matrix.

Many of these reactions are complex and are still only qualitatively understood.

As irrigation water moves through an arid zone soil profile the reactions that will occur include:

- a) Cation exchange involving both the organic and inorganic colloidal complex of the soil.
- b) The precipitation and/or dissolution of various compounds

commonly found in soil such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$.

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is not only found naturally in many soils of arid regions, but it can precipitate from irrigation water if the solubility product of gypsum is exceeded in the soil during an irrigation cycle. The lime minerals (CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$) similarly can be precipitated from irrigation water percolating through the soil and, can also exist abundantly as indigenous soil minerals.

Thus both gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and lime (CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$) minerals can be regarded as either a source or sink for Ca^{++} ion in the soil solution during irrigation.

Because of the difference in relative solubility between gypsum and the lime minerals, the effect of these minerals on the composition of irrigation water percolating through the soil is considerably different. The effect of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 on the composition of the soil solution during irrigation is the basis of this study.

Objective

The research reported here is a laboratory soil column study to determine primarily:

1) If by chemical analysis of the soil column effluent it is possible to predict if $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or CaCO_3 controls the Ca^{2+} concentration in the percolating water.

2) Is it possible to quantify the dissolution or precipitation of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or CaCO_3 during irrigation by calculating the solubility product of these compounds from soil column effluent.

CHAPTER II

LITERATURE REVIEW

Most of the studies reported for determining the solubility and the solubility product of gypsum ($\text{Ca SO}_4 \cdot 2\text{H}_2\text{O}$), and Lime (Ca CO_3) are based on the analysis of aqueous solutions. Particularly in the studies no attention was given to the possibility of ion-pair formation that could strongly affect solubility.

Cameron in (1901) studied the solubility of gypsum in aqueous solution of sodium chloride at various temperatures and various concentrations of salt. The following conclusions were made.

1. The maximum solubility of gypsum in aqueous solution of NaCl was at 37.5°C .
2. At 23°C , the maximum solubility of gypsum takes place in a solution containing from 135 to 140 gm/L NaCl.
3. The solubility of gypsum at 23°C in solution containing 135 gm/L NaCl is about 9.3 gm. L.
4. The solubility of gypsum in solution containing less than 140 gm/L NaCl is very little affected by a change of temperature.
5. The maximum in the solubility curve, which he plotted, still persisted even when the solubility was calculated on the basis of weight of solvent present rather than on the volume of the solution.

The time required for equilibrium was often great at ordinary temperatures due to the slow rate of gypsum dissolution.

Frear and Johnston in 1929 measured the solubility of calcium carbonate (lime) at 25°C in presence of carbon dioxide at pressures that varied from 3×10^{-4} to 1.0 atmosphere in a series of solutions of NaCl and $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$ gypsum including solutions saturated with respect to gypsum $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$. The following expression was used to calculate the solubility product of lime when the calcium carbonate was at equilibrium with the aqueous solution.

$$K_c = (\text{Ca}^{2+})(\text{CO}_3^{2-})$$

Where

K_c = the solubility product of calcium carbonate

(Ca^{2+}) = activity of calcium

(CO_3^{2-}) = activity of carbonate

For gypsum

$$K_G = (\text{Ca}^{2+})(\text{SO}_4^{2-})$$

Where

K_G = The solubility product of gypsum

$(\text{Ca}^{2+}) =$ activity of calcium

$(\text{SO}_4^{2-}) =$ activity of sulfate

The unsaturated solutions of gypsum, the solubility of CaCO_3 depended upon the common ion effect and upon the total ion concentration as it affected the activities of the chemical species involved in the equilibrium. They found out the solubility product of CaCO_3 at 25°C in water saturated with carbon dioxide at pressure range from 3×10^{-4} to 1 atmosphere in terms of ionic activities was (4.8×10^{-9}) .

The solubility of CaCO_3 in an aqueous solution of saturated calcium sulfate and sodium chloride was greater than that found in an unsaturated solution.

The standard entropy and free energy of solution of aqueous sulfate ion was investigated by Lattimer, Ghickes and Philips in (1937) using three solutions:

- a) Silver sulfate
- b) Calcium sulfate
- c) Barium sulfate

The standard entropy value of the sulfate ion was considered to be more reliable when determined in the calcium sulfate system than when determined in the silver sulfate or barium sulfate systems.

The following expression was used to calculate the standard free energy of solution

$$\Delta F^{\circ} = \Delta H^{\circ} + T\Delta S^{\circ}$$

Where

ΔF° = Standard free energy of solution

ΔH° = Standard heat of solution

$$\Delta F^{\circ} = -RT \ln K_{sp}$$

ΔS° = Standard entropy of solution

Jacob Kielland (1937) investigated the activity coefficients of ions in aqueous solutions, which had largely been computed by independent means. The Debye-Huckel formula was used to calculate the activity coefficient of the ions.

$$\text{Log } f_i = \frac{-0.3582_i^2 \sqrt{I}}{1 + 10^8 a_i 0.2325 \sqrt{I}} = \text{Log } \gamma_i + \text{Log} \left(1 + 0.018 \sum_{i=1}^S m_i \right)$$

Where

f_i = Denotes the rational activity coefficient of the i th ion.

γ_i = The practical activity coefficient of i th ion with valence Z_i

I = The ionic strength

$$I = \sum c_i Z_i^2$$

C_i = The concentration of ion in moles/Liter.

The a_i factor (distance of closest approach between ions) was calculated approximately by different methods.

Bonion and Centola (1933) suggested the following formula for ionic activity coefficient up to an ionic concentration of about $I = 0.2$.

$$\text{Log } \gamma_i = 0.5 Z_i^2 I^{\frac{1}{2}} / 1 + I^{\frac{1}{2}}$$

Which is equal to $(-0.354 Z_i^2 I^{\frac{1}{2}} / (1 + 3.4 \times 0.2325I)^{\frac{1}{2}})$

This expression is based on the assumption that $a_i = 3A^0$ for all ionic species.

Denman (1961) obtained accurate gypsum solubility data under conditions of varying salt content (gypsum common ion salts and non common ion salts). Common ion salts usually did not exceed 30 epm (equivalent parts per million) and non-common ion salts rarely exceeded 40 epm (equivalent parts per million). Common ion salts were Na_2SO_4 or MgSO_4 ; non-common salt was predominately NaCl . The temperature of the solubility studies was that existing in cooling water of evaporative cooling systems. He considered the activity coefficients when he calculated gypsum solubility in the mixture of these salts. Agreement was found between the experimental and calculated values.

He showed that the solubility of gypsum decreased in presence of Na_2SO_4 and MgSO_4 while it increased in presence of NaCl . Thus he concluded that the solubility of gypsum decreased in presence of common ions while it increased in the presence of non common -ions salts.

Moreno and Osborn (1963) studied the solubility isotherm of gypsum and calculated its solubility product and the solubility of dicalcium phosphate dihydrate (C. Cp. D) in presence of gypsum, and its behavior in soil and in aqueous solutions.

The activity of sulfate was calculated by using the following expression:

$$(\text{SO}_4^{2-}) = \frac{[\text{SO}_4^{2-}]}{\frac{1}{\gamma_{\text{SO}_4^{2-}}} + \frac{(\text{H}^+)}{K_s \gamma_{\text{HSO}_4}} + \frac{[\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}}}{K_d}}$$

Where

(SO_4^{2-}) is the activity of sulfate

γ_i = The activity coefficient of the *i*th ion

$K_s = 1.03 \times 10^{-2}$ (constant)

$K_d =$ The ion-pair dissociation constant of $\text{CaSO}_4^0 = 4.9 \times 10^{-3}$

The activity coefficient (γ_i) was calculated by the following formula

$$\text{Log } \gamma_i = \frac{0.508 Z_i^2 I^{\frac{1}{2}}}{1 + 0.3 a_i I^{\frac{1}{2}}}$$

Where

a_i = The ionic radius parameter

I = The ionic strength

Z = The valence of the ionic species

To calculate the activity of the complex (CaSO_4^0) the following expression was used.

$$(\text{CaSO}_4^0) = \frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]\gamma_{\text{SO}_4^{2-}}}{K_d} = \frac{K_g}{K_d}$$

Where

(CaSO_4^0) is the activity of ion-pair complex (CaSO_4^0)

$[\text{Ca}^{2+}]$ is the concentration of calcium in moles/Liter

$[\text{SO}_4^{2-}]$ is the concentration of sulfate ion in moles/Liter.

K_g is the solubility of product gypsum

K_d is the dissociation constant of CaSO_4^0

Then

$$K_g = [\text{Ca}^{2+}][\text{SO}_4^{2-}]\gamma_{\text{Ca}^{2+}}$$

The solubility product of gypsum calculated from this research was found to be 2.45×10^{-5} .

Dutt (1964) investigated the effect of small amounts of gypsum in soil on the composition soil column effluents. Calcium-saturated Yolo Loam was used for this study. Various amounts of gypsum were placed to soil columns, and the columns were leached with a solution containing 50 mg MgCl_2 .

After the chemical analysis of the effluents was done, he found that the presence of gypsum has a little effect on the Na^+ in the effluent. However, the concentration of Mg^{2+} was dependent on the amount of gypsum present in the system. The concentration of Mg^{2+} in the effluent increased to a value approaching the concentration of the input solution entering the soil when the gypsum added was leached from the soil column.

Ostroff and Metler (1966) determined the solubility of calcium sulfate dihydrate in system $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$ at 28, 38, 50, 70 and 90°C and in range of concentration up to 5.5 molal NaCl and 6.34 molal MgCl_2 in admixtures.

They showed that the solubility of calcium sulfate in distilled water decreased with an increase in temperature.

The presence of small amounts of MgCl_2 in a NaCl solution markedly influenced gypsum solubility up to approximately 2.5m (molal) NaCl, and a higher molalities of NaCl the effect of MgCl_2 decreased.

The highest concentrations of NaCl used was 4 molal.

They did not observe any difference in gypsum solubility between the NaCl solution and the mixed NaCl and Mg Cl₂ solution.

The solubility and solubility product for gypsum were calculated as follows:

$$S = a + b (m \text{ NaCl}) + C (m \text{ NaCl})^2 + d (m \text{ NaCl})^3 + e (m \text{ NaCl})^4$$

Where

a, b, c, d, and e are empirical parameters determined at various temperatures.

S is the solubility of gypsum in moles/L

Then

$$\text{Log } K_{sp} = \frac{-AZ_i^2 \sqrt{I}}{1 + Ba_i \sqrt{I}} + 2 \text{ Log } m$$

Where

K_{sp} is the solubility product of gypsum

A is a constant at a given temperature.

Z is the valance of Ca²⁺ or SO₄²⁻

B is a constant

a_i is a constant

I is the ionic strength

m is the molality

Marshall and Slusher (1966) studied the solubility of calcium sulfate dihydrate in aqueous solution of sodium chloride (NaCl).

They concluded that the variation of the gypsum solubility could be described to high ionic strength (2m) at temperatures from 0 to 100°C by only one parameter commonly referred to as the ionic size parameter α . This evaluation yielded a constant value of 4-5Å for α over the entire range of temperature. At ionic strengths above (2m) and at low temperature, the gypsum solubility showed negative deviations from the one parameter expression in contradiction to the expected behavior for the association of Ca^{2+} or SO_4^{2-} with Na^+ or Cl^- ions.

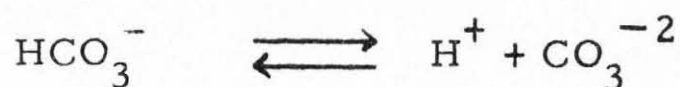
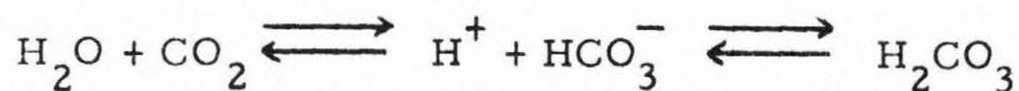
Meites, Pode and Thomas (1966) investigated the relationship between the solubilities and solubility products for some chemical compounds.

They said that this relationship is a very distant one indeed. They observed both the effect of ions pairs and common ions. A comparison between the solubility products which were calculated by using the concentration and the activity of each ion species was made.

They concluded that the solubility products which depended on ionic activity is more suitable and reasonable than that which depended on the total concentration due to the effect of ion-pairs formation.

Olsen and Watanabe (1959) determined the solubility of calcium carbonate in calcareous soils. They examined the application to various calcite solubility equations to calcareous soils. Deviations from these equations was noted because of a higher than expected solubility of the calcareous material in soils.

The following equations were used to relate PCO_2 , HCO_3^- , H^+ and Ca^{2+} in the pure calcite system. They assumed that the system involved the simultaneous equilibria of CO_2 and H_2O and solubility of CaCO_3 in H_2O



$$K_{1A} = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{CO}_2)(\text{H}_2\text{O})} \quad (1)$$

Where

K_{1A} is the first ionization constant for carbonic acid. (H^+) , (HCO_3^-) , (CO_2) , (H_2O) are the activities of H^+ , HCO_3^- , CO_2 , and H_2O , respectively.

It is assumed that γ_{CO_2} is unity in H_2O , thus (CO_2) can be replaced by m_{CO_2}

$\text{H}_2\text{CO}_3 = C_{\text{PCO}_2}$ where C = Henry's Law Constant and PCO_2 = partial pressure of CO_2 in atmospheres. Therefore,

$$K_{1A} = \frac{(\text{H}^+)(\text{HCO}_3^-)}{C_{\text{PCO}_2}} \quad (2)$$

Where

$$K_{1A} = 4.45 \times 10^{-7}$$

$$C = 0.0344 \text{ at } 25^{\circ}\text{C}$$

Now

$$K_2 = \frac{(\text{H}^+)(\text{CO}_3^{2-})}{(\text{HCO}_3^-)} \quad (3)$$

Where

K_2 is the ionization constant of HCO_3^- and equal to 4.69×10^{-11} at 25°C . The solubility product of calcite is

$$K_{sp} = (\text{Ca}^{2+})(\text{CO}_3^{2-}) \quad (4)$$

Where

K_{sp} is the solubility product of calcite with value of 4.82×10^{-9} at 25°C .

By substituting equations (2) and (3) into (4) equation (5) is obtained

$$\frac{K_{sp}}{K_{1A} K_2 C} = \frac{(\text{Ca}^{2+})}{(\text{H})^2} \text{PCO}_2 \quad (5)$$

Equation (2) and (5) show that (pH) is a function of both (Ca^{2+}) and (HCO_3^-) but these ion have opposite effect on pH at constant CO_2 pressure.

An increase in (HCO_3^-) will increase the pH. The effect of a change in (Ca^{2+}) on pH is less than that of (HCO_3^-) .

The pH was calculated from the activity of HCO_3^- by using the following formula.

$$\text{pH} = \text{pK}_{1A} - 0.509\sqrt{I} + \text{Log} (\text{HCO}_3^-) - \text{Log} \text{CPCO}_2$$

Where

I is the ionic strength and was calculated assuming a 2:1 electrolyte as $\text{Ca}(\text{HCO}_3)_2$.

$$\text{Log} \gamma_{\pm} = -0.509\sqrt{I}$$

γ_{\pm} is the mean activity coefficient of CaCO_3 which calculated from the Deby-Huckel Limiting Law.

Tanji (1969) determined solubility of gypsum in aqueous electrolytes as affected by ion association and ionic strength up to 0.15 M and at $25^\circ\text{C} \pm 1$. The saturated solutions of gypsum were filtered and the filtrates were analyzed for Ca^{2+} , pH, activity of sodium, activity of Ca^{2+} and activity of $\text{Ca}^{2+} + \text{Mg}^{2+}$ and sulfate concentration was determined gravimetrically as BaSO_4 . A computer program was used to predict ion association and solubility of gypsum in simple and mixed aqueous electrolyte systems.

(K_{sp}) of gypsum (solubility product of gypsum) and $K_d \text{CaSO}_4^0$, $K_d \text{MgSO}_4^0$ and $K_d \text{NaSO}_4^0$ (dissociation constants of CaSO_4^0 , MgSO_4^0 , NaSO_4^0

ion-pairs respectively) were considered simultaneously. Ionic strength, single ion activity coefficients, ionic activities, and other solution parameters were calculated, until equilibrium is attained. The solubility product of gypsum was partly described by

$$K_{sp} = \frac{(Ca^{2+})(SO_4^{2-})(H_2O)^2}{(CaSO_4 \cdot 2H_2O)} [Ca^{2+}] \gamma_{Ca^{2+}} [SO_4^{2-}] \gamma_{SO_4^{2-}} \quad (1)$$

The activity of (H_2O) and $(CaSO_4 \cdot 2H_2O)$ were arbitrarily taken at unity. Ionic activity coefficients were computed from the following expression.

$$\text{Log} \gamma_i = -0.509 Z_i^2 (I^{1/2} / (1 + I^{1/2}) - bu) \quad (2)$$

A fixed value of 3A for a^0 parameter (ion size parameters) was taken so that Ba^0 reduce to unity and assumed a value of 0.3 for b.

The dissociation constant of $CaSO_4^0$ was computed from the following expression

$$K_d^{CaSO_4^0} = \frac{[Ca^{2+}] \gamma_{Ca^{2+}} [SO_4^{2-}] \gamma_{SO_4^{2-}}}{[CaSO_4^0] \gamma_{CaSO_4^0}} \quad (3)$$

Where $\gamma_{CaSO_4^0}$ was assumed to be unity. The dissociation constant for $MgSO_4^0$ is defined by

$$K_d \text{MgSO}_4^0 = \frac{[\text{Mg}^{2+}] \gamma_{\text{Mg}^{2+}} [\text{SO}_4^{2-}] \gamma_{\text{SO}_4^{2-}}}{[\text{MgSO}_4^0] \gamma_{\text{MgSO}_4^0}} \quad (4)$$

in which $\gamma_{\text{MgSO}_4^0}$ was taken as unity. The dissociation constant for NaSO_4^- was described by

$$K_D = \frac{[\text{Na}^+] \gamma_{\text{Na}^+} [\text{SO}_4^{2-}] \gamma_{\text{SO}_4^{2-}}}{[\text{NaSO}_4^-] \gamma_{\text{NaSO}_4^-}} \quad (5)$$

The concentration of $\gamma_{\text{NaSO}_4^-}$ was calculated from $[\text{NaSO}_4^-]$ was included in (I) ionic strength. They concluded that the mean ionic activity coefficients calculated by the computer program were in close agreement with literature γ_{\pm} values for all concentration of NaCl but not so close for other electrolytes, particularly MgSO_4 . They said that this deviation was due to the use of equation (2) in which a^0 was taken as $3A$ for all ions and $b = 0.2$ for all electrolytes.

Gypsum solubility was greater in MgCl_2 than in NaCl solutions due to a high (I) and greater association of MgSO_4^0 , as compared to NaSO_4^- which further reduce the activity of SO_4^{2-} .

In case of the common ion Ca^{2+} from CaCl_2 or SO_4^{2-} from Na_2SO_4 and MgSO_4 , the solubility of gypsum was decreased as a result of an increase in activity of common ion and decrease in activity of other ions, SO_4^{2-} or Ca^{2+} , respectively.

The dissolution of gypsum in each solution was less than in Na_2SO_4 solution because of MgSO_4^0 association is stronger than NaSO_4^0 .

Ponnamperama, Tianco and Loy (1966) showed that there is a simple linear relation between the electrical conductivity of a solution and its ionic strength.

Utilizing extracts of flooded soils and electrolyte solutions of ionic strength less than 0.06 mole/L.

They derived the following expression

$$I = 16EC$$

Where EC is the specific conductance in mhos/cm at 25°C. The ionic strength is a measure of the intensity of the electrical field in an electrolyte solution. Correction of the analytical concentrations used to compute ionic strength for natural ion-pair species and ion pair of reduce charge are necessary to provide an accurate measure of the ionic strength electrical conductance relation.

Griffin and Jurinak (1973) modify Ponnamperuma's equation to include correction for ion-pair formation and to extend the investigation to waters and soil extract of higher salt contents more representative of semiarid ecosystems, and they compared activity coefficients predicted from EC measurements with (a) those determined from specific ion electrode measurements (b) those calculated from total chemical analysis using both the Debye-Huckel and Davies equations.

The chemical analysis of soil extract for three soils and 124

river waters were used in this study. The electrical conductivity and ion concentration were determined. The measured ionic concentration were corrected for ion-pair formation.

They showed that there were a high correlation between electrical conductivity and ionic strength with all samples. The linear regression for all natural waters and soil extract was

$$Y = .0127 x - .0003 \quad (1)$$

$$r = 0.996 \quad (2)$$

or

$$I = 0.013 \text{ EC} \quad (3)$$

Where ionic strength I , is in moles/Liter and EC is in millimhos/cm at 25°C.

The relation shown in equation (2) differs from the findings of Ponnumperuma et al (1966).

They got good agreement between the experimental calcium ion activity coefficient as calculated using equation (2) and the actual values determined using ion-pair corrected chemical analyses with both the Debye-Huckel and Davies equations. The Ca^{2+} ion activity coefficient values calculated from the activity of Ca^{2+} obtained by the calcium-specific ion electrode were consistently higher than the values obtained by the other methods.

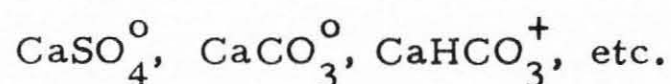
CHAPTER III

THEORY

The theory of Debye-Huckel allows one to correct ionic concentration for long range electrostatic interactions in relatively dilute solutions of electrolytes.

The correction factor is called the activity coefficient γ_i . However, derivations from the Debye-Huckel theory are not uncommon.

The activity coefficient correction alone is not always sufficient to correct molar concentrations to ionic activities. This fact lead to the concept of ion pair formation which is the short-range interaction of two oppositely charged ions producing a soluble but undissociated complex as:



In this study the concept of ion-pair formation is coupled with the activity coefficient concept to convert soil column effluent concentration data to activities thus allowing calculation of the solubility product of the solid phase, gypsum or lime, which controls the composition of the effluent.

The ionic strength, I , of the soil column effluent was estimated by (Griffin and Jurinak, 1973)

$$I = .0127 \text{ EC}$$

Where EC = mmhos/cm at 25°C.

The activity coefficient γ_i was calculated for the individual ions by means of the following equation

$$-\text{Log} \gamma_i = \frac{A Z_i^2 (I)^{\frac{1}{2}}}{1 + B_a^0 (I)^{\frac{1}{2}}}$$

Where:

$$A = .509 \text{ constant}$$

$$Z = 2 = \text{valence of the ion}$$

$$B = 3.3 \times 10^{-7} \text{ at } 25^\circ\text{C}$$

$$a^0 = 6 \times 10^{-8} \text{ for } \text{Ca}^{2+}$$

$$a^0 = 4 \times 10^{-8} \text{ for } \text{SO}_4^{2-}$$

The individual ion activity, a_i is defined as:

$$a_i = \gamma_i m_i$$

Where:

m_i = the concentration of species in moles/L

The calculations used to determine ion activities from analytical

data and how the solubility of gypsum and lime were determined is now discussed.

a) When the effluent is in equilibrium with gypsum, the total calcium in solution $[Ca^{2+}]_T$ is given by.

$$a) \quad [Ca^{2+}]_T = [Ca^{2+}] + CaSO_4^0 \quad (a-1)$$

Where

$$CaSO_4^0 = \frac{(Ca^{2+})(SO_4^{2-})}{K_{dSO_4}} \quad (a-2)$$

and

$$(Ca^{2+}) = \frac{K_{dSO_4} CaSO_4^0}{(SO_4^{2-})}$$

or

$$\frac{(Ca^{2+})}{\gamma_{Ca^{2+}}} = \frac{K_{dSO_4} CaSO_4^0}{(SO_4^{2-}) \gamma_{Ca^{2+}}} = [Ca^{2+}] \quad (a-3)$$

Substituting equation (a-3) into (a-1) gives

$$[\text{Ca}^{2+}]_T = \frac{K_{d\text{SO}_4} \text{CaSO}_4^{\circ}}{(\text{SO}_4^{2-}) (\gamma_{\text{Ca}^{2+}})} + \text{CaSO}_4^{\circ} \quad (\text{a-4})$$

Re-arranging

$$\frac{[\text{Ca}^{2+}]}{\text{CaSO}_4^{\circ}} = 1 + \frac{K_{d\text{SO}_4}}{(\text{SO}_4^{2-}) \gamma_{\text{Ca}^{2+}}} = \frac{(\text{SO}_4^{2-}) \gamma_{\text{Ca}^{2+}} + K_{d\text{SO}_4}}{(\text{SO}_4^{2-}) \gamma_{\text{Ca}^{2+}}} \quad (\text{a-5})$$

Inverting

$$\frac{\text{CaSO}_4^{\circ}}{[\text{Ca}^{2+}]_T} = \frac{(\text{SO}_4^{2-}) (\gamma_{\text{Ca}^{2+}})}{(\text{SO}_4^{2-}) \gamma_{\text{Ca}^{2+}} + K_{d\text{SO}_4}} = \frac{1}{1 + \frac{K_{d\text{SO}_4}}{(\text{SO}_4^{2-}) (\gamma_{\text{Ca}^{2+}})}}$$

or

$$\text{CaSO}_4^{\circ} = [\text{Ca}]_T \frac{1}{1 + \frac{K_{d\text{SO}_4}}{(\text{SO}_4^{2-}) \gamma_{\text{Ca}^{2+}}}} = \frac{K_{sp}}{K_{d\text{SO}_4}}$$

b) For the case where the effluent is in equilibrium with both CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the total calcium concentration is given by:

$$[\text{Ca}]_T = [\text{Ca}^{2+}] + [\text{CaSO}_4^0] + [\text{CaSO}_3^0] + [\text{CaHCO}_3^+] + [\text{CaOH}^+] \quad (\text{b-1})$$

The contribution of $[\text{CaHCO}_3^+]$ and (CaOH^+) to the calcium concentration is less than 0.01%, as shown by the following calculations, and is not considered in further calculations.

at pH 8.1 (pOH 5.9) the activity of the (CaOH^+) ion-pair is.

$$(\text{CaOH}^+) = \frac{(\text{Ca}^{2+})(\text{OH})}{K_{\text{dOH}}} = \frac{(\text{Ca}^{2+})(10^{-5.9})}{10^{-1.37}} = (\text{Ca}^{2+})(2.9 \times 10^{-5})$$

The activity of (CaHCO_3^+) is at pH 8.1

$$(\text{CaHCO}_3^+) = \frac{K_{\text{A1}} K_{\text{H}}^{\text{P}} \text{CO}_2 (\text{Ca}^{2+})}{(\text{H}^+) + K_{\text{dHCO}_3}} = \frac{(\text{Ca}^{2+})(\text{HCO}_3^-)}{K_{\text{dHCO}_3}}$$

$$\begin{aligned} (\text{CaHCO}_3^+) &= \frac{10^{-6.35} 10^{-1.47} 10^{-3.5} (\text{Ca}^{2+})}{10^{-8.1} + 10^{-1.25}} = 10^{-10.1} (\text{Ca}^{2+}) \\ &= 7.9 \times 10^{-11} (\text{Ca}^{2+}) \end{aligned}$$

The dissociation constants for $[\text{CaSO}_4^0]$ and $[\text{CaCO}_3^0]$ are:

$$K_{\text{dSO}_4} = \frac{(\text{Ca}^{2+})(\text{SO}_4^{2-})}{(\text{CaSO}_4^0)} = 5.25 \times 10^{-3}$$

$$K_{\text{dCO}_3} = \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{(\text{CaCO}_3^0)} = 6.3 \times 10^{-4}$$

Solving for CaSO_4^0 and CaCO_3^0 and substituting in equation (b-1) gives

$$[\text{Ca}^{2+}]_{\text{T}} = [\text{Ca}^{2+}] + \frac{(\text{Ca}^{2+})(\text{SO}_4^{2-})}{K_{\text{dSO}_4}} + \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_{\text{dCO}_3}} \quad (\text{b-3})$$

$$[\text{Ca}]_{\text{T}} = \frac{(\text{Ca}^{2+})}{\gamma_{\text{Ca}^{2+}}} + \frac{(\text{Ca}^{2+})(\text{SO}_4^{2-})}{K_{\text{dSO}_4}} + \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_{\text{dCO}_3}}$$

Collecting (Ca^{2+}) terms gives:

$$[\text{Ca}]_{\text{T}} = (\text{Ca}^{2+}) \left[1/\gamma_{\text{Ca}^{2+}} + \frac{(\text{SO}_4^{2-})}{K_{\text{dSO}_4}} + \frac{(\text{CO}_3^{2-})}{K_{\text{dCO}_3}} \right] \quad (\text{b-4})$$

or

$$[\text{Ca}]_T = (\text{Ca}^{2+}) / B \quad (\text{b-5})$$

where

$$B = \left[1/\gamma_{\text{Ca}} + \frac{(\text{SO}_4^{2-})}{K_{\text{dSO}_4}} + \frac{(\text{CO}_3^{2-})}{K_{\text{dCO}_3}} \right] \quad (\text{b-6})$$

To solve for the activity of sulfate ion, (SO_4^{2-}) , one uses the relation for gypsum in equilibrium with water

$$(\text{Ca}^{2+}) = K_{\text{spSO}_4} / (\text{SO}_4^{2-}) \quad (\text{b-7})$$

Substituting in equation (b-5) gives

$$[\text{Ca}]_T = \left[K_{\text{spSO}_4} / (\text{SO}_4^{2-}) \right] [B]^{-1}$$

The total concentration of sulfate $(\text{SO}_4^{2-})_T$ is given by

$$[\text{SO}_4^{2-}]_T = [\text{SO}_4^{2-}] + \text{CaSO}_4^0 \quad (\text{b-8})$$

or

$$[\text{SO}_4^{2-}]_T = \frac{(\text{SO}_4^{2-})}{\gamma_{\text{SO}_4}} + \frac{(\text{Ca}^{2+})(\text{SO}_4^{2-})}{K_{\text{dSO}_4}}$$

Which gives

$$[\text{SO}_4^{2-}]_T = (\text{SO}_4^{2-}) \left[\frac{1}{\gamma_{\text{SO}_4^{2-}}} + \frac{(\text{Ca}^{2+})}{K_{\text{dSO}_4}} \right] \quad (\text{b-9})$$

From (b-5) we know:

$$(\text{Ca}^{2+}) = [\text{Ca}]_T / B$$

Substituting in equation (b-9) gives

$$(\text{SO}_4^{2-}) = [\text{SO}_4^{2-}]_T / \left[\frac{1}{\gamma_{\text{SO}_4^{2-}}} + \frac{[\text{Ca}]_T}{BK_{\text{dSO}_4}} \right] \quad (\text{b-10})$$

or

$$(\text{SO}_4^{2-}) = [\text{SO}_4^{2-}]_T \left/ \frac{1}{\gamma_{\text{SO}_4^{2-}}} + \frac{[\text{Ca}]_T}{\frac{1}{\gamma_{\text{Ca}}} + \frac{(\text{SO}_4^{2-})}{K_{\text{dSO}_4}} + \frac{(\text{Ca}_3^{2-})}{K_{\text{dSO}_3}} K_{\text{dSO}_4}} \right. \quad (\text{b-11})$$

For the case when the effluent is in equilibrium with lime (CaCO_3), the total calcium concentration is given as

$$[\text{Ca}^{2+}]_T = [\text{Ca}^{2+}] + [\text{CaHCO}_3^+] + [\text{CaCO}_3^0] + [\text{CaOH}^+] \quad (\text{c-1})$$

in terms of activities (c-1) is

$$[\text{Ca}^{2+}]_T = \frac{(\text{Ca}^{2+})}{\gamma_{\text{Ca}^{2+}}} + \frac{(\text{CaHCO}_3^+)}{\gamma_{\text{CaHCO}_3^+}} + \frac{(\text{CaOH}^+)}{\gamma_{\text{CaOH}^+}} + \frac{(\text{CaCO}_3^0)}{\gamma_{\text{CaCO}_3^0}} \quad (\text{c-2})$$

Since CaCO_3^0 is uncharged the value of $\gamma_{\text{CaCO}_3^0}$ is taken as unity. It is also assumed that γ_{CaOH^+} and $\gamma_{\text{CaHCO}_3^+}$ are equal to $\gamma_{\text{HCO}_3^-}$.

Thus (c-2) becomes

$$[\text{Ca}^{2+}]_T = \frac{(\text{Ca}^{2+})}{\gamma_{\text{Ca}^{2+}}} + \frac{(\text{CaHCO}_3^+)}{\gamma_{\text{HCO}_3^-}} + \frac{(\text{CaOH}^+)}{\gamma_{\text{HCO}_3^-}} + \text{CaCO}_3^0 \quad (\text{c-3})$$

Writing the activity of each in pair in terms of its respective K_d value gives

$$[\text{Ca}^{2+}]_T = (\text{Ca}^{2+}) \left[\frac{1}{\gamma_{\text{Ca}^{2+}}} + \frac{(\text{HCO}_3^-)}{K_{d_2} \gamma_{\text{HCO}_3^-}} + \frac{(\text{OH}^-)}{K_{d_3} \gamma_{\text{HCO}_3^-}} + \frac{(\text{CO}_3^{2-})}{K_{d_1}} \right] \quad (\text{c-4})$$

Where

$$(\text{CaCO}_3^0) = \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_{d_1}} \text{ and } K_{d_1} = 6.3 \times 10^{-4}$$

$$(\text{CaHCO}_3^+) = \frac{(\text{Ca}^{2+})(\text{HCO}_3^-)}{K_{d_2}} \text{ and, } K_{d_2} = 5.5 \times 10^{-2}$$

$$(\text{CaOH}^+) = \frac{(\text{Ca}^{2+})(\text{OH}^-)}{K_{d_3}} \text{ and, } K_{d_3} = 4.25 \times 10^{-2}$$

Equation (c-4) is now written

$$(\text{Ca}^{2+}) = [\text{Ca}^{2+}]_T / B \quad (\text{c-5})$$

Where

$$B' = \left[\frac{1}{\gamma_{Ca^{2+}}} + \frac{(HCO_3^-)}{K_{d2} \gamma_{HCO_3^-}} + \frac{(OH^-)}{K_{d3} \gamma_{HCO_3^-}} + \frac{(CO_3^{2-})}{K_{d1}} \right]$$

D) Calculation of the solubility products

1. For a system in equilibrium with gypsum

$$(Ca^{2+}) = (SO_4^{2-}) = (2.4 \times 10^{-5})^{\frac{1}{2}} \quad (d-1)$$

From equation (b-6)

$$(Ca^{2+}) = [Ca^{2+}]_T / B \quad (d-2)$$

Where

$$B = \left[\frac{1}{\gamma_{Ca}} + \frac{(SO_4^{2-})}{5.25 \times 10^{-3}} + \frac{(CO_3^{2-})}{6.3 \times 10^{-4}} \right]$$

From equation (b-9)

$$(SO_4^{2-}) = [SO_4^{2-}]_T / \left[\frac{1}{\gamma_{SO_4^{2-}}} + \frac{(Ca^{2+})}{K_{dSO_4}} \right] \quad (d-3)$$

Iteration is required to solve equations (d-2) and (d-3).

2. For a system in equilibrium with CaCO_3

$$(\text{Ca}^{2+}) = (\text{CO}_3^{2-}) = (4.45 \times 10^{-9})^{\frac{1}{2}} \quad (\text{d-6})$$

From equation (c-5)

$$(\text{Ca}^{2+}) = [\text{Ca}^{2+}]_{\text{T}} / B' \quad (\text{d-7})$$

Where

$$B' = \left[\frac{1}{\gamma_{\text{Ca}^{2+}}} + \frac{(\text{HCO}_3^-)}{(5.5 \times 10^{-2}) \gamma_{\text{HCO}_3^-}} + \frac{(\text{OH}^-)}{(4.25 \times 10^{-2}) \gamma_{\text{HCO}_3^-}} + \frac{(\text{CO}_3^{2-})}{6.3 \times 10^{-4}} \right]$$

and (CO_3^{2-}) is calculated from

$$(\text{CO}_3^{2-}) = \frac{K_{A1} K_{A2} K_4 P_{\text{CO}_2}}{[\text{H}^+]^2} \quad (\text{d-8})$$

The solubility product of gypsum is then calculated from

$$(\text{Ca}^{2+})(\text{SO}_4^{2-}) = 2.4 \times 10^{-5} = K_{\text{spSO}_4}$$

and for CaCO_3 (lime)

$$(\text{Ca}^{2+})(\text{CO}_3^{2-}) = 4.45 \times 10^{-9} = K_{\text{spCO}_3}$$

CHAPTER IV

MATERIALS AND METHODS

The data were obtained from the analysis of effluent from soil column studies conducted in the laboratory.

Two type of soils were used in this study.

1. Yolo loam soil which is a non-calcareous, non-gypsiferous soil from central California.

2. Vernal soil which is a calcareous soil from eastern Utah.

The Yolo loam soil was Ca-saturated by leaching with 0.1 N CaCl_2 , then leaching with distilled water until the effluent was free of chloride as determined by the AgNO_3 test.

The soil was air-dried and then passed through a 2mm sieve. Reagent grade, CaCO_3 , was added to portions of the prepared soil to bring the lime content to one percent. Reagent grade, CaSO_4 was also added to bring the gypsum content to one or two percent.

All additions were based on the air dried weight of the soil. Vernal soil was used in its natural condition.

Soil column studies

The soil column consisted of an infiltration tube 25cm high and 5.5cm in diameter. The outflow end consisted of a fritted glass disc

over which was placed two layers of filter paper to protect the disc from the overlying soil. The columns drained into an automatic fraction collector.

The fraction collector was set to take 10ml aliquots. Water was added to the columns by a constant head device. Most studies were conducted under saturated moisture conditions though a limited number of unsaturated flow studies were conducted. Usually 100 grams of soil (air-dried) was used in the saturated flow studies whereas 50 grams of air-dried soil was used in unsaturated moisture studies. The characteristics of soil columns are shown in Tables 1, 2, and 3.

The effluent were analysed for calcium by the atomic absorption spectrophotometry using a model 303 Perkin-Elmer instrument. The electrical conductivity [EC] was measured with a Beckman model RC-19 conductivity bridge using a 2ml pipette cell which had a cell constant of unity. The pH was measured by means of a glass-electrode and sulfate was determined gravimetrically (U. S. Salinity Laboratory, 1954).

In this study three types of water were used to leach the soil columns.

1. Logan river water. EC = 0.278 mmhos/cm.
2. KCl solution. EC = 2.89 mmhos/cm.
3. K_2SO_4 solution, EC = 2.67 mmhos/cm.

Table 1. Characteristics of Vernal soil columns

Soil Column	Leaching solution	Flow rate	Pore volume %	Bulk density
Vernal soil (unsaturated moisture studies)	Logan river water	15cc/day	51.1	1.29
Vernal soil (Saturated moisture studies)	Logan river water	10cc/hour	52.0	1.21

Table 2. Characteristics of Yolo soil columns. Saturated moisture studies.

Soil Column	Leaching solution	Flow rate cc/hour	Pore volume %	Bulk density
No treatment	Logan river water	6-7	44.7	1.31
1% gypsum + 1% lime	Logan river water	6-8	44.8	1.30
2% gypsum + 1% lime	Logan river water	8-5-10	45.2	1.22
2% gypsum + 1% lime	KCl	10	45.1	1.24
2% gypsum + 1% lime	K_2SO_4	10	45.0	1.25

Table 3. The flow rate and the moisture content under unsaturated moisture studies of Yolo and Vernal soils columns.

Soil Column	Moisture Content	Flow Rate
Yolo soil (1% gypsum + 1% lime)	Upper part 36.2%	15cc/day
	Lower part 28.3%	
Vernal soil	Upper part 35.1%	15cc/day
	Lower part 29.3%	

The unsaturated flow studies were conducted by adding water dropwise on the top of the column while maintaining a 25 cm tension on the outflow end of the column. This tension was produced by a hanging water column.

CHAPTER V
RESULTS AND DISCUSSION

Initial studies were conducted to determine the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 in the waters used to leach the soil columns. The chemical data and the K_{sp} values calculated are shown in Table 4. The K_{sp} values were calculated from data that were corrected for both ion-pair formation and the salt effect (activity coefficient) and from the same data which assumed that the total concentration of ions analyzed were equivalent to their activities.

It is noted that the highest concentration of calcium was found in the KCl solution and the lowest concentration was found in the K_2SO_4 solution when the salt was gypsum. The lower solubility of gypsum in the K_2SO_4 solution is considered to be a common ion effect which overwhelmed the formation of ion-pairs and the salt effect both of which would increase the solubility of gypsum. The high solubility in the KCl solutions is ascribed to the salt effect. It is of interest to note that when the gypsum and lime were present together in a given water, the EC value tended to be less than if gypsum were present alone. The calcium in all solutions decreased slightly when both salts were present as compared to when gypsum was present alone. This trend was also followed by the sulfate concentration except in the case of the K_2SO_4 solution

Table 4. Solubility of CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in waters used in this study

Leaching water	Salt	E. C. mmhog/cm at 25C	pH	[Ca] T	[SO ₄] T	I	$\gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}}$	K _{sp} with correction	K _{sp} without correction
Logan river water	CaCO_3	0.321	8.23	4.5×10^{-4}	2.7×10^{-4}	4.07×10^{-3}	0.763	3.12×10^{-9}	4.21×10^{-9}
Logan river water	$\text{CaSO}_4 + \text{CaCO}_3$	2.10	7.87	1.215×10^{-2}	1.192×10^{-2}	2.66×10^{-2}	0.54	1.63×10^{-5}	4.223×10^{-5}
Logan river water	CaSO_4	2.10	7.57	1.34×10^{-2}	1.33×10^{-2}	2.667×10^{-2}	0.54	1.93×10^{-5}	5.275×10^{-5}
KCl	CaCO_3	2.89	8.23	5.2×10^{-4}		3.64×10^{-2}	0.506	3.5×10^{-9}	3.82×10^{-9}
KCl	$\text{CaSO}_4 + \text{CaCO}_3$	4.70	7.85	1.79×10^{-2}	1.73×10^{-2}	5.93×10^{-2}	0.440	1.9×10^{-5}	5.99×10^{-5}
KCl	CaSO_4	4.78	7.5	2.09×10^{-2}	1.82×10^{-2}	6.07×10^{-2}	0.443	2.34×10^{-5}	7.28×10^{-5}
K_2SO_4	CaCO_3	2.623	8.23	1.05×10^{-3}	1.162×10^{-2}	3.32×10^{-2}	0.52	3.25×10^{-9}	6.61×10^{-9}
K_2SO_4	$\text{CaSO}_4 + \text{CaCO}_3$	3.722	7.92	1.06×10^{-2}	2.84×10^{-2}	4.6×10^{-2}	0.45	1.6×10^{-5}	6.66×10^{-5}
K_2SO_4	CaSO_4	3.859	7.62	1.175×10^{-2}	2.84×10^{-2}	4.7×10^{-2}	0.45	1.66×10^{-5}	6.76×10^{-5}

where no difference in sulfate concentration could be detected. As one might suspect however, in a mixed salt system, the solubility of gypsum dominated the chemical composition of the water.

The solubility of CaCO_3 as effected by the three waters (solutions) follows the expected trend. The KCl solution (EC = 2.9 mmhos/cm) increased the concentration of calcium by 115%. This is due to the salt effect. Using a K_2SO_4 solution of approximately the same salinity (EC = 2.7 mmhos/cm), the solubility of CaCO_3 was increased by 233%. At the same time the equilibrium conductivity and ionic strength, I, in the K_2SO_4 system was less than in the KCl system. These data show the strong effect of ion-pair formation (CaSO_4^0) on the solubility of CaCO_3 . The presence of soluble CaSO_4^0 increased dramatically the total calcium concentration while it reduced the presence of charged calcium ions (EC) in solution relative to the KCl water.

The K_{sp} calculations show the affect of correcting analytical data for ion-pair formation and the presence of salt. The K_{sp} for CaCO_3 could not be calculated without corrections because the CO_3^- activity was theoretically determined as described in the Theory section. The calculated corrected K_{sp} values for CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are compared to the theoretical K_{sp} values of 4.45×10^{-9} and 2.4×10^{-5} , respectively. The values obtained are considered to be in reasonable agreement with theory, but refinement is still required in terms of analytical technique, additional corrections, or assumptions used in this study.

Figure 1A shows EC of Yolo soil column effluent plotted against

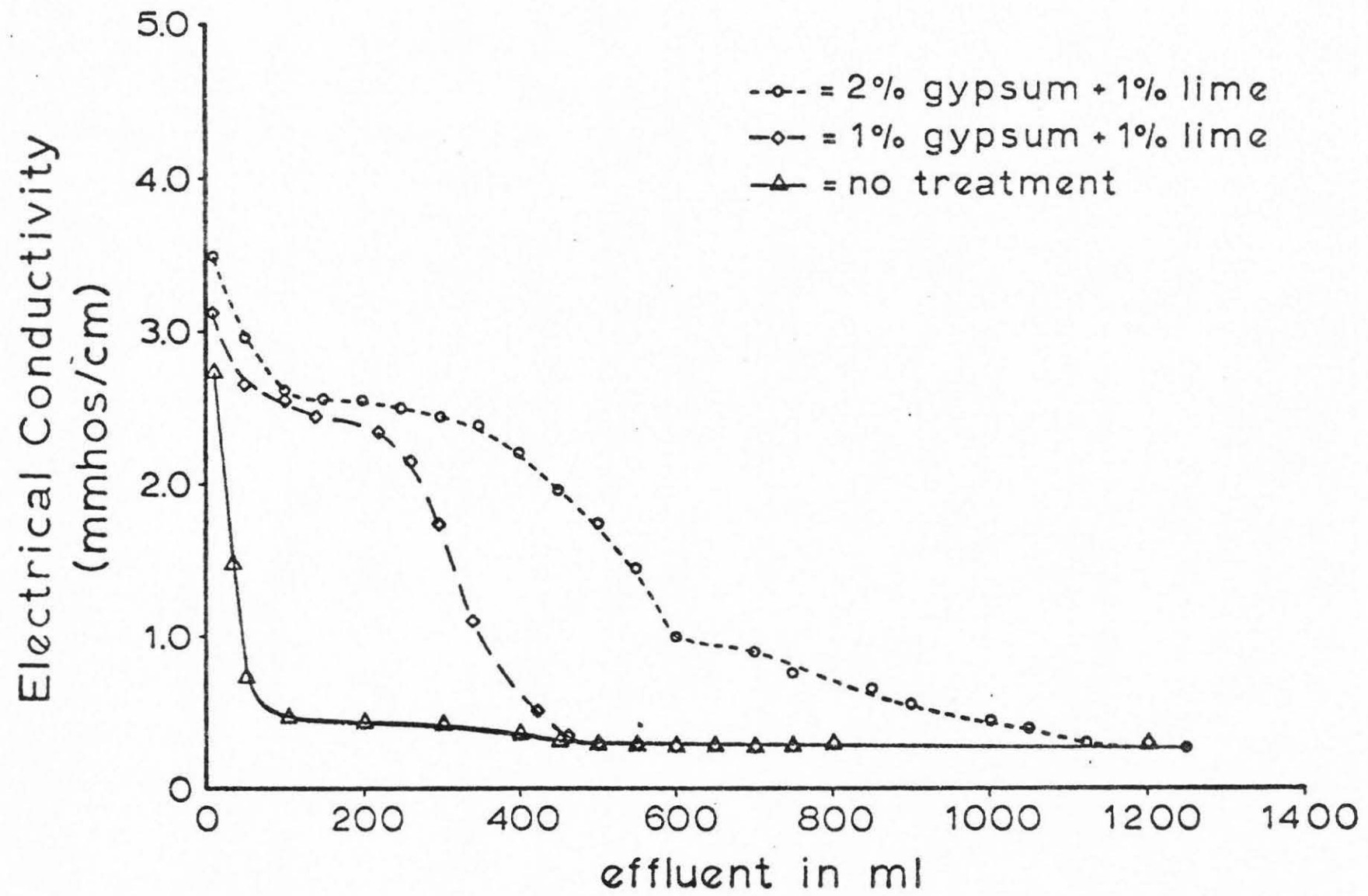


Figure 1A. Electrical conductivity of the effluent of Yolo soil columns leached with Logan river water under saturated conditions.

the volume of effluent. The water used was Logan river water which is regarded as a reference water of good quality in this study. The data are from columns of untreated soil and from columns of soil to which 1 or 2% gypsum plus 1% lime had been added.

Figure 1B shows the same data except the negative log of the calcium ion concentration pC_{Ca} in the effluent is plotted vs ml of effluent. The affect of increasing the gypsum content of the soil to 2% is evident in both the EC and pC_{Ca} values. These data show that analysis of calcium in the leachate is more useful in determining when the water is equilibrium with solid phase gypsum or lime than using the criteria of EC. Two distinct plateaus (Figure 1B) are evident, the first at $pC_{Ca} = 1.5$ suggests equilibrium with gypsum while the second at $pC_{Ca} = 2.7$ suggests equilibrium with lime.

Figure 2A shows the EC of Yolo soil column (2% gypsum plus 1% lime) effluent plotted vs ml of effluent where three types of water were used. The greater initial EC values noted when using the KCl solution compared to that attained when using the K_2SO_4 solution is considered to be a function of the indifferent salt effect on the solubility of gypsum. When K_2SO_4 solution was used the common ion effect produced the solubility of gypsum. These conclusions are corroborated in Figure 2B which shows the greater amount of Ca^{2+} in solution in the presence of the KCl solution than in the presence of the K_2SO_4 solution when gypsum is being dissolved, i. e., at $pC_{Ca} = 1.5$. However, Figure 2B shows that the situation is reversed when $CaCO_3$ is dissolving ($pC_{Ca} = 2.6$). In

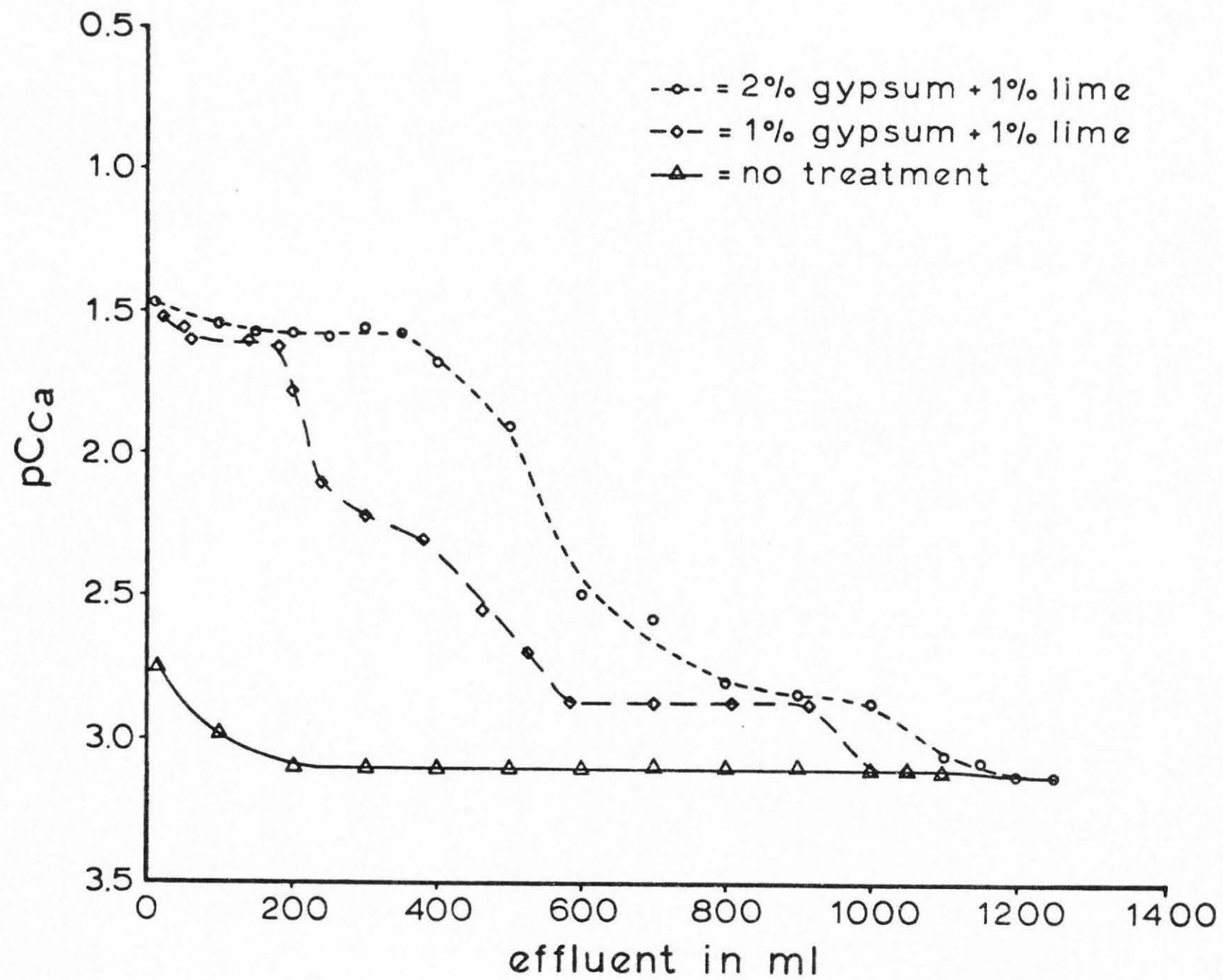


Figure 1 B. pC_{Ca} of the effluent of Yolo soil columns leached with Logan river water under saturated conditions.

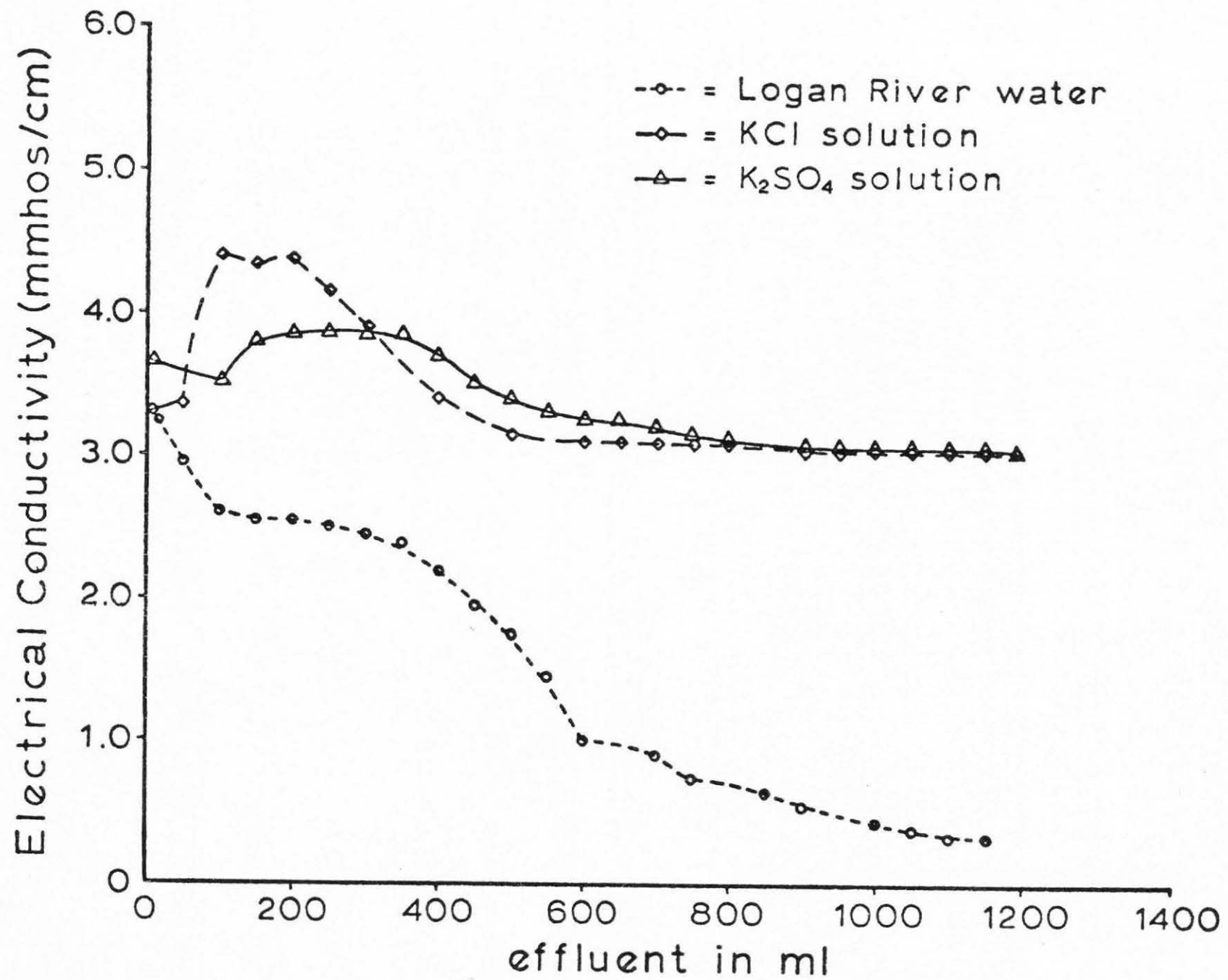


Figure 2A. Electrical conductivity of the effluent of Yolo soil (2% gypsum + 1% lime) columns leached under saturated conditions.

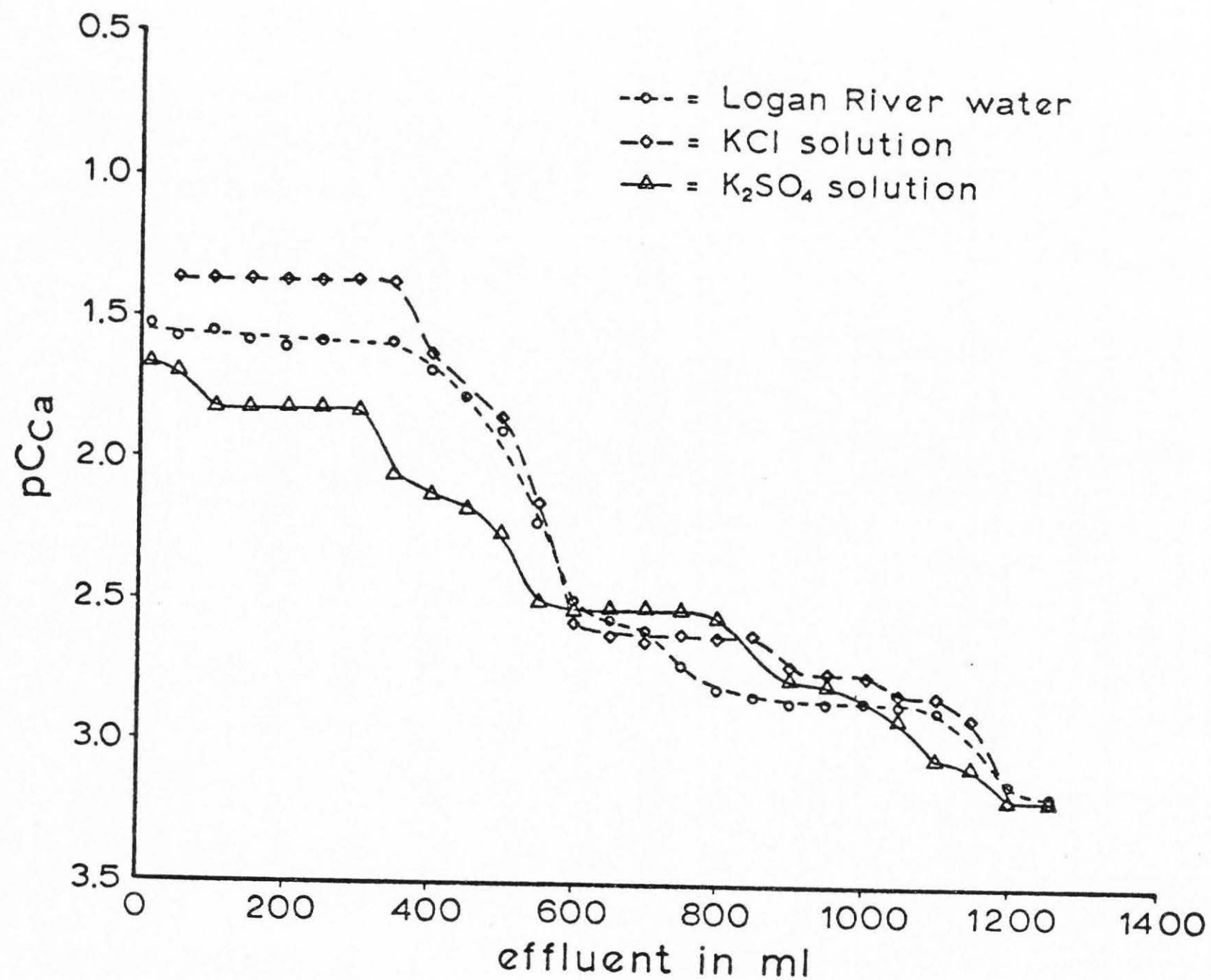


Figure 2B. pC_{Ca} of the effluent of Yolo soil (2% gypsum + 1% lime) columns leached under saturated conditions.

this case the formation of CaSO_4^0 complex produces a greater concentration of Ca^{2+} in the K_2SO_4 effluent than in the KCl effluent.

Most of the Ca^{2+} ion released from the exchange complex by the presence of the K^+ ion is considered to occur in the initial stages of leaching, thus the calcium concentration initially analysed necessarily incorporated both calcium due to exchange and that which resulted from the dissolution of gypsum.

Tables 5, 6 and 7 show the data used to calculate the solubility product, K_{sp} , of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 . The analytical data were corrected from both the salt effect and ion-pair formation as described in the Theory section. The K_{sp} values given are the average of six data points taken in the region where the Ca^{2+} ion concentration appeared to assume a steady state value. In all cases, the calculated K_{sp} value for gypsum a lime underestimated the theoretical value by about 30 to 40%.

Figure 3A shows the EC analysis of effluent from a Yolo column under conditions of saturated and unsaturated moisture flow. The water used was Logan river water. A pore volume in the column under saturated and non-saturated flow was 47 and 46% respectively. The moisture content (on a dry weight basis) of the unsaturated column varied between 28.5% on the top of the column to 36.2% on the bottom. The data show the efficiency of using unsaturated flow to remove salt from soil. The data are not directly comparable since 100g of dry soil was used in the saturated flow case whereas 50 g was used in the unsaturated study.

Figure 3B shows the concentration of calcium in the effluent under

Table 5. Solubility product data for Yolo loam soil column with 2% gypsum and 1% lime leached with Logan river water

ml of effluent	E. C. mmhos/cm at 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	(SO_4^{2-})	pH
The calculated solubility product of gypsum = $1.85 \pm 0.75 \times 10^{-5}$								
50	2.623	3.329×10^{-2}	.54	1.47×10^{-2}	4.55×10^{-2}	1.32×10^{-2}	4.19×10^{-3}	8.0
100	2.572	3.266×10^{-2}	.55	1.42×10^{-2}	4.437×10^{-3}	1.28×10^{-2}	4.14×10^{-3}	8.0
150	2.542	3.288×10^{-2}	.55	1.46×10^{-2}	4.5×10^{-3}	1.72×10^{-2}	3.95×10^{-3}	8.0
200	2.50	3.175×10^{-2}	.55	1.45×10^{-2}	4.5×10^{-3}	1.23×10^{-2}	3.98×10^{-3}	8.0
250	2.45	3.45×10^{-2}	.554	1.44×10^{-2}	4.48×10^{-3}	1.2×10^{-2}	3.9×10^{-3}	8.0
300	2.37	3.039×10^{-2}	.556	1.44×10^{-2}	4.47×10^{-3}	1.21×10^{-2}	3.9×10^{-3}	8.0

Table 5. (Continued)

ml. of effluent	E.C. mmhos/cm at 25°C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	(CO_3^{2-})	pH
The calculated solubility product of lime $4.4 \pm 0.3 \times 10^{-9}$								
600	.430	5.23×10^{-3}	.726	1.7×10^{-3}	1.10×10^{-3}	1.1×10^{-3}	3.98×10^{-6}	8.15
650	.380	4.6998×10^{-3}	.746	1.55×10^{-3}	1.10×10^{-3}	1.02×10^{-3}	3.98×10^{-6}	8.15
700	.365	4.635×10^{-3}	.7516	1.55×10^{-3}	0.95×10^{-3}	9.1×10^{-4}	3.98×10^{-6}	8.15
750	.350	4.445×10^{-3}	.754	1.51×10^{-3}	0.95×10^{-3}	8.2×10^{-4}	5.01×10^{-6}	8.2
800	.338	4.292×10^{-3}	.756	1.51×10^{-3}	0.93×10^{-3}	7.5×10^{-4}	5.01×10^{-6}	8.2
850	.332	4.216×10^{-3}	.759	1.5×10^{-3}	0.86×10^{-3}	7.1×10^{-4}	5.91×10^{-6}	8.2

Table 6. Solubility product data for Yolo loam soil column with 2% gypsum and 1% lime leached with K_2SO_4

ml. of effluent	E. C. mmhos/cm at 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	(SO_4^{2-})	pH
The calculated solubility product of gypsum 2.27×10^{-5}								
50	3.36	4.27×10^{-2}	.48	1.9×10^{-2}	5.327×10^{-3}	1.8×10^{-2}	5.04×10^{-3}	7.9
100	4.39	5.57×10^{-2}	.462	1.63×10^{-2}	4.8×10^{-3}	1.63×10^{-2}	4.5×10^{-3}	7.9
150	4.34	5.52×10^{-2}	.463	1.63×10^{-2}	4.8×10^{-3}	1.6×10^{-2}	4.2×10^{-3}	7.9
200	4.34	5.52×10^{-2}	.463	1.61×10^{-2}	4.62×10^{-3}	1.61×10^{-2}	4.28×10^{-3}	7.9
250	4.13	5.24×10^{-2}	.469	1.61×10^{-2}	4.61×10^{-3}	1.60×10^{-2}	4.35×10^{-3}	7.9
300	3.88	4.924×10^{-2}	.479	1.71×10^{-2}	4.5×10^{-3}	1.524×10^{-2}	4.32×10^{-3}	7.9

Table 6. (Continued)

ml. of effluent	E. C. mmhos/cm at 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	CO_3^{2-}	pH
The calculated solubility product of lime 4.2×10^{-9}								
550	3.6	4×10^{-2}	.492	4.1×10^{-3}	1.427×10^{-3}	3.5×10^{-3}	1.99×10^{-6}	8.0
600	3.10	3.937×10^{-2}	.493	3.8×10^{-3}	1.320×10^{-3}	3.2×10^{-3}	1.99×10^{-6}	8.0
650	3.10	3.937×10^{-2}	.495	3.8×10^{-3}	1.42×10^{-3}	2.1×10^{-3}	3.16×10^{-6}	8.10
700	3.092	3.926×10^{-2}	.50	3.8×10^{-3}	1.42×10^{-3}	1.8×10^{-3}	3.16×10^{-6}	8.10
750	3.072	3.9×10^{-2}	.501	3.75×10^{-3}	1.42×10^{-3}	$.92 \times 10^{-4}$	3.16×10^{-6}	8.10
800	3.080	3.91×10^{-2}	.501	3.8×10^{-3}	1.33×10^{-3}	$.90 \times 10^{-4}$	3.16×10^{-6}	8.10

Table 7. Solubility product data for Yolo loam soil column with 2% gypsum and 1% lime leached with KCl

ml. of effluent	E.C. mmhos/cm at 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	(SO_4^{2-})	pH
The calculated solubility product of gypsum $1.84 \pm 0.2 \times 10^{-5}$								
50	3.68	4.104×10^{-2}	.474	1.285×10^{-2}	3.67×10^{-3}	1.98×10^{-2}	5.5×10^{-3}	7.9
100	3.685	4.12×10^{-2}	.475	1.1825×10^{-2}	3.98×10^{-3}	1.89×10^{-2}	5.12×10^{-3}	7.9
150	3.61	4.117×10^{-2}	.476	1.195×10^{-2}	3.57×10^{-3}	1.88×10^{-2}	5.12×10^{-3}	7.9
200	3.50	4.15×10^{-2}	.479	1.092×10^{-2}	3.78×10^{-3}	1.82×10^{-2}	5.03×10^{-3}	7.9
250	3.38	4.15×10^{-2}	.480	1.11×10^{-2}	3.46×10^{-3}	1.82×10^{-2}	5.03×10^{-3}	7.9
300	3.278	4.15×10^{-2}	.481	1.007×10^{-2}	3.46×10^{-3}	1.71×10^{-2}	4.77×10^{-3}	7.9

Table 7. (Continued)

ml. of effluent	E.C. mmhos/cm at 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	(CO_3^{2-})	pH
The calculated solubility product of lime 3.02×10^{-9}								
700	3.272	4.15×10^{-2}	.48	4.85×10^{-3}	1.34×10^{-3}	9.8×10^{-3}	1.99×10^{-6}	8.0
750	3.270	4.15×10^{-2}	.486	4.7×10^{-3}	1.30×10^{-3}	8.2×10^{-3}	1.99×10^{-6}	8.0
800	3.270	4.15×10^{-2}	.486	4.83×10^{-3}	1.34×10^{-3}	7.3×10^{-3}	3.16×10^{-6}	8.1
850	3.242	4.11×10^{-2}	.49	4.6×10^{-3}	1.28×10^{-2}	5.2×10^{-3}	3.16×10^{-6}	8.1
900	3.25	4.12×10^{-2}	.49	3.92×10^{-3}	1.12×10^{-2}	5.6×10^{-3}	3.16×10^{-6}	8.1
950	3.235	4.1×10^{-2}	.50	3.67×10^{-3}	1.1×10^{-2}	5.1×10^{-3}	3.16×10^{-6}	8.1

Table 8. Solubility product data for Yolo loam soil column with 1% gypsum and 1% lime leached with Logan river water (unsaturated flow)

ml. of effluent	E. C. mmhos/cm 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	(SO_4^{2-})	pH
The calculated solubility product of gypsum = 1.77×10^{-5}								
44	3.08	3.91×10^{-2}	.492	1.72×10^{-2}	5.02×10^{-3}	1.2×10^{-2}	4.125×10^{-3}	8.0
64	2.99	3.797×10^{-2}	.50	1.55×10^{-2}	4.76×10^{-3}	1.19×10^{-2}	3.74×10^{-3}	8.0
70	2.979	3.77×10^{-2}	.50	1.38×10^{-2}	4.45×10^{-3}	1.18×10^{-2}	3.70×10^{-3}	8.0
77	2.960	3.759×10^{-2}	.50	1.38×10^{-2}	4.369×10^{-3}	1.17×10^{-2}	3.70×10^{-3}	8.0
87	2.74	3.479×10^{-2}	.510	1.378×10^{-2}	4.43×10^{-3}	1.17×10^{-2}	3.48×10^{-3}	8.0
104	2.72	3.47×10^{-2}	.51	1.382×10^{-2}	4.05×10^{-3}	1.17×10^{-2}	3.7×10^{-3}	8.0

Table 8. (Continued)

ml. of effluent	E. C. mmhos/cm at 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	(CO_3^{2-})	pH
The calculated solubility product of lime = 4.12×10^{-9}								
215	0.464	5.89×10^{-3}	.729	1.33×10^{-3}	8.71×10^{-4}	1.1×10^{-3}	3.98×10^{-6}	8.15
231	0.464	5.89×10^{-3}	.729	1.425×10^{-4}	9×10^{-4}	1.1×10^{-3}	5.01×10^{-6}	8.2
241	0.464	5.89×10^{-3}	.729	1.415×10^{-3}	8.84×10^{-4}	1.08×10^{-3}	5.01×10^{-6}	8.2
258	0.452	5.68×10^{-3}	.732	1.355×10^{-3}	8.84×10^{-4}	9.0×10^{-4}	5.01×10^{-6}	8.2
282	0.446	5.66×10^{-3}	.735	1.405×10^{-3}	8.86×10^{-4}	8.25×10^{-4}	5.01×10^{-6}	8.2
293	0.442	5.61×10^{-3}	.738	1.348×10^{-3}	8.8×10^{-4}	8.1×10^{-4}	5.01×10^{-6}	8.2

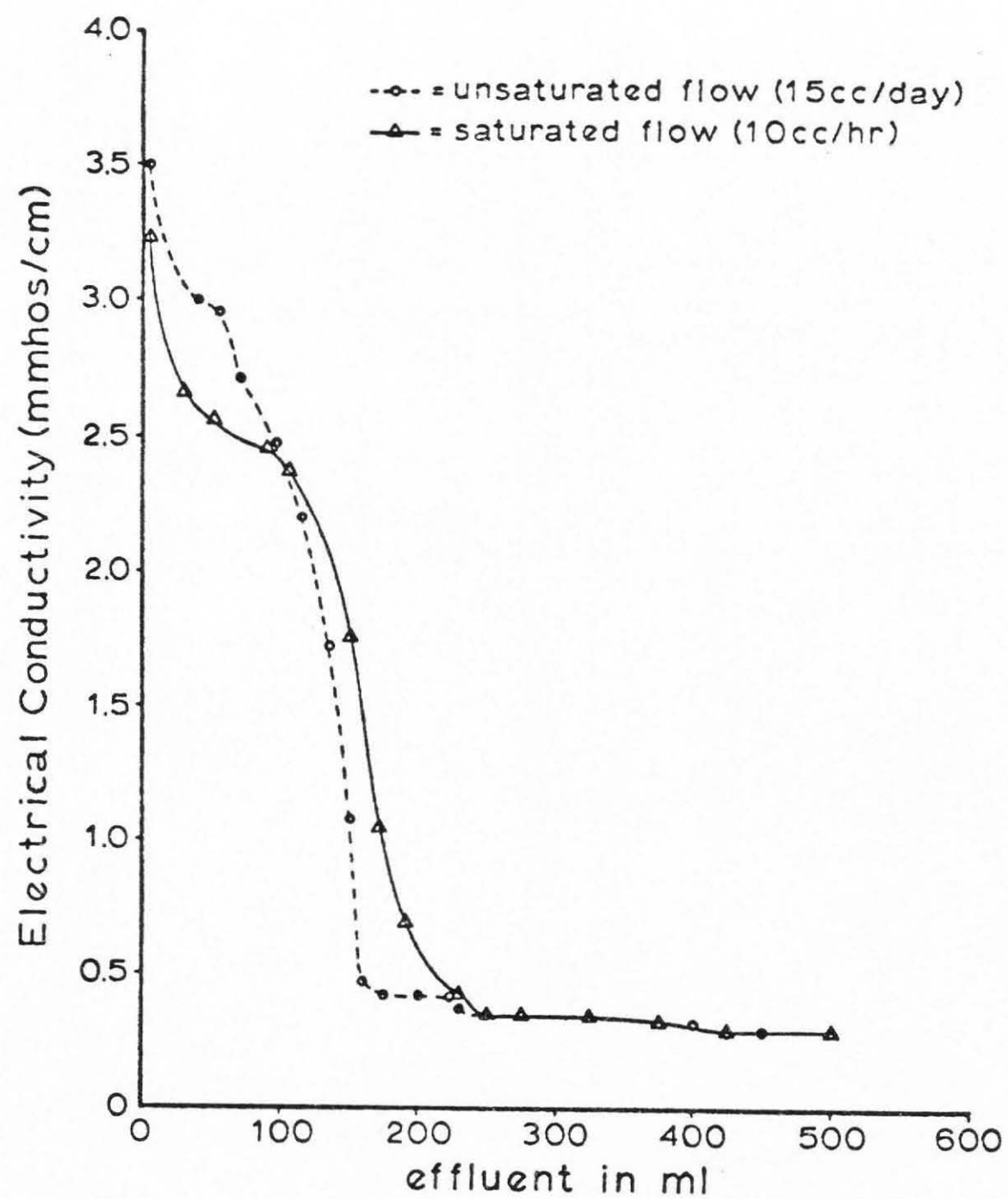


Figure 3A. Electrical conductivity of the effluent of Yolo soil (1% gypsum + 1% lime) columns leached with Logan river water.

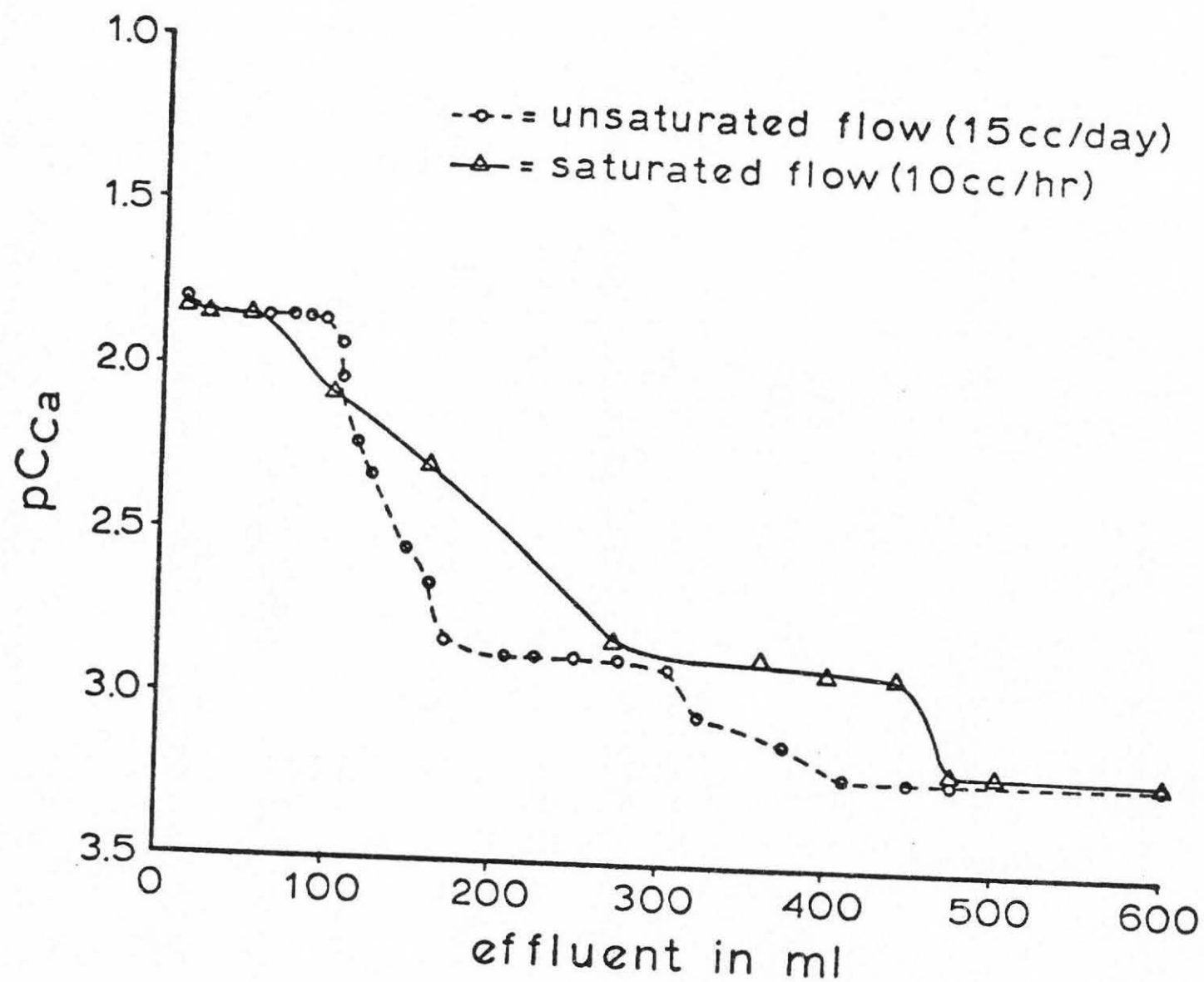


Figure 3B. pC_{Ca} of the effluent of Yolo soil (1% gypsum + 1% lime) columns leached with Logan river water.

Table 9. Solubility product data for Yolo soil with 1% gypsum and 1% lime leached with Logan river water (saturated flow)

ml. of effluent	E. C. mmhos/cm at 25°C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	$[SO_4^{2-}]_T$ mole/L	(SO_4^{2-})	pH
The calculated solubility product of gypsum = 1.6×10^{-5}								
50	2.8	3.556×10^{-2}	.509	1.427×10^{-2}	4.1×10^{-3}	1.36×10^{-2}	4.0×10^{-3}	7.95
70	2.65	3.3655×10^{-2}	.515	1.4×10^{-2}	4.11×10^{-3}	1.32×10^{-2}	4.1×10^{-3}	7.95
90	2.598	3.238×10^{-2}	.52	1.41×10^{-2}	4.17×10^{-3}	1.3×10^{-2}	3.98×10^{-3}	7.95
110	2.55	3.238×10^{-2}	.52	1.4×10^{-2}	4.17×10^{-3}	1.28×10^{-2}	3.97×10^{-3}	8.0
150	2.06	3.175×10^{-2}	.523	1.4×10^{-2}	4.25×10^{-3}	1.28×10^{-3}	3.93×10^{-3}	8.0
ml. of effluent	E. C. mmhos/cm at 25°C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	(CO_3^{2-})		pH
The calculated solubility product of lime = 3.83×10^{-3}								
550	.3284	4.17×10^{-3}	.73	1.275×10^{-3}	8.17×10^{-4}	5.01×10^{-6}		8.15
570	.328	4.17×10^{-3}	.732	1.275×10^{-3}	8.17×10^{-4}	5.01×10^{-6}		8.15
590	.3260	4.14×10^{-3}	.75	1.3×10^{-3}	8.25×10^{-4}	3.98×10^{-6}		8.2
620	0.325	4.14×10^{-3}	.75	1.275×10^{-3}	8.5×10^{-4}	3.98×10^{-6}		8.2
650	0.324	4.13×10^{-3}	.76	1.270×10^{-3}	8.48×10^{-4}	3.98×10^{-6}		8.2

both saturated and unsaturated flow conditions. It is noted that the curves intersected after the gypsum was removed from the soil. Again, the unsaturated flow appears more efficient in removal of calcium from the system. Tables 8 and 9 show the calculated values for the solubility products of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_3 from the experimental data. Table 8 is for the unsaturated column and Table 9 is for the saturated column. The data from the unsaturated column approximates more closely the theoretical K_{sp} values particularly in the case of CaCO_3 .

Figures 4A and 4B show how the EC and pC_{Ca} of the effluent vary with volume of effluent when Vernal soil columns were leached with Logan river water under saturated and unsaturated flow conditions. This soil, which originated from Utah State University's experimental plots in Ashley Valley, Utah was assumed to be gypsiferous. However, the surface soil from which the sample for this study was obtained, did not show any distinct evidence of gypsum. The unsaturated flow curves do suggest a possibility of a trace of gypsum though the data are not conclusive. The porosity for the unsaturated and saturated column was 45 and 43%, respectively. The moisture gradient from the top to the bottom of the unsaturated column varied from 28.1 to 36.1%. The K_{sp} for CaCO_3 calculated from the analytical data are shown in Tables 10 and 11. The values calculated are in reasonable agreement with the theoretical K_{sp} value of 4.45×10^{-9} .

Figures 5A and 5B compare the effluent data for the unsaturated flow, using Logan river water, for both Vernal soil and Yolo loam soil

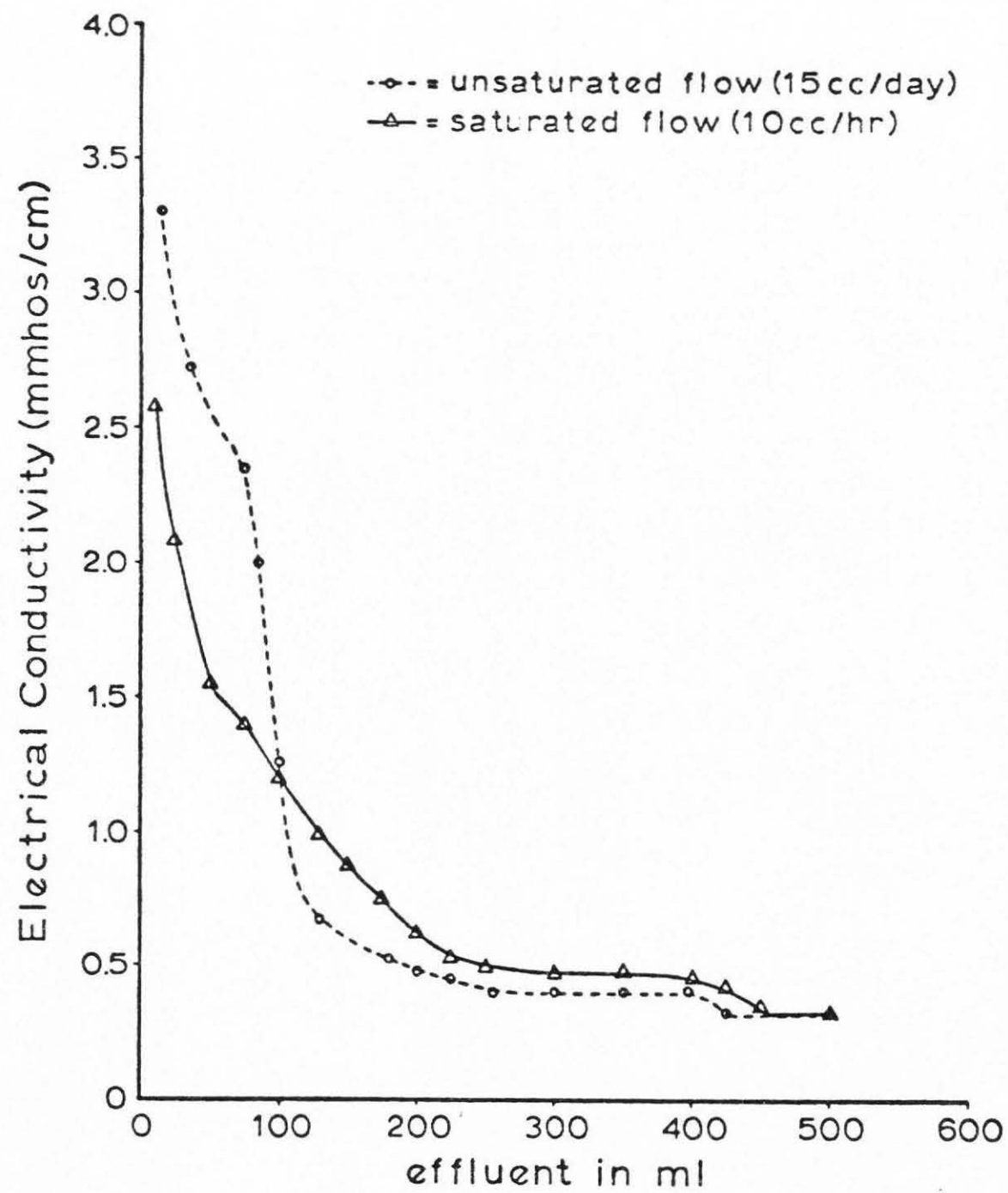


Figure 4A. Electrical conductivity of the effluent of Vernal soil columns leached with Logan river water.

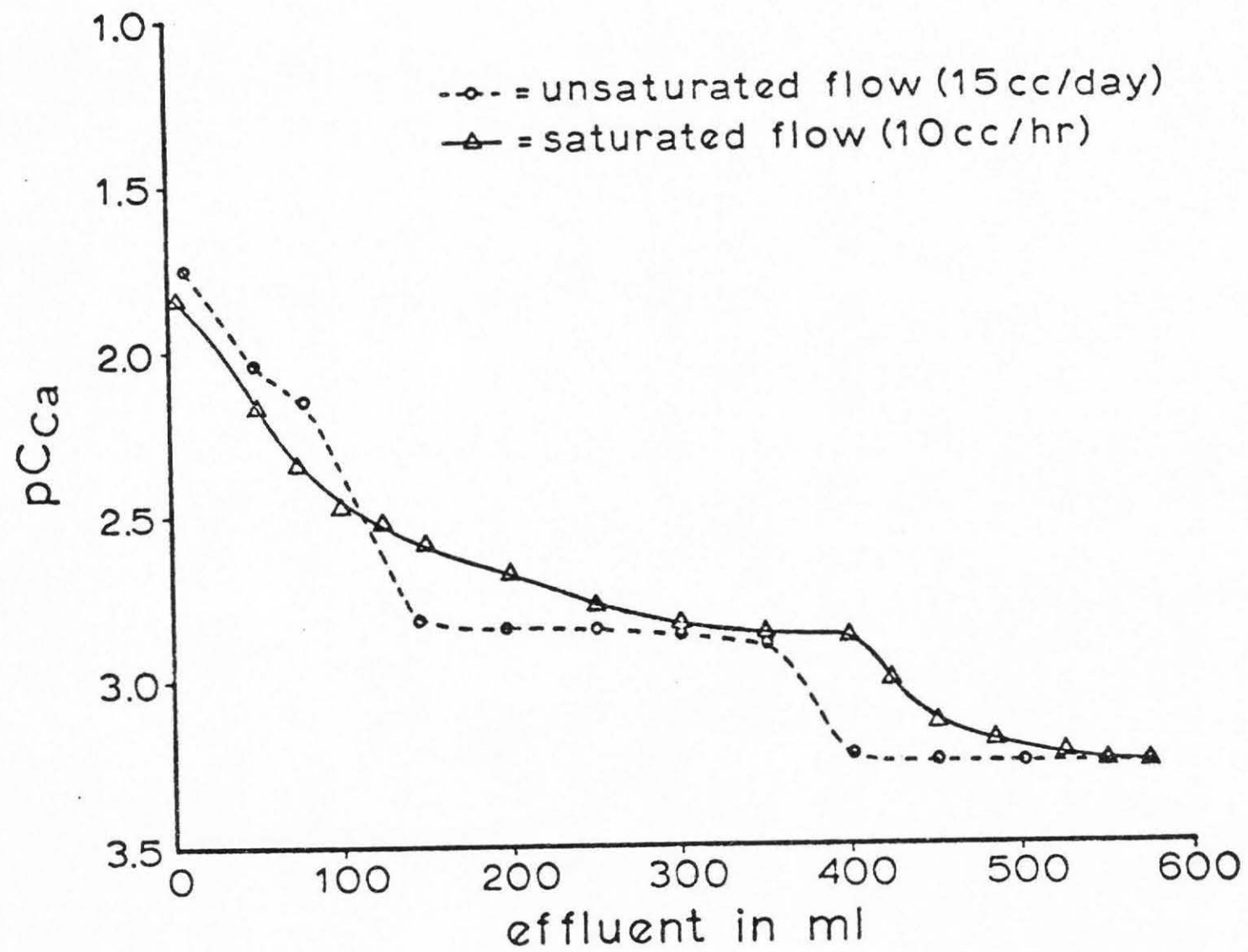


Figure 4B. pC_{Ca} of the effluent of Vernal soil columns leached with Logan river water.

Table 10. The solubility product data for Vernal soil leached with Logan river water (saturated flow)

ml. of effluent	E. C. mmhos/cm at 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	(CO_3^{2-})	pH
The calculated solubility product of lime = $4.07 \times 10^{-9} + 0.3 \times 10^{-9}$							
310	.4451	4.89×10^{-3}	.740	1.53×10^{-3}	9.5×10^{-4}	3.98×10^{-6}	8.18
360	.397	4.78×10^{-3}	.742	1.51×10^{-3}	9.3×10^{-4}	3.98×10^{-6}	8.18
410	.382	4.7×10^{-3}	.743	1.52×10^{-3}	9.1×10^{-4}	3.98×10^{-6}	8.18
460	.388	4.67×10^{-3}	.75	1.53×10^{-3}	8.9×10^{-4}	5.01×10^{-6}	8.2
510	.363	4.61×10^{-3}	.751	1.49×10^{-3}	8.67×10^{-4}	5.01×10^{-6}	8.2
560	.364	4.58×10^{-3}	.752	1.49×10^{-3}	8.61×10^{-4}	5.01×10^{-6}	8.2
610	.363	4.57×10^{-3}	.755	1.48×10^{-3}	8.52×10^{-4}	5.01×10^{-6}	8.20

Table 11. The solubility product data for Vernal soil leached with Logan river water (unsaturated flow)

ml. of effluent	E. C. mmhos/cm at 25C	Ionic strength	$\gamma_{Ca^{2+}}$ $\gamma_{SO_4^{2-}}$	$[Ca^{2+}]_T$ mole/L	(Ca^{2+})	(CO_3^{2-})	pH
The calculated solubility product of lime = 4.35×10^{-9}							
170	.453	5.3×10^{-3}	.732	1.55×10^{-3}	1×10^{-3}	5.01×10^{-6}	8.2
190	.459	4.8×10^{-3}	.742	1.52×10^{-3}	9.5×10^{-4}	5.01×10^{-6}	8.2
210	.457	4.8×10^{-3}	.742	1.5×10^{-3}	9.4×10^{-4}	5.01×10^{-6}	8.2
240	.456	4.72×10^{-3}	.743	1.48×10^{-3}	9.1×10^{-4}	5.01×10^{-6}	8.2
270	.452	4.6×10^{-3}	.75	1.51×10^{-3}	9.2×10^{-4}	5.01×10^{-6}	8.2
340	.449	4.6×10^{-3}	.751	1.42×10^{-3}	8.8×10^{-4}	5.01×10^{-6}	8.2

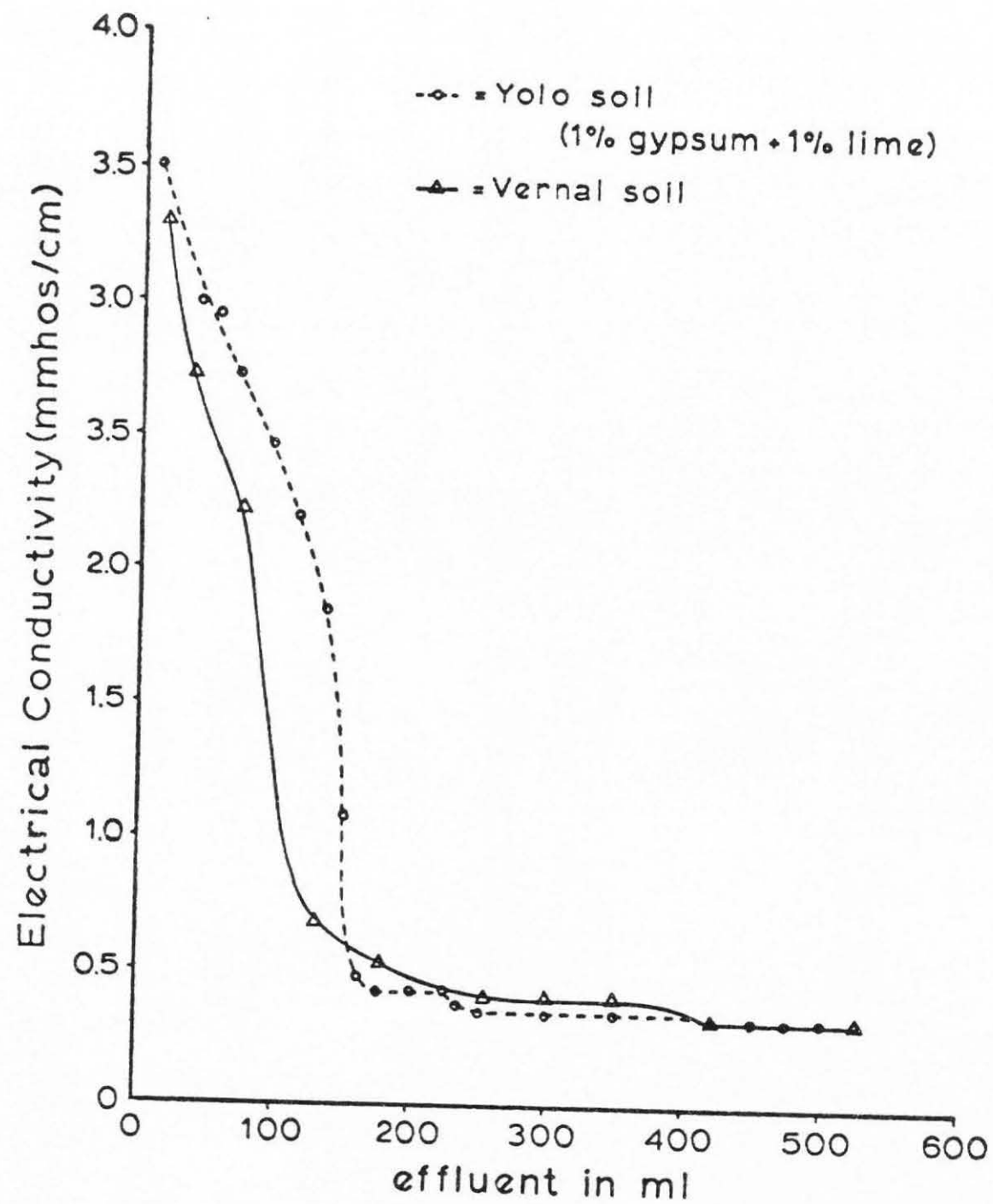


Figure 5A. Electrical conductivity of the effluent of soil columns leached under unsaturated conditions with Logan river water.

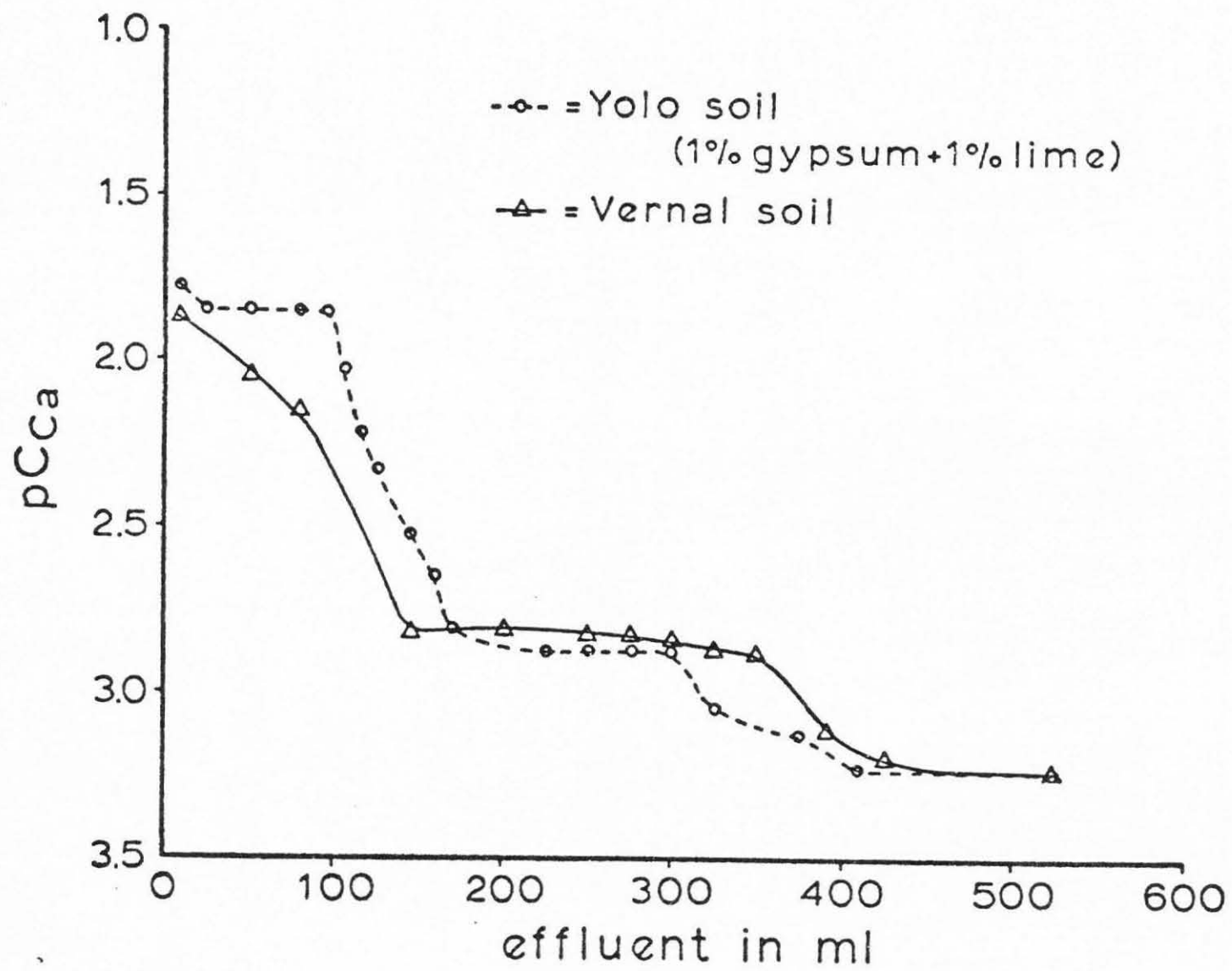


Figure 5B. pC_{Ca} of the effluent of soil columns leached under unsaturated conditions with Logan river water.

1% gypsum plus 1% lime). Figure 5A shows that at low levels of gypsum, the EC values cannot be used to indicate whether gypsum is present or not however, the pC_{Ca} data (Figure 5B) show a distinct plateau for a soil with the 1% gypsum. The close agreement between the solubility of naturally occurring lime (Vernal soil) and added reagent grade $CaCO_3$ (Yolo soil) is noted in Figure 5B.

It was of interest to devise a means of calculating a relative efficiency of removing Ca^{2+} from the soil columns by various waters and moisture regimes. This was achieved by estimating the amount of Ca^{2+} that was removed by 1000ml (one liter) of effluent. After this amount of leaching had occurred most of the salt removal was effected. An example of how this was accomplished is now given.

The system considered is the Yolo loam column (2% gypsum plus 1% lime) and the problem is to estimate the amount of Ca^{2+} removed by 1000ml of KCl solution. The original data are found in Figure 2B. The data from Figure 2B was replotted as shown in Figure 6A. The total area (a) encompassed by the dashed line is equaled to the maximum amount (mg) of Ca^{2+} that could be removed in 1000ml of effluent, i. e. 760 mg Ca^{2+} in the example described. The area (c) generated by the experimental Ca^{2+} release curve represents the unknown amount (X_{mg}) of Ca^{2+} leached from the soil by 1000ml of leaching solution. The relationship solved to find the Ca^{2+} released is

$$\frac{\text{Area A}}{760 \text{ mg}} = \frac{\text{Area C}}{X_{\text{mg}}} \quad (1)$$

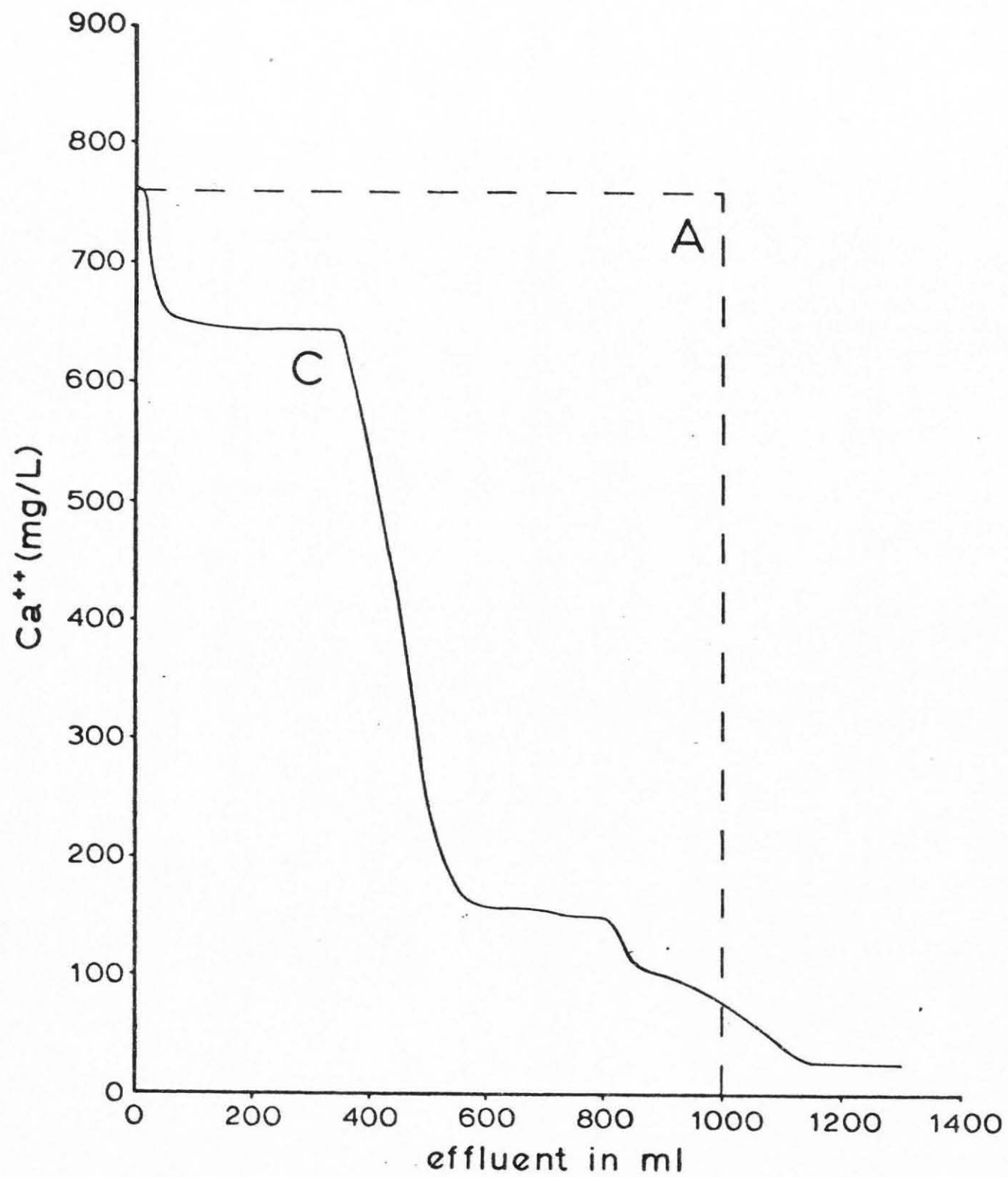


Figure 6A. Calcium concentration of the effluent of a Yolo soil (2% gypsum + 1% lime) column leached with KCl solution under saturated conditions.

A relative measure of areas A and C was obtained by cutting out the appropriate curve from a plot and weighing the cutout portion on an analytical balance. The weight is proportional to the area under the curve. The results are given in Table 12. Column 4 in Table 12 gives the Ca^{2+} removed as predicted from equation (1), column 5 gives the total amounts of Ca^{2+} added as gypsum and lime. It was assumed exchangeable Ca^{2+} was negligible in the total column mass balance. The fraction of Ca^{2+} removed by 1000ml of effluent is shown in column 6. These data correlate the data shown in Figure 2B. The KCl solution was the most efficient in leaching out gypsum followed by Logan river water. The K_2SO_4 solution was the least effective. It is noted that KCl removed 398 mg (46%) of the total calcium added as 2% gypsum and 1% lime. The amount of Ca^{2+} added as gypsum was 464 mg thus a maximum of 86% of the total gypsum added is accounted for assuming all calcium released came from gypsum. Figure 6B shows the sulfate release data for the same column. Using the relative area method it was determined (See Table 12) that 368 mg (99%) of the sulfate added had been removed. These data strongly suggest that a portion (at least 15%) of the Ca^{2+} resulting from gypsum dissolution reprecipitated as CaCO_3 in the column. Since the effluent contains Ca^{2+} which originates both from the presence of soil minerals and the exchange complex it is reasonable to assume that more than 15% of the Ca^{2+} release from gypsum dissolution precipitated as CaCO_3 .

Table 12 also shows, using the relative area method, the greater efficiency of unsaturated flow in salt removal as compared to saturated flow.

Table 12. Calcium and sulfate removal from treated Yolo loam soil

Water	Weight gm.		mg, Ca ²⁺ removal (R)	mg, Ca ²⁺ Original (O)	Fraction removal R/O
	C	A			
Yolo loam soil with 2% gypsum and 1% lime					
Logan river water	.7814	1.3801	334	864	0.39
KCl	.9098	1.7398	398	864	0.46
K ₂ SO ₄	0.6456	1.3194	269	864	0.31
Flow	Weight gm.		mg, Ca ²⁺ removal (R)	mg, Ca ²⁺ Original (O)	Fraction removal R/O
	C	A			
Yolo loam soil with 1% gypsum and 1% lime leached with Logan river water					
Saturated	0.475	1.4467	187	632	0.29
Unsaturated	0.226	0.6145	253	632	0.4

Table 12 (Continued)

Water	Weight gm		SO ₄ ²⁻	SO ₄ ²⁻	Fraction removal R/O
	C	A	removal (R)	Original (O)	
Sulfate removal from treated Yolo loam soil with 2% gypsum and 1% lime, leached with KCl solution					
KCl	.3110	1.4538	368.4692	372	0.985

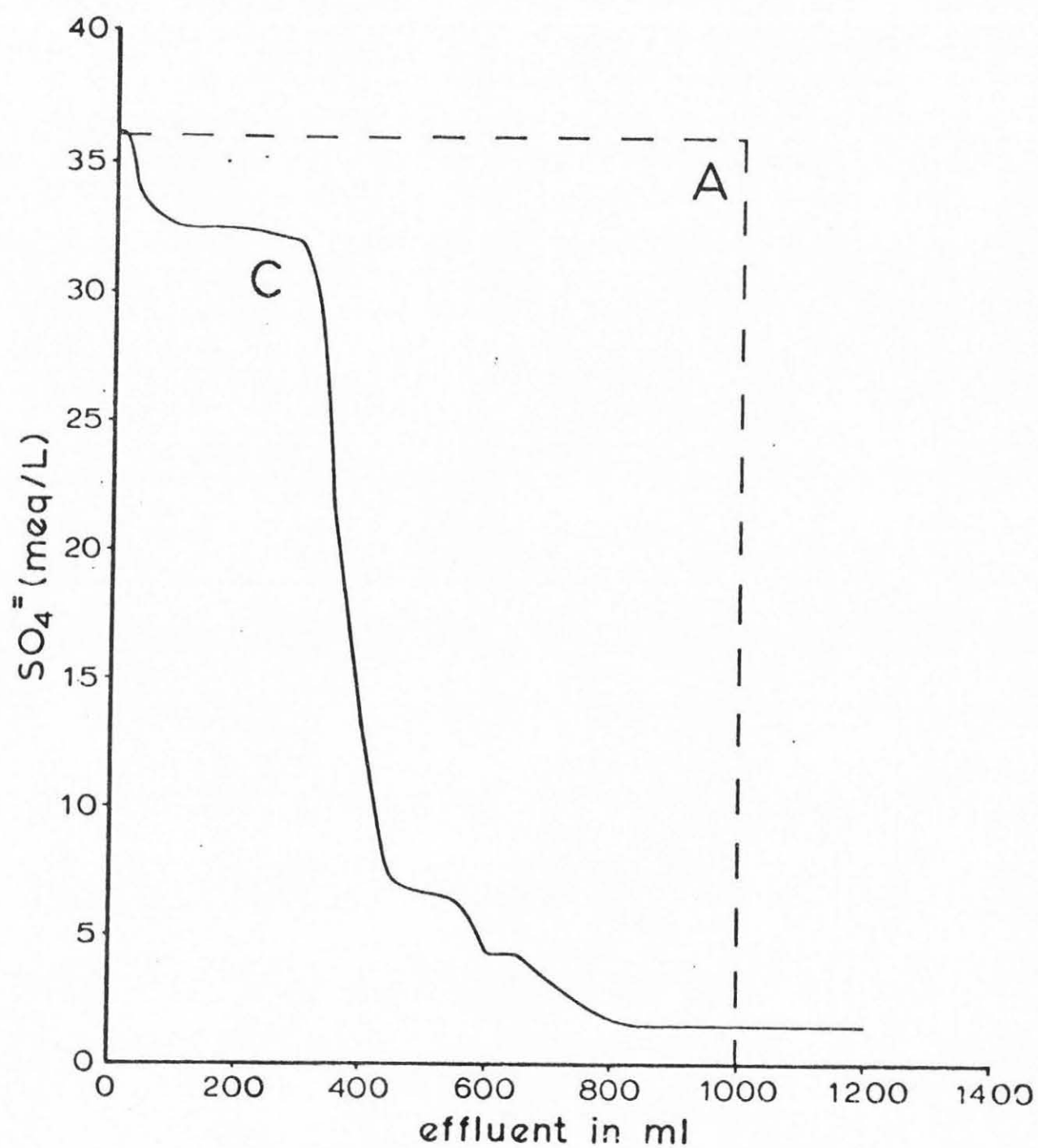


Figure 6B. Sulfate concentration of the effluent of a Yolo soil (2% gypsum + 1% lime) column leached with KCl solution under saturated condition.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Two soils were used in this soil column study, Yolo loam soil a non-calcareous, non-gypsiferous soil from central California and Vernal soil a calcareous soil from eastern Utah.

Initial studies were conducted where the solubilities of pure CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were determined in the presence of Logan river water, a KCl solution (2.8mmhos/cm), and a K_2SO_4 solution (2.7mmhos/cm). Gypsum was more soluble in the KCl solution due to the indifferent salt effect whereas, lime was more soluble in the K_2SO_4 solution because of the formation of CaSO_4^0 ion pairs. The solubility product of both $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 were determined from the analytical data. Equations were developed which took into account both the salt effect and the formation of CaSO_4^0 and CaCO_3^0 in pairs which were assumed to be the most important complex ions present. The calculated K_{sp} values were less than the theoretical values obtained from literature however, agreement was considered reasonable.

Using the three waters to leach a column of Yolo loam to which was added 2% gypsum + 1% lime essentially the same results were obtained as in the pure systems. The solubility of gypsum was greatest using KCl leaching solution and least using K_2SO_4 solution, Logan river

water was intermediate. The CaCO_3 in soil was most soluble in the K_2SO_4 leaching solution and less in the KCl solution.

The soil column studies showed that an EC measurement was not adequate to locate the region of a salt release curve that was in equilibrium or steady state with a given soil mineral. It was found that measuring the Ca^{2+} concentration in the effluent was a more reliable index to a steady state condition.

Unsaturated flow removed more salt per unit volume of effluent than saturated flow. The time required to remove a given amount of salt however was about 17 times longer when unsaturated flow was used.

All solubility products calculated underestimated the K_{sp} values for both $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 which suggested that even with unsaturated moisture flow, equilibrium may not be reached with gypsum on lime. This assumes all calculations and analytical data are valid.

Using a relative area method to analyze the KCl effluent of a Yolo loam soil (2% gypsum + 1% lime) under saturated moisture flow it was shown that a certain amount of Ca^{2+} derived from gypsum dissolution precipitated in the column as CaCO_3 . This reaction accounted for greater than 15% of the Ca^{2+} from gypsum. Because the K-Ca exchange was not monitored in the column the contribution of Ca^{2+} from the exchange complex is not known.

This study points out certain problems in studying the dissolution and precipitation of soil compounds. Equilibrium with compound like $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ may require more time than realized. The theoretical

K_{sp} values for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 can be approximated from experimental data but are difficult to duplicate. This in part may be due to the fact that the exchange mechanism was not accounted for in the calculations. Considerable work is still required to quantify the movement of Ca^{2+} ions in soil in the presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 .

LITERATURE CITED

- Adams, F. 1971. Ionic concentrations and activities in soil solutions. *Soil Sci. Soc. Am. Proc.* 35:420-426.
- Benion, G. B., and G. Centola. 1933. *Mem. Accad. Italia* 4, 445.
- Cameron, F. Frank., 1901. Solubility of gypsum in aqueous solution of sodium chloride. *Jour. Phys. Chem.* 5, 557-576.
- Denman, W. L. 1961. Maximum re-use of cooling water based on gypsum content and solubility. *Ind. Engr. Chem.* 53:817-822.
- Dutt, Gordon. 1964. Effect of small amounts of gypsum in soils on the solutes in effluents. *Soil Sci. Soci. Am. Proc.* 4, 754-757.
- Fear, J., and R. F. Johnston. 1929. The solubility of calcium carbonate at 25°C in presence of carbon dioxide at pressure varied from 3×10^4 to 1.0 atmosphere. *Ind. Eng. Chem.*
- Griffin, R. A., and J. J. Jurinak. 1973. Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. *Soil Sci. Soc. Am. Proc.* 116.
- Kielland, J. 1937. Individual activity coefficients of Ions in aqueous solution. *Am. Chem. Soci. J.* 59, 1675-1678.
- Marshall, W. L., and R. Slusher. 1966. Thermodynamics of calcium sulfate dihydrate in aqueous sodium chloride solution, 0-110°. *Jour. Phys. Chem.* 70:4015-4027.
- Meites, Louis, J. S. F. Pode and Henry C. Thomas. 1966. Are solubilities and solubility products related. *Jour. Chem. End.* 43, 667-672.
- Moreno, E. C., and E. C. Oborn. 1963. The solubility isotherm of gypsum, the solubility product and the solubility of (D-C-p-D). *Soil Soci. Am. Proc.* 27, 614-19.
- Olsen, R. Sterling and Frank S. Watanabe. 1959. Solubility of calcium carbonate in calcareous soils. *Soil Sci.* 88, 123-132.

Ostroff, A. G., and A. V. Metler. 1966. Solubility of calcium sulfate dihydrate in the system NaCl-MgCl-H₂O from 28° to 70° C. Jour. Chem. Engr. Data 11:346-350.

Ponnamperuma, F. N., E. M. Tianco, and T. A. Loy. 1966. Ionic strengths of the solutions of flooded soils and other natural aqueous solutions from specific conductance. Soil Sci. 102: 408-413.

Tanji, K. K. 1969. Determination of solubility of gypsum in aqueous electrolytes as affected by ion association and ionic strength up to 0.15M and at 25°C. Envi. Sci, 3:656-661.

U. S. Salinity Laboratory. 1954. Design and improvement of saline and alkali soils, U.S.D.A. Handbook 60.

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