

June 1975

WRRRI Report No. 056

**AQUIFER PARAMETERS BY A CHEMICAL TRACER  
TECHNIQUE NONLINEAR MIXING IN THE ROSWELL  
CONFINED AQUIFER**

Technical Completion Report  
Project No. B-038-NMEX

AQUIFER PARAMETERS BY A CHEMICAL TRACER TECHNIQUE

Nonlinear Mixing in the Roswell Confined Aquifer

Vernon LeFebre, Associate Professor  
Department of Physics

TECHNICAL COMPLETION REPORT

Project No. B-038-NMEX

New Mexico Water Resources Research Institute  
in cooperation with  
Department of Geoscience, New Mexico Institute  
of Mining and Technology  
Socorro, New Mexico

June 1975

The work upon which this publication is based was supported in part by funds provided through the New Mexico Water Resources Research Institute by the United States Department of the Interior, Office of Water Research and Technology, as authorized under the Water Resources Research Act of 1964, Public Law 88-379, under project number: B-038-NMEX.

## ABSTRACT

Soil column tests and chemical analyses of water samples from the Roswell ground water basin indicate that water is saturated with calcite before entering the aquifer. It is postulated that calcite precipitation and dissolution occurring within the aquifer result from nonlinear mixing effects. Four such effects are developed and applied to the Roswell ground water basin. One result is that mixing caused by leakage from the unconfined to the confined aquifer is clogging the confined aquifer with a calcite precipitate.

## TABLE OF CONTENTS

	<u>Page</u>
Abstract	ii
List of Figures	iv
List of Tables	v
Explanatory Note	1
Introduction	2
Study Area	3
Unsaturated Zone	5
Analysis Methods	12
Aquifer Water	13
Nonlinear Mixing Effects	16
Common Ion Saturation Curve	16
Carbon Dioxide Saturation Curve	18
Temperature Saturation Curve	20
Inert Ion Saturation Curve	22
Aquifer Mixing Modes	27
Confined Aquifer	27
Unconfined Aquifer	29
Coupling Between Aquifers	29
References	33

## LIST OF FIGURES

Figure		Page
1	Representative north-south section of the Roswell Basin.	4
2	Carbon dioxide content of distilled water after passing through 50 cm soil columns collected in the Roswell Basin.	10
3	Calcite saturation as a function of gypsum content	19
4	Calcite saturation as a function of carbon dioxide pressure	21
5	Calcite saturation as a function of temperature	23
6	Calcite saturation as a function of inert salt (NaCl) concentration	26

## LIST OF TABLES

Table		Page
I	Concentration of selected ionic species in distilled water after passing through 50 cm soil columns	8
II	Chemical composition and temperature for water samples taken from wells	14
III	Gypsum content of water samples from the Oasis Well	31

## EXPLANATORY NOTE

This project was initiated with A. Mercado, G. G. Billings, and G. W. Gross as principal investigators, with the last-named to provide mainly logistical support. When the first two investigators left New Mexico Institute of Mining and Technology, V. LeFebre, who had previously been assisting informally with the mathematical formulation of the kinetic theory, agreed to carry the project to completion.

## INTRODUCTION

This is the completion report for Project No. 3109-140, B-038-NMEX. It was originally proposed<sup>1</sup> that the calcium content of groundwater in the confined limestone aquifer underlying Roswell, New Mexico, be examined as a possible indicator of groundwater residence time. In theory, the limestone matrix of the aquifer dissolves, increasing the calcium content of the groundwater flowing through the aquifer. However, field measurements indicate that water is saturated with calcite before entering the aquifer. Therefore, the postulated monotonic increase in the calcium concentration does not occur.

Changes do occur in the calcium content of the aquifer water. These changes can be related to four nonlinear mixing effects. A preliminary examination of these effects is given in this report. It is still possible that the calcium content of groundwater in a limestone aquifer reflects the residence time of the water in the aquifer but the connection is not as straightforward as originally proposed.



## STUDY AREA

The Roswell groundwater basin is mainly located west of the Pecos river valley in eastern New Mexico and extends beyond the cities of Roswell in the north and Artesia in the south. On the east, the basin is bounded by the High Plains and on the west by the Sacramento Mountains.

### Aquifer Structure

Two aquifers have been recognized in the Roswell groundwater basin (Fig. 1), a deep confined aquifer and a shallow unconfined aquifer. The deep aquifer is located in the San Andres Formation of Permian age. It contains a large fraction of evaporites (dolomite, limestone, gypsum) and is characterized by abundant solution features. The shallow aquifer is located in valley alluvium. Considerable amounts of gypsum and calcium carbonate are in the alluvium. The shallow and the deep aquifer are separated by a relatively impermeable sequence composed of limestones, dolomites, mudstones, and sandstones. These formations make up the Artesia Group and form the aquitard above the confined aquifer. Along the western edge of the basin is the recharge area for the confined aquifer. Limestone outcrops and a thin barren soil cover characterize most of this area. In the northern sections of the recharge area, sink holes indicated the presence of dissolving gypsum deposits beneath the surface. Northeast of Roswell the water table (unconfined aquifer) is at the land surface and has formed brackish lakes and ponds (Bitter Lakes).

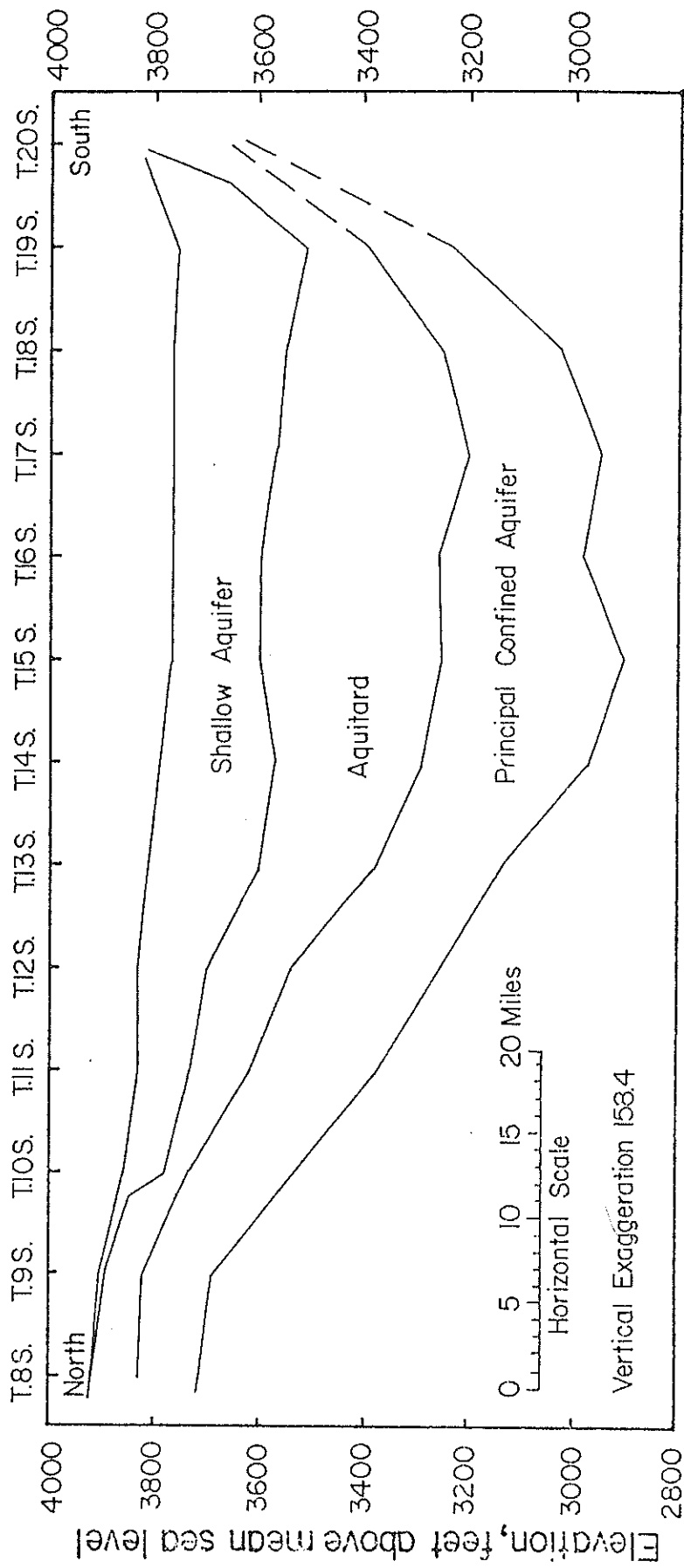


Figure 1. Representative north-south cross section of the Roswell Basin (after Saleem and Jacob, WRI Report No. 10, 1971, Fig. 5).

## UNSATURATED ZONE

Water, before reaching either the confined or the unconfined aquifer, must first pass through the upper layers of the ground. Flow through this zone is relatively slow and usually occurs in the presence of air (unsaturated flow).

Above the unconfined (shallow) aquifer, the zone of unsaturated flow is composed of soil. The recharge area for the confined aquifer, where unsaturated flow to this aquifer occurs, is composed of limestone outcrops, sink holes, and soil.

All water entering the unconfined aquifer will first flow through a soil zone. Water entering the confined aquifer in the recharge area may flow through fractures and joints in the limestone outcrops, or it may flow down a sink hole, or, finally, it may infiltrate through soil. The chemical composition of water entering an aquifer will depend on the physical as well as the chemical structure of the flow path through the unsaturated zone.

The carbon dioxide content of water in the unsaturated zone is determined by the organic debris and root concentration in the upper layers of the zone. This concentration is greatest in soil, much less in rock fractures and joints, and relatively negligible in the shafts of sink holes. Therefore, the carbon dioxide content of the water entering the aquifer depends on the physical structure of the flow path. In addition to calcium carbonate, the rocks and soil in the Roswell basin contain variable amounts of calcium sulfate in the form of gypsum. Most of the gypsum in the aquifer water is acquired as the water flows through the unsaturated

zone. The gypsum concentration in the aquifer water is dependent on the amount of gypsum in the soil zone (i.e. chemical structure of the soil zone).

Since three physically different flow paths exist in the unsaturated zone of the recharge area for the confined aquifer, waters of at least three different carbon dioxide contents will enter this aquifer. Water entering the unconfined aquifer will have a more uniform carbon dioxide content since only one physical type of flow path exists in the unsaturated zone above this aquifer.

The dissolution rate of a solid in water depends directly on the surface area of the solid. Soils present much more surface area to infiltrating water than either sink holes or fractures and joints. Therefore, water infiltrating through soils will reach saturation with respect to the dissolvable minerals found in the soil faster than water infiltrating through fractures, joints, or sink holes in a solid matrix of similar composition. If the infiltration rates are roughly comparable, the faster dissolution rates in the soil indicate that chemical saturation is achieved at a shallower depth in soil zones. Actually, flow through joints, fractures, and sink holes is much faster than through soils, thereby increasing the difference in depth to chemical saturation. It is conceivable that water flowing through joints, fractures and sink holes may reach the confined aquifer before achieving chemical equilibrium with respect to calcite. However, all water taken from the confined aquifer is saturated with calcite, even water

taken from directly under the recharge area. Consequently, even though water infiltrating through fractures, joints, and sink holes requires greater infiltration distances before reaching saturation, the actual infiltration distances in the recharge area (approximately 400 ft.) are sufficient to cause saturation with respect to calcite. Gypsum dissolves at a considerably faster rate than calcite (approximately by a factor of 100). The gypsum content of the unsaturated zone, although highly variable, is usually much less than the calcite concentration, and the water entering either aquifer is unsaturated with respect to gypsum.

An attempt was made to quantify the preceding arguments using soil samples taken from various locations and depths in the Roswell basin. Soil samples were taken from hill tops and gully bottoms in the recharge area and from irrigated and unirrigated fields in the alluvium. In addition, soil samples were taken from various depths below an unirrigated field in the alluvium. The soils were loosely placed in cylindrical plastic columns 10 cm in diameter and 80 cm long, and leached with distilled water. The leachant was collected and analyzed for  $H^+$ ,  $HCO_3^-$ ,  $Ca^{+2}$  and  $SO_4^{-2}$ . The results are summarized in Table I.

All soil samples gave a leachant that was saturated with calcite after passing through 50 cm of sample. Samples taken from deeper locations in the alluvium yielded water that was saturated with gypsum. Calculated  $CO_2$  concentrations in the leachant were approximately ten times the atmospheric amount for surface soil

Table I

## Soil Water

Location	depth meters	pH	Ca <sup>+2</sup> ppm	HCO <sub>3</sub> <sup>-</sup> ppm	SO <sub>4</sub> <sup>-2</sup> ppm	P <sub>CO<sub>2</sub></sub> x 10 <sup>3</sup> atm	Leachant vol. ml
Alluvium Irrigated field	0	8.0 8.4	100 50	152 222	197 110	1.6 .9	5.3 x 10 <sup>2</sup>
Alluvium Unirrigated field	0	7.7 8.4	325 10	116 183	670 11	2.7 .8	2.7 x 10 <sup>3</sup>
Alluvium Unirrigated field	1	7.6 7.6	350 350	44 44	2000 2000	1.0 .7	3.0 x 10 <sup>3</sup>
Alluvium Unirrigated field	3	7.7 8.0	330 330	51 44	2000 2000	.7 .7	9.0 x 10 <sup>2</sup>
Recharge Creek bottom	0	7.8 8.0	118 22	146 140	171	2.4 1.4	1.6 x 10 <sup>3</sup>
Recharge Hill top	0	7.8 8.3	112 31	195 184	155 71	2.1 .9	1.2 x 10 <sup>3</sup>

Concentrations of selected ionic species found in singly distilled water (initial pH 6.5) after passing through 50 cm of soil collected at the indicated locations. Beginning and final concentrations are listed in the left and right columns under each species heading. The final concentration was measured after the passage of the listed leachant volume. All measurements indicate saturation with respect to calcite and the samples from 1 and 3 meters below the surface (unirrigated field) were also saturated with respect to gypsum. Alluvium samples were collected near the city of Roswell in the northern part of the basin and the recharge samples were collected 30 miles west of Artesia, a city in the southern half of the basin.

samples and three times the atmospheric amount for deeper soil samples (Fig. 2). The actual amount of gypsum in the soil samples can be gauged by the changes in the  $\text{SO}_4^{+2}$  or  $\text{Ca}^{+2}$  concentration in the leachant as a function of leachant volume. Deeper soil samples were not leached of gypsum after the passage of 3,000 ml of leachant, surface samples, however, were depleted of gypsum after the passage of 300 ml of leachant.

It is unlikely that any part of the aquifer water infiltrated through the tested soil samples. Probably most of the water infiltrating the soil does so over a small fraction of the total area. The location of these infiltration areas is determined by topographic and permeability conditions. In such infiltration areas the gypsum content is very much depleted and the saturation with respect to gypsum indicated by the deep soil sample tests would not occur. In addition, such infiltration areas will sustain more plant growth and therefore contribute more carbon dioxide to the infiltrating water. It is likely that the behavior of these infiltration areas with respect to calcite dissolution is very similar to the behavior exhibited by the soil columns.

In summary, water infiltrating a soil zone will be saturated with calcite after passing through 50 cm of soil. The carbon dioxide content will increase several orders of magnitude in the upper soil layers and gypsum will be acquired from soil located 1 to 2 meters below the soil surface. Water infiltrating through joints, fractures, and sink holes will acquire calcite at a slower rate but it will be saturated with calcite when it reaches the

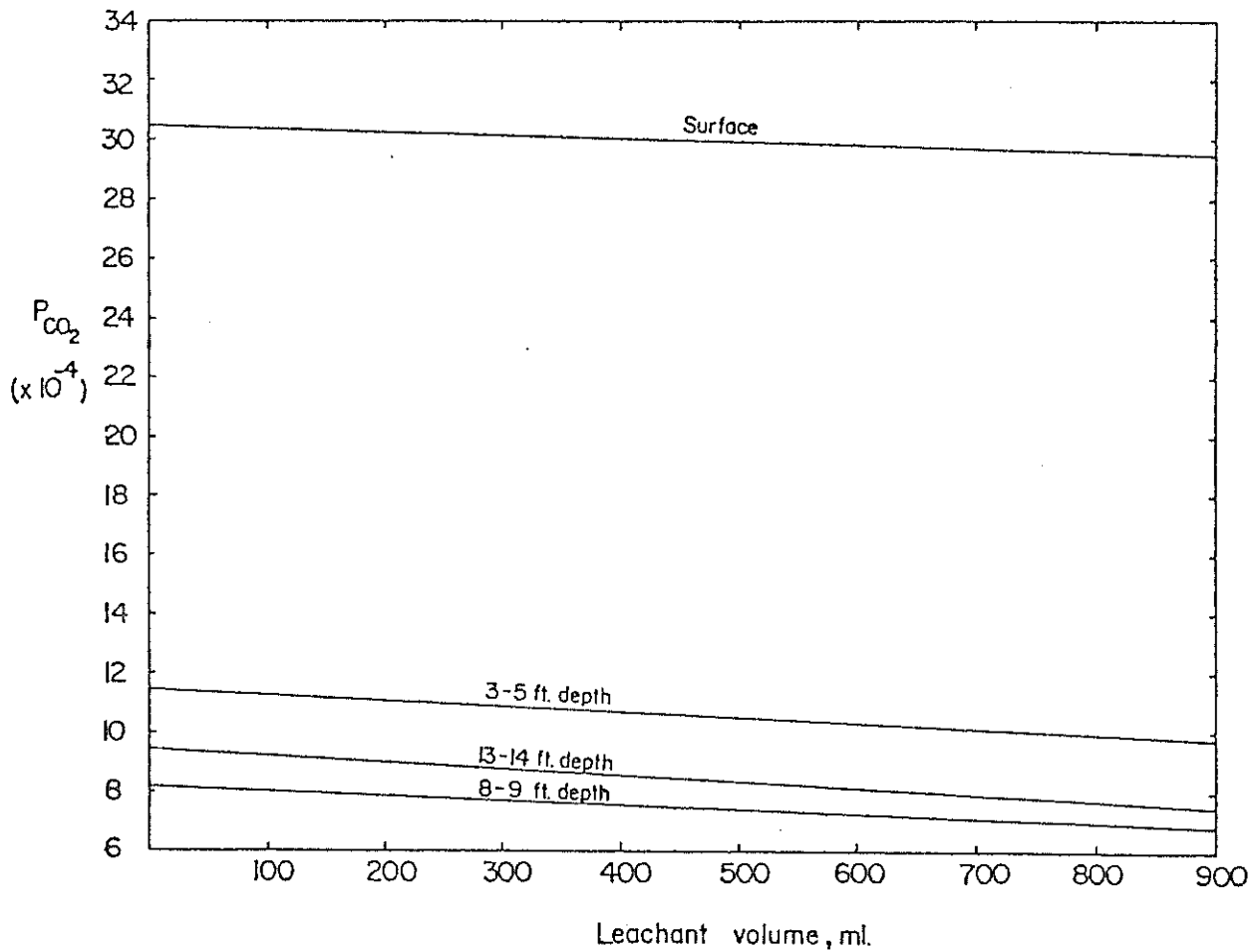


Figure 2.-Carbon dioxide content of distilled water after passing through 50 cm of soil collected from the indicated depth intervals in the alluvium under an unirrigated field in the Roswell Basin.



aquifer. Probably most of the solutes found in the groundwater in the Roswell basin are acquired before the water reaches the aquifers. Further chemical changes occur in the aquifers but these are of a smaller magnitude and result from nonlinear effects during the mixing of waters of different chemical composition and temperatures. It is also possible that the concentrations of sparingly soluble elements that dissolve at slow rates continue to increase in the aquifer.

## ANALYSIS METHODS

During the spring and summer of 1973, sixty-five groundwater samples were collected. Temperature and pH were determined at the collection site. The samples were titrated with .02 N H<sub>2</sub>SO<sub>4</sub> to a pH of 4.5 to determine P<sub>CO<sub>2</sub></sub> and [HCO<sub>3</sub><sup>-</sup>]; this was also done at the collection site.

In the laboratory, cation concentrations (Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+1</sup>, and Na<sup>+1</sup>) were determined using a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer, SO<sub>4</sub><sup>-2</sup> concentrations were determined turbidimetrically, and Cl<sup>-</sup> concentrations were determined using a mercuric nitrate titration.

## AQUIFER WATER

All water samples taken from the confined and unconfined aquifers and the recharge area for the confined aquifer are saturated with calcite and contain approximately 100 times the atmospheric amount of dissolved carbon dioxide (Table II). Water taken from the unconfined aquifer is approximately 2°C cooler and contains more gypsum than water taken from the confined aquifer. This is especially true in the southern part of the basin (samples 16 to 25). The northern part of the Roswell confined aquifer and all parts of the recharge area exhibit large fluctuations in the concentrations of chemical species found in the groundwater. These variations in composition can be attributed to chemical variations in the unsaturated zone of the recharge area and to the high flow velocities found in the northern part of the confined aquifer which prevent diffusional mixing of chemical differences acquired in the unsaturated zone. Slower velocities<sup>2</sup> result in the greater chemical uniformity found in the southern part of the basin (Samples 24 and 25, Table II). In addition, the aquitard above the confined aquifer in the northern part of the basin has a greater leakage. During the pumping season, for a given drawdown, the amount of leakage from the unconfined aquifer, which has a higher gypsum content, will be greater in the northern part of the basin. Since the leakage is probably distributed randomly over the confined aquifer, the result will be a random input of high gypsum concentration giving rise to the variable gypsum ( $\text{SO}_4^{2-}$ ) content that is observed in the northern part of the confined

Table II. - Chemical compositions and temperatures for water samples taken from wells in the confined (C) and unconfined (U) aquifers and in the recharge area (CR) for the confined aquifer.

Date	No.	Location <sup>1</sup>	Aquifer	Temp	pH	Ca <sup>2</sup>	Mg	Na	K	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	Pco <sub>2</sub> <sup>3</sup>	CaSat <sup>4</sup>
5/26/73	1	11-25-15-343	C	20.5	7.2	207	90	320	1.8	375	512	224	15.3	2.2
	2	11-25-15-333	C	20.5	7.3	193	85	719	2.0	385	440	208	11.2	2.2
	3	11-25-23-111	C	20.6	7.1	279	104	600	3.4	770	632	208	17.8	2.0
	4	11-24-25-341	C	20.5	7.5	228	37.4	42	1.5	100	190	214	8.2	3.2
	5	11-24-25-312	C	20.7	7.4	163	64.	34	1.2	56	312	230	8.9	2.5
	6	11-24-23-443	C	20.7	7.4	168	69	41	2.6	75	362	274	10.0	2.7
	7	11-24-23-433	C	19.6	7.4	230	124	59	1.4	100	572	232	10.0	3.1
	8	12-23-5	CR	18.5	7.2	327	127	64	1.8	---	890	330	22.5	4.0
	9	12-23-5	CR	-----	7.4	132	57	28	2.5	60	202	266	11.4	1.7
	10	8-23-17	CR	24.0	7.0	535	264	420	3.0	530	1442	299	32.0	3.1
	11	8-22-12	CR	20.5	7.5	136	83	420	1.4	470	342	185	50.0	2.3
	7/10/73	12	7-23-31	CR	22.0	7.5	348	116	400	3.0	605	682	165	56.0
13		11-23- 1-433	U	19.1	7.0	220	81	80	1.7	185	542	212	22.9	1.5
14		11-24-24-334	U	17.2	7.1	400	216	114	1.5	105	1242	264	22.8	2.8
15		11-23- 1-413	U	19.5	7.3	220	88	98	1.6	175	472	217	11.8	2.5
16		17-26-10-331	C	21.2	7.3	223	77	185	3.5	175	750	224	9.69	2.9
17		17-26-10-133	C	24.0	7.1	273	96	195	2.6	400	650	233	20.0	1.7
18		17-26-10-433	C	23.8	7.2	243	63.7	52	3.0	45	600	228	15.5	1.8
19		17-26-14-211	C	23.6	7.3	244	116	87	3.7	160	659	220	11.9	2.9
20		17-26-11-433	C	23.0	7.3	226	78	110	2.8	80	571	222	12.0	2.5
21		15-18-17-143	CR	16.6	7.4	151	32.1	46	2.4	25	170	299	13.7	2.7
22		15-17-14-312	CR	18.4	7.1	554	87	32	2.4	30	1440	290	24.8	4.9
23		17-23-30-123	CR	-----	7.5	180	41.7	135	4.1	40	370	238	8.55	3.0
24		17-26-15-113	U	18.6	6.9	375	139	270	2.6	215	1390	292	37.1	2.42
25	17-26-15-211	U	18.8	7.3	278	91	135	2.9	190	802	220	10.6	4.0	

<sup>1</sup>Sample locations are given using a numbering system which identifies the township, range, section, and tract.  
<sup>2</sup>Ionic species are given in ppm.

<sup>3</sup>Pco<sub>2</sub> when multiplied by 10<sup>-3</sup> gives the effective CO<sub>2</sub> pressure in atmospheres.

<sup>4</sup>CaSat is defined as (Calcium measured/calcium required for calcite saturation). The first fifteen samples were taken from the northern part of the basin, the last ten samples were taken from the southern part.

aquifer.

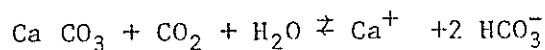
Because the unconfined aquifer is completely covered by its recharge area, inhomogeneities in the water from the unsaturated zone are never completely damped out along the stream lines in the unconfined aquifer. The high gypsum concentration in this aquifer is caused by the relatively large gypsum content of the soils above the aquifer.

## NONLINEAR MIXING EFFECTS

Consider the mixing of two solutions, both saturated with calcite, but either containing different amounts of gypsum, dissolved carbon dioxide, or inert ionic species, (that is, ions not involved in the common-ion effect) or having different temperatures. Invariably, the resulting mixture will not be saturated with calcite. The mixture will be either over or undersaturated depending on the differences between the two solutions being mixed. This change in degree of calcite saturation during mixing arises because the saturation curve for calcite is a nonlinear function of carbon dioxide, gypsum, and inert ion concentrations, and temperature. In the following section, four nonlinear saturation curves will be constructed using elementary considerations. These curves will be related to the behavior of groundwater in the Roswell basin.

Common Ion Saturation Curve

The chemical behavior of calcite in solutions having a pH near 7 is given by



where  $\text{CaCO}_3$  is a solid,  $\text{CO}_2$  is a gas, and both  $\text{Ca}^{+2}$  and  $\text{HCO}_3^{-}$  exist as ions in solution. The concentrations and pressure of components displayed in the chemical equation are related by the mathematical equation

$$\frac{[\text{Ca}^{+2}][2\text{HCO}_3^{-}]^2}{P_{\text{CO}_2}} = K \quad (1)$$

where brackets indicate molar concentrations of the bracketed species,  $P_{\text{CO}_2}$  is the pressure of carbon dioxide measured in atmospheres, and the value of  $K$  is approximately  $1.2 \times 10^{-6}$ .

Consider one liter of solution containing  $y$  moles of  $\text{CaCO}_3$  and  $x$  moles of  $\text{CaSO}_4$ . Assume that the dissolved calcite content is much greater than the hydrogen ion concentration

$$y \gg [\text{H}^+]$$

The ionic concentrations can be written as

$$[\text{Ca}^{+2}] = y+x$$

$$[\text{HCO}_3^-] = 2y$$

Substitution into the mathematical equilibrium equation gives

$$\frac{(y+x)(2y)^2}{P_{\text{CO}_2}} = K$$

After rearranging terms, a cubic equation results

$$y^3 + y^2x - \frac{K P_{\text{CO}_2}}{4} = 0$$

Two limiting cases are easily examined. First, if no gypsum is present.,  $x = 0$  and

$$y = \left\{ \frac{K P_{\text{CO}_2}}{4} \right\}^{\frac{1}{3}} \quad (2)$$

Second, if

$$x \gg y$$

the equilibrium expression can be written as

$$x 4y^2 = K P_{\text{CO}_2}$$

or

$$y = \sqrt{\frac{K P_{\text{CO}_2}}{4}} \frac{1}{\sqrt{x}} \quad (3)$$

Obviously, as  $x$  gets large,  $y$  approaches zero.

A plot of calcite concentration as a function of gypsum concentration is given in Figure 3. The curve is concave upward, indicating that the mixing of any two saturated solutions with different gypsum contents will give a final solution that is oversaturated with respect to calcite. If such mixing occurs within an aquifer, a deposit of calcite will appear in the mixing zone.

#### Carbon Dioxide Saturation Curve

The amount of calcite held in solution at equilibrium depends on the pressure of the carbon dioxide in the solution. If no gypsum is present in the solution, the dissolved calcite concentration is given by Eq. (2).

$$y = \left\{ \frac{K}{4} \right\}^{\frac{1}{3}} P_{\text{CO}_2}^{\frac{1}{3}}$$

A plot of this equation is displayed in Figure 4. The curve is concave downwards. Therefore, the mixing of two saturated calcite solutions containing different carbon dioxide pressures will result in an undersaturated solution. This is indicated by the straight line connecting the points representing the initial solution concentrations. In regions of the aquifer where this type of mixing occurs, further dissolution of calcite from the aquifer matrix will take place.



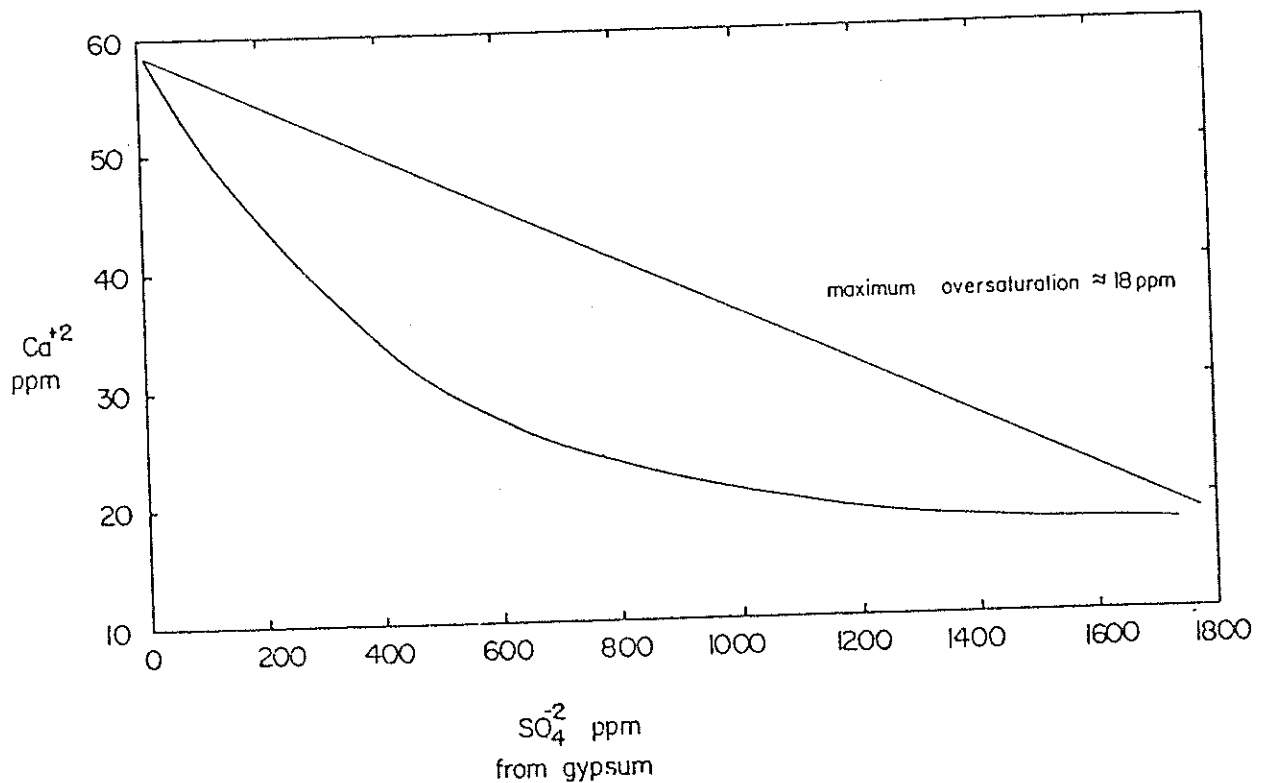
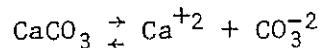


Figure 3.-Calcite saturation as a function of gypsum content (curved line). The mixing of two saturated calcite solutions with different gypsum contents (0 and 1800 ppm  $\text{SO}_4^{-2}$ ) gives a final calcite content (listed as ppm  $\text{Ca}^{+2}$  from calcite) that is located on the straight line. The position of the mixture on the straight line is determined by the relative amounts of the two solutions mixed. Maximum oversaturation (18 ppm) occurs if 2/3 of the mixture is the saturated calcite solution with no gypsum (0 ppm  $\text{SO}_4^{-2}$ ).

### Temperature Saturation Curve

Another way to display the dissolution of calcite is given by the chemical equation



The equation must be satisfied at equilibrium. The mathematical version of this chemical equation is

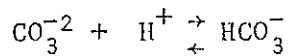
$$[\text{Ca}^{+2}][\text{CO}_3^{-2}] = K_{sp} \quad (4)$$

where  $K_{sp}$  is the solubility product constant

$$K_{sp} = 10^{-(8.3389 + .0022T + .0005T^2)}$$

and T is the temperature of the solution in degrees Centigrade.

The  $\text{CO}_3^{-2}$  liberated during dissolution reacts with hydrogen ions in the solution producing bicarbonate ions



This reaction has the equilibrium constant  $K_2$

$$K_2 = \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{-2}][\text{H}^+]}$$

Solving for  $[\text{CO}_3^{-2}]$  and substituting into Eq. (4)

$$[\text{Ca}^{+2}][\text{HCO}_3^-] = K_{sp} K_2 [\text{H}^+]$$

If  $[\text{HCO}_3^-] \gg [\text{H}^+] \sim 10^{-7}$  molar

then

$$2[\text{Ca}^{+2}] = [\text{HCO}_3^-]$$

and

$$[\text{Ca}^{+2}] = \left\{ \frac{K_{sp}}{2} \right\}^{\frac{1}{2}} \left\{ K_2 [\text{H}^+] \right\}^{\frac{1}{2}} \quad (5)$$

The temperature dependence of the calcium or calcite concentration

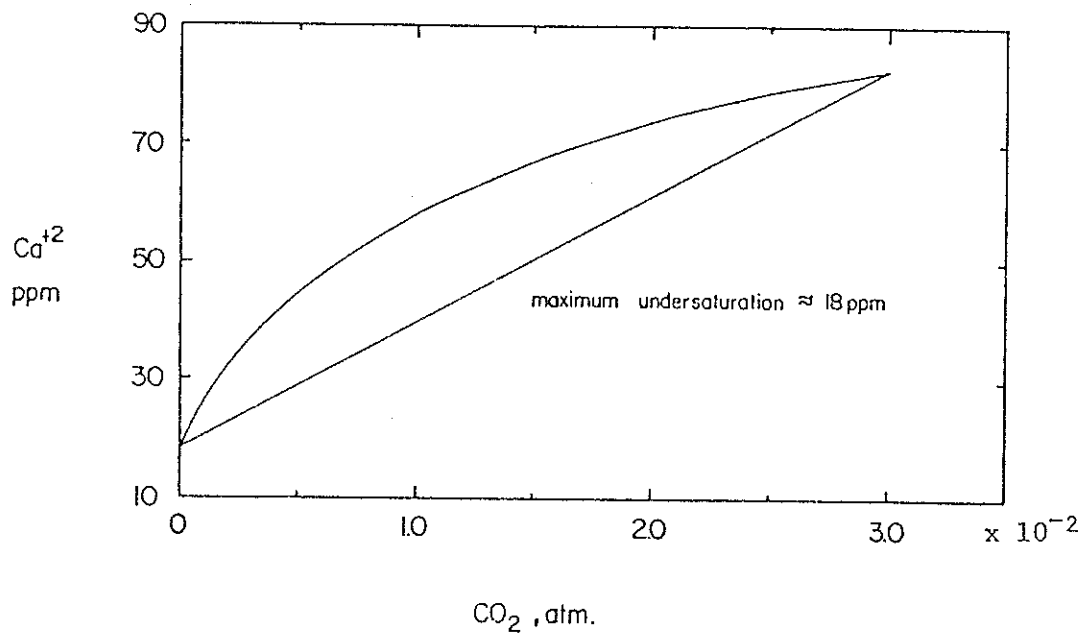


Figure 4.-Calcite saturation as a function of carbon dioxide pressure. Mixtures are undersaturated with calcite (straight line). The maximum undersaturation is about 18 ppm  $\text{Ca}^{+2}$ .

is given by

$$[\text{Ca}^{+2}] = \left\{ \frac{K_2 [\text{H}^+]}{2} \right\}^{\frac{1}{2}} (10^{-(4.1694 + .0011T + .0002T^2)}). \quad (6)$$

The saturation curve, Figure 5, is concave upward at high temperatures and concave downward at low temperatures. In the temperature range of interest, 15°C to 25°C, the curve is almost a straight line. As a result, no change in saturation will occur during mixing. However, the development that is presented fails to consider the thermal energy contained in the solid aquifer matrix. Although difficult to quantify, it is apparent that when the aquifer matrix is considered, water entering a warmer region of the aquifer will become oversaturated. In the Roswell basin, water flowing from the unconfined to the warmer confined aquifer will be oversaturated by a maximum of 6 ppm calcium. Flow in the opposite direction will result in the same amount of undersaturation.

#### Inert Ion Saturation Curve

Thermodynamic equilibrium equations are derived in terms of a rather nebulous quantity called activity. For sufficiently dilute solutions the activity is the same as the concentration and this simplification has been made in Equations 2, 3, and 5. However, to be perfectly precise, the calcium concentrations given by these equations should be the calcium activities. The calcium activity is related to the calcium concentration by the activity coefficient

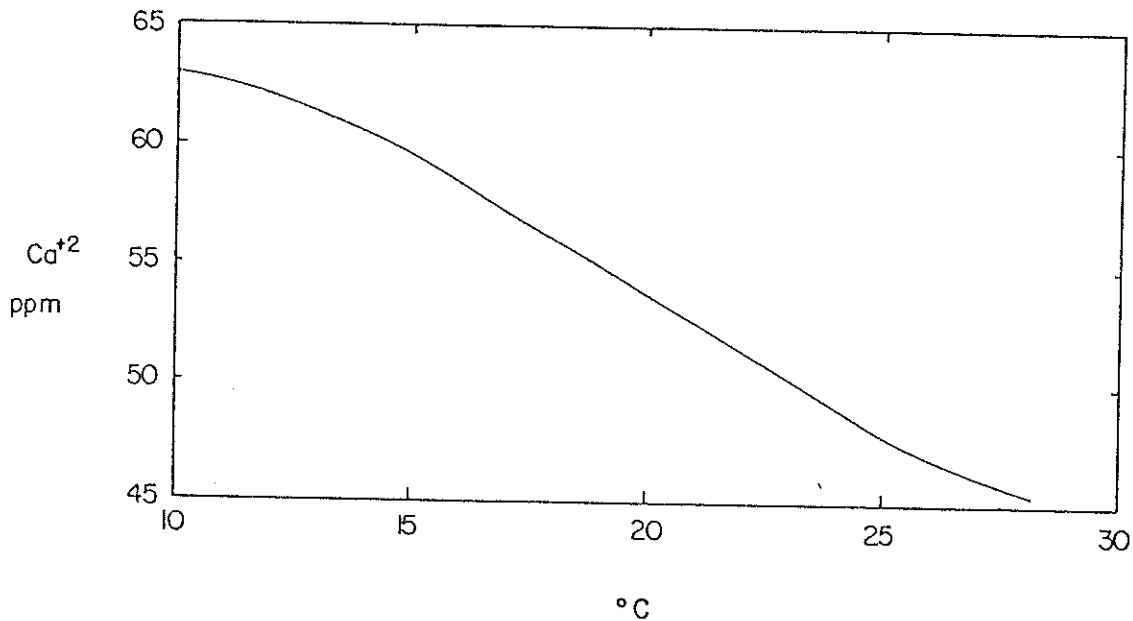


Figure 5.-Calcite saturation as a function of temperature. In the temperature range of interest (15 to 23°C) the saturation curve is a straight line. No change in saturation will result from mixing in this temperature range.

$$a = \gamma m$$

where  $a$  is the activity,  $\gamma$  is the activity coefficient and  $m$  is the concentration given as molality (moles per  $10^3$  gm of solution).

For dilute solutions

$$m = c$$

where  $c$  is concentration as molarity (moles per liter of solution).

Therefore, for dilute solutions

$$a = \gamma c$$

A more correct version of Equation (5) would be

$$\gamma[\text{Ca}^{+2}] = \left(\frac{K_{\text{SP}}}{2}\right)^{\frac{1}{2}} (K_2 a_{\text{H}^+})^{\frac{1}{2}}$$

or

$$[\text{Ca}^{+2}] = \gamma^{-1} \left(\frac{K_{\text{SP}}}{2} K_2 a_{\text{H}^+}\right)^{\frac{1}{2}} \quad (7)$$

Various empirical formulas have been developed for the evaluation of  $\gamma$ , the most common being

$$\gamma = \exp \left\{ - \frac{A |Z_+ Z_-| I^{\frac{1}{2}}}{1 - B d I^{\frac{1}{2}}} \right\} \quad (8)$$

where  $A$ ,  $B$ , and  $d$  are properly chosen parameters,  $Z_+$  and  $Z_-$  are the charges found on the positive and negative ion pair being considered, and  $I$  is the ionic strength

$$I = \frac{1}{2} \sum_i m_i Z_i^2$$

where  $m$  is the molality of the  $i^{\text{th}}$  species, and the summation is carried over all ionic species found in the solution. Non-reactive (inert) ions such as  $\text{Na}^+$  and  $\text{Cl}^-$  increase the ionic

strength, decrease the activity coefficient (Eq. 8), and increase the calcium concentration at equilibrium (Eq. 7). A plot of Equation 7 is given in Figure 6. The curve is concave downward so that the mixing of two saturated solutions with different ionic strengths produces an unsaturated solution.

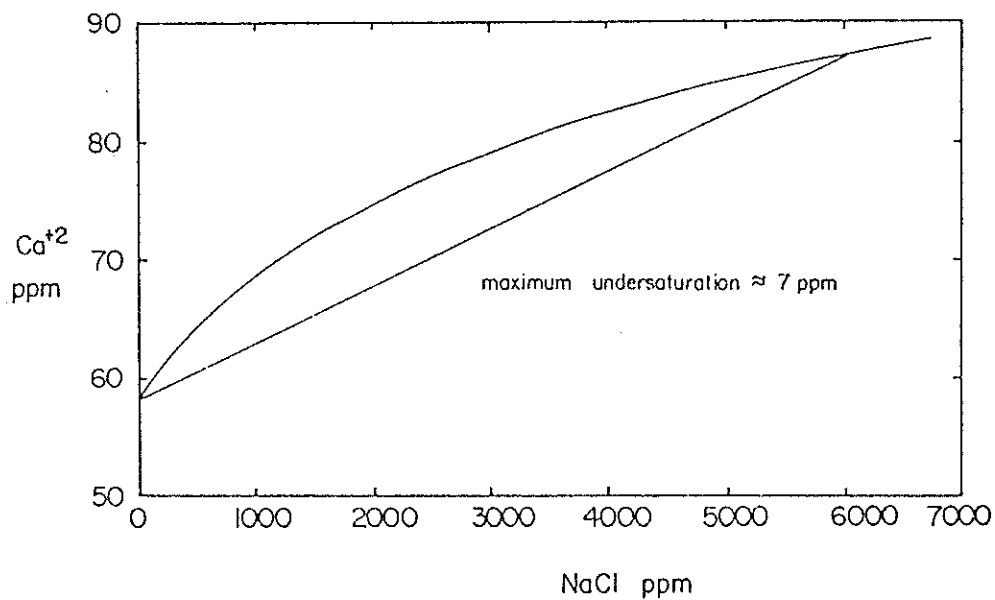


Figure 6.-Calcite saturation as a function of inert salt (NaCl) concentration.

Mixing results in undersaturation (straight line). The maximum undersaturation is about 7 ppm  $\text{Ca}^{+2}$ .



## AQUIFER MIXING MODES

Aquifers in karst formations can be visualized as a maze of interconnecting tubes. Wherever two tubes connect, waters of different composition may be brought together and mixing will occur downstream from the junction. Depending on the flow velocity, mixing will be turbulent or diffusional. Turbulent mixing is more efficient but less likely since flow velocities are usually too slow to initiate this process. Mixing efficiency is characterized by a mixing length, usually the length of fluid flow path required to reduce concentration differences in adjacent regions to  $\frac{1}{e}$  of their initial value. It is conceivable that the mixing length is longer than any flow path through the aquifer.

Confined Aquifer

Water entering the confined aquifer through the recharge area will contain variable amounts of gypsum and carbon dioxide. (Calcite is always saturated). Carbon dioxide variations have been attributed to differences in the physical structure of the available infiltration paths through the unsaturated zone. Gypsum variations reflect the heterogeneous distribution of gypsum in the unsaturated zone.

Variations in the carbon dioxide content of the sampled groundwater appears to be random with perhaps a slight increase along any flow line from the recharge area to the Pecos River. Since carbon dioxide concentration is calculated from the pH and alkalinity of the groundwater which are determined in the field,

the random variations are probably a reflection of the relatively large errors in the carbon dioxide determination. All samples have  $\text{CO}_2$  concentrations that are approximately 100 times the atmospheric value. Any large variations in  $\text{CO}_2$  content (due to variations in the physical structure of infiltration path) were not observed. This implies that if the postulated variations in the physical path do occur, they occur over a relatively small surface area so that the mixing length is very short. Carbon dioxide variations in the water entering the aquifer cause further calcite dissolution. The dissolution will occur immediately under the unsaturated zone in the recharge area. Since no  $\text{CO}_2$  heterogeneities are transported into lower sections of the confined aquifer near the Pecos River, no calcite dissolution caused by carbon dioxide mixing will occur in this region.

Gypsum variations in the water contained in the northern part of the aquifer are large, even near the Pecos River. This indicates that the mixing length may be longer than the flow path in this section of the aquifer.

Measurements made in the confined aquifer in the southern part of the basin, east of Artesia, yield a uniform gypsum content. The 30 mile flow path from the recharge area to this location is sufficient to complete the mixing process. Therefore, the mixing length is less than 30 miles in this region. Tritium measurements indicate that the flow velocity in the southern part of the aquifer is considerably slower than in the northern part

so that diffusional mixing may be important in the southern part of the confined aquifer.

In summary, gypsum variations in the recharge area will precipitate calcite throughout the northern part of the confined aquifer and in the region west of Artesia in the southern part of the confined aquifer.

#### Unconfined Aquifer

The water reaching the unconfined aquifer in the valley alluvium contains a variable but high gypsum content; it is never less than 500 ppm  $\text{SO}_4^{-2}$  and may be as great as 1400 ppm  $\text{SO}_4^{-2}$ . Mixing occurs by dispersion and diffusion, but since the entire unconfined aquifer is covered by its recharge area, sources of high gypsum concentration occur over the entire aquifer so that along any flow path in the aquifer the gypsum content will never reach a constant value. This variation in the gypsum concentration will cause calcite precipitation throughout the unconfined aquifer.

#### Coupling Between Aquifers

Hydraulic heads at the interface (aquitard) between the confined and unconfined aquifers are not identical so there is flow through the aquitard. In the past, the confined aquifer always had the higher head and the flow was always from the confined to the unconfined aquifer. However, in recent years, due to intense pumping of the confined aquifer during the summer months, the pressure has been reduced causing water to flow from the unconfined

to the confined aquifer. During the winter months pumping is stopped, water pressure in the confined aquifer recovers, and the flow across the aquitard is reversed. This artificially induced cycling of water across the aquitard causes the mixing of high gypsum water from the unconfined aquifer with lower gypsum water from the confined aquifer. The result is the deposition of calcite in the mixing zone on both sides of the aquitard. Core samples taken from a well drilled on the eastern side of Roswell contain vugs that are lined with a calcite druse<sup>3</sup>, resulting from this mixing effect. In addition, flow from the unconfined to the confined aquifer is causing an increase in the gypsum content of water in the confined aquifer. This increase is illustrated for the Oasis well near Roswell in Table III.

In recent years, the sodium chloride concentration of water in the northeast section of the confined aquifer has rapidly increased. Since anomalous sodium chloride concentrations are not found in the recharge area, the sodium chloride increase must result from the mixing of confined aquifer water with water that has a very high sodium chloride content. This section of the aquifer is under a region of salt lakes and marshes and it is highly probably, although not definitely proven, that the salt water or brine is intruding from above as a result of pressure reduction in the confined aquifer due to pumping. In any case, the introduction of an inert salt such as sodium chloride increases the equilibrium concentration of calcite causing further

Table III

Changes in the gypsum content (measured as ppm  $\text{SO}_4^{-2}$ ) of water taken from the Oasis (Clardy) Well (location 11.25.15.333). This well, which is approximately 800 ft. deep, is located near Roswell and taps the confined aquifer. The gradual increase in the gypsum content may be indicative of an increasing leakage rate from the upper unconfined aquifer.

date	ppm $\text{SO}_4^{-2}$
5/10/28	291
7/3/38	297
2/9/39	283
4/10/40	321
8/30/48	300
3/11/52	303
8/12/52	305
7/12/55	329
10/26/71	410
5/25/73	512

calcite dissolution. However, the intruding brine is probably also rich in gypsum and has a relatively low temperature, especially if from the upper aquifer, so that calcite solubility is reduced through the common ion and temperature effects. Since three effects are operating simultaneously, it is difficult to predict the solubility change.

Throughout the confined aquifer, waters with variable gypsum concentrations are being mixed. The gypsum variations originate in the recharge area or through leakage from the unconfined aquifer. As a result, calcite precipitation is occurring in most of the confined aquifer. If this process continues, the permeability of the confined aquifer will be reduced.

## REFERENCES

1. Mercado, A., 1972, The Kinetics of Mineral Dissolution in Aquifers and Their Use for Hydrologic Investigations. Ph.D. Dissertation, New Mexico Institute of Mining and Technology, Socorro, 221 pp.
2. Rabinowitz, D. D. and Gerardo Wolfgang Gross, 1972, Environmental Tritium as a Hydrometeorologic Tool in the Roswell Basin, New Mexico. New Mexico Water Resources Research Institute, Report No. 016, 268 pp.
3. Havenor, K. C., 1968. Structure, Stratigraphy, and Hydrogeology of the Northern Roswell Artesian Basin, Chaves County, New Mexico. New Mexico State Bureau of Mines and Mineral Resources, Socorro, Circular 93. (The author erroneously identifies the vug linings as anhydrite, X-ray analysis indicates calcite).