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Calcium Carbonate Dissolution and Precipitation in Water: Factors Affecting the Carbonate Saturometer Method

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CALCIUM CARBONATE DISSOLUTION AND PRECIPITATION IN WATER: FACTORS AFFECTING THE CARBONATE SATUROMETER METHOD

by

Lyle M. Dabb

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

of

MASTER OF SCIENCE

in

Soil Chemistry

Approved:

UTAH STATE UNIVERSITY
Logan, Utah

1971

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I thank my wife, Sandy, for keeping our home affairs running so smoothly and for her understanding and patience.

Lyle M. Dabb

Lyle M. Dabb

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ABSTRACT

Calcium Carbonate Dissolution and Precipitation In Water: Factors Affecting the Carbonate Saturometer Method

by

Lyle M. Dabb, Master of Science

Utah State University, 1971

Major Professor: Dr. Jerome J. Jurinak
Department: Soils and Meteorology

The carbonate saturometer method developed by Weyl (1961) was studied in respect to the effect of several variables on the solubility of carbonates. The solubility of three solid carbonate materials was measured in four different salt solutions, at four ionic strengths, and at two different temperatures. The solids studied included: calcite, dolomite, and a calcareous soil.

It was found that the three solid carbonate materials varied in solubility from a low in the soil carbonates to a high in dolomite.

Increasing the ionic strength of the solution increased the solubility of most of the solid carbonate materials.

By decreasing the temperature, the solubility was increased.

When $SO_4^=$ was present in solution, the solubility of both calcium carbonate and dolomite increased. When Mg^{++} was present in solution the solubility of calcium carbonate was increased more than was the solubility of dolomite.

(45 pages)

INTRODUCTION

The concentration of calcium and magnesium compounds in water determines its hardness. The hardness of water is an important criteria for determining water quality. Cities are concerned with the degree of water hardness because hardness limits the use of water for culinary purposes.

One of the characteristics of hard water is the ability to precipitate Ca-Mg carbonates from solution under certain conditions. The precipitation of carbonates from irrigation water is not regarded as totally favorable even though the removal of Ca^{++} and Mg^{++} from solution reduces the total salt lead. Carbonate precipitation also lowers the Ca/Na ratio in the water making it less beneficial for subsequent agricultural use. Agriculture is concerned because of the ultimate effect of a low Ca/Na ratio of irrigation water on the physical properties of soil.

Langelier (1936) derived a simple index to indicate whether a water should precipitate or dissolve calcium carbonate in a closed system. His saturation index was computed by subtracting the pH that the water would have at equilibrium with calcium carbonate, (pH_c), from the actual pH of the water, (pH_a).

$$\text{Saturation Index} = pH_a - pH_c$$

Negative values indicate that the water will dissolve calcium carbonate and positive values indicate that calcium carbonate will precipitate.

In other words, positive values indicate the water is supersaturated with respect to calcium carbonate and negative values indicate that the water is undersaturated with respect to calcium carbonate.

The Saturation Index of Langlier was modified by Bower et al. (1965) and applied to water percolating through soils. The modification of the saturation index consisted simply of substituting the pH of the highly-buffered soil, (pH_s), for the actual pH of the poorly buffered irrigation water, (pH_a).

$$\text{(Modified) Saturation Index} = pH_s - pH_c$$

To put the saturation index on a more quantitative basis, Weyl (1961) described the carbonate saturometer method for determining the solubility of carbonates. This method makes use of the fact that the hydrogen ion activity of a solution will change if a carbonate is either dissolved or precipitated. Therefore, changes in the amount of carbonate dissolved can be measured by measuring changes in the hydrogen ion activity.

This is a study to determine some of the factors that affect measurements made by the carbonate saturometer method.

REVIEW OF LITERATURE

Carbonate chemistry is complex. Much work has been done to obtain a better understanding of the principles involved. Weyl (1961), and Garrels and Christ (1965), list five equations that are important in calcium carbonate equilibrium. The associated equilibrium constants, K, at 25°C are cited from Garrels and Christ.

$$CaCO_3 \rightleftarrows Ca^{++} + CO_3^{=} \qquad \frac{[Ca^{++}][CO_3^{=}]}{[CaCO_3]} = K_{CaCO_3} = 10^{-8.3} \tag{1}$$

$$H_2CO_3 \rightleftarrows HCO_3^{-} + H^{+} \qquad \frac{[H^{+}][HCO_3^{-}]}{[H_2CO_3]} = K_{H_2CO_3} = 10^{-6.4} \tag{2}$$

$$HCO_3^{-} \rightleftarrows CO_3^{=} + H^{+} \qquad \frac{[H^{+}][CO_3^{=}]}{[HCO_3^{-}]} = K_{HCO_3^{-}} = 10^{-10.3} \tag{3}$$

$$H_2O \rightleftarrows H^{+} + OH^{-} \qquad \frac{[H^{+}][OH^{-}]}{[H_2O]} = K_{H_2O} = 10^{-14.0} \tag{4}$$

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \qquad \frac{H_2CO_3}{P_{CO_{2(g)}}} = K_{CO_2} = 10^{-1.47} \tag{5}$$

The above equations show that a number of system variables are involved in studies of carbonate solubility. These variables must be defined before the solubility of carbonates can be determined and understood. Garrels and Christ (1965) also outlines five different cases or sets of conditions of carbonate equilibrium. This study will be concerned primarily with case two and to a lesser extent with cases four and five. These cases show that external variables also play an important role in determining the final equilibrium state of the system. The five cases are:

1. The reaction involved in placing pure calcite in pure water, with negligible gas present.
2. The reaction of calcite in pure water, but with the system open to CO_2; i.e., in contact with a reservoir, such as the atmosphere, of fixed partial pressure of CO_2.
3. Equilibrium relations in a system with a fixed quantity of dissolved carbonate species, but with pH arbitrarily fixed, i.e., controlled by other reactions in the system.
4. Equilibrium in a system connected to an external reservoir of fixed partial pressure of CO_2, but with pH arbitrarily determined.
5. Equilibrium resulting from addition of $CaCO_3$ to a system originally open to a CO_2 reservoir, but closed to that reservoir before addition of $CaCO_3$.

When magnesium ion is added to the carbonate system, it becomes even more complicated because of the distinct possibility of Ca-Mg carbonate interaction. In addition, ion pair formation must be considered as a factor affecting carbonate solubility. Garrels and Christ (1965) gave the following list of ion pairs that influenced carbonate equilibrium in solution.

$$MgCO_3^\circ,\ CaCO_3^\circ,\ MgSO_4^\circ,\ CaSO_4^\circ,\ \text{and}\ NaHCO_3^\circ.$$

They pointed out that there is apparently no complexing of $CaCl_2$ or $MgCl_2$ in solutions at 25°C. Nakayama (1968), reported that $CaCO_3^\circ$ made up 20 percent of the Ca^{++} in solution when water containing $CaCO_3$ is in equilibrium with the atmosphere.

Akin and Lagerwerff (1965) reported that the solubility of $CaCO_3$ was enhanced in the presence of Mg^{++} and $SO_4^{=}$. They pointed out that calcium carbonate is polymorphic and that calcite is the least soluble form, with aragonite, vaterite, monohydrate, and hexahydrate forms being more soluble. The concluded that these metastable forms will develop more readily in the presence of Mg^{++} and $SO_4^{=}$. They stated that the literature on the solubility of calcite is voluminous. It has been studied in systems of extremely low partial pressures of CO_2 as well as in systems where the CO_2 partial pressures reached 100 atm. Calcite solubility in water from 0°C to 100°C has been measured as well.

Walton (1965) studied the effects of supersaturation on the solubility of calcium carbonate. He found that supersaturation must exist before precipitation starts because of the presence of an energy barrier. Once the solution is sufficiently supersaturated, to form what he terms a "critical cluster," irreversible crystal growth is started. Crystal growth continues until the solution is at equilibrium with the precipitating solid.

Equilibrium is slowly attained in liquid-solid mixtures of carbonates. Weyl (1967) concluded that the slow kinetics of calcite dissolution in the presence of Ca^{++} and Mg^{++} must be at the liquid-solid interface because in pure liquids, equilibrium is rapidly attained. Gortikov and Panteleva (1937) found that the rate of solution of calcite increased as the speed of stirring increased. Brooks, Clark and Thurston (1950) also pointed out the marked effect of stirring on the nature of $CaCO_3$ precipitated from solutions that were supersaturated.

A simple yet precise method for determining the factors affecting the precipitation and solubility of calcium carbonate, under a variety of environmental conditions, is needed. The carbonate saturometer, first described by Weyl (1961), appears to be a suitable method. This technique is based upon the fact that the pH of a solution changes when $CO_3^=$ is added or removed from solution. The reactions involved are:

$$HCO_3^- \rightleftarrows H^+ + CO_3^=$$

$$\begin{array}{c} Ca^{++} + CO_3^= \rightleftarrows CaCO_{3(s)} \\ \hline Ca^{++} + HCO_3^- \rightleftarrows H^+ + CaCO_3(s) \end{array}$$

If a water is undersaturated with respect to a solid phase carbonate, the carbonate dissolves producing $CO_3^=$ which combines with H^+ thus increasing the pH of the solution. If a water is supersaturated with respect to a solid carbonate, the carbonate precipitates, causing HCO_3^- to dissociate into H^+ and $CO_3^=$, thus decreasing the pH. If a water is saturated with respect to a solid carbonate, the pH of the solution remains unchanged.

METHODS AND MATERIALS

The method used in this study, for the determination of the solubility of calcium carbonate, was the one developed by Weyl (1961), as modified by Hassett (1970), and further modified by the author. The primary reaction chamber was a 250 ml tall-form beaker, fitted with a size 13 rubber stopper. The solid phase carbonate and soil additions were made through an access hole in the stopper. A small hole in the stopper allowed for the escape of gases. The reaction chamber was submerged in a thermostat to the level of the solution inside the reaction chamber. The thermostat was a two gallon earthenware crock, filled with water regulated at ±.1°C. The reaction chamber, when placed in the water bath, was seated on a submerged, water-powered, magnetic stirrer. This arrangement allowed the reaction solutions to be uniformly stirred during a given experiment. The magnetic stirrer was powered by a water pump on a Haake E51 temperature regulator. The water pumped through the stirrer also circulated the water in the thermostat. Temperatures below room temperature were obtained by heating against a cooling coil placed within the thermostat.

The pH measurements were taken with a Corning, semi-micro combination electrode, with triple-purpose glass membrane. The glass electrode was inserted through an opening in the reaction chamber stopper. The electrode was coupled to a model EUW-301 Heath recording pH meter.

The solution in the reaction chamber was aerated by a stream of water-saturated air. The air was treated in the following manner:

First, the air passed through a flask containing glass wool to remove grease and particulates. The dry air was then passed through a flowmeter and maintained at a rate of 500 ml/min. After regulating the flow, the air was saturated with water vapor by passing it through two gas scrubbers in series. An open flask was then placed in the line to trap any excess water. The saturated air was dispersed, in the solution to be studied, by means of a fritted glass sparger.

To obtain carbonate solubility data the following procedures were used: A 100 ml sample of a water was pipetted into the reaction chamber which was clamped in the water bath over the magnetic stirrer: then a teflon coated bar was placed in the chamber and the speed of rotation checked. The rubber stopper containing the solution aerator was attached. Prior to the insertion of the combination electrode into the solution, it was washed with a dilute HCL solution, followed by several washings with distilled water. The electrode was lightly blotted with a tissue. After washing, the electrode was inserted through a hole in the stopper and placed in the solution. The depth of the electrode in the solution was adjusted so that the stirring bar would not make contact. Sufficient time was allowed for the reaction chamber containing the solution to come in thermal equilibrium with the water bath before readings were taken. After the aerated solution had reached thermal equilibrium and the pH of the solution had reached a constant value (defined as the starting pH), a weighed amount of solid carbonate material was added through the access hole. This addition usually altered the pH of the solution. When the pH of the altered solution had reached a constant value (equilibrium), this was defined as the ending pH. By subtracting the starting pH from the ending pH, a ΔpH value was determined. A positive ΔpH value indicated dissolution of carbonate, a negative ΔpH value indicated precipitation of carbonate. To obtain a quantitative measurement of the change in dissolved carbonate concentration, the calculated ΔpH value was compared to the data obtained by titrating the original water (solution) with $NaHCO_3$. In this study only water undersaturated with respect to $CaCO_3$ was studied.

To observe the factors which affect carbonate solubility in water, four different salt solutions at four ionic strengths were added to three different types of solid phase carbonate material.

The four salts used were: NaCl, a 1:1 salt; Na_2SO_4, a 1:2 salt; $MgSO_4$, a 2:2 salt; and $MgCl_2$, a 2:1 salt. These four salts were used to determine if sulfate and magnesium ions had any specific effects on the dissolution of carbonates above and beyond the effect of ionic strength. Akin and Lagerwerff (1965) observed that the sulfate ion as well as the magnesium ion cause an inordinate increase in the solubility of calcium carbonate.

The four ionic strengths used were: $I = .00$ (de-ionized water), $I = .05$, $I = .10$, and $I = .20$. The ionic strength, I, was calculated according to the equation

$$I = 1/2 \; \Sigma \; C_i \; Z_i^2$$

where C_i = concentration of the solution species (+ and -) and Z_i is the valence of that solution specie.

The three different types of solid carbonate used were: a reagent grade calcium carbonate (Mallinckrodt, lot TEJ); a dolomite (coarse crystalline, white, New York); and a calcareous soil (from Vernal, Utah) containing 10-12 percent carbonates. Solubilities were measured at 15°C and 23°C.

RESULTS AND DISCUSSION

A preliminary experiment was conducted to determine if the amount of solid added to the aqueous solution affected the value obtained from the saturometer. Vernal soil, in varying amounts, was added to two different waters. One water was undersaturated with respect to calcium carbonate and the other water was supersaturated with respect to calcium carbonate. These waters were Numbers 1 and 6, respectively, (Tables 3 and 4) and represent natural irrigation waters from Vernal, Utah. A sample of a given water was aerated to a constant pH. Then a given amount of calcareous Vernal soil was added and aeration was continued to an equilibrium pH. The ΔpH value was calculated as explained in Methods and Materials.

The data are shown in Figures 1 and 2. It was observed that the equilibrium ΔpH values are a function of sample weight. In the unsaturated and saturated water a sample weight of at least 0.1 gram was required to obtain a ΔpH value which appeared independent of sample mass. In the unsaturated water (Figure 1) it was noted that at the larger sample weights the solution appeared initially to be supersaturated with carbonate; with time this condition disappeared. This effect is believed to be caused by the non-equilibrium conditions which existed between the soil carbonate and the atmospheric CO_2 dissolved in the aerated water. As aeration was continued the pH of the solution decreased as equilibrium was established with the atmospheric CO_2. In the supersaturated water (Figure 2) the larger sample weights of soil tended to produce an over precipitation of carbonate. The precipitated

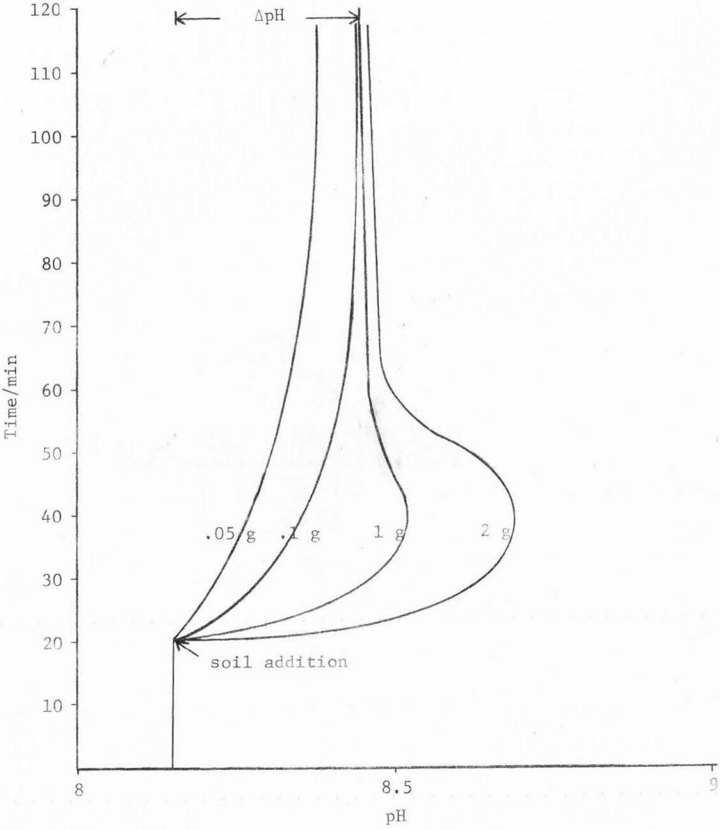

Figure 1. Simulated curves drawn by the recording pH meter for different masses of Vernal soil added to an undersaturated water.

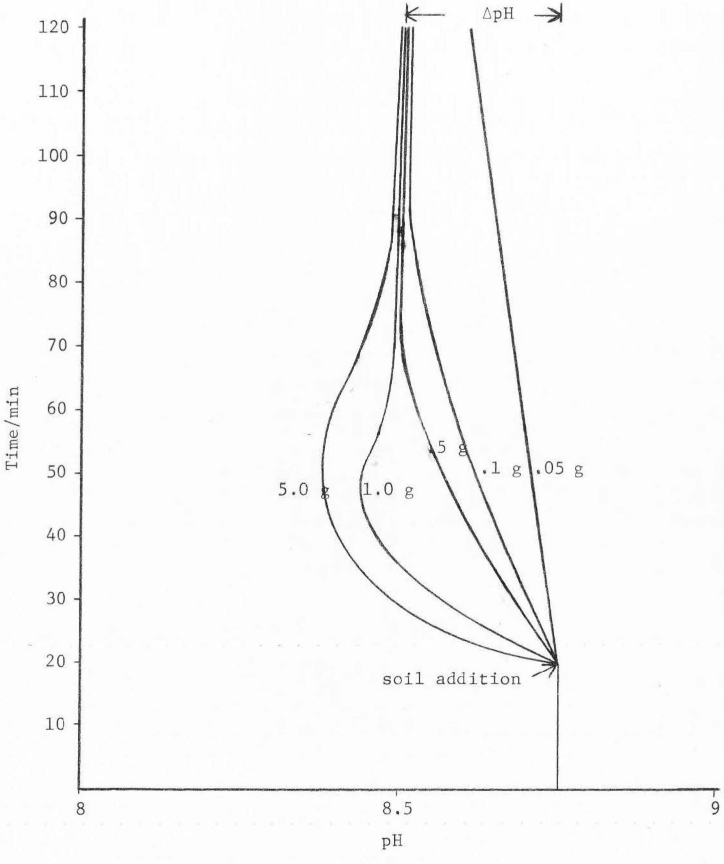

Figure 2. Simulated curves drawn by the recording pH meter for different masses of Vernal soil added to a supersaturated water.

carbonate redissolved as equilibrium was reached with the CO_2 in the atmosphere. The higher sample weights in both systems reached equilibrium faster than the smaller sample weights. From the results of these data one gram of carbonate material was selected as the sample weight added in all studies.

The results of the solubility experiment are summarized in Tables 1 and 2. In Figures 3 through 16, the data of carbonate solubility are plotted in two different ways. Figures 3 through 10 show the solubility of all solid carbonates in an aqueous solution of a particular salt. In Figures 11 through 16, the data show the effect of various salt solutions on a given carbonate material. In comparing Figures 3 and 4 against 5 and 6, and also Figures 7 and 8 against 9 and 10, it was noted that in solutions of sodium salts, dolomite is much more soluble than calcium carbonate. However, in aqueous solutions of magnesium salts there is little difference between the solubility of dolomite and calcium carbonate. In fact, in several cases at the higher ionic strengths, the solubility of calcium carbonate is slightly higher than dolomite. These data suggest that magnesium salts influence carbonate solution beyond the simple ionic strength effect. From their solubility products alone, dolomite would be expected to be slightly more soluble than calcium carbonate. The data suggest that at the higher concentrations of Mg^{++} the common ion effect influences dolomite solubility. At the lower temperature (15°C), the presence of sulfate ion had a large influence on increasing carbonate solubility as compared with the chloride anion. This suggests a specific reaction of sulfate with carbonate.

Table 1. ΔpH values and mmoles of dissolved carbonate for three solid carbonates and four aqueous salt solutions at different ionic strengths, at 23°C

		$CaCO_3$		Dolomite		Vernal soil	
Salt	I	ΔpH	$\frac{mmoles}{L}$	ΔpH	$\frac{mmoles}{L}$	ΔpH	$\frac{mmoles}{L}$
NaCl							
	.00	2.95	1.65	3.15	2.33	3.02	1.90
	.05	2.82	3.20	2.95	4.60	2.78	2.80
	.10	2.76	3.70	2.90	5.00	2.71	3.50
	.20	2.67	4.40	2.74	5.50	2.61	3.90
Na_2SO_4							
	.00	2.95	1.65	3.15	2.33	3.02	1.90
	.05	2.50	1.90	2.69	3.50	2.46	1.70
	.10	2.31	1.80	2.50	4.00	2.19	1.40
	.20	2.09	2.20	2.34	4.00	2.04	2.00
$MgSO_4$							
	.00	2.95	1.65	3.15	2.35	3.02	1.90
	.05	2.66	1.90	2.85	3.00	2.45	1.20
	.10	2.62	1.75	2.75	2.40	2.38	.90
	.20	2.53	1.90	2.60	2.25	2.25	.85
$MgCl_2$							
	.00	2.95	1.65	3.15	2.35	3.02	1.90
	.05	2.98	1.50	3.03	1.60	2.81	.90
	.10	2.97	2.20	3.03	2.50	2.79	1.40
	.20	2.99	2.50	2.92	2.20	2.75	1.50

Table 2. ΔpH values and mmoles of dissolved carbonate for three solid carbonates and four aqueous salt solutions at different ionic strengths, at 15°C

		$CaCO_3$		Dolomite		Vernal soil	
Salt	I	ΔpH	$\frac{\text{mmoles}}{\text{L}}$	ΔpH	$\frac{\text{mmoles}}{\text{L}}$	ΔpH	$\frac{\text{mmoles}}{\text{L}}$
NaCl							
	.00	2.85	2.00	3.03	3.25	2.75	1.60
	.05	2.93	2.30	3.05	4.50	2.83	2.00
	.10	3.08	3.00	3.15	5.00	2.91	1.70
	.20	3.10	3.70	3.15	6.00	2.90	2.00
Na_2SO_4							
	.00	2.85	2.00	3.03	3.25	2.75	1.60
	.05	2.92	1.80	3.15	6.00	2.81	1.40
	.10	2.88	2.50	3.00	7.50	2.78	2.80
	.20	2.76	5.80	2.88	8.30	2.58	2.30
$MgSO_4$							
	.00	2.85	2.00	3.03	3.25	2.75	1.60
	.05	2.99	3.50	3.00	3.75	2.80	1.50
	.10	2.89	7.50	2.85	6.80	2.62	2.80
	.20	2.86	7.50	2.85	7.3	2.52	2.00
$MgCl_2$							
	.00	2.85	2.00	3.03	3.25	2.75	1.60
	.05	2.89	2.00	2.96	2.60	2.69	1.20
	.10	2.88	2.20	2.94	2.70	2.66	1.25
	.20	2.86	2.70	2.84	2.60	2.63	1.40

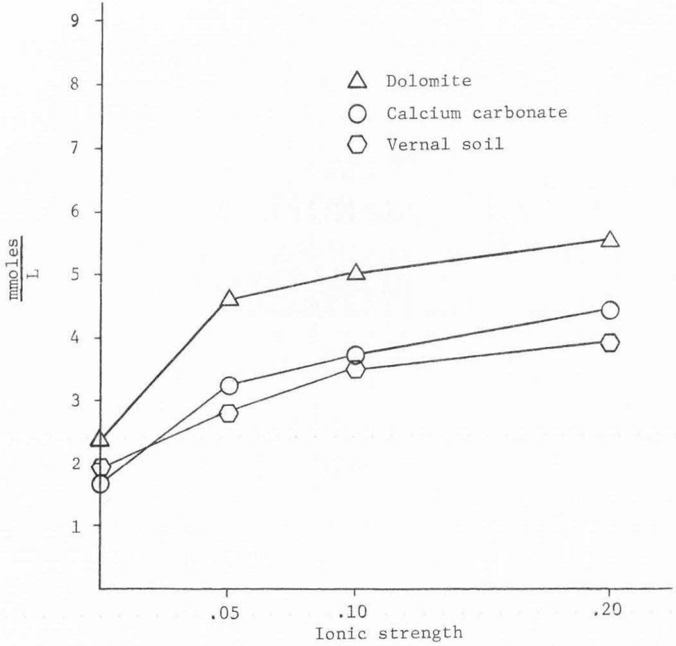

Figure 3. Three solid carbonate additions to sodium chloride solutions at various ionic strengths, at 23°C.

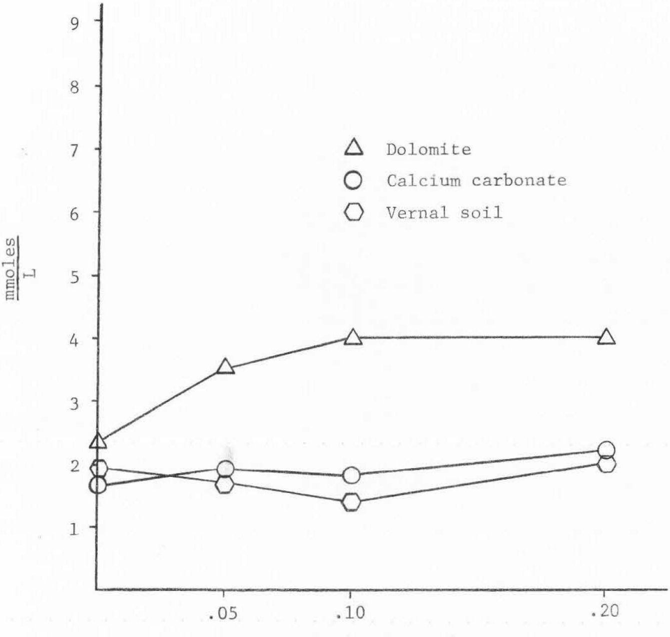

Figure 4. Three solid carbonate additions to sodium sulfate solutions at various ionic strengths, at 23°C.

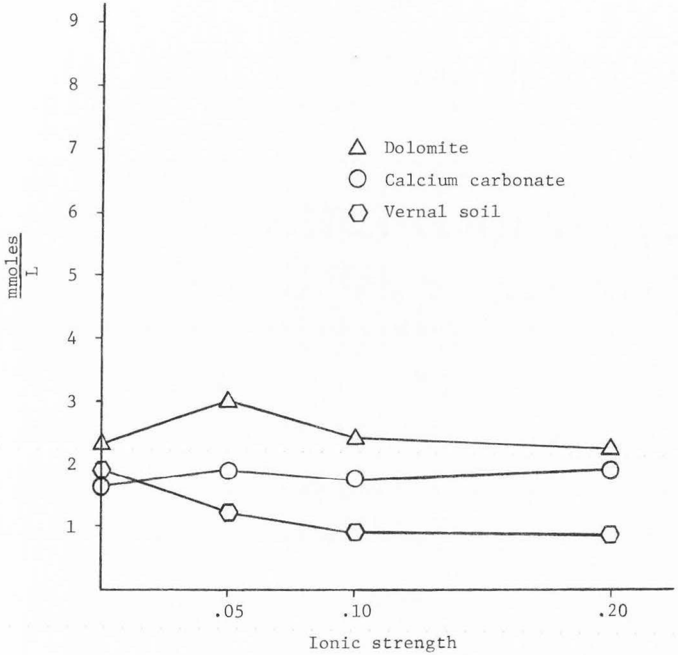

Figure 5. Three solid carbonate additions to magnesium sulfate solutions at various ionic strengths, at 23°C.

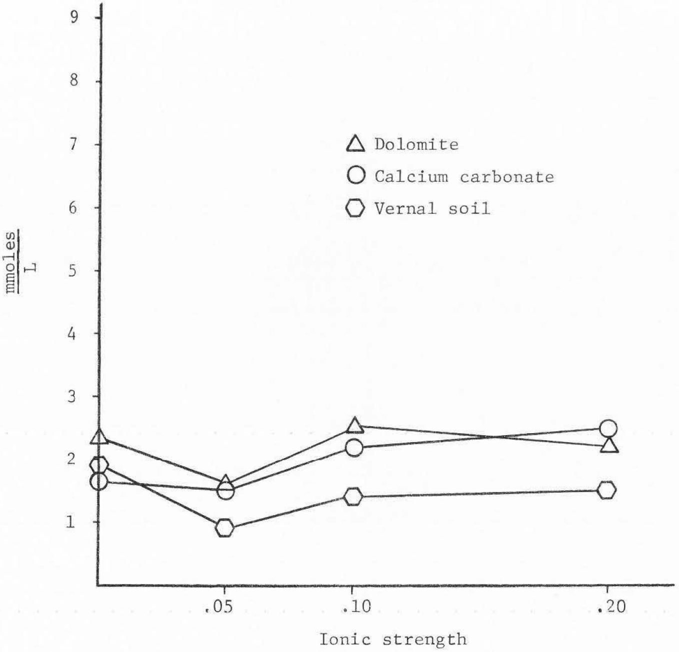

Figure 6. Three solid carbonate additions to magnesium chloride solutions at various ionic strengths, at 23°C.

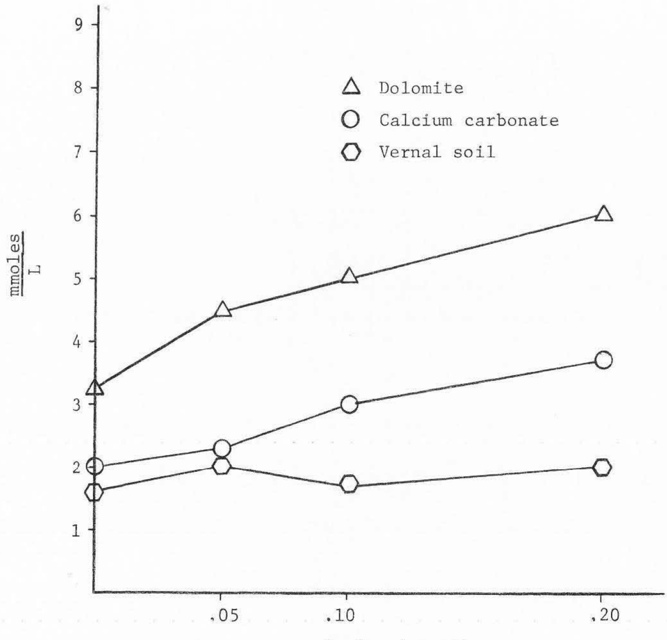

Figure 7. Three solid carbonate additions to sodium chloride solutions at various ionic strengths, at 15°C.

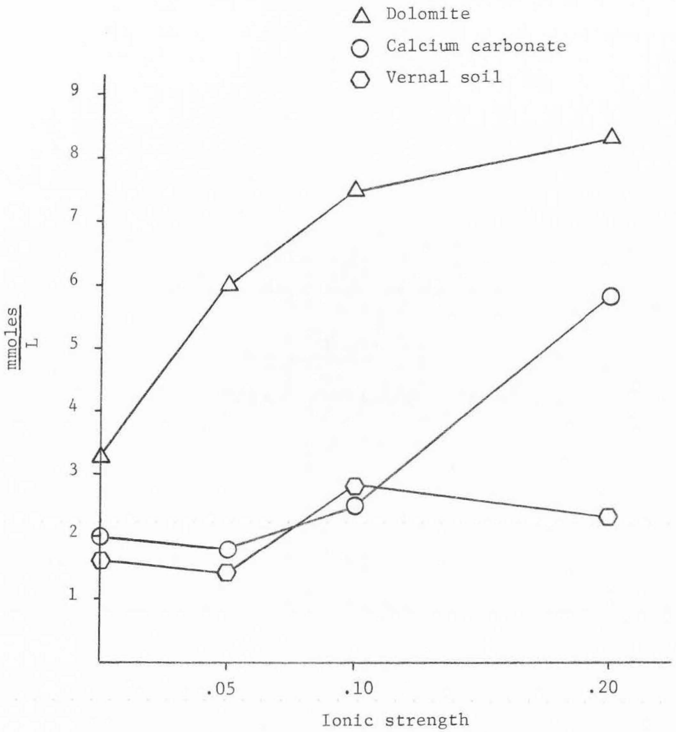

Figure 8. Three solid carbonate additions to sodium sulfate solutions at various ionic strengths, at 15°C.

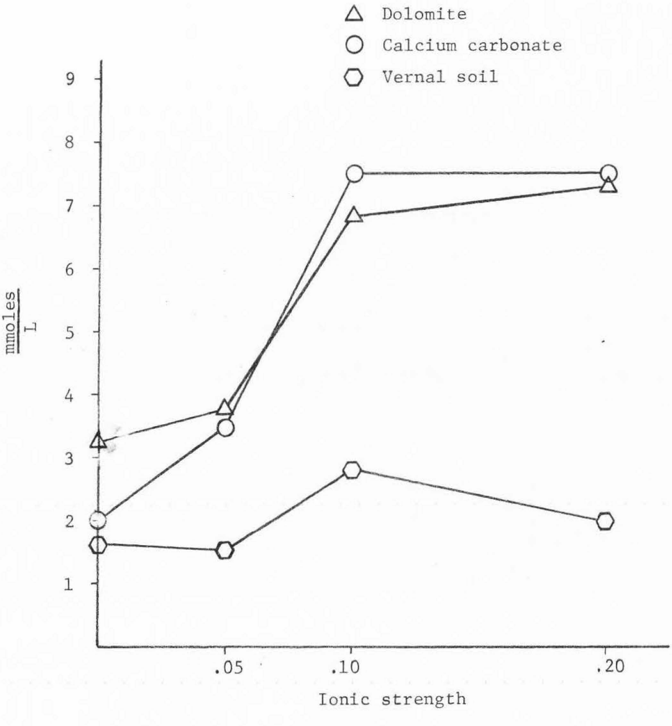

Figure 9. Three solid carbonate additions to magnesium sulfate solutions at various ionic strengths, at 15°C.

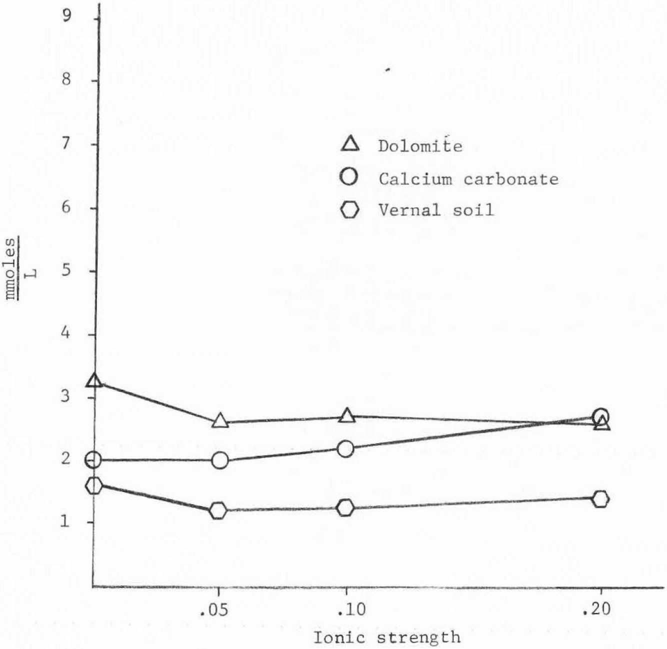

Figure 10. Three solid carbonate additions to magnesium chloride solutions at various ionic strengths, at 15°C.

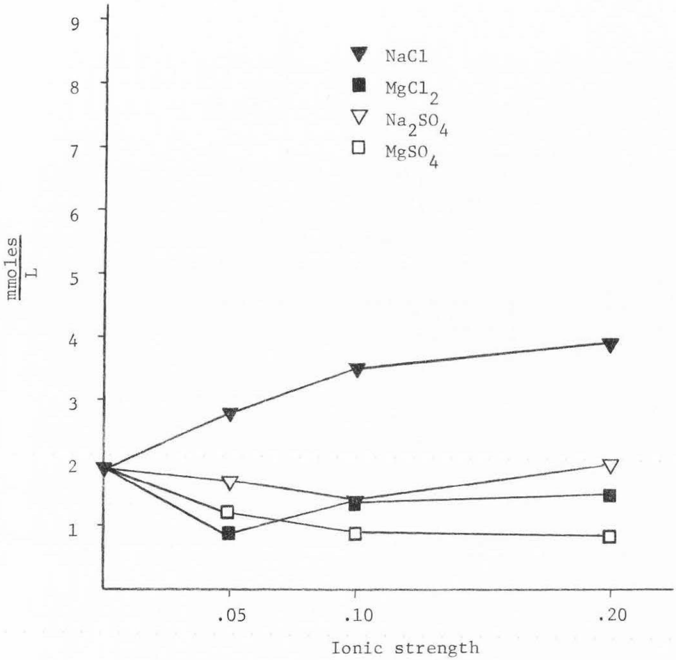

Figure 11. Calcium carbonate additions to four salt solutions at various ionic strengths, at 23°C.

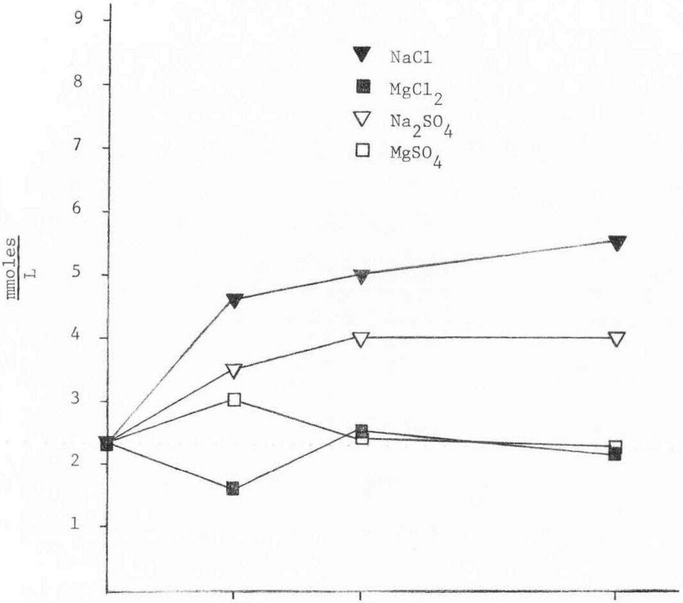

Figure 12. Dolomite additions to four salt solutions at various ionic strengths, at 23°C.

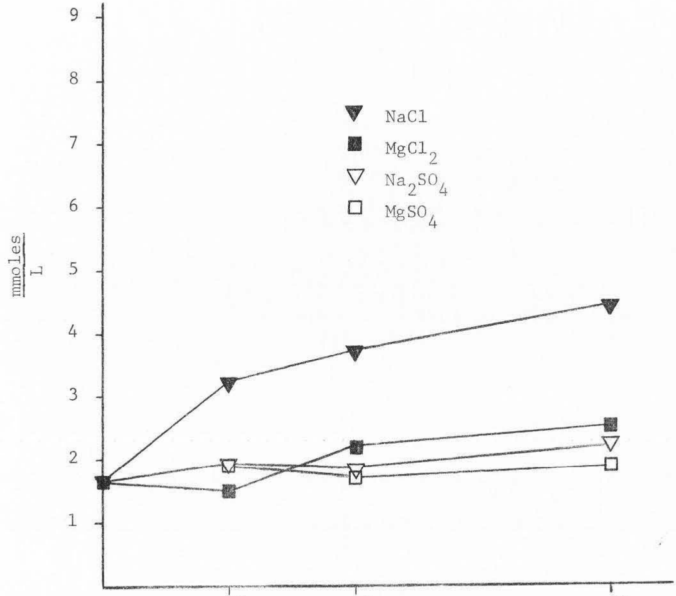

Figure 13. Vernal soil additions to four salt solutions at various ionic strengths, at 23°C.

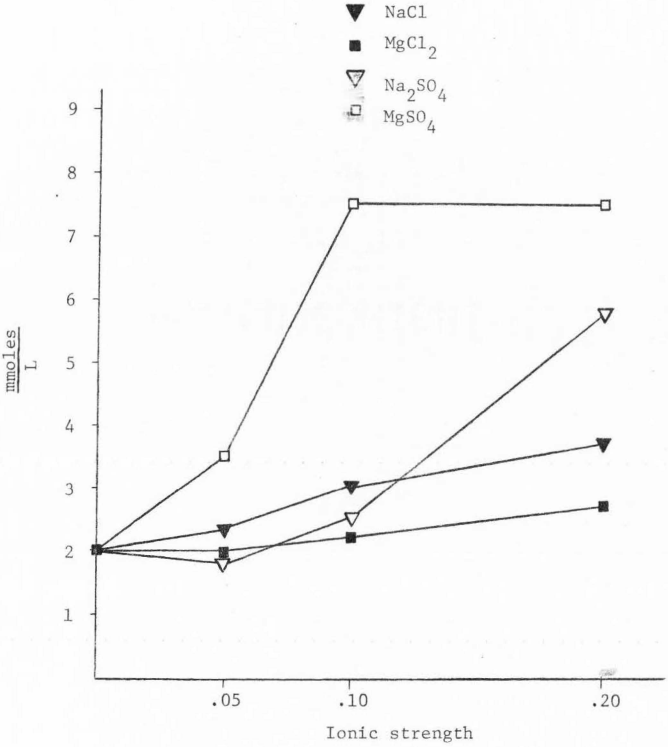

Figure 14. Calcium carbonate addition to four salt solutions at various ionic strengths, at 15°C.

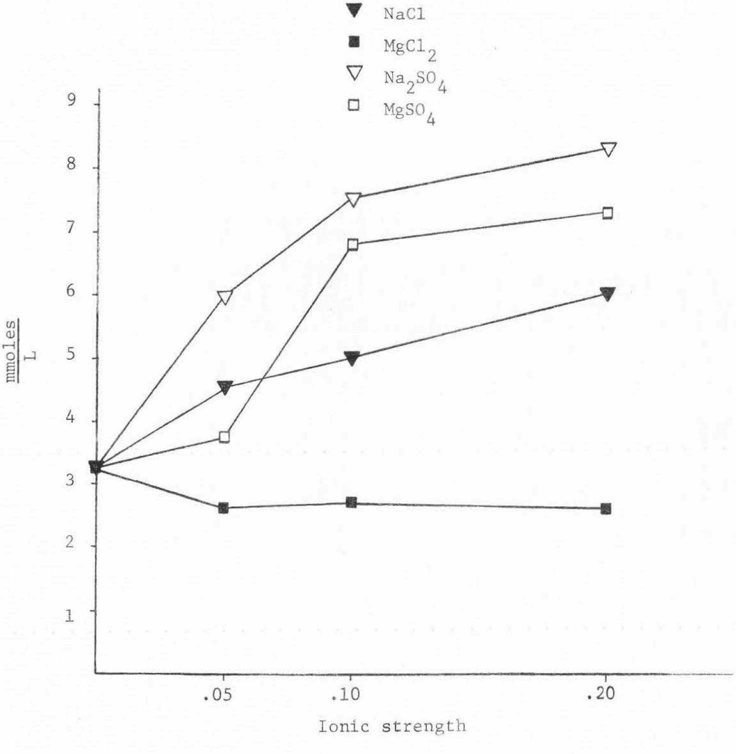

Figure 15. Dolomite additions to four salt solutions at various ionic strengths, at 15°C.

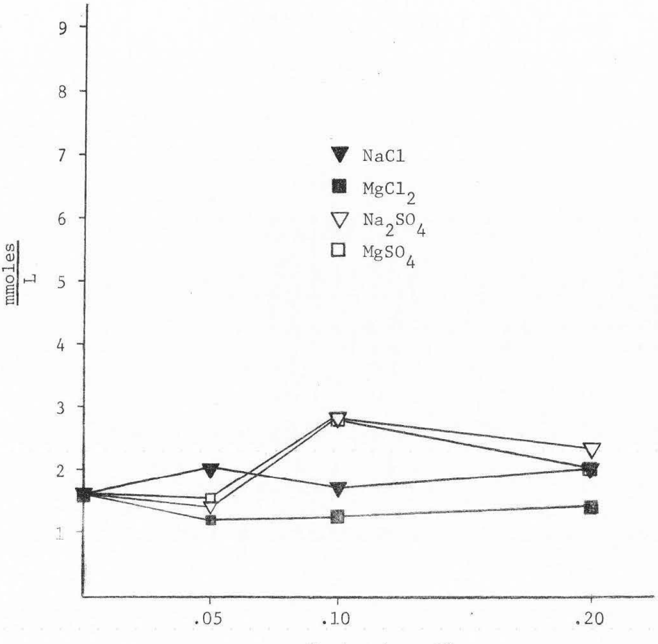

Figure 16. Vernal soil additions to four salt solutions at various ionic strengths, at 15°C.

The solubility of the carbonates in the Vernal soil was less in any given salt solution than the solubility of dolomite or calcium carbonate. This was not expected. One possible explanation of the lower solubility of the soil carbonates in comparison to dolomite and calcium may be that the soil carbonates are coated by the precipitation of a less soluble compound. Olsen and Watanabe (1959) concluded that phosphates in calcareous soils are predominately in the form of insoluble calcium phosphates. It is possible that calcium phosphate was precipitated or absorbed at the carbonate interface, effectively reducing the apparent solubility of the soil carbonates. Another aspect of the reduced solubility of carbonates in soil is the presence of excess calcium ion in the system which acts as a common ion with respect to calcium carbonate.

In general, it was noted that the solubility of carbonates was increased as the temperature was lowered from 23°C to 15°C. This effect was expected since the concentration of CO_2 dissolved in water also increases with decreasing temperatures.

In Figures 14, 15, and 16 it is noted that the solubility of the three solid carbonates was highest in the waters containing the sulfate ion. This indicated that sulfate ion also increased the solubility of carbonates as pointed out by Akin and Lagerwerff (1965). Again, in Figures 11 and 12, we see that calcium carbonate is more soluble in the $MgSO_4$ solution. With the dolomite mineral, the solubility was highest in the waters with Na_2SO_4 and lower in the solution made with $MgSO_4$. This suggests that both Mg^{++} and $SO_4^=$ increase the solubility of calcium carbonate but that Mg^{++} tends to decrease the solubility of dolomite in comparison with calcium carbonate. Again, this can be explained by the common ion effect.

EIGHT NATURAL WATERS FROM VERNAL, UTAH

To determine the applicability of the saturometer method on natural irrigation waters, eight water sources were sampled near Vernal. the eight water samples were collected June 4, 1970. Chemical data for the waters are given in Table 4. The carbonate saturometer method (as described in the Methods and Materials section) was used to obtain ΔpH values. The ΔpH values listed in Table 3, give an indication of the waters' potential to dissolve or precipitate carbonates. Positive ΔpH values mean the water was undersaturated with respect to carbonates. Negative ΔpH values show that the water was supersaturated with respect to the added solid carbonate. Zero ΔpH values were assumed to mean that the water was at equilibrium with respect to the added solid carbonate. From the ΔpH values given in Table 3, we note that as the water in Ashley Creek came into the valley, it was undersaturated with respect to calcium carbonate and soil carbonates, as evidenced by the positive ΔpH values. Waters two, three, and four were surface waters that had been stored in Steinaker Reservoir. The measured ΔpH values show that these waters were saturated with respect to the soil carbonates and supersaturated with respect to calcium carbonate. This indicates that water quality changes during storage prior to use. Waters five through eight are drainage waters and have passed through the soil. They are supersaturated with respect to soil carbonates and calcium carbonate as evidenced by the negative ΔpH values. By comparing the ΔpH values for the different solid carbonate additions, we see that the soil carbonates are more soluble in any given water than is calcium

Table 3. ΔpH values for Vernal soil and calcium carbonate additions to eight natural irrigation waters

Water	Natural water temp °F	Location	Soil ΔpH	$CaCO_3$ ΔpH
1	52	Ashley creek point of diversion	.290	.220
2	71	Steinaker Reservoir	.000	-.065
3	64	Canal	.000	-.110
4	63	Irrigation water above #5	.000	-.075
5	61	Ground water spring below #4	-.160	-.190
6	68	Naples drain	-.250	-.475
7	67	Drain water below Naples	-.030	-.350
8	71	Ashley Creek outflow	-.165	-.405

Table 4. Chemical composition of eight natural waters from Vernal, Utah

Water	E.C. µmhos/cm	Ca^{++}	Mg^{++}	Na^{+}	NO_3^-	Cl^-	Boron
		ppm					
1	81	11.4	2.7	1.7	.6	5.5	.05
2	228	33.1	9.8	6.0	.3	6.4	.10
3	288	38.9	13.4	9.6	.3	7.1	.08
4	204	30.7	10.7	4.2	.6	5.7	.05
5	620	79.6	45.1	15.7	5.5	11.9	.10
6	2100	317.7	153.9	120.1	1.2	25.9	.77
7	2200	302.6	173.1	136.7	1.1	23.4	1.21
8	1280	136.5	89.2	84.4	3.5	18.3	.38

carbonate in that water. The eight waters all followed the same trends in the amount of carbonate dissolved or precipitated, the magnitude of the electrical conductivity readings, ppm of calcium, and ppm of magnesium. The only water departing from this trend was water 7. The seemingly low values for this water could have been the result of precipitation of carbonate after the readings were made for the composition determination of the water, but before the carbonate saturometer readings were made. This could have happened at the high degree of supersaturation expected in water 7 from its high calcium and magnesium concentrations. Titration curves were not made for these waters due to the difficulty of working with supersaturated waters. They would be necessary to get quantitative results of changes in the carbonate concentrations. The ΔpH values are sufficient to indicate trends in the solubility.

SUMMARY AND CONCLUSIONS

The carbonate saturometer method developed by Weyl (1961) was studied in respect to the effect of several variables on the solubility data obtained. The solubility of three solid carbonate materials were measured, in four different salt solutions, at four ionic strengths and at two different temperatures.

The results confirmed that the solubility of carbonates increased as the ionic strength of the solution increased from .05 to .20.

The solubility of calcium carbonate was increased by the presence of Mg^{++} and $SO_4^{=}$ in agreement with Akin and Lagerwerff (1965). The solubility of dolomite was increased in the presence of $SO_4^{=}$. Dolomite did not show as large an increase in solubility in the presence of Mg^{++} as did calcium carbonate. The effects of various salt solutions on the solubility of soil carbonates were less pronounced. In general the lowering of the temperature increased the solubility of all the solid carbonates.

The carbonate saturometer was used to study the degree of saturation in eight natural irrigation waters. Good correlation was found between the ΔpH values obtained and the degree of saturation as measured by other methods.

If proper attention is given to the variables that affect the saturometer method, it could be a useful tool in the study of carbonate dissolution and precipitation in natural as well as artificial systems.

SUGGESTIONS FOR FUTURE RESEARCH

The saturometer method seems to be a useful tool for determining whether a water will dissolve or precipitate carbonate. However, to make the results obtained more meaningful, the experimental error must be reduced.

One area requiring improvement is the aeration system. The water saturated air entering the reaction chamber is at room temperature. This could have an effect on measurements taken at other than room temperature. Another problem in the aeration system is washing the spargers free of carbonate between samples. Washing the sparger in an HCl wash and then in deionized water seemed to remove the carbonate completely from spargers used to aerate samples containing calcium carbonate. However, when the same washing procedure was used on spargers that had aerated samples containing dolomite or soil, evidence indicated that a trace of carbonate remained. Dolomite reacts more slowly in cold HCl than calcite. It may be necessary to wash the spargers in warm HCl to get a more rapid and complete reaction between the acid and the carbonate.

Later work has indicated that a capillary tube type aeration system may eliminate the washing problems. However, with the capillary tube system, a longer time was required to obtain equilibrium.

It has been reported by Brooks, Clark and Thurston (1950) that the rate of dissolution of carbonates increases as the speed of stirring increases. The speed of stirring may also affect the amount of carbonate dissolved. Therefore, the speed of stirring should be maintained constant.

Working with more dilute solutions would possibly yield more meaningful results, as an ionic strength of .20 is on the upper concentration limits for the Debye-Huckle theory to be valid.

It was observed by the author that the starting ΔpH values drifted slightly for several days after water solutions were made. Allowing the water solutions to stand for several days before using them gave a more reproducible starting pH.

To determine the effects of plant growth on the solubility or precipitation of calcium carbonate in soil, a column study is proposed. Set up triplicate columns of a soil, saturate two with a predetermined water and incubate them. Leach one, with no plant growth. Leach the second after the same incubation period but with an actively growing plant cover. Leach a third column with no incubation period. Measure the solubility of carbonates in various leaching fractions. Expand the experiment by varying the water, plant growth, soil treatment, or the temperature.

An attempt should be made to correlate data on the solubility of carbonates by the saturometer method with other methods that determine the amount of Ca^{++} and Mg^{++} in solution. Changes in solubility could be checked with a calcium electrode, a conductivity bridge, or a determination of Ca^{++} and Mg^{++} by the atomic absorption spectrophotometer.

It has been suggested that calcium carbonate after dissolution precipitates as a different form of lesser solubility. X-ray defraction could be used to check for changes in form before and after precipitation. This could also be used for determining whether magnesium or calcium carbonates were precipitating.

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