DISSOLUTION AND PRECIPITATION OF GYPSUM
IN THE SOIL UNDER IRRIGATION

by

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

MASTER OF SCIENCE

in

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$\alpha_i$ Activity of ionic specie $i$

$[\cdot]$ Concentration of ionic specie in the solution (moles/Liter)

$K_h$ Henry's Law constant

$(\cdot)$ Activity of ionic specie in solution

$I$ Ionic strength (moles/Liter)

$\gamma_i$ Activity coefficient of specie $i$

$[\cdot]_T$ Total analytical concentration of ionic specie in solution

$K_{dHCO_3}$ Dissociation constant of Bicarbonate complex

$K_{dCO_3}$ Dissociation constant of carbonate complex

$K_{dSO_4}$ Dissociation constant of sulfate complex

$K_{dOH}$ Dissociation constant of hydroxyle complex

$K_{spSO_4}$ Solubility product of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

$K_{spCO_3}$ Solubility product of $\text{CaCO}_3$

$K_{A1}$ First dissociation constant of $\text{H}_2\text{CO}_3$

$K_{A2}$ Second dissociation constant of $\text{H}_2\text{CO}_3$

$P_{CO_2}$ Partial pressure of $\text{CO}_2$ (atmosphere)

$P_{Ca} = -\log [\text{Ca}]_T$
ABSTRACT

Dissolution and Precipitation of Gypsum in the Soil Under Irrigation

by

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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 CaSO$_4 \cdot 2$H$_2$O were determined in the presence of Logan river water, a KCl solution (2.8 mmhos/cm) and a K$_2$SO$_4$ solution (2.7 mmhos/cm). Gypsum was more soluble in the KCl solution than in the K$_2$SO$_4$ 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 K₂SO₄ leaching solution. Logan river water gave intermediate values.

Calcium carbonate was most soluble in the K₂SO₄ leaching solution and less in the KCl solution. It was found that measuring the Ca²⁺ 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 Ca²⁺ derived from gypsum dissolution precipitated in the column as CaCO₃. This amount was greater than 15% of the Ca²⁺ dissolved from gypsum.
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 qualitively 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 \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \), \( \text{CaCO}_3 \) and \( \text{CaMg(CO}_3\text{)}_2 \).

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 (\( \text{CaCO}_3 \) and \( \text{CaMg(CO}_3\text{)}_2 \)) 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 (\( \text{CaCO}_3 \) and \( \text{CaMg(CO}_3\text{)}_2 \)) minerals can be regarded as either a source or sink for \( \text{Ca}^{++} \) 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 \( \text{CaCO}_3 \) 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 \( \text{CaCO}_3 \) controls the \( \text{Ca}^{2+} \) 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 \( \text{CaCO}_3 \) 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 (Ca\(\text{SO}_4 \cdot 2\text{H}_2\text{O}\)), and Lime (Ca\(\text{CO}_3\)) 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 $3 \times 10^{-4}$ 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

$$K_c = \text{the solubility product of calcium carbonate}$$

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

$$(\text{CO}_3^{2-}) = \text{activity of carbonate}$$

For gypsum

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

Where

$$K_G = \text{The solubility product of gypsum}$$
\((Ca^{2+}) = \text{activity of calcium}\)

\((SO_4^{2-}) = \text{activity of sulfate}\)

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 \(3 \times 10^{-4}\) to 1 atmosphere in terms of ionic activities was \(4 \cdot 8 \times 10^{-9}\).

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
\[ \Delta F^o = \Delta H^o + T\Delta S \]

Where

\[ \Delta F^o = \text{Standard free energy of solution} \]

\[ \Delta H^o = \text{Standard heat of solution} \]

\[ \Delta F^o = -RT \ln K_{sp} \]

\[ \Delta S^o = \text{Standard entropy of solution} \]

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.

\[
\log f_i = \frac{-0.3582 \cdot i^{\frac{2}{1}}}{1 + 10^{8} a_i 0.2325 \sqrt{I}} = \log \gamma_i + \log (1 + 0.018 \sum_{i=1}^{S} m_i)
\]

Where

- \( f_i \) = Denotes the rational activity coefficient of the ith ion.
- \( \gamma_i \) = The practical activity coefficient of ith 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 $I = 0.2$.

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

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

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. C.p. 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:

\[
(SO_4^{2-}) = \frac{[SO_4^{2-}]}{\gamma_{SO_4^{2-}}} + \frac{(H^+)}{K_s \gamma_{HSO_4}} + \frac{[Ca^{2+}] \gamma_{Ca^{2+}}}{K_d}
\]

Where

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

\[\gamma_i\] = The activity coefficient of the ith ion

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

\[K_d = \text{The ion-pair dissociation constant of } CaSO_4^0 = 4.9 \times 10^{-3}\]

The activity coefficient \[\gamma_i\] was calculated by the following formula

\[
\log \gamma_i = \frac{0.508 Z_i^{2\frac{1}{2}}}{1 + 0.3 a_i^{\frac{1}{2}}}
\]
Where

\[ a_i = \text{The ionic radius parameter} \]

\[ I = \text{The ionic strength} \]

\[ Z = \text{The valence of the ionic species} \]

To calculate the activity of the complex \( (\text{CaSO}_4) \) the following expression was used.

\[
(CaSO_4^0) = \frac{[Ca^{2+}][SO_4^{2-}](\gamma SO_4^{2-})}{K_d} = \frac{K_G}{K_d}
\]

Where

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

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

\( [SO_4^{2-}] \) 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

\[
K_g = [Ca^{2+}][SO_4^{2-}](\gamma Ca^{2+})
\]
The solubility product of gypsum calculated from this research was found to be $2.45 \times 10^{-5}$.

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 NaCl-MgCl$_2$-$H_2O$ 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 2.5 m (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 MgCl₂ 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

\[ \log K_{sp} = \frac{-AZ^2 \sqrt{I}}{1 + B \sqrt{I}} + 2 \log m \]

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 "a." This evaluation yielded a constant value of 4-5Å for "a" 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 \( \text{Ca}^{2+} \) or \( \text{SO}_4^{2-} \) with \( \text{Na}^+ \) or \( \text{Cl}^- \) 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 $\text{PCO}_2$, $\text{HCO}_3^-$, $\text{H}^+$ and $\text{Ca}^{2+}$ in the pure calcite system. They assumed that the system involved the simultaneous equilibria of $\text{CO}_2$ and $\text{H}_2\text{O}$ and solubility of $\text{CaCO}_3$ in $\text{H}_2\text{O}$

$$
\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3
$$

$$
\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{-2}
$$

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

Where

$K_{1\text{A}}$ is the first ionization constant for carbonic acid. $(\text{H}^+)$, $(\text{HCO}_3^-)$, $(\text{CO}_2)$, $(\text{H}_2\text{O})$ are the activities of $\text{H}^+$, $\text{HCO}_3^-$, $\text{CO}_2$, and $\text{H}_2\text{O}$, respectively.

It is assumed that $\gamma\text{CO}_2$ is unity in $\text{H}_2\text{O}$, thus $(\text{CO}_2)$ can be replaced by $m\text{CO}_2$

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

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

Where

$$
K_{1\text{A}} = 4.45 \times 10^{-7}
$$
C = 0.0344 at 25°C

Now

\[ K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} \]  

(3)

Where

\( K_2 \) is the ionization constant of \( HC_0^3 \) and equal to \( 4.69 \times 10^{-11} \) at 25°C. The solubility product of calcite is

\[ K_{sp} = (Ca^{2+})(CO_3^{2-}) \]  

(4)

Where

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

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

\[ \frac{K_{sp}}{K_1 A K_2 C} = \frac{(Ca^{2+})}{(H^+)^2} \cdot PCO_2 \]  

(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 \( (\text{HCO}_3^-) \) will increase the pH. The effect of a change in \( (\text{Ca}^{2+}) \) on pH is less than that of \( (\text{HCO}_3^-) \).

The pH was calculated from the activity of \( \text{HCO}_3^- \) by using the following formula.

\[
\text{pH} = pK_{1A} - 0.509 \sqrt{I} + \log (\text{HCO}_3^-) - \log \text{CPCO}_2
\]

Where

\[
\log \gamma_+ = -0.509 \sqrt{I}
\]

\( \gamma_+ \) is the mean activity coefficient of \( \text{CaCO}_3 \) 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 atC. These solubility studies were carried out at 25°C ± 1. The saturated solutions of gypsum were filtered and the filtrates were analyzed for \( \text{Ca}^{2+} \), pH, activity of sodium, activity of \( \text{Ca}^{2+} \) and activity of \( \text{Ca}^{2+} + \text{Mg}^{2+} \) and sulfate concentration was determined gravimetrically as \( \text{BaSO}_4 \). 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 \( K_{d \text{CaSO}_4}, K_{d \text{MgSO}_4} \) and \( K_{d \text{NaSO}_4} \) (dissociation constants of \( \text{CaSO}_4 \), \( \text{MgSO}_4 \), \( \text{NaSO}_4 \)).
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

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

The activity of (H$_2$O) and (CaSO$_4 \cdot 2H_2$O) were arbitrarily taken at unity. Ionic activity coefficients were computed from the following expression.

$$\log y_i = -0.509 \frac{Z_i^2}{1/(1 + 2^2) - bu}$$ (2)

A fixed value of 3A for $\sigma$ parameter (ion size parameters) was taken so that $B\sigma$ reduce to unity and assumed a value of 0.3 for $b$.

The dissociation constant of CaSO$_4^\circ$ was computed from the following expression

$$K_{d_{CaSO_4^\circ}} = \frac{[Ca^{2+}] [SO_4^{2-}]^{2} \gamma_{CaSO_4^\circ}}{[CaSO_4^\circ] \gamma_{CaSO_4^\circ}}$$ (3)

Where $\gamma_{CaSO_4^\circ}$ was assumed to be unity. The dissociation constant for MgSO$_4^\circ$ is defined by
in which $\gamma_{\text{MgSO}_4^0}$ was taken as unity. The dissociation constant for NaSO$_4^-$ was described by

$$K_D\text{MgSO}_4^0 = \frac{[\text{Mg}^2+]\gamma_{\text{Mg}^2+}[\text{SO}_4^{2-}]\gamma_{\text{SO}_4^{2-}}}{[\text{MgSO}_4^0]\gamma_{\text{MgSO}_4^0}}$$

(4)

The concentration of $\gamma_{\text{NaSO}_4^-}$ was calculated from $[\text{NaSO}_4^-]$ was included in (I) ionic strength. The concluded that the mean ionic activity coefficients calculated by the computer program were in close agreement with literature $\gamma^+$ 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$_2$SO$_4$ 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 \( \text{Na}_2\text{SO}_4 \) solution because of \( \text{MgSO}_4^0 \) association is stronger than \( \text{NaSO}_4^0 \).

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

\[ I = 16 \text{EC} \]

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 specification 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

\[ Y = 0.0127x - 0.0003 \]  

(1)

\[ r = 0.996 \]  

(2)

or

\[ I = 0.013 \text{ EC} \]  

(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 \( \text{Ca}^{2+} \) ion activity coefficient values calculated from the activity of \( \text{Ca}^{2+} \) 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 $\gamma_i$. 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:

$$\text{CaSO}_{4}^{0}, \text{CaCO}_{3}^{0}, \text{CaHCO}_{3}^{+}, \text{etc.}$$

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 EC

Where EC = mmhos/cm at 25°C.

The activity coefficient $\gamma_i$ was calculated for the individual ions by means of the following equation

$$-\log \gamma_i = \frac{A Z_i^2 (I)^{\frac{1}{2}}}{1 + B_i^0 (I)^{\frac{1}{3}}}$$

Where:

- $A = .509$ constant
- $Z = 2 =$ valence of the ion
- $B = 3.3 \times 10^{-7}$ at 25°C
- $a^0 = 6 \times 10^{-8}$ for $Ca^{2+}$
- $a^0 = 4 \times 10^{-8}$ for $SO_4^{2-}$

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.

\[
[a] \quad [Ca^{2+}]_T = [Ca^{2+}] + CaSO_4^0
\]  

(a-1)

Where

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

and

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

or

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

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

\[
[Ca^{2+}]_T = \frac{K_{dSO_4}CaSO_4^0}{(SO_4^{2-} / Ca^2+)} + CaSO_4^0
\]  \hspace{1cm} (a-4)

Inverting

\[
\frac{CaSO_4^0}{[Ca^{2+}]_T} = \frac{(SO_4^{2-} / Ca^2+)}{(SO_4^{2-} / Ca^2+ + K_{dSO_4} / Ca^2+)} = \frac{1}{K_{dSO_4} \left( \frac{1}{SO_4^{2-} / Ca^2+} + \frac{1}{SO_4^{2-} / Ca^2+} \right)}
\]  \hspace{1cm} (a-5)

or

\[
CaSO_4^0 = [Ca]_T \frac{1}{K_{dSO_4} \left( \frac{1}{SO_4^{2-} / Ca^2+} + \frac{1}{SO_4^{2-} / Ca^2+} \right)} = \frac{K_{sp}}{K_{dSO_4}}
\]
b) For the case where the effluent is in equilibrium with both \( \text{CaCO}_3 \) and \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \), the total calcium concentration is given by:

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

The contribution of \([\text{CaHCO}_3^+]\) and \([\text{CaOH}^+]\) 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 \([\text{CaOH}^+]\) 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 \([\text{CaHCO}_3^+]\) is at pH 8.1

\[
[\text{CaHCO}_3^+] = \frac{K_{\text{Al}}K_{\text{HCO}_3^2}(\text{Ca}^{2+})}{(H^+)[\text{HCO}_3^-]} = \frac{K_{\text{Al}}K_{\text{HCO}_3^2}(\text{Ca}^{2+})}{(H^+)[\text{HCO}_3^-]}
\]

\[
[\text{CaHCO}_3^+] = \frac{-6.35 \times 10^{-1.47} \times 10^{-3.5}(\text{Ca}^{2+})}{10^{-8.1} + 10^{-1.25}} = 10^{-10.1} \times (\text{Ca}^{2+})
\]

\[
= 7.9 \times 10^{-11}(\text{Ca}^{2+})
\]
The dissociation constants for $[\text{CaSO}_4^0]$ and $[\text{CaCO}_3^0]$ are:

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

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

Solving for $\text{CaSO}_4^0$ and $\text{CaSO}_3$ and substituting in equation (b-1) gives

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

$$[\text{Ca}]_T = \frac{[\text{Ca}^{2+}]}{\gamma_{\text{Ca}^{2+}}} + \frac{(\text{Ca}^{2+})(\text{SO}_4^{2-})}{K_{d\text{SO}_4}} + \frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_{d\text{CO}_3}}$$

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

$$[\text{Ca}]_T = (\text{Ca}^{2+}) \left[ \frac{1}{\gamma_{\text{Ca}^{2+}}} + \frac{(\text{SO}_4^{2-})}{K_{d\text{SO}_4}} + \frac{(\text{CO}_3^{2-})}{K_{d\text{CO}_3}} \right] \quad \text{(b-4)}$$
or

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

where

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

To solve for the activity of sulfate ion, \((\text{SO}_4^{2-})\), one uses the relation for gypsum in equilibrium with water

\[ (\text{Ca}^{2+}) = K_{sp\text{SO}_4} / (\text{SO}_4^{2-}) \quad \text{(b-7)} \]

Substituting in equation (b-5) gives

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

The total concentration of sulfate \((\text{SO}_4^{2-})_T\) is given by
\[ [\text{SO}_4^{2-}]_T = [\text{SO}_4^{2-}] + \text{CaSO}_4^0 \]  \hspace{1cm} \text{(b-8)}

or

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

Which gives

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

From (b-5) we know:

\[ (\text{Ca}^+) = \frac{[\text{Ca}]_T}{B} \]

Substituting in equation (b-9) gives

\[ (\text{SO}_4^{2-}) = [\text{SO}_4^{2-}]_T \left/ \left[ \frac{1}{\gamma_{\text{SO}_4}} + \frac{[\text{Ca}]_T}{BK_{d\text{SO}_4}} \right] \right. \]  \hspace{1cm} \text{(b-10)}
or

\[ \frac{[\text{SO}_4^{2-}]}{[\text{SO}_4^{2-}]} = \frac{1}{\gamma_{\text{SO}_4}} + \frac{[\text{Ca}]}{K_{d\text{SO}_4}} + \frac{[\text{Ca}_3^{2-}]}{K_{d\text{SO}_4}} \]  

(b-11)

For the case when the effluent is in equilibrium with lime (CaCO\(_3\)), the total calcium concentration is given as

\[ [\text{Ca}^{2+}]_T = [\text{Ca}^{2+}] + [\text{CaHCO}_3^+] + [\text{CaCO}_3^0] + [\text{CaOH}^+] \]  

(c-1)

in terms of activities (c-1) is

\[ [\text{Ca}^{2+}]_T = \frac{[\text{Ca}^{2+}]}{\gamma_{\text{Ca}}} + \frac{[\text{CaHCO}_3^+]}{\gamma_{\text{CaHCO}_3}} + \frac{[\text{CaOH}^+]}{\gamma_{\text{CaOH}^+}} + \frac{[\text{CaCO}_3^0]}{\gamma_{\text{CaCO}_3}} \]  

(c-2)

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

Thus (c-2) becomes
\[
[Ca^{2+}]_T = \frac{(Ca^{2+})}{\gamma^{2+}_{Ca^2+}} + \frac{(CaHCO_3^-)}{\gamma^{HCO_3^-}_{HCO_3}} + \frac{(CaOH^+)}{\gamma^{OH^-}_{HCO_3}} + CaCO_3^0 \quad (c-3)
\]

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

\[
[Ca^{2+}]_T = (Ca^{2+}) \left[ \frac{1}{\gamma^{2+}_{Ca^2+}} + \frac{(HCO^-_3)}{K_d^{HCO^-}_{d_2} \gamma^{HCO^-}_{HCO_3}} + \frac{(OH^-)}{K_d^{OH^-}_{d_3} \gamma^{HCO^-}_{HCO_3}} + \frac{(CO_3^{2-})}{K_d^{CO_3^{2-}}_{d_1}} \right] \quad (c-4)
\]

Where

\[
(CaCO_3^0) = \frac{(Ca^{2+}) (CO_3^{2-})}{K_d^{d_1}} \quad \text{and} \quad K_d^{d_1} = 6.3 \times 10^{-4}
\]

\[
(CaHCO_3^+) = \frac{(Ca^{2+}) (HCO^-_3)}{K_d^{d_2}} \quad \text{and,} \quad K_d^{d_2} = 5.5 \times 10^{-2}
\]

\[
(CaOH^+) = \frac{(Ca^{2+}) (OH^-)}{K_d^{d_3}} \quad \text{and,} \quad K_d^{d_2} = 4.25 \times 10^{-2}
\]

Equation (c-4) is now written

\[
(Ca^{2+}) = \frac{[Ca^{2+}]_T}{B} \quad (c-5)
\]
Where

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

D) Calculation of the solubility products

1. For a system in equilibrium with gypsum

\[ (Ca^{2+}) = (SO_4^{2-}) = (2.4 \times 10^{-5})^2 \]

(d-1)

From equation (b-6)

\[ (Ca^{2+}) = \left[ Ca^{2+}\right]_T / B \]

(d-2)

Where

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

From equation (b-9)

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

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

2. For a system in equilibrium with CaCO₃

\[
(Ca^{2+}) = (CO_3^{2-}) = (4.45 \times 10^{-9})^{\frac{1}{2}} \tag{d-6}
\]

From equation (c-5)

\[
(Ca^{2+}) = \frac{[Ca^{2+}]_T}{B'} \tag{d-7}
\]

Where

\[
B' = \left[ \frac{1}{y_{Ca^{2+}}} + \frac{(HCO_3^-)}{(5.5 \times 10^{-2})^2} \frac{y_{HCO_3}}{y_{(OH^-)}} \right] + \left[ \frac{(OH^-)}{(4.25 \times 10^{-2})^2} \frac{y_{HCO_3}}{y_{(OH^-)}} \right] + \frac{(CO_3^2-)}{(6.3 \times 10^{-4})^2} \tag{d-8}
\]

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

\[
(CO_3^{2-}) = \frac{K_{A1} K_{A2} K_{PCO}}{[H^+]^2} \tag{d-8}
\]

The solubility product of gypsum is then calculated from

\[
(Ca^{2+})(SO_4^{2-}) = 2.4 \times 10^{-5} = K_{spSO_4} \]
and for CaCO$_3$ (lime)

\[
(Ca^{2+})(CO_3^{2-}) = 4.45 \times 10^{-9} = K_{spCO_3}.
\]
CHAPTER IV
MATERIALS AND METHODS

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

Two types 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 CaCl₂, then leaching with distilled water until the effluent was free of chloride as determined by the AgNO₃ test.

The soil was air-dried and then passed through a 2mm sieve. Reagent grade, CaCO₃, was added to portions of the prepared soil to bring the lime content to one percent. Reagent grade, CaSO₄ 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 gravimeterically (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.
Table 1. Characteristics of Vernal soil columns

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

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

<table>
<thead>
<tr>
<th>Soil Column</th>
<th>Leaching solution</th>
<th>Flow rate cc/hour</th>
<th>Pore volume %</th>
<th>Bulk density</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment</td>
<td>Logan river water</td>
<td>6-7</td>
<td>44.7</td>
<td>1.31</td>
</tr>
<tr>
<td>1% gypsum + 1% lime</td>
<td>Logan river water</td>
<td>6-8</td>
<td>44.8</td>
<td>1.30</td>
</tr>
<tr>
<td>2% gypsum + 1% lime</td>
<td>Logan river water</td>
<td>8-5-10</td>
<td>45.2</td>
<td>1.22</td>
</tr>
<tr>
<td>2% gypsum + 1% lime</td>
<td>KCl</td>
<td>10</td>
<td>45.1</td>
<td>1.24</td>
</tr>
<tr>
<td>2% gypsum + 1% lime</td>
<td>K₂SO₄</td>
<td>10</td>
<td>45.0</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Table 3. The flow rate and the moisture content under unsaturated moisture studies of Yolo and Vernal soils columns.

<table>
<thead>
<tr>
<th>Soil Column</th>
<th>Moisture Content</th>
<th>Flow Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yolo soil (1% gypsum + 1% lime)</td>
<td>Upper part 36.2%</td>
<td>15cc/day</td>
</tr>
<tr>
<td></td>
<td>Lower part 28.3%</td>
<td></td>
</tr>
<tr>
<td>Vernal soil</td>
<td>Upper part 35.1%</td>
<td>15cc/day</td>
</tr>
<tr>
<td></td>
<td>Lower part 29.3%</td>
<td></td>
</tr>
</tbody>
</table>

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 CaSO$_4$·2H$_2$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$_2$SO$_4$ solution when the salt was gypsum. The lower solubility of gypsum in the K$_2$SO$_4$ solution is considered to be a common in 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$_2$SO$_4$ solution.
Table 4. Solubility of $\text{CaCO}_3$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in waters used in this study

<table>
<thead>
<tr>
<th>Leaching water</th>
<th>Salt</th>
<th>E.C. mmho/cm at 25°C</th>
<th>pH</th>
<th>$[\text{Ca}]_T$</th>
<th>$[\text{SO}_4]_T$</th>
<th>$I$</th>
<th>$K_{\text{sp}}$ with correction</th>
<th>$K_{\text{sp}}$ without correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Logan river water</td>
<td>$\text{CaCO}_3$</td>
<td>0.321</td>
<td>8.23</td>
<td>$4.5 \times 10^{-4}$</td>
<td>$2.7 \times 10^{-4}$</td>
<td>$4.07 \times 10^{-3}$</td>
<td>0.763</td>
<td>$3.12 \times 10^{-9}$</td>
</tr>
<tr>
<td>Logan river water</td>
<td>$\text{CaSO}_4 + \text{CaCO}_3$</td>
<td>2.10</td>
<td>7.87</td>
<td>$1.215 \times 10^{-2}$</td>
<td>$1.192 \times 10^{-2}$</td>
<td>$2.66 \times 10^{-2}$</td>
<td>0.54</td>
<td>$1.63 \times 10^{-5}$</td>
</tr>
<tr>
<td>Logan river water</td>
<td>$\text{CaSO}_4$</td>
<td>2.10</td>
<td>7.57</td>
<td>$1.34 \times 10^{-2}$</td>
<td>$1.33 \times 10^{-2}$</td>
<td>$2.667 \times 10^{-2}$</td>
<td>0.54</td>
<td>$1.93 \times 10^{-5}$</td>
</tr>
<tr>
<td>KCl</td>
<td>$\text{CaCO}_3$</td>
<td>2.89</td>
<td>8.23</td>
<td>$5.2 \times 10^{-4}$</td>
<td>$3.64 \times 10^{-2}$</td>
<td>$0.506$</td>
<td>$3.5 \times 10^{-9}$</td>
<td>$3.82 \times 10^{-9}$</td>
</tr>
<tr>
<td>KCl</td>
<td>$\text{CaSO}_4 + \text{CaCO}_3$</td>
<td>4.70</td>
<td>7.85</td>
<td>$1.79 \times 10^{-2}$</td>
<td>$1.73 \times 10^{-2}$</td>
<td>$5.93 \times 10^{-2}$</td>
<td>0.440</td>
<td>$1.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>KCl</td>
<td>$\text{CaSO}_4$</td>
<td>4.78</td>
<td>7.5</td>
<td>$2.09 \times 10^{-2}$</td>
<td>$1.82 \times 10^{-2}$</td>
<td>$6.07 \times 10^{-2}$</td>
<td>0.443</td>
<td>$2.34 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{K}_2\text{SO}_4$</td>
<td>$\text{CaCO}_3$</td>
<td>2.623</td>
<td>8.23</td>
<td>$1.05 \times 10^{-3}$</td>
<td>$1.162 \times 10^{-2}$</td>
<td>$3.32 \times 10^{-2}$</td>
<td>0.52</td>
<td>$3.25 \times 10^{-9}$</td>
</tr>
<tr>
<td>$\text{K}_2\text{SO}_4$</td>
<td>$\text{CaSO}_4 + \text{CaCO}_3$</td>
<td>3.722</td>
<td>7.92</td>
<td>$1.06 \times 10^{-2}$</td>
<td>$2.84 \times 10^{-2}$</td>
<td>$4.6 \times 10^{-2}$</td>
<td>0.45</td>
<td>$1.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{K}_2\text{SO}_4$</td>
<td>$\text{CaSO}_4$</td>
<td>3.859</td>
<td>7.62</td>
<td>$1.175 \times 10^{-2}$</td>
<td>$2.84 \times 10^{-2}$</td>
<td>$4.7 \times 10^{-2}$</td>
<td>0.45</td>
<td>$1.66 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
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 CaCO₃ 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 K₂SO₄ solution of approximately the same salinity (EC = 2.7 mmhos/cm), the solubility of CaCO₃ was increased by 233%. At the same time the equilibrium conductivity and ionic strength, I, in the K₂SO₄ system was less than in the KCl system. These data show the strong effect of ion-pair formation (CaSO₄°) on the solubility of CaCO₃. The presence of soluble CaSO₄° increased dramatically the total calcium concentration while it reduced the presence of charged calcium ions (EC) in solution relative to the KCl water.

The Ksp calculations show the affect of correcting analytical data for ion-pair formation and the presence of salt. The Ksp for CaCO₃ could not be calculated without corrections because the CO₃ = activity was theoretically determined as described in the Theory section. The calculated corrected Ksp values for CaCO₃ and CaSO₄·2H₂O are compared to the theoretical Ksp values of 4.45x10⁻⁹ and 2.4x10⁻⁵, 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 1B. $pC_{Ca}$ 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 $\text{CaSO}_4^0$ complex produces a greater concentration of $\text{Ca}^{2+}$ in the $\text{K}_2\text{SO}_4$ effluent than in the KCl effluent.

Most of the $\text{Ca}^{2+}$ ion released from the exchange complex by the presence of the $\text{K}^+$ 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 $\text{CaCO}_3$. 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 $\text{Ca}^{2+}$ 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 50g 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

<table>
<thead>
<tr>
<th>ml of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{\text{Ca}^{2+}}$ mole/L</th>
<th>$[\text{Ca}^{2+}]_T$ mole/L</th>
<th>$[\text{SO}_4^{2-}]_T$ mole/L</th>
<th>pH</th>
<th>$[\text{SO}_4^{2-}]$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.623</td>
<td>3.329x$10^{-2}$</td>
<td>0.54</td>
<td>1.47x$10^{-2}$</td>
<td>4.55x$10^{-2}$</td>
<td>1.32x$10^{-2}$</td>
<td>4.19x$10^{-3}$</td>
<td>8.0</td>
</tr>
<tr>
<td>100</td>
<td>2.572</td>
<td>3.266x$10^{-2}$</td>
<td>0.55</td>
<td>1.42x$10^{-2}$</td>
<td>4.437x$10^{-3}$</td>
<td>1.28x$10^{-2}$</td>
<td>4.14x$10^{-3}$</td>
<td>8.0</td>
</tr>
<tr>
<td>150</td>
<td>2.542</td>
<td>3.288x$10^{-2}$</td>
<td>0.55</td>
<td>1.46x$10^{-2}$</td>
<td>4.5x$10^{-3}$</td>
<td>1.72x$10^{-2}$</td>
<td>3.95x$10^{-3}$</td>
<td>8.0</td>
</tr>
<tr>
<td>200</td>
<td>2.50</td>
<td>3.175x$10^{-2}$</td>
<td>0.55</td>
<td>1.45x$10^{-2}$</td>
<td>4.5x$10^{-3}$</td>
<td>1.23x$10^{-2}$</td>
<td>3.98x$10^{-3}$</td>
<td>8.0</td>
</tr>
<tr>
<td>250</td>
<td>2.45</td>
<td>3.45x$10^{-2}$</td>
<td>0.554</td>
<td>1.44x$10^{-2}$</td>
<td>4.48x$10^{-3}$</td>
<td>1.2x$10^{-2}$</td>
<td>3.9x$10^{-3}$</td>
<td>8.0</td>
</tr>
<tr>
<td>300</td>
<td>2.37</td>
<td>3.039x$10^{-2}$</td>
<td>0.556</td>
<td>1.44x$10^{-2}$</td>
<td>4.47x$10^{-3}$</td>
<td>1.21x$10^{-2}$</td>
<td>3.9x$10^{-3}$</td>
<td>8.0</td>
</tr>
</tbody>
</table>

The calculated solubility product of gypsum = $1.85 \pm 0.75x10^{-5}$
Table 5. (Continued)

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{Ca}^{2+}$</th>
<th>$[Ca^{2+}]_T$ mole/L</th>
<th>$[SO_4^{2-}]_T$ mole/L</th>
<th>$[CO_3^{2-}]$ mole/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
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<td>0.430</td>
<td>5.23x10^{-3}</td>
<td>0.726</td>
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<td>3.98x10^{-6}</td>
</tr>
<tr>
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<td>0.746</td>
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<td>1.10x10^{-3}</td>
<td>1.02x10^{-3}</td>
<td>3.98x10^{-6}</td>
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<tr>
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<td>0.365</td>
<td>4.635x10^{-3}</td>
<td>0.7516</td>
<td>1.55x10^{-3}</td>
<td>0.95x10^{-3}</td>
<td>9.1x10^{-4}</td>
<td>3.98x10^{-6}</td>
</tr>
<tr>
<td>750</td>
<td>0.350</td>
<td>4.445x10^{-3}</td>
<td>0.754</td>
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<td>0.95x10^{-3}</td>
<td>8.2x10^{-4}</td>
<td>5.01x10^{-6}</td>
</tr>
<tr>
<td>800</td>
<td>0.338</td>
<td>4.292x10^{-3}</td>
<td>0.756</td>
<td>1.51x10^{-3}</td>
<td>0.93x10^{-3}</td>
<td>7.5x10^{-4}</td>
<td>5.01x10^{-6}</td>
</tr>
<tr>
<td>850</td>
<td>0.332</td>
<td>4.216x10^{-3}</td>
<td>0.759</td>
<td>1.5x10^{-3}</td>
<td>0.86x10^{-3}</td>
<td>7.1x10^{-4}</td>
<td>5.91x10^{-6}</td>
</tr>
</tbody>
</table>

The calculated solubility product of lime $4.4+ 0.3x10^{-9}$
Table 6. Solubility product data for Yolo loam soil column with 2% gypsum and 1% lime leached with K₂SO₄

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>( \gamma_{\text{Ca}^{2+}} )</th>
<th>([ \text{Ca}^{2+} ]_T ) mole/L</th>
<th>([ \text{SO}_4^{2-} ]_T ) mole/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.36</td>
<td>4.27x10⁻²</td>
<td>.48</td>
<td>1.9x10⁻²</td>
<td>5.327x10⁻³</td>
<td>1.8x10⁻²</td>
</tr>
<tr>
<td>100</td>
<td>4.39</td>
<td>5.57x10⁻²</td>
<td>.462</td>
<td>1.63x10⁻²</td>
<td>4.8x10⁻³</td>
<td>1.63x10⁻²</td>
</tr>
<tr>
<td>150</td>
<td>4.34</td>
<td>5.52x10⁻²</td>
<td>.463</td>
<td>1.63x10⁻²</td>
<td>4.8x10⁻³</td>
<td>1.6x10⁻²</td>
</tr>
<tr>
<td>200</td>
<td>4.34</td>
<td>5.52x10⁻²</td>
<td>.463</td>
<td>1.61x10⁻²</td>
<td>4.62x10⁻³</td>
<td>1.61x10⁻²</td>
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<tr>
<td>250</td>
<td>4.13</td>
<td>5.24x10⁻²</td>
<td>.469</td>
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<td>4.61x10⁻³</td>
<td>1.60x10⁻²</td>
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<tr>
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<td>3.88</td>
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<td>1.71x10⁻²</td>
<td>4.5x10⁻³</td>
<td>1.524x10⁻²</td>
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</table>

The calculated solubility product of gypsum 2.27x10⁻⁵
Table 6. (Continued)

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{Ca}^{2+}$</th>
<th>[Ca$^{2+}$]$_T$ mole/L</th>
<th>$\gamma_{SO_4}^{2-}$</th>
<th>[SO$_4^{2-}$]$_T$ mole/L</th>
<th>[CO$_3^{2-}$]</th>
<th>pH</th>
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<tbody>
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</tr>
<tr>
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<td>3.937x10^-2</td>
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<td>8.0</td>
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<tr>
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<td>3.937x10^-2</td>
<td>.495</td>
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<td>1.42x10^-3</td>
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</tr>
<tr>
<td>700</td>
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<tr>
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</tr>
</tbody>
</table>

The calculated solubility product of lime 4.2$^+$ 2x10$^{-9}$
Table 7. Solubility product data for Yolo loam soil column with 2% gypsum and 1% lime leached with KCl

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{\text{Ca}^2+}$</th>
<th>$[\text{Ca}^2+]_T$ mole/L</th>
<th>$[\text{SO}_4^{2-}]_T$ mole/L</th>
<th>(Ca)</th>
<th>(SO$_4^{2-}$)</th>
<th>pH</th>
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</thead>
<tbody>
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</tr>
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<td>3.50</td>
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<td>1.092x10$^{-2}$</td>
<td>3.78x10$^{-3}$</td>
<td>1.82x10$^{-2}$</td>
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<td>1.82x10$^{-2}$</td>
<td>5.03x10$^{-3}$</td>
<td>7.9</td>
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<tr>
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<td>1.007x10$^{-2}$</td>
<td>3.46x10$^{-3}$</td>
<td>1.71x10$^{-2}$</td>
<td>4.77x10$^{-3}$</td>
<td>7.9</td>
</tr>
</tbody>
</table>

The calculated solubility product of gypsum $1.84 \pm 0.2x10^{-5}$
Table 7. (Continued)

<table>
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<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25C</th>
<th>Ionic strength</th>
<th>( \gamma_{\text{Ca}^2+} )</th>
<th>( [\text{Ca}^2+]_T ) mole/L</th>
<th>( (\text{Ca}^2+) ) mole/L</th>
<th>( [\text{SO}_4^{2-}]_T ) mole/L</th>
<th>( (\text{CO}_3^2-) ) mole/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>3.272</td>
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<td>4.85x10^-3</td>
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<td>1.99x10^-6</td>
<td>8.0</td>
</tr>
<tr>
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<td>3.270</td>
<td>4.15x10^-2</td>
<td>.486</td>
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<td>8.2x10^-3</td>
<td>1.99x10^-6</td>
<td>8.0</td>
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<td>.486</td>
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<td>3.16x10^-6</td>
<td>8.1</td>
</tr>
<tr>
<td>900</td>
<td>3.25</td>
<td>4.12x10^-2</td>
<td>.49</td>
<td>3.92x10^-3</td>
<td>1.12x10^-2</td>
<td>5.6x10^-3</td>
<td>3.16x10^-6</td>
<td>8.1</td>
</tr>
<tr>
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<td>3.235</td>
<td>4.1x10^-2</td>
<td>.50</td>
<td>3.67x10^-3</td>
<td>1.1x10^-2</td>
<td>5.1x10^-3</td>
<td>3.16x10^-6</td>
<td>8.1</td>
</tr>
</tbody>
</table>

The calculated solubility product of lime 3.02x10^-9
Table 8. Solubility product data for Yolo loam soil column with 1% gypsum and 1% lime leached with Logan river water (unsaturated flow)

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/gm 25C</th>
<th>Ionic strength</th>
<th>$\gamma_{\text{Ca}^{2+}}$</th>
<th>$[\text{Ca}^{2+}]_T$</th>
<th>$[\text{SO}_4^{2-}]_T$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>3.08</td>
<td>3.91x10^{-2}</td>
<td>.492</td>
<td>1.72x10^{-2}</td>
<td>5.02x10^{-3}</td>
<td>8.0</td>
</tr>
<tr>
<td>64</td>
<td>2.99</td>
<td>3.797x10^{-2}</td>
<td>.50</td>
<td>1.55x10^{-2}</td>
<td>4.76x10^{-3}</td>
<td>8.0</td>
</tr>
<tr>
<td>70</td>
<td>2.979</td>
<td>3.77x10^{-2}</td>
<td>.50</td>
<td>1.38x10^{-2}</td>
<td>4.45x10^{-3}</td>
<td>8.0</td>
</tr>
<tr>
<td>77</td>
<td>2.960</td>
<td>3.759x10^{-2}</td>
<td>.50</td>
<td>1.38x10^{-2}</td>
<td>4.369x10^{-3}</td>
<td>8.0</td>
</tr>
<tr>
<td>87</td>
<td>2.74</td>
<td>3.479x10^{-2}</td>
<td>.510</td>
<td>1.378x10^{-2}</td>
<td>4.43x10^{-2}</td>
<td>8.0</td>
</tr>
<tr>
<td>104</td>
<td>2.72</td>
<td>3.47x10^{-2}</td>
<td>.51</td>
<td>1.382x10^{-2}</td>
<td>4.05x10^{-3}</td>
<td>8.0</td>
</tr>
</tbody>
</table>

The calculated solubility product of gypsum = $1.77 \pm 0.4 \times 10^{-5}$
Table 8. (Continued)

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{\text{Ca}^{2+}}$</th>
<th>$[\text{Ca}^{2+}]_T$</th>
<th>$[\text{SO}_4^{2-}]_T$</th>
<th>$[\text{CO}_3^{2-}]$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>215</td>
<td>0.464</td>
<td>5.89x10^{-3}</td>
<td>0.729</td>
<td>1.33x10^{-3}</td>
<td>8.71x10^{-4}</td>
<td>1.1x10^{-3}</td>
<td>3.98x10^{-6}</td>
</tr>
<tr>
<td>231</td>
<td>0.464</td>
<td>5.89x10^{-3}</td>
<td>0.729</td>
<td>1.425x10^{-4}</td>
<td>9x10^{-4}</td>
<td>1.1x10^{-3}</td>
<td>5.01x10^{-6}</td>
</tr>
<tr>
<td>241</td>
<td>0.464</td>
<td>5.89x10^{-3}</td>
<td>0.729</td>
<td>1.415x10^{-3}</td>
<td>8.84x10^{-4}</td>
<td>1.08x10^{-3}</td>
<td>5.01x10^{-6}</td>
</tr>
<tr>
<td>258</td>
<td>0.452</td>
<td>5.68x10^{-3}</td>
<td>0.732</td>
<td>1.355x10^{-3}</td>
<td>8.84x10^{-4}</td>
<td>9.0x10^{-4}</td>
<td>5.01x10^{-6}</td>
</tr>
<tr>
<td>282</td>
<td>0.446</td>
<td>5.66x10^{-3}</td>
<td>0.735</td>
<td>1.405x10^{-3}</td>
<td>8.86x10^{-4}</td>
<td>8.25x10^{-4}</td>
<td>5.01x10^{-6}</td>
</tr>
<tr>
<td>293</td>
<td>0.442</td>
<td>5.61x10^{-3}</td>
<td>0.738</td>
<td>1.348x10^{-3}</td>
<td>8.8x10^{-4}</td>
<td>8.1x10^{-4}</td>
<td>5.01x10^{-6}</td>
</tr>
</tbody>
</table>

The calculated solubility product of lime = $4.12 \pm 0.3 \times 10^{-9}$
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)

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{Ca}^{2+}$</th>
<th>$\gamma_{SO_4^{2-}}$</th>
<th>$[Ca^{2+}]_T$ mole/L</th>
<th>$[SO_4^{2-}]_T$ mole/L</th>
<th>(Ca$^+$)</th>
<th>(SO$_4^{2-}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.8</td>
<td>3.556x10^-2</td>
<td>0.509</td>
<td>1.427x10^-2</td>
<td>4.1x10^-3</td>
<td>1.36x10^-2</td>
<td>4.0x10^-3</td>
<td>7.95</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>2.65</td>
<td>3.365x10^-2</td>
<td>0.515</td>
<td>1.4x10^-2</td>
<td>4.11x10^-3</td>
<td>1.32x10^-2</td>
<td>4.10^-3</td>
<td>7.95</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>2.598</td>
<td>3.238x10^-2</td>
<td>0.52</td>
<td>1.41x10^-2</td>
<td>4.17x10^-3</td>
<td>1.3x10^-2</td>
<td>3.98x10^-3</td>
<td>7.95</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>2.55</td>
<td>3.238x10^-2</td>
<td>0.52</td>
<td>1.4x10^-2</td>
<td>4.17x10^-3</td>
<td>1.28x10^-2</td>
<td>3.97x10^-3</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>2.06</td>
<td>3.175x10^-2</td>
<td>0.523</td>
<td>1.4x10^-2</td>
<td>4.25x10^-3</td>
<td>1.28x10^-3</td>
<td>3.93x10^-3</td>
<td>8.0</td>
<td></td>
</tr>
</tbody>
</table>

The calculated solubility product of gypsum = 1.6x10^-5

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{Ca}^{2+}$</th>
<th>$\gamma_{SO_4^{2-}}$</th>
<th>$[Ca^{2+}]_T$ mole/L</th>
<th>(Ca$^+$)</th>
<th>(CO$_3^{2-}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>0.3284</td>
<td>4.17x10^-3</td>
<td>0.73</td>
<td>1.275x10^-3</td>
<td>8.17x10^-4</td>
<td>5.01x10^-6</td>
<td>8.15</td>
<td></td>
</tr>
<tr>
<td>570</td>
<td>0.328</td>
<td>4.17x10^-3</td>
<td>0.732</td>
<td>1.275x10^-3</td>
<td>8.17x10^-4</td>
<td>5.01x10^-6</td>
<td>8.15</td>
<td></td>
</tr>
<tr>
<td>590</td>
<td>0.3260</td>
<td>4.14x10^-3</td>
<td>0.75</td>
<td>1.3x10^-3</td>
<td>8.25x10^-4</td>
<td>3.98x10^-6</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>620</td>
<td>0.325</td>
<td>4.14x10^-3</td>
<td>0.75</td>
<td>1.275x10^-3</td>
<td>8.5x10^-4</td>
<td>3.98x10^-6</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>0.324</td>
<td>4.13x10^-3</td>
<td>0.76</td>
<td>1.270x10^-3</td>
<td>8.48x10^-4</td>
<td>3.98x10^-6</td>
<td>8.2</td>
<td></td>
</tr>
</tbody>
</table>

The calculated solubility product of lime = 3.83+ 0.3x10^-3
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 $\text{CaSO}_3$ 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 $\text{CaCO}_3$.

Figures 4A and 4B show how the EC and $pC_{\text{Ca}}$ 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 $\text{CaCO}_3$ 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 $4.45 \times 10^{-9}$.

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>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E.C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{Ca^{2+}}$</th>
<th>$[Ca^{2+}]_T$</th>
<th>$\gamma_{SO_4^{2-}}$</th>
<th>(Ca$^{2+}$)</th>
<th>(Ca$^{2+}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>.4451</td>
<td>4.89x10$^{-3}$</td>
<td>.740</td>
<td>1.53x10$^{-3}$</td>
<td>9.5x10$^{-4}$</td>
<td>3.98x10$^{-6}$</td>
<td>8.18</td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>.397</td>
<td>4.78x10$^{-3}$</td>
<td>.742</td>
<td>1.51x10$^{-3}$</td>
<td>9.3x10$^{-4}$</td>
<td>3.98x10$^{-6}$</td>
<td>8.18</td>
<td></td>
</tr>
<tr>
<td>410</td>
<td>.382</td>
<td>4.7x10$^{-3}$</td>
<td>.743</td>
<td>1.52x10$^{-3}$</td>
<td>9.1x10$^{-4}$</td>
<td>3.98x10$^{-6}$</td>
<td>8.18</td>
<td></td>
</tr>
<tr>
<td>460</td>
<td>.388</td>
<td>4.67x10$^{-3}$</td>
<td>.75</td>
<td>1.53x10$^{-3}$</td>
<td>8.9x10$^{-4}$</td>
<td>5.01x10$^{-6}$</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>510</td>
<td>.363</td>
<td>4.61x10$^{-3}$</td>
<td>.751</td>
<td>1.49x10$^{-3}$</td>
<td>8.67x10$^{-4}$</td>
<td>5.01x10$^{-6}$</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>560</td>
<td>.364</td>
<td>4.58x10$^{-3}$</td>
<td>.752</td>
<td>1.49x10$^{-3}$</td>
<td>8.61x10$^{-4}$</td>
<td>5.01x10$^{-6}$</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>610</td>
<td>.363</td>
<td>4.57x10$^{-3}$</td>
<td>.755</td>
<td>1.48x10$^{-3}$</td>
<td>8.52x10$^{-4}$</td>
<td>5.01x10$^{-6}$</td>
<td>8.20</td>
<td></td>
</tr>
</tbody>
</table>

The calculated solubility product of lime $= 4.07 \pm 0.3 \times 10^{-9}$
Table 11. The solubility product data for Vernal soil leached with Logan river water (unsaturated flow)

<table>
<thead>
<tr>
<th>ml. of effluent</th>
<th>E. C. mmhos/cm at 25°C</th>
<th>Ionic strength</th>
<th>$\gamma_{Ca}^{2+}$</th>
<th>$[Ca]_T^{2+}$ mole/L</th>
<th>$\gamma_{SO_4}^{2-}$</th>
<th>$(Ca)^{2+}$</th>
<th>$(CO_3)^{2-}$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>.453</td>
<td>5.3x10^{-3}</td>
<td>.732</td>
<td>1.55x10^{-3}</td>
<td>1x10^{-3}</td>
<td>5.01x10^{-6}</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>.459</td>
<td>4.8x10^{-3}</td>
<td>.742</td>
<td>1.52x10^{-3}</td>
<td>9.5x10^{-4}</td>
<td>5.01x10^{-6}</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>.457</td>
<td>4.8x10^{-3}</td>
<td>.742</td>
<td>1.5x10^{-3}</td>
<td>9.4x10^{-4}</td>
<td>5.01x10^{-6}</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>.456</td>
<td>4.72x10^{-3}</td>
<td>.743</td>
<td>1.48x10^{-3}</td>
<td>9.1x10^{-4}</td>
<td>5.01x10^{-6}</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>270</td>
<td>.452</td>
<td>4.6x10^{-3}</td>
<td>.75</td>
<td>1.51x10^{-3}</td>
<td>9.2x10^{-4}</td>
<td>5.01x10^{-6}</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>.449</td>
<td>4.6x10^{-3}</td>
<td>.751</td>
<td>1.42x10^{-3}</td>
<td>8.8x10^{-4}</td>
<td>5.01x10^{-6}</td>
<td>8.2</td>
<td></td>
</tr>
</tbody>
</table>

The calculated solubility product of lime = $4.35 \pm 0.03 \times 10^{-9}$
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\textsubscript{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 \textit{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\textsuperscript{2+} from the soil columns by various waters and moisture regimes. This was achieved by estimating the amount of Ca\textsuperscript{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\textsuperscript{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\textsuperscript{2+} that could be removed in 1000ml of effluent, i.e. 760 mg Ca\textsuperscript{2+} in the example described. The area (c) generated by the experimental Ca\textsuperscript{2+} release curve represents the unknown amount \(X_{\text{mg}}\) of Ca\textsuperscript{2+} leached from the soil by 1000ml of leaching solution. The relationship solved to find the Ca\textsuperscript{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

<table>
<thead>
<tr>
<th>Water</th>
<th>Weight gm.</th>
<th>$\text{mg, Ca}^{2+}$ removal</th>
<th>$\text{mg, Ca}^{2+}$ Original</th>
<th>Fraction removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>A</td>
<td>(R)</td>
<td>(O) R/O</td>
</tr>
<tr>
<td>Yolo loam soil with 2% gypsum and 1% lime</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Logan river water</td>
<td>.7814</td>
<td>1.3801</td>
<td>334</td>
<td>864 0.39</td>
</tr>
<tr>
<td>KCl</td>
<td>.9098</td>
<td>1.7398</td>
<td>398</td>
<td>864 0.46</td>
</tr>
<tr>
<td>$\text{K}_2\text{SO}_4$</td>
<td>0.6456</td>
<td>1.3194</td>
<td>269</td>
<td>864 0.31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow</th>
<th>Weight gm.</th>
<th>$\text{mg, Ca}^{2+}$ removal</th>
<th>$\text{mg, Ca}^{2+}$ Original</th>
<th>Fraction removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>A</td>
<td>(R)</td>
<td>(O) R/O</td>
</tr>
<tr>
<td>Yolo loam soil with 1% gypsum and 1% lime leached with Logan river water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturated</td>
<td>0.475</td>
<td>1.4467</td>
<td>187</td>
<td>632 0.29</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>0.226</td>
<td>0.6145</td>
<td>253</td>
<td>632 0.4</td>
</tr>
<tr>
<td>Water</td>
<td>Weight gm</td>
<td>$\text{SO}_4^{2-}$ removal</td>
<td>$\text{SO}_4^{2-}$ Original</td>
<td>Fraction removal</td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>C</td>
<td>A</td>
<td>$(R)$</td>
<td>$(O)$</td>
<td>$R/O$</td>
</tr>
</tbody>
</table>

Sulfate removal from treated Yolo loam soil with 2% gypsum and 1% lime, leached with KCl solution

KCl  | .3110  | 1.4538  | 368.4682  | 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-calcereous, non-gypsiferous soil from central California and Vernal soil a calcereous soil from eastern Utah.

Initial studies were conducted where the solubilities of pure CaCO$_3$ and CaSO$_4$·2H$_2$O were determined in the presence of Logan river water, a KCl solution (2.8mmhos/cm), and a K$_2$SO$_4$ 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$_2$SO$_4$ solution because of the formation of CaSO$_4$ ion pairs. The solubility product of both CaSO$_4$·2H$_2$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$_4$ and CaCO$_3$ 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$_2$SO$_4$ solution, Logan river
water was intermediate. The \( \text{CaCO}_3 \) in soil was most soluble in the 
\( \text{K}_2\text{SO}_4 \) leaching solution and less in the \( \text{KCl} \) 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 \( \text{Ca}^{2+} \) 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 \( \text{CaCO}_3 \) 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 \( \text{Ca}^{2+} \) derived from gypsum dissolution precipitated in the column as \( \text{CaCO}_3 \). This reaction accounted for greater than 15% of the \( \text{Ca}^{2+} \) from gypsum. Because the K-Ca exchange was not monitored in the column the contribution of \( \text{Ca}^{2+} \) 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 CaSO$_4 \cdot 2H_2O$ 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 CaSO$_4 \cdot 2H_2O$ and CaCO$_3$. 
LITERATURE CITED


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