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SOLUBILITIES OF  
CALCIUM SULFATE DIHYDRATE  
AT 25°C IN BRACKISH WATERS  
AND THEIR CONCENTRATES;  
EFFECT OF CALGON ADDITIVE  
AND PREDICTIONS FOR  
REVERSE OSMOSIS PROCESSES

LeRoy B. Yeatts  
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REACTOR CHEMISTRY DIVISION

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AND PREDICTIONS FOR REVERSE OSMOSIS PROCESSES\*

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William L. Marshall

\*Research supported by the Membrane Processes Division, U.S. Office of Saline Water, and performed at the Oak Ridge National Laboratory operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

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SEPTEMBER 1973

OAK RIDGE NATIONAL LABORATORY  
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## FOREWORD

This experimental study was made during the period of January 1, 1972, to December 31, 1972, for the Office of Saline Water, Department of the Interior. The research was done under Work Order 30, interagency agreement No. 14-30-2535, and is Part I of a two part study. Part II, titled "Calcium Sulfate Scaling in Reverse Osmosis (Hyperfiltration) of Brackish Waters by Hollow-Fiber and Spiral-Wound Modules" (ORNL-4330; July, 1973) and authored by R. E. Minturn with a section by L. Dresner, presents results and interpretations of the reverse osmosis dynamic studies that were coordinated with the equilibrium investigations of Part I. Part II was performed under the Water Research Program of ORNL, J. S. Johnson, Jr., Director.



## ABSTRACT

The solubility of calcium sulfate dihydrate, a substance which can impede reverse osmosis (RO) processes by saturation precipitation in RO membrane pores, was determined at 25°C in three typical brackish water compositions and their concentrates. These waters were synthetically prepared, and corresponded to compositions and concentrates of well waters used by the Office of Saline Water RO plants at Gillette, Wyoming, and Webster, South Dakota, and those of a post-irrigation water from the Wellton-Mohawk Canal in Arizona. In this present study, a commercial solid polyphosphate preparation, Calgon, was shown when added in small amounts (5-40 ppm in unconcentrated solutions) to initially produce an apparent increase in the saturation concentration of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (the solid phase). Later (2-6 days), the solution concentration of  $\text{CaSO}_4$  decreased to near the expected solubilities in the absence of Calgon. The method of calculation of the solubility of  $\text{CaSO}_4$  and its hydrates in various saline waters, which has been used successfully for several years, is found to apply equally well to the calculation of saturation limits of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in the present waters and concentrates. Calculations and verifications of maximum possible water recoveries and of other parameters that are of direct application to RO processes are presented. Included also is the computer program for making the calculations.

## 1. INTRODUCTION

The Office of Saline Water (OSW) has seriously considered the reverse osmosis (RO), or hyperfiltration, process to produce potable water from brackish waters, and has had pilot plants in operation at Gillette, Wyoming, and Webster, South Dakota, for several years. The extent to which any saline feed water can be efficiently concentrated by this process (or by distillation) in recovering pure water is limited by the saturation precipitation of particular substances, usually calcium sulfate or its two hydrates. In a reverse osmosis process, the precipitating substance fills the pores of the RO membrane, and thus the efficiency of the process decreases sharply. In a distillation plant, scale forms on heat exchanger surfaces thereby greatly decreasing the operating efficiency.

Most naturally occurring brackish waters contain calcium, magnesium, and sulfate ions, and usually a small amount of hydroxide ion. Some of the substances of low solubility that may precipitate from these waters, for example  $Mg(OH)_2$ ,  $Ca(OH)_2$ ,  $MgCO_3$ , and  $CaCO_3$ , can be eliminated by small additions of acid to the saline feed water. Calcium sulfate, however, is not so readily eliminated, and knowledge of its solubility or solubility product in the concentrates is of primary concern in establishing the extent of concentration that may be obtained before saturation by calcium sulfate occurs.

Of equally important concern with solubility is the qualitatively observed effect of very small amounts of additives, for example, sodium hexametaphosphate (the commercial product, Calgon) in retarding over short periods of time the precipitation of calcium sulfate and other substances. Although the mechanism of this process may be related predominantly to a kinetic rather than equilibrium behavior, controlled laboratory studies have appeared to be needed for understanding more about effects of particular additives. The

ensuing results and their interpretation could then be used to predict the precipitation behavior of calcium sulfate both in the waters under study and, or greater importance, in brackish waters in general where they as feed waters are treated with additives.

It was the purpose of this investigation to determine the solubility at 25°C of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum) in three representative brackish waters and their concentrates and also to determine quantitatively the effect on  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  solubility of added Calgon to these waters. The waters selected were those used in the OSW RO plants at Gillette, Wyoming, and at Webster, South Dakota, and that from the Wellton-Mohawk post-irrigation Canal in Arizona. As background knowledge, many solubility studies of  $\text{CaSO}_4$  and its two hydrates in sea water and its concentrates, and also in multicomponent salt systems, have been made over the past fifteen years. From a fundamental interpretation of these earlier studies, a generalized computer program was developed for calculating solubility limits of  $\text{CaSO}_4$  and its hydrates at temperatures from 0 to 350°C.<sup>1</sup> A modified version for application to the present studies is given in Table XIII A in the Appendix. Nevertheless, calculations of this type had not been confirmed experimentally for the brackish waters considered in this present study. It was the additional purpose, therefore, to establish further the confidence with which solubility limits could be calculated in advance. This study has indeed further confirmed the reliable prediction of solubility limits of calcium sulfate and its hydrates in saline waters, with particular application to reverse osmosis processes.

## 2. EXPERIMENTAL

An eight times (8X) concentrated, synthetic stock solution of each of the three brackish waters listed in the Introduction was prepared from dried "analytical grade" reagents and demineralized water. Dilutions of each stock solution were made volumetrically with demineralized water to produce the lower concentrates, as well as the 1X solutions, of these brackish waters (see Tables I, IV, and VII). The synthetic 1X solutions differed only slightly in composition from the naturally occurring waters whose compositions are given in Table IA of the Appendix. The different analytical results in Table 1A for the same water are most likely real since the composition of a natural water can be expected to change, for example, with the season of the year, the amount of recent rainfall, and the rate of usage. The synthetic solutions were made slightly acid, i.e.,  $\text{pH} \approx 5.5$ , to simulate the treatment of a feed water used in a pilot plant for reverse osmosis (hyperfiltration). At this pH the equilibrium concentration of  $\text{HCO}_3^-$  ion is approximately 35 ppm.

The additive, whose effect upon solubility was studied, was the commercial product Calgon (a water conditioner) manufactured by Calgon Corporation, a subsidiary to Merck and Co., Inc. Calgon is essentially solid sodium hexametaphosphate, but it contains carbonates as impurities corresponding to approximately 6 wt %  $\text{CO}_2$ , and also contains trace quantities (<0.1 wt %) of aluminum, iron, and silicon. Dilute aqueous solutions of Calgon have a pH near 7. One to two hours before its use in a solubility experiment, a moderately concentrated solution of Calgon in demineralized water was prepared.

In general, excess solid  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Mallinckrodt, analytical reagent grade), the stable saturating solid at  $25^\circ\text{C}$ , was equilibrated with a brackish water and its several concentrates placed separately in 50 ml polyethylene bottles. These

bottles and their contents were rocked overnight (16-18 hr) or longer in a constant temperature water bath regulated at  $25 \pm 0.1^\circ\text{C}$ . After the rocking was stopped, the solution phase of each mixture was sampled through a porous Pyrex glass filter fused to Pyrex tubing. One small known volume of each sample was evaporated to dryness for determining the weight of water per ml of solution, enabling one to convert molarities to molalities. Another small known volume of each filtered solution phase was used to obtain the equilibrium concentration of calcium. This value was established by determining the combined calcium plus magnesium concentration from a semimicro potentiometric titration with standard disodium ethylenediamine tetraacetate solution (EDTA;  $\sim 0.01\text{ M}$ ). The known initial concentration of magnesium in the brackish water was subtracted from this total concentration to obtain the equilibrium concentration of calcium. In preliminary work, calcium was determined also by atomic absorption spectroscopy. However, this latter method required the preparation of standard calcium solutions, the determination of a standard curve(s) daily, and the accurate dilution of each solution sample before analysis. No increase in precision was observed, and therefore the method using EDTA was chosen since it appeared to require less time in our particular procedures. The presence of Calgon, at the 5-160 ppm levels used, was found not to interfere with the quantitative determination of calcium by either of the above methods. Additional details of the experimental procedure have been presented previously.<sup>1,2</sup>

### 3. RESULTS AND DISCUSSION

3.1 General- Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  in aqueous NaCl solutions were determined early in this research effort in order to assess the analytical technique used henceforth for the quantitative determination of calcium in these brackish waters. The assessment was possible because solubilities deter-

mined previously at 25°C at this laboratory have been compared with those of several other investigators.<sup>3</sup> The results of this present study are listed in Table IIA, Appendix, and are plotted in Figure 1. The continuous curve drawn in Figure 1 is given elsewhere<sup>3</sup> to best represent all available solubility data at 25°C. The straight line portion of the curve has a slope equal to the Debye-Hückel limiting slope, in molal units, for a 2-2 electrolyte. The assumption was made that dissolved calcium sulfate is completely ionized, contrary to experimental evidence presented previously.<sup>4</sup> However, this procedure appears to be justified for these present descriptions and calculations as supported by the previous studies.<sup>1,3,5</sup> The terms  $Q_{\text{fsp}}$  and  $K_{\text{fsp}}$  are used where,

$Q_{\text{fsp}}$  = formal solubility product = total calcium molality x total sulfate molality  
and

$K_{\text{fsp}}$  = formal solubility product = formal solubility product quotient at zero ionic strength, a hypothetical state.

The ionic strength,  $I$ , is equal to  $1/2 \sum_i m_i z_i^2$ , where  $m_i$  is the molality of the ion  $i$  which has a charge of  $z$ . The term  $I^{1/2}/(1+1.5I)^{1/2}$  is from the extended Debye-Hückel equation, with the  $A$  parameter set equal to 1.5, discussed in detail previously.<sup>1,5</sup> Note that the solubility data from the present study which are plotted in Figure 1 adhere extremely well to the curve presented earlier.<sup>3</sup> This curve is used throughout the paper as a reference since its form has been confirmed by the data of several investigators over the years using different analytical methods<sup>3</sup> and because this present study involves the determination of the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25°C in a natural water which is high in NaCl (see Table VII).

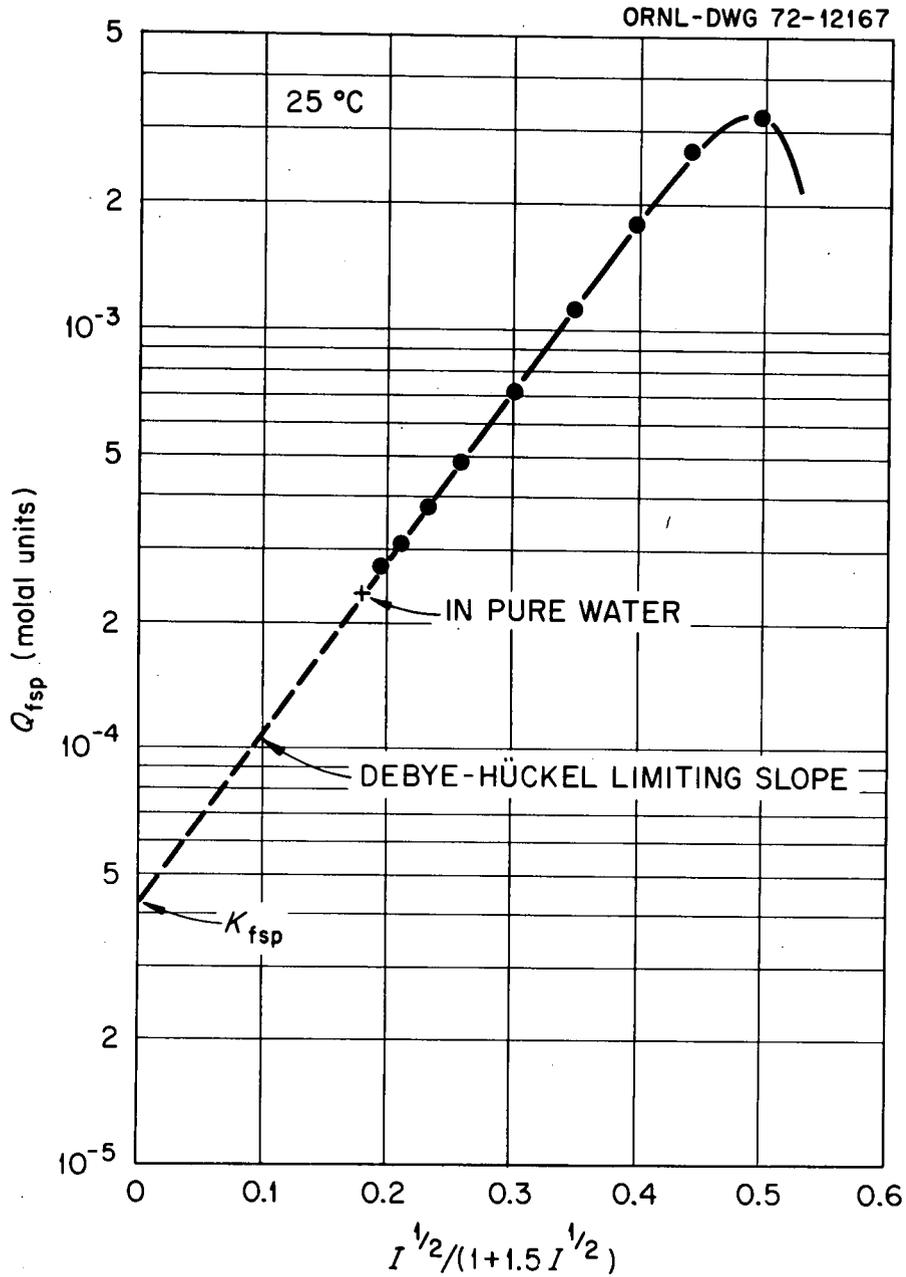


Figure 1 Formal Solubility Product Quotients of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Aqueous NaCl Solutions as a Function of  $I^{1/2}/(1+1.5 I^{1/2})$  at 25 °C.

Since all three waters considered have relatively high concentrations of  $\text{SO}_4^{2-}$  ion, it seemed desirable also to determine the solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous  $\text{Na}_2\text{SO}_4$  solutions at  $25^\circ\text{C}$  and to compare the results with those of earlier investigations.<sup>4,6</sup> The data are given in Table IIIA (Appendix) and are plotted in Figure 2 as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  solubilities vs  $\text{Na}_2\text{SO}_4$  molalities. Again, the results of this present study to 2 molal (m)  $\text{Na}_2\text{SO}_4$  are in excellent agreement with the previous data, and further support both the equilibration procedure and the analytical method. The continuing decrease in solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  as the molality of  $\text{Na}_2\text{SO}_4$  increases to 0.13 m is due to the increasing molality of the common ion,  $\text{SO}_4^{2-}$ , while the increase in solubility at higher  $\text{Na}_2\text{SO}_4$  molalities results from a dominant ionic strength effect.

Throughout this work, with few exceptions, the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  in water alone was redetermined with each set of experiments to assure that the contact time was sufficiently long, the electrodes for titration were in good condition, and the analytical reagents and end-point indicator had not become contaminated or diluted. The average solubility in water at  $25^\circ\text{C}$  from these results was  $0.0152 \pm 0.0001$  m (average deviation), which is in excellent agreement with the result reported earlier of  $0.01523 \pm 0.00016$  m (av. dev.).<sup>2</sup> This agreement should indicate the confidence which can be placed in these present experimental results.

3.2 Gillette, Wyoming, Brackish Well Water - The composition of the Gillette, Wyoming, brackish well water which was synthesized for the solubility studies is given in Table I. Calcium and magnesium are the cations present in greatest concentration, and are nearly equal in molarity, while sulfate is the dominant anion even prior to acidification (see Table IA). A trace amount only of iron is present. The solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in this water and its

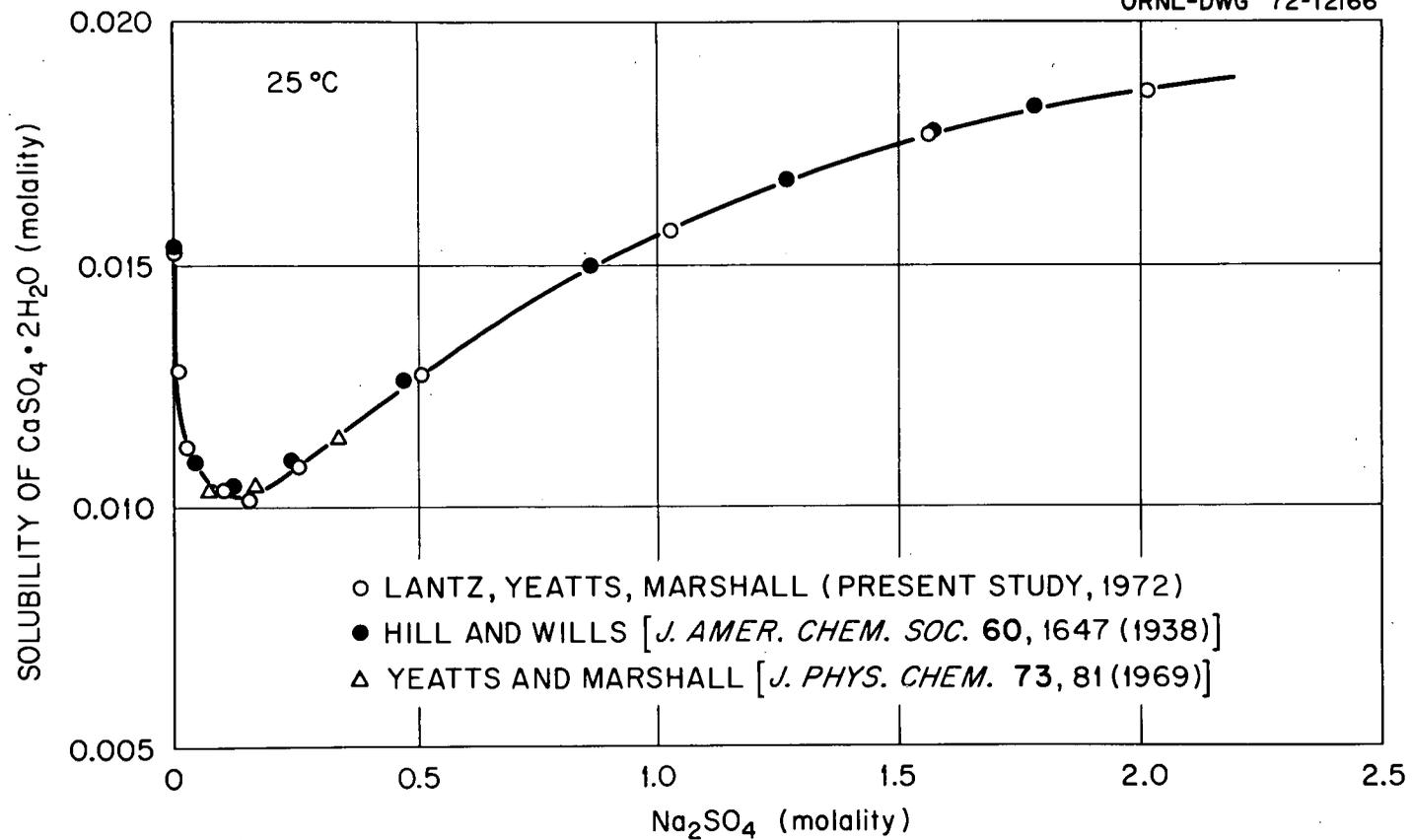


Figure 2 Solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Aqueous  $\text{Na}_2\text{SO}_4$  Solutions at 25 °C.

Table I. Molal Composition of Synthetic Gillette, Wyoming, Brackish Well Water Used for Solubility Studies of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25°C and pH of 5.5

Component	Units of Composition		
	(ppm)	(mmoles/l)	(molality)
Na	58.9	2.56	0.00258
K	14	0.35	0.00035
Ca	429	10.70	0.01078
Mg	215	8.84	0.00891
Fe	3.9	0.07	0.00007
Cl	10.6	0.30	0.00030
$\text{SO}_4^*$	2017	21.00	0.02116
$\text{SiO}_2^{**}$	52	0.87	0.00087
$\text{HCO}_3^-$	6	0.10	0.00010
F	0.95	0.05	0.00005
Ionic Strength	-	-	0.0840

\*Total sulfate after acidification with  $\text{H}_2\text{SO}_4$  to pH = 5.5.

\*\* $\text{HCO}_3^-$  content after acidification.

concentrates as high as 6X are tabulated in Table II. These solubilities at 25°C are converted to formal solubility product quotients, which are plotted on a logarithmic scale as a function of  $I^{1/2}/(1+1.5I^{1/2})$  in Figure 3. The dashed line is the curve associated with the solubilities in aqueous NaCl solution, discussed in Section 3.1, while the continuous curve represents the best curve drawn through the experimental data. The figure shows that  $Q_{fsp}$  in a given concentrate of this brackish water is slightly higher than in a sodium chloride solution of the same ionic strength. This greater solubility in the brackish well water is due largely to the presence of  $Mg^{2+}$  ions which form  $MgSO_4^0$  neutral molecules or ion pairs, thereby reducing the  $SO_4^{2-}$  ion concentration. This reduction requires the dissolution of additional  $CaSO_4 \cdot 2H_2O$  to satisfy the value of  $Q_{fsp}$ .<sup>1</sup> The results given in Table II and shown in Figure 3 were determined by two different investigators, with each investigator preparing solutions and making analyses independent of the other investigator. Most of the duplicate determinations for the solubilities of  $CaSO_4 \cdot 2H_2O$  agree within  $\pm 1\%$ .

Figure 4 (see Table IVA) indicates the effect which the presence of Calgon at the low level of 5 ppm/C.F. (concentration factor) has upon the solubility of  $CaSO_4 \cdot 2H_2O$  in Gillette water. Although the effect is not great, it seems remarkable that Calgon in trace quantities produces a discernible apparent increase in the solubilities in all concentrates of the well water and in water alone. The solubilities in the presence of Calgon are not nearly as reproducible as those obtained in the absence of Calgon; it is not unusual for the former values to vary by 25% and at times by a factor of two.

Table II. Comparison of the Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  in Acidified Concentrates of Gillette, Wyoming, Brackish Well Water Obtained by Two Different Investigations

Concentration Factor	$\text{CaSO}_4$ (m)	$\text{SO}_4$ (total) (m)	$Q_{\text{fsp}}^*$	$I^{**}$ (molal units)	$I^{1/2}/(1+1.5I^{1/2})$
By Investigator #1					
1	0.0133	0.0237	$3.14 \times 10^{-4}$	0.0941	0.210
1.5	0.0123	0.0278	3.41	0.110	0.222
2	0.0119	0.0327	3.90	0.130	0.234
2.5	0.0114	0.0374	4.27	0.148	0.244
3	0.0110	0.0422	4.65	0.167	0.253
3.5	0.0108	0.0471	5.07	0.186	0.262
4	0.0104	0.0519	5.41	0.205	0.270
5	0.00980	0.0617	6.04	0.244	0.284
6	0.0102	0.0725	7.36	0.286	0.297
$\text{H}_2\text{O}$	0.0151	0.0151	2.28	0.0604	0.180
By Investigator #2					
1	0.0132	0.0236	$3.11 \times 10^{-4}$	0.0927	0.209
2	0.0120	0.0328	3.95	0.129	0.233
4	0.0113	0.0530	5.99	0.208	0.271
6	0.0102	0.0726	7.37	0.285	0.297
$\text{H}_2\text{O}$	0.0152	0.0152	2.31	0.0608	0.181

\* $Q_{\text{fsp}}$  = formal solubility product quotient = total calcium molality x total sulfate molality.

\*\*I = ionic strength

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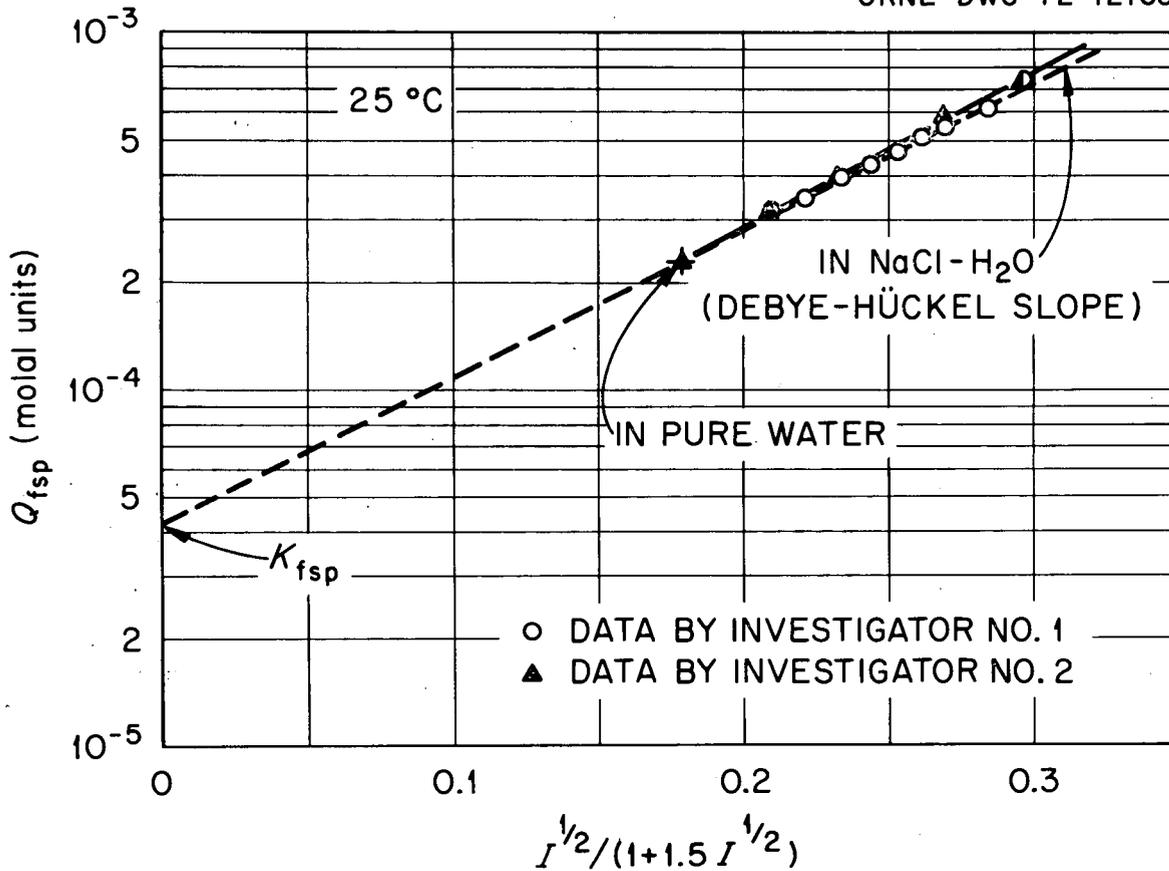


Figure 3 Formal Solubility Product Quotients of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Aqueous NaCl Solutions and Concentrates of Gillette, Wy., Brackish Well Water vs  $I^{1/2}/(1+1.5 I^{1/2})$  at 25 °C.

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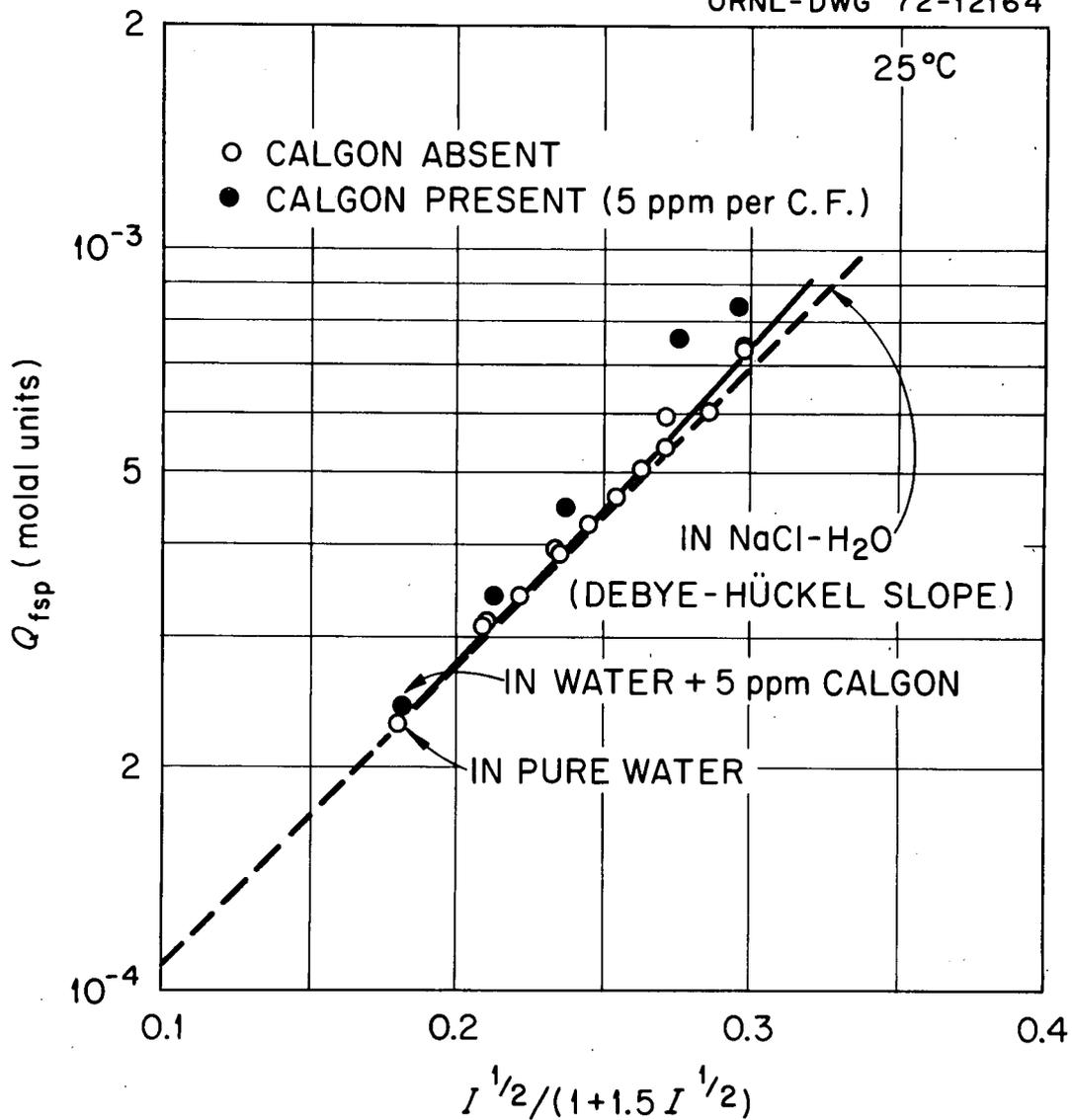


Figure 4 Comparison of Formal Solubility Product Quotients as a Function of  $I^{1/2}/(1+1.5 I^{1/2})$  for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25 °C in Concentrates of Gillette, Wy., Brackish Well Water With and Without Calgon Present.

The polyethylene bottles containing excess solid  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Gillette water concentrates, and Calgon from the preceding experiment were left undisturbed at room temperature for 12 days. At the end of this period they were placed again in the water bath at  $25^\circ\text{C}$  and "re-equilibrated" by rocking for 19 hours. The results in Table IVA2, when compared with those obtained by investigator No. 2 in Table II, appear now to have no Calgon present since the solubilities in the two tables are nearly the same. Apparently, the polyphosphate, which is the "active" ingredient in Calgon, hydrolyzed to form the ortho-phosphate upon standing at room temperature over an extended period of time. Although tertiary calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is insoluble, the concentration of phosphate ion from the hydrolysis of Calgon precipitates too little, if any, calcium to make the decrease in concentration of calcium detectable by our analytical method.

A depletion of the calcium concentration of Gillette water before using it as a feed for the plant has been considered. It then would be possible to concentrate the well water to a greater extent, and thus recover more potable water per unit volume of feed before  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  precipitates. The data in Table II, by investigator No. 1, for the solubility at  $25^\circ\text{C}$  of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Gillette, Wyoming, brackish well water are plotted in Figure 5 to show the effect of calcium depletion upon the degree to which solutions can be concentrated before precipitation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  occurs. The lines radiating from the origin and through concentration factor (C.F.) equal 1 represent the increase in concentration of dissolved  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  as the C.F.'s for the solutions increase, i.e., as more water is removed from the systems.<sup>7</sup> Each line denotes a different concentration of calcium in the starting or feed solution (C.F. = 1). The point at which a given line intersects the solubility

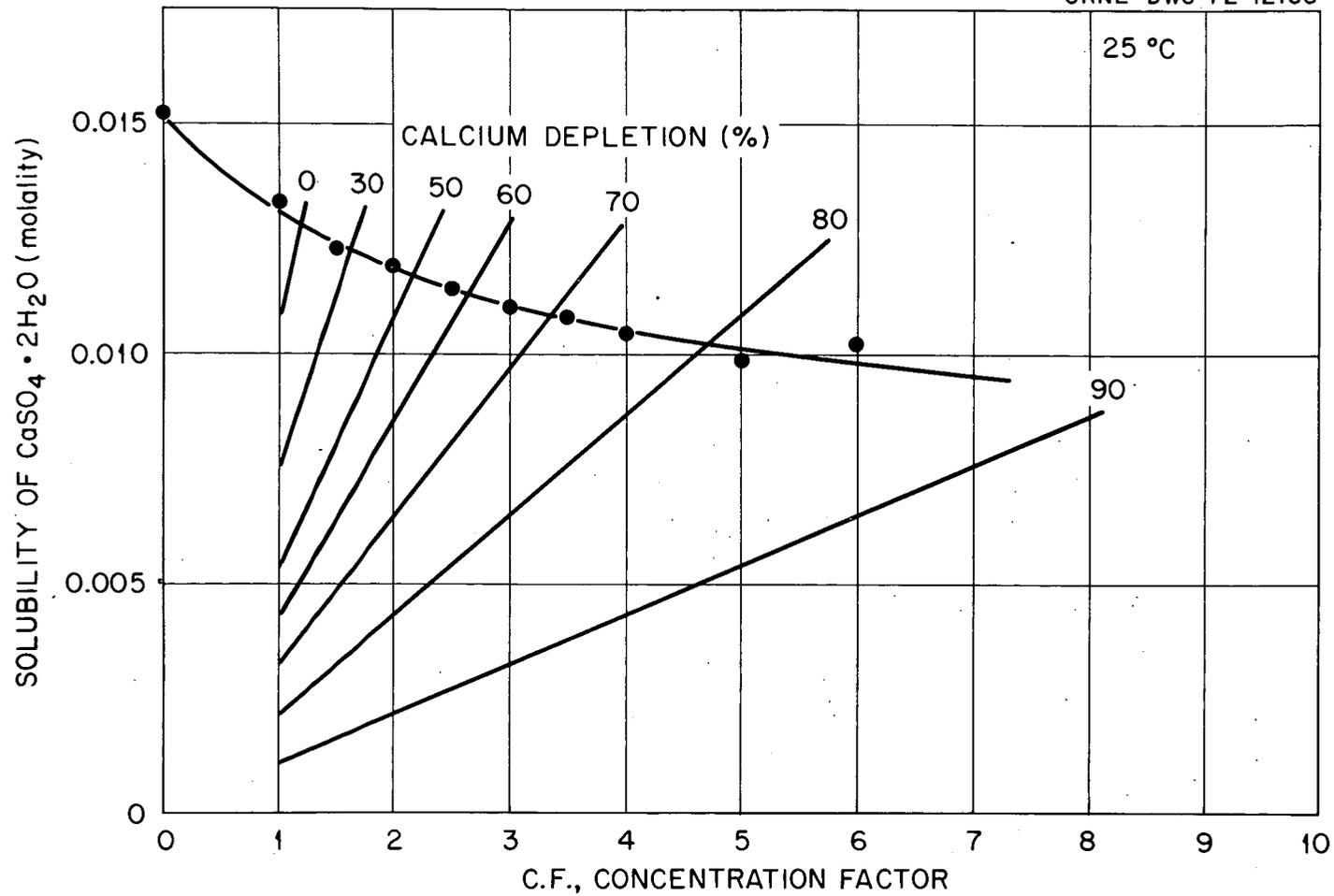


Figure 5 Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25 °C in Concentrates of Gillette, Wy., Brackish Well Water.

curve for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  indicates the concentration factor at which  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  precipitates from that particular solution. The computer program published earlier<sup>1</sup> was modified slightly to enable calculations of the saturation concentration factors at various levels of calcium depletion in this same brackish well water (see Table VA). A comparison of the results read from Figure 5 with the calculated values is given in Table III. Although the agreement between calculated and experimental values of C.F. is not as good as one might hope, they do predict a limited concentration range over which precipitation may be expected to take place.

These results show that the water taken directly from the well can be concentrated very little before precipitation begins. Nearly 50% of the initial calcium must be removed from this brackish well water to enable the saturation C.F. to be doubled. (Since ion exchange replacement of calcium by sodium is the method likely to be used in depleting calcium from a brackish water, appropriate changes were made in the ionic strengths before saturation C.F.'s were calculated.)

The percent maximum water recovery is calculated using the following equation

$$\text{Maximum water recovery (\%)} = 100\% - 100\% / \text{sat'n. C.F.} \quad (1)$$

From Table III it is apparent that only about 17% of the initial feed water can be recovered as potable water before  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  precipitates if no calcium is depleted from the brackish well water.

It is of interest to observe the effect of dissolved magnesium salts upon the saturation C.F. A plot of the calculated saturation C.F. both as a function of (a) calcium depletion and of (b) equal depletion of calcium and magnesium in Figure 6 reveals that Gillette water can be concentrated to a slightly greater extent before  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  precipitates if only the calcium is depleted rather

Table III. Effect at 25°C of Calcium Depletion on Maximum Water Recovery and Saturation Concentration Factor for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Acidified Concentrates of Gillette, Wy., Brackish Well Water

Calcium Depletion %	Saturation C.F.		Maximum Water Recovery*	
	Calc.	Exp.	Calc.	Exp.
0	1.22	1.19	18.0	16.0
20	1.43	-	30.1	--
30	1.56	1.64	35.9	39.0
50	1.99	2.16	49.7	53.7
60	2.35	2.67	57.4	62.5
70	2.93	3.36	65.9	70.2
80	4.00	4.70	75.0	78.7
90	6.97	-	85.7	--

\* Calculated and experimental values here are the results obtained upon substituting the calculated and experimental C.F. values, respectively, into eq. 1.

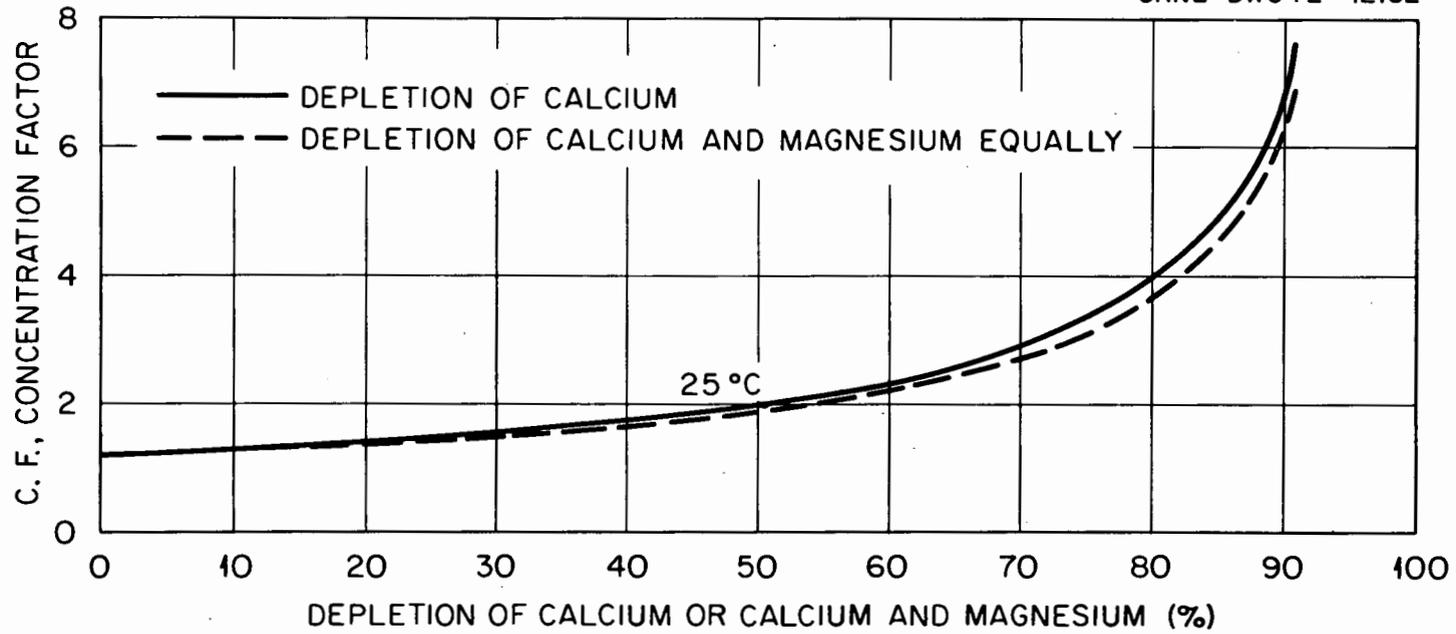


Figure 6 Effect of Calcium and Calcium Plus Magnesium Depletion upon the Saturation Concentration Factor of Gillette, Wy., Brackish Well Water at 25 °C.

than if calcium and magnesium are both depleted. This behavior results from the formation of  $\text{MgSO}_4^0$  ion pairs when magnesium is present, which effectively lowers the concentration of  $\text{SO}_4^{2-}$  ions and permits a slightly higher concentration of  $\text{Ca}^{2+}$  ions to remain in solution.<sup>1,8</sup> At 60% depletion (Figure 6), the saturation concentration factors with and without equal removal of magnesium vary only by ~6%, while the maximum water recovery at this 60% depletion is calculated to be ~57% when calcium is depleted and ~55% when calcium and magnesium are both depleted (see equation 1). (For ionic strength considerations, it was assumed that each calcium or magnesium ion removed was replaced by two sodium ions. Also, a reading of 20%, for example, on the abscissa for the depletion of calcium and magnesium means that 20% of the calcium and 20% of the magnesium have been removed from the initial well water.)

It was desirable also to calculate the effect of concentration polarization upon the saturation concentration factors in Gillette water as the concentration of calcium is reduced in the well water. The concentration polarization factor (C.P.F.) is defined as the ratio of the concentration of a given ion at the wall or membrane surface to that in the bulk solution. Although the C.P.F. is known to differ for each ion, the approximation was made that it is the same for all ions in this particular water in order to simplify the calculations. The calculated results (see Table VIA) for Gillette water are plotted in Figure 7. Where no calcium is removed initially and the C.P.F. has increased from 1.0 to 1.5, the saturation C.F. is decreased from 1.22 to 0.82, respectively. The maximum water recovery calculated with equation 1 is reduced from ~18% to 0%. At 50% calcium depletion, as the C.P.F. increases from 1.0 to 1.5, the maximum water recovery decreases from ~50% to ~25%. Figure 6 shows that the removal of both calcium and magnesium from the well water makes so little difference in the saturation C.F. values from those when only calcium

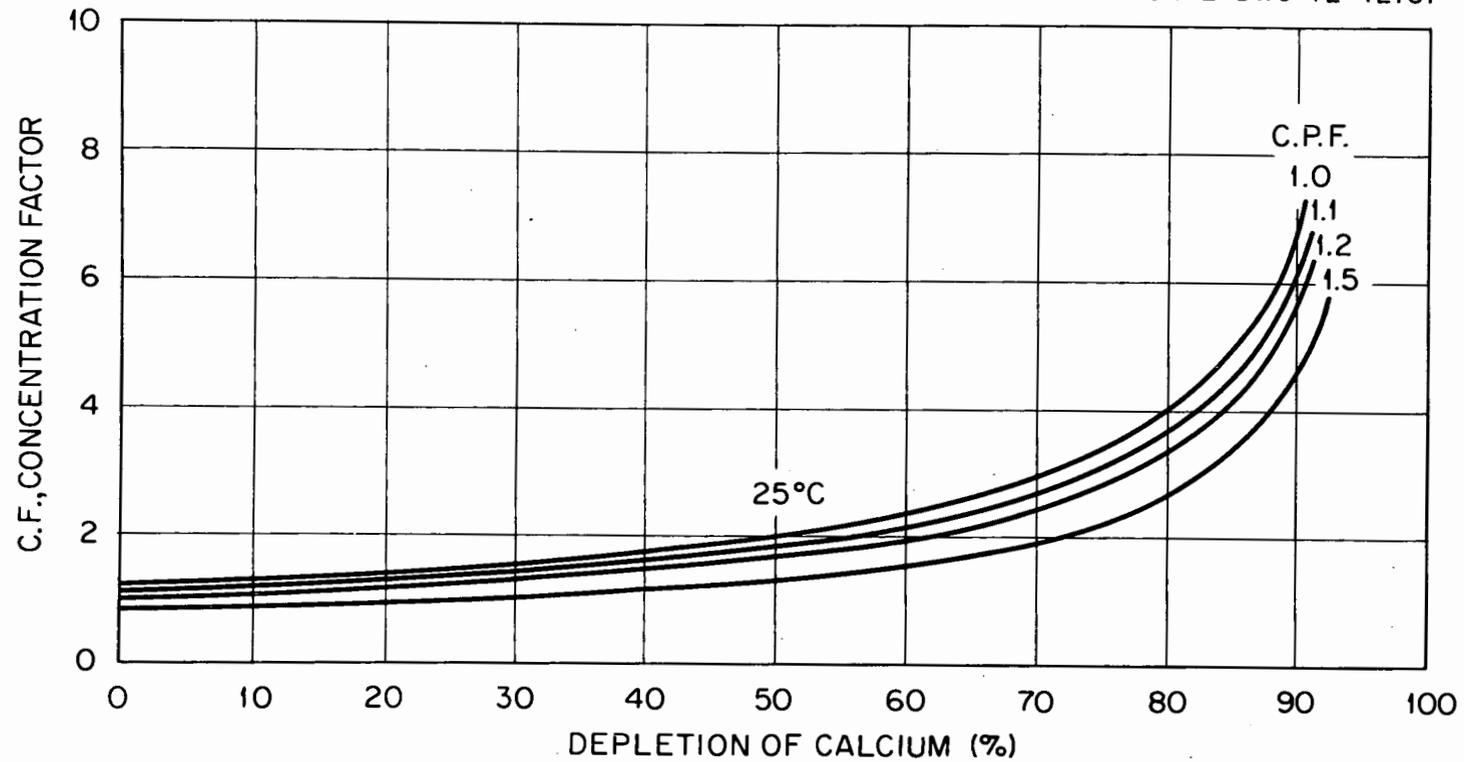


Figure 7 Effect of Removing Calcium from Gillette, Wy. Brackish Well Water upon the Saturation Concentration Factor at Various Concentration Polarization Factors (C.P.F.) and 25°C.

is removed that the former effect was not considered here.

3.3 Webster, South Dakota, Brackish Well Water - The composition of the synthesized brackish well water made to simulate the Webster, South Dakota, water (see Table IA) is given in Table IV. The dominant cations in decreasing order of concentration are sodium, magnesium, calcium, and potassium, with only trace amounts of manganese and iron present, while sulfate ion is the anion found in greatest concentration, by far. The solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  in this water and its concentrates to 8X, determined after two different times and by two different equilibration methods, are presented in Table V. The results are so nearly identical for the two different methods that equilibrium in the system is practically assured. The formal solubility product quotients ( $Q_{\text{fsp}}$ ) from part 1 of Table V are plotted on a logarithmic scale in Figure 8 as a function of  $I^{1/2}(1+1.5I^{1/2})$ , with the solubilities in  $\text{NaCl-H}_2\text{O}$  serving as the reference line (see Section 3.1). The higher solubilities in Webster water than in  $\text{NaCl-H}_2\text{O}$  solutions at the same ionic strength reflect the presence of magnesium ions in the former which associate with  $\text{SO}_4^{2-}$  ions to form  $\text{MgSO}_4^0$  ion pairs. Additional  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  thereby dissolves to satisfy the value of  $Q_{\text{fsp}}$  as explained in Section 3.2 and elsewhere.<sup>1,8</sup>

Figure 9 shows the effects of added Calgon upon the formal solubility product quotients of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (see Table VIIA). The presence of Calgon in Webster water appears to increase somewhat the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . This increase is quite regular and reproducible as the concentration of Calgon is increased from 5 ppm in 1X water to 40 ppm in 8X water (5 ppm/C.F.). However, Figure 9 (again, see Table VIIA) clearly indicates that a 4X increase in Calgon to 20 ppm/C.F. does not lead to a 4X increase in solubility (or a corresponding 16X increase in  $Q_{\text{fsp}}$ ); in fact, there is an obvious, erratic or irregular effect upon solubility. These results in the presence of 20 ppm

Table IV. Molal Composition of Synthetic Webster, South Dakota, Brackish Well Water Used for Solubility Studies of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  and pH of 5.5

Component	Units of Composition		
	(ppm)	(mmoles/l)	(molality)
Na	118	5.14	0.00518
K	16	0.41	0.00041
Ca	140	3.49	0.00353
Mg	105	4.32	0.00436
Mn	1.1	0.02	0.00002
Fe	0.3	0.0054	0.00001
Cl	9.9	0.28	0.00028
$\text{SO}_4^*$	1009	10.51	0.01062
$\text{SiO}_2$	51	0.85	0.00086
$\text{HCO}_3^{**}$	~35	~ 0.57	~0.00058
Ionic Strength	-	-	0.0409

\* Total sulfate after acidification with  $\text{H}_2\text{SO}_4$  to pH = 5.5

\*\*  $\text{HCO}_3^-$  content after acidification.

Table V. Comparison of the Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  Obtained at  $25^\circ\text{C}$  by Two Different Methods of Equilibrating this Solid with Concentrates of Webster, S. Dak., Brackish Well Water

Concentration Factor	$\text{CaSO}_4$ (m)	$\text{SO}_4$ (total) (m)	$Q_{\text{fsp}}^*$	$I^{**}$	$I^{1/2}/(I+1.5I^{1/2})$ (molal units)
1. Phases equilibrated by rocking overnight (16 hr)					
1	0.0136	0.0207	$2.82 \times 10^{-4}$	0.0812	0.200
1.5	0.0132	0.0238	3.13	0.0926	0.209
2	0.0128	0.0269	3.43	0.104	0.218
3	0.0121	0.0333	4.03	0.128	0.233
4	0.0118	0.0401	4.74	0.154	0.247
5	0.0117	0.0470	5.48	0.180	0.259
6	0.0117	0.0542	6.32	0.207	0.270
7	0.0116	0.0612	7.12	0.233	0.280
8	0.0113	0.0677	7.62	0.258	0.288
$\text{H}_2\text{O}$	0.0152	0.0152	2.31	0.0608	0.180
2. Phases equilibrated by stirring for 1 hr.					
1	0.0137	0.0207	$2.84 \times 10^{-4}$	0.0813	0.200
1.5	0.0132	0.0238	3.13	0.0927	0.209
2	0.0129	0.0270	3.48	0.105	0.218
3	0.0120	0.0332	3.99	0.128	0.233
4	0.0118	0.0400	4.71	0.153	0.247
5	0.0117	0.0470	5.49	0.180	0.259
6	0.0116	0.0540	6.28	0.206	0.270
7	0.0116	0.0611	7.12	0.233	0.280
8	0.0114	0.0680	7.78	0.259	0.289
$\text{H}_2\text{O}$	0.0151	0.0151	2.27	0.0604	0.179

\*  $Q_{\text{fsp}}$  = formal solubility product quotient = total calcium molality x total sulfate molality.

\*\* I = ionic strength.

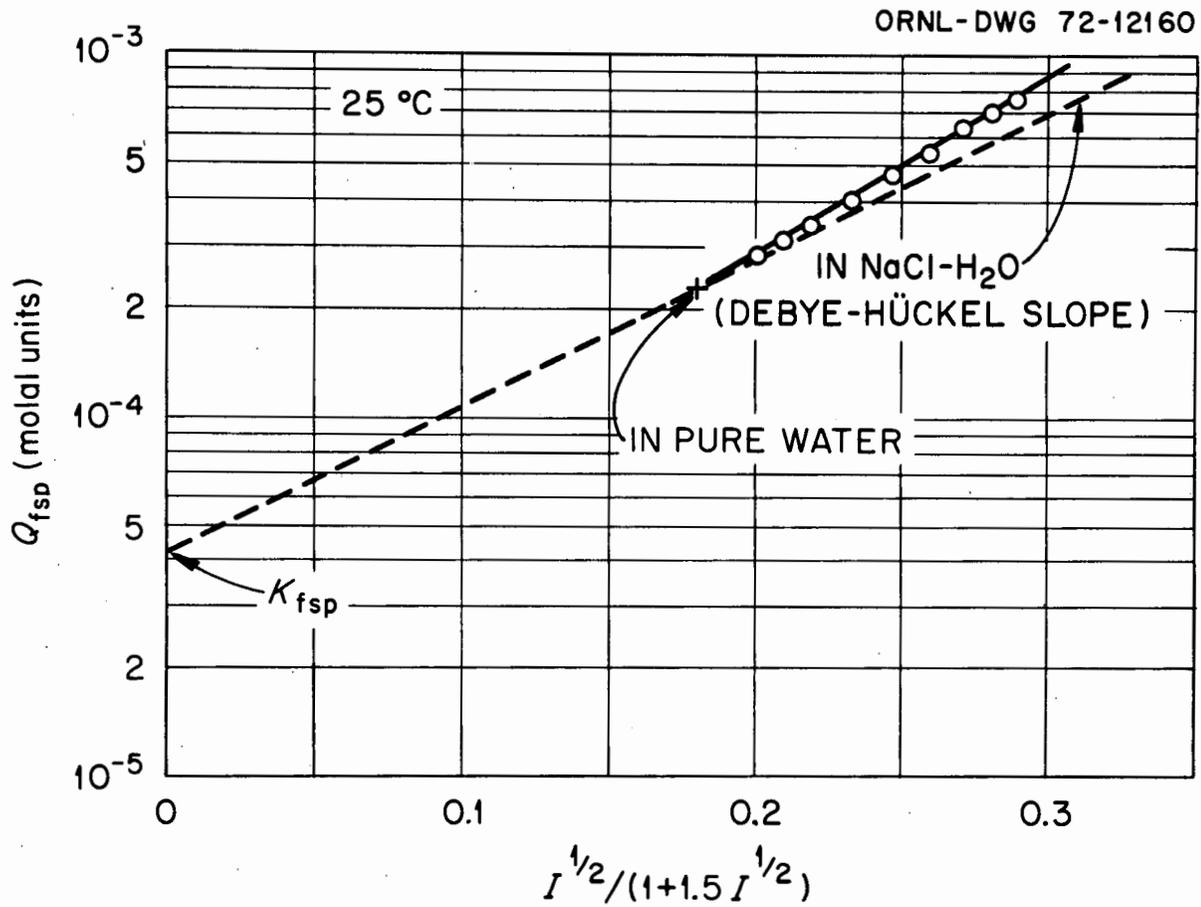


Figure 8 Formal Solubility Product Quotients of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Aqueous NaCl Solutions and Concentrates of Webster, S. Dak., Brackish Well Water vs  $I^{1/2}/(1+1.5 I^{1/2})$  at 25 °C.

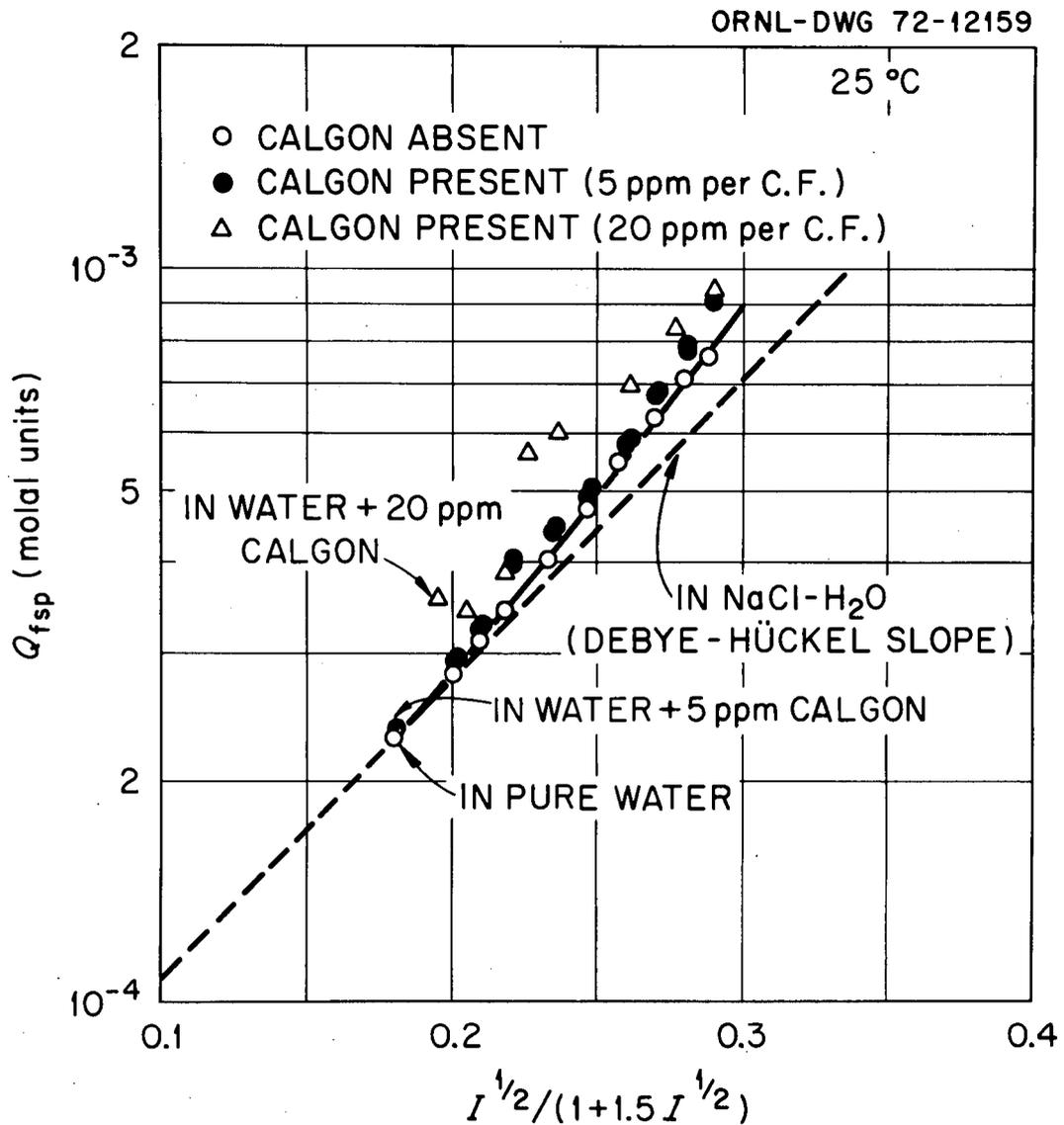


Figure 9 Comparison of Formal Solubility Product Quotients as a Function of  $I^{1/2}/(1+1.5 I^{1/2})$  for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25 °C in Concentrates of Webster, S. Dak., Brackish Well Water With and Without Calgon Present.

Calgon/C.F. were obtained by equilibrating the phases overnight (16 hr.) with gentle rocking. Table VIIIA of the Appendix shows that an experimental run where stirring for 1 hr. was used to equilibrate the phases did not produce any more regular pattern to the solubility data.

The solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  in Webster brackish well water and its concentrates taken from Table V, Part 1, are plotted in Figure 10 as a function of the concentration factor. The point of intersection between the experimental solubility curve and a given straight line indicates the extent to which the initial well water, from which a given percentage of the calcium has been removed, can be concentrated before  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is precipitated.<sup>7</sup> Both experimentally derived and calculated (see Section 3.2; also Tables VIIIA and XIIB) values for the saturation C.F. are given in Table VI. Although there appears to be a moderate difference between the two sets of values for the saturation C.F., the experimental and calculated values for maximum water recovery (Table VI) are in good agreement. The results in Table VI show that the initial well water can be concentrated by a factor of 3.3, or 70% of the water may be recovered before  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  can be expected to precipitate. Or if the initial calcium content of the well water is depleted by 50%, about 83% of the water is recoverable.

Figure 11 (Table VIIIA) shows that it makes little difference in the saturation C.F. whether calcium alone or equal amounts of calcium and magnesium are removed from the well water; at 50% depletion the two calculated values vary only by ~5%. Also, the maximum water recovery is 82% when calcium **only** is depleted by 50%, and 81% when calcium and magnesium are depleted equally by 50%.

The effect of different concentration polarization factors (C.P.F.) upon the saturation C.F. of this brackish water, as the concentration of calcium is reduced, is depicted in Figure 12 (Table IXA). When no calcium is removed from the brackish well water, the saturation C.F. decreases from 3.32 to 2.21 as the C.P.F.

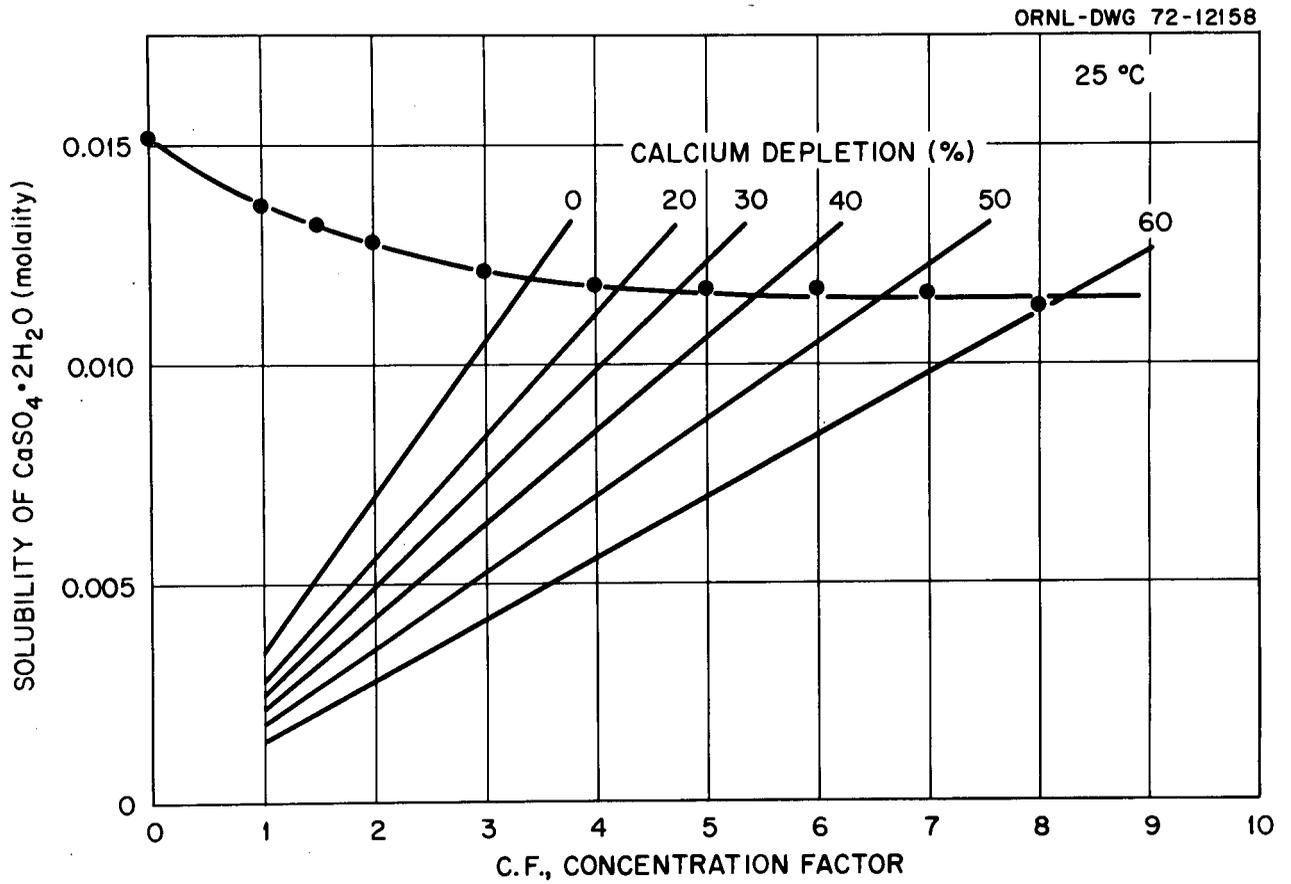


Figure 10 Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25 °C in Concentrates of Webster, S. Dak., Brackish Well Water.

Table VI. Effect of Calcium Depletion at 25°C on Maximum Water Recovery and Saturation Concentration Factor for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Concentrates of Webster, S. Dak., Brackish Well Water

Calcium Depletion (%)	Saturation C.F.		Maximum Water Recovery* (%)	
	Calc.	Exp.	Calc.	Exp.
0	3.32	3.38	69.9	70.4
20	3.90	4.22	74.4	76.3
30	4.30	4.74	76.7	78.9
40	4.83	5.44	79.3	81.6
50	5.56	6.56	82.0	84.8
60	6.59	8.22	84.8	87.8
70	8.25	--	87.9	--

\* Calculated and experimental values here are the results obtained upon substituting the calculated and experimental C.F. values, respectively, into eq. 1.

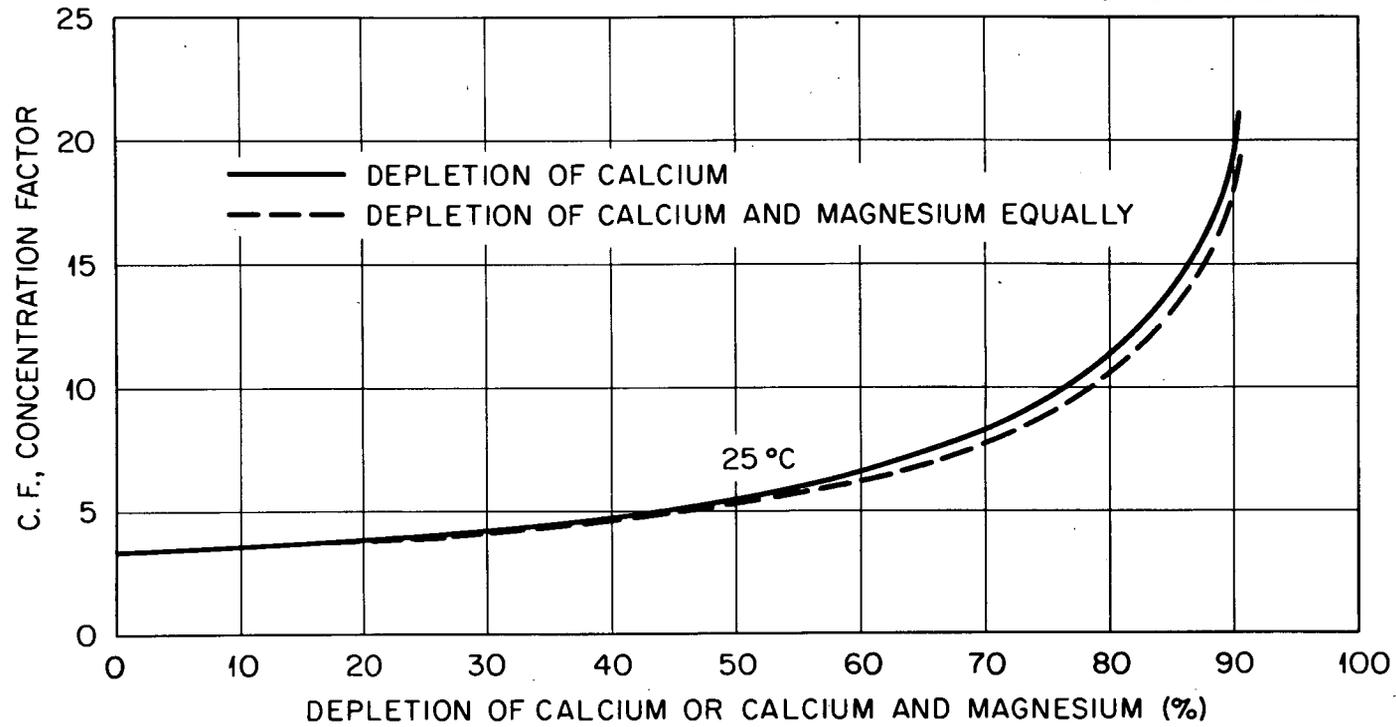


Figure 11 Effect of Calcium and Calcium Plus Magnesium Depletion upon the Saturation Concentration Factor of Webster, S. Dak., Brackish Well Water at 25°C.

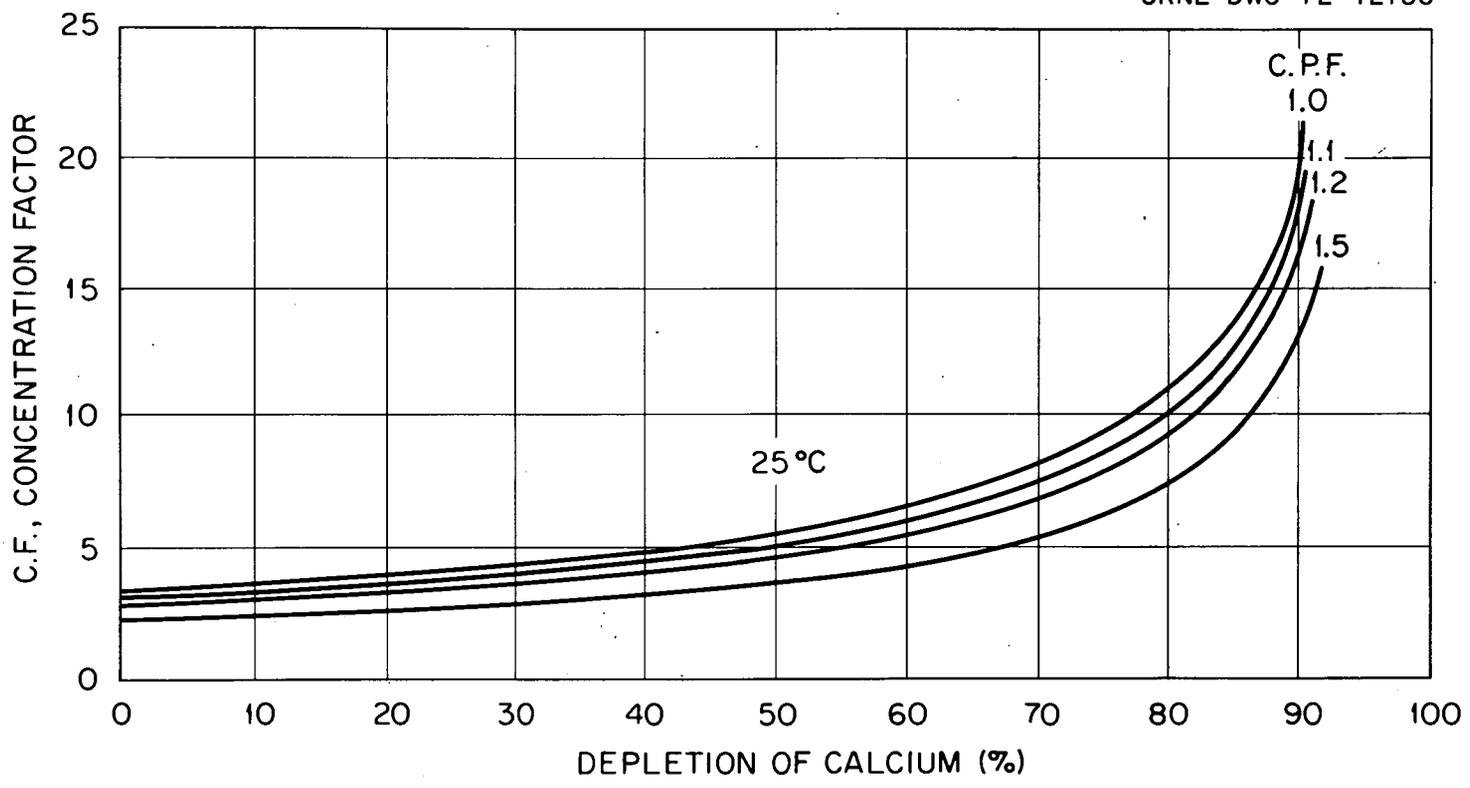


Figure 12 The Effect of Removing Calcium from Webster S. Dak., Brackish Well Water upon the Saturation Concentration Factor at Various Concentration Polarization Factors (C.P.F.) and 25°C.

increases from 1.0 to 1.5; or, put another way, the maximum water recovery decreases from 70% to 55% as the C.P.F. rises from 1.0 to 1.5. At 50% calcium depletion the maximum water recovery decreases from ~82% to ~73% as the C.P.F. rises from 1.0 to 1.5.

3.4 Wellton-Mohawk Post-Irrigation Canal in Arizona - Table IA gives the analysis of a water taken from the Wellton-Mohawk Canal in Arizona. This water originates from irrigation waters that have percolated through the soil to wells from which they have been pumped for disposal in the canal. The composition of the synthetic post-irrigation water which closely approximates the Wellton-Mohawk water and which was used for the solubility studies is given in Table VII. Of the cations, sodium is present in the highest concentration along with appreciable quantities of calcium and magnesium; chloride is the predominant anion while the sulfate ion molarity is approximately 1/3 that of the  $\text{Cl}^-$  ion. The solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25°C in this water and its concentrates to 8X are listed in Table VIII. A plot of the  $Q_{\text{fsp}}$ 's on the logarithmic scale vs.  $I^{1/2}/(1+1.5I^{1/2})$  in Figure 13 indicates clearly that these values are very nearly the same as those obtained earlier in  $\text{NaCl-H}_2\text{O}$  solutions. The slightly higher values for  $Q_{\text{fsp}}$  in this post-irrigation water, essentially a saline water, are attributed to the presence of magnesium in the water which forms  $\text{MgSO}_4^0$  ion pairs, thus reducing the  $\text{SO}_4^{2-}$  ion concentration and allowing additional  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to dissolve (see Section 3.2)<sup>1,8</sup>

The effect of added Calgon in apparently increasing the  $Q_{\text{fsp}}$ 's at the different concentration levels is observed in Figure 14 (Table XA). However, the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in the concentrates of Wellton-Mohawk water above about 2X does not seem to be affected any more by Calgon at the concentration of 20 ppm/C.F. than at the 5 ppm/C.F. level. In the water concentrates below 2X and in pure water itself, Calgon at 20 ppm/C.F. increases the apparent solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  more than does Calgon at 5 ppm/C.F., but the increase is not by the factor of 4 which the Calgon concentration undergoes.

Table VII. Molal Composition of Synthetic Wellton-Mohawk, Arizona, Post-irrigation Water Used for Solubility Studies of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25°C and pH of 5.5

Component	Units of Composition		
	(ppm)	(mmoles/l)	(molality)
Na	933	40.6	0.04077
K	16	0.41	0.00041
Ca	244	6.09	0.00612
Mg	88	3.62	0.00364
B	1.7	0.16	0.00016
Cl	1210	34.13	0.03430
$\text{SO}_4^*$	1229	12.80	0.01287
$\text{SiO}_2$	28	0.47	0.00047
$\text{HCO}_3^{**}$	4.4	0.07	0.00007
$\text{NO}_3$	8	0.13	0.00013
F	2	0.11	0.00011
$\text{PO}_4$	2.7	0.028	0.00003
Ionic strength	--	--	0.0838

\*Total sulfate after acidification with  $\text{H}_2\text{SO}_4$  to pH = 5.4.

\*\* $\text{HCO}_3^-$  content after acidification.

Table VIII. Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25°C in Acidified, Synthetic Wellton-Mohawk, Ariz., Post-irrigation Water and Its Concentrates

Concentration Factor	$\text{CaSO}_4$ (m)	$\text{SO}_4$ (total) (m)	$Q_{\text{fsp}}^*$	$I^{**}$	$I^{1/2}/(1+1.5I^{1/2})$ (molal units)
1	0.0160	0.0228	$3.66 \times 10^{-4}$	0.124	0.230
1.5	0.0163	0.0264	4.31	0.154	0.247
2	0.0165	0.0300	4.95	0.185	0.261
3	0.0167	0.0371	6.22	0.246	0.284
4	0.0167	0.0439	7.34	0.305	0.302
5	0.0170	0.0511	8.70	0.367	0.317
6	0.0170	0.0579	9.84	0.426	0.330
8	0.0168	0.0700	11.8	0.534	0.349
$\text{H}_2\text{O}$	0.0152	0.0152	2.30	0.0608	0.180

\* $Q_{\text{fsp}}$  = formal solubility product quotient = total calcium molality x total sulfate molality.

\*\* $I$  = ionic strength.

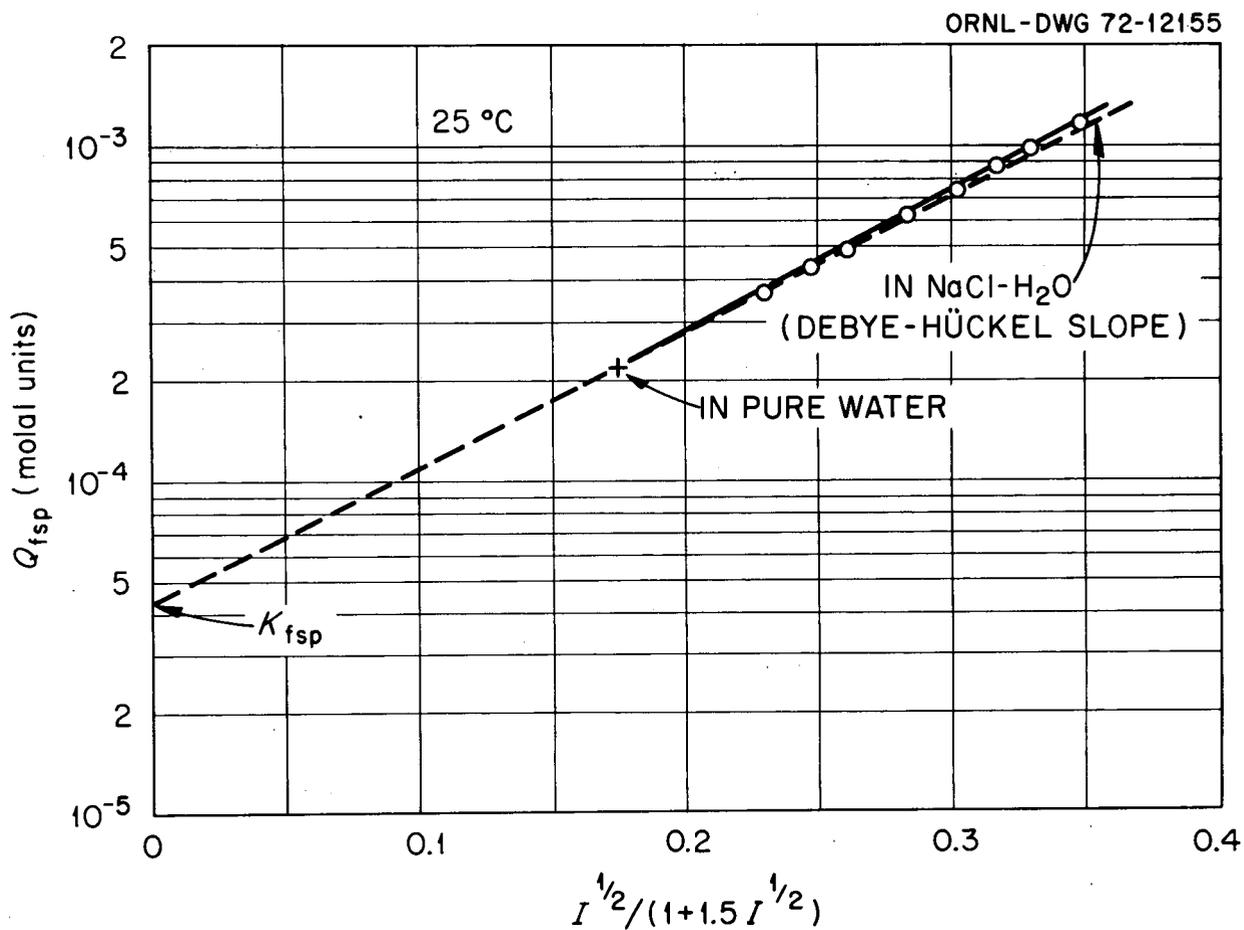


Figure 13 Formal Solubility Product Quotients of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Aqueous NaCl Solutions and Concentrates of Wellton-Mohawk., Ariz., Post-Irrigation Water vs  $I^{1/2}/(1+1.5 I^{1/2})$  at 25 °C.

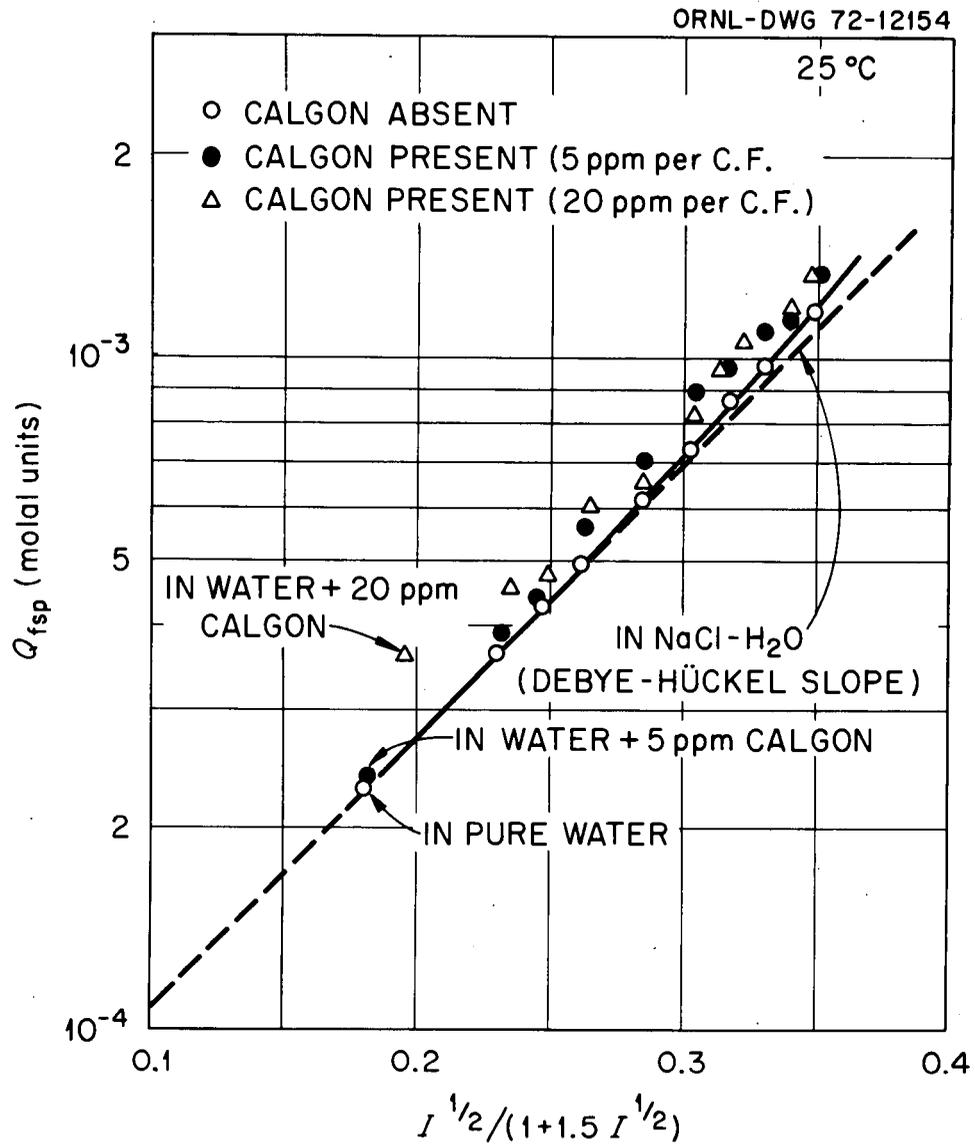


Figure 14 Comparison of the Formal Solubility Product Quotients for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25 °C in Concentrates of Wellton-Mohawk, Ariz., Post-Irrigation Water With and Without Calgon Present.

Figure 15 represents a determination of the extent to which Wellton-Mohawk water may be concentrated, after various degrees of calcium depletion (0 - 70%), before precipitation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  begins. This determination is based on the experimental solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  found for this water (Table VIII). These saturation concentration factors (C.F.) are compared in Table IX with those calculated after modifying the computer program (Table XIII A) published earlier.<sup>1</sup> It can be seen that the original water can be concentrated nearly 3X at 25°C before precipitation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is expected. That is, 63% of the water can be recovered from the original Wellton-Mohawk post-irrigation water before  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  will precipitate at 25°C. The water recovery can be increased to about 80% at the cost of removing 50% of the initial calcium content. The agreement between experimental and calculated saturation C.F.'s is good up to the point where 30% of the initial calcium is removed; beyond this point the divergence between the two sets of results becomes rather great. Of course, the experimental values are preferred for use.

The curves in Figure 16 (Table XIA) are drawn through the saturation concentration factors calculated for this water after various amounts of calcium, or calcium and magnesium, were removed from the original Wellton-Mohawk water. A significantly increased saturation C.F. appears unattainable for Wellton-Mohawk water by removing equal amounts of both calcium and magnesium instead of calcium alone. At 20% calcium depletion, a maximum water recovery of 69.5% is calculated versus a 69.9% recovery when both calcium and magnesium are depleted by 20%.

The effect of calcium depletion upon the saturation C.F.'s was calculated and is shown graphically in Figure 17 for various concentration polarization factors. Throughout the range of calcium depletion plotted here, the value for the C.F. at a C.P.F. of 1.5 is approximately 2/3 that at a C.P.F. of 1.0, when

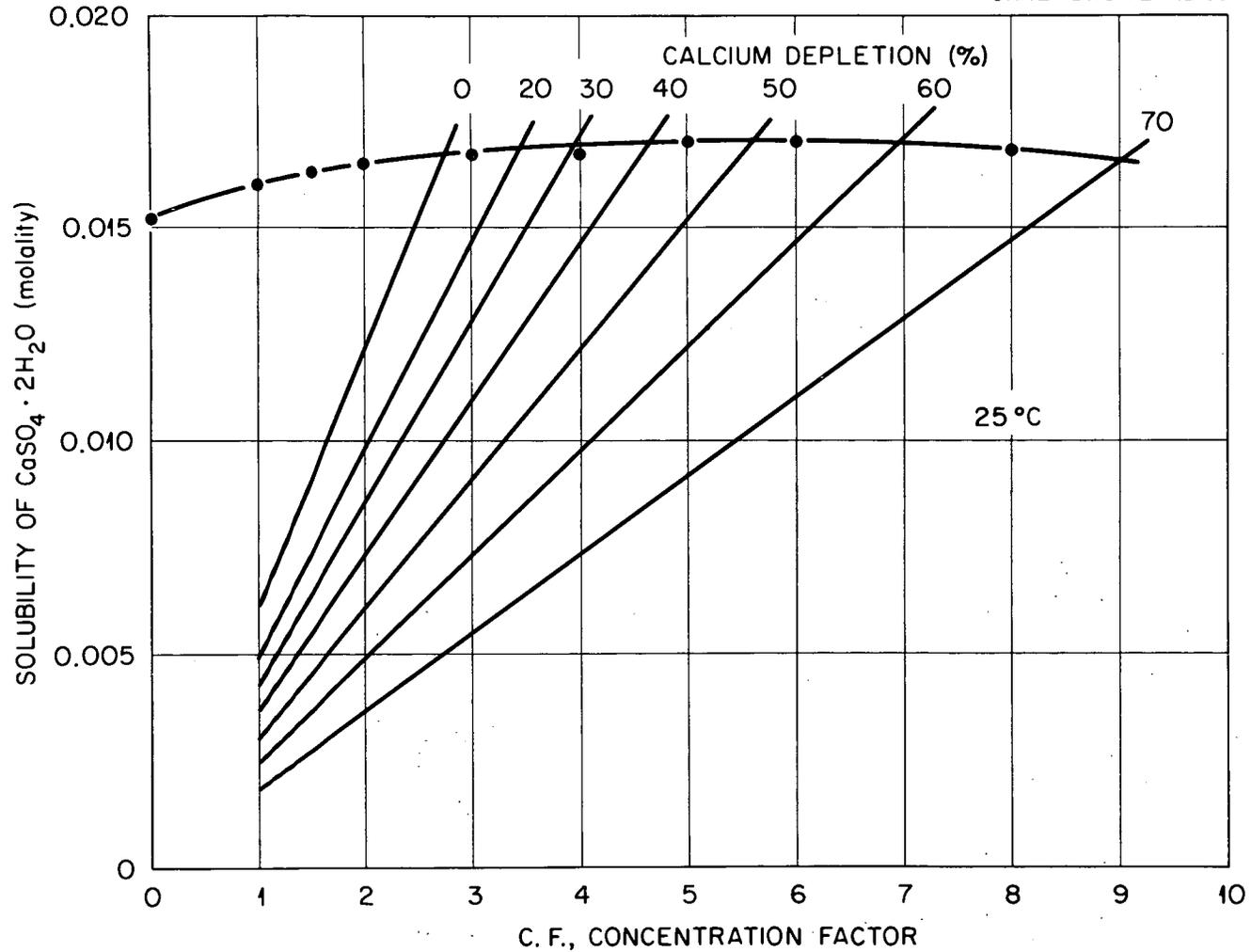


Figure 15 Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25°C in Concentrates of Wellton - Mohawk, Ariz., Water.

Table IX. Effect of Calcium Depletion at 25°C Maximum Water Recovery and Saturation Concentration Factor for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in a Wellton-Mohawk, Ariz., Post-irrigation Water

Calcium Depletion (%)	Saturation C.F.		Maximum Water Recovery* (%)	
	Calc.	Exp.	Calc.	Exp.
0	2.79	2.72	64.2	63.2
20	3.32	3.45	69.9	71.0
30	3.78	3.96	73.5	74.7
40	4.16	4.66	76.0	78.5
50	4.81	5.62	79.2	82.2
60	5.74	6.96	82.6	85.6
70	7.22	9.02	86.1	88.9

\*Calculated and experimental values here are the results obtained upon substituting the calculated and experimental C.F. values, respectively, into eq. 1.

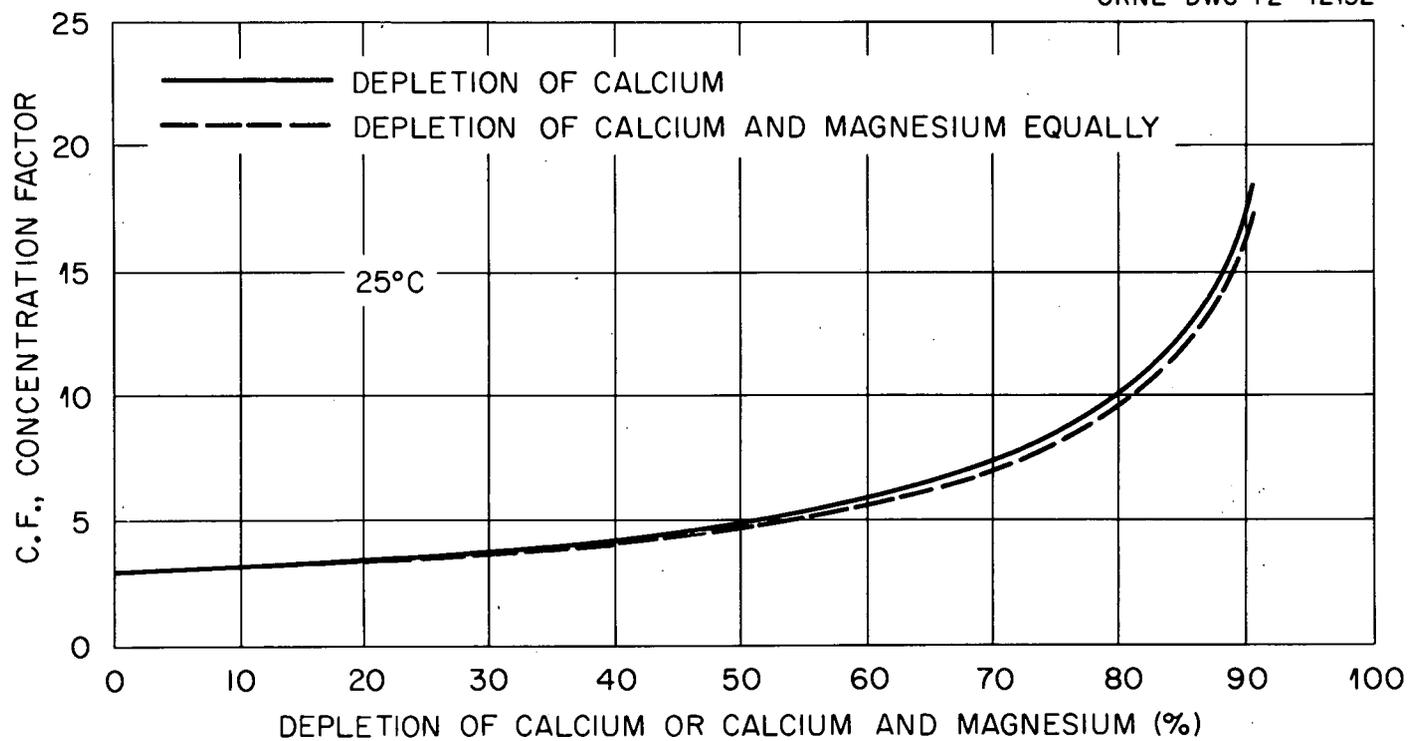


Figure 16 Effect of Calcium and Calcium Plus Magnesium Depletion Upon the Saturation Concentration Factor of Wellton - Mohawk, Ariz., Water at 25°C.

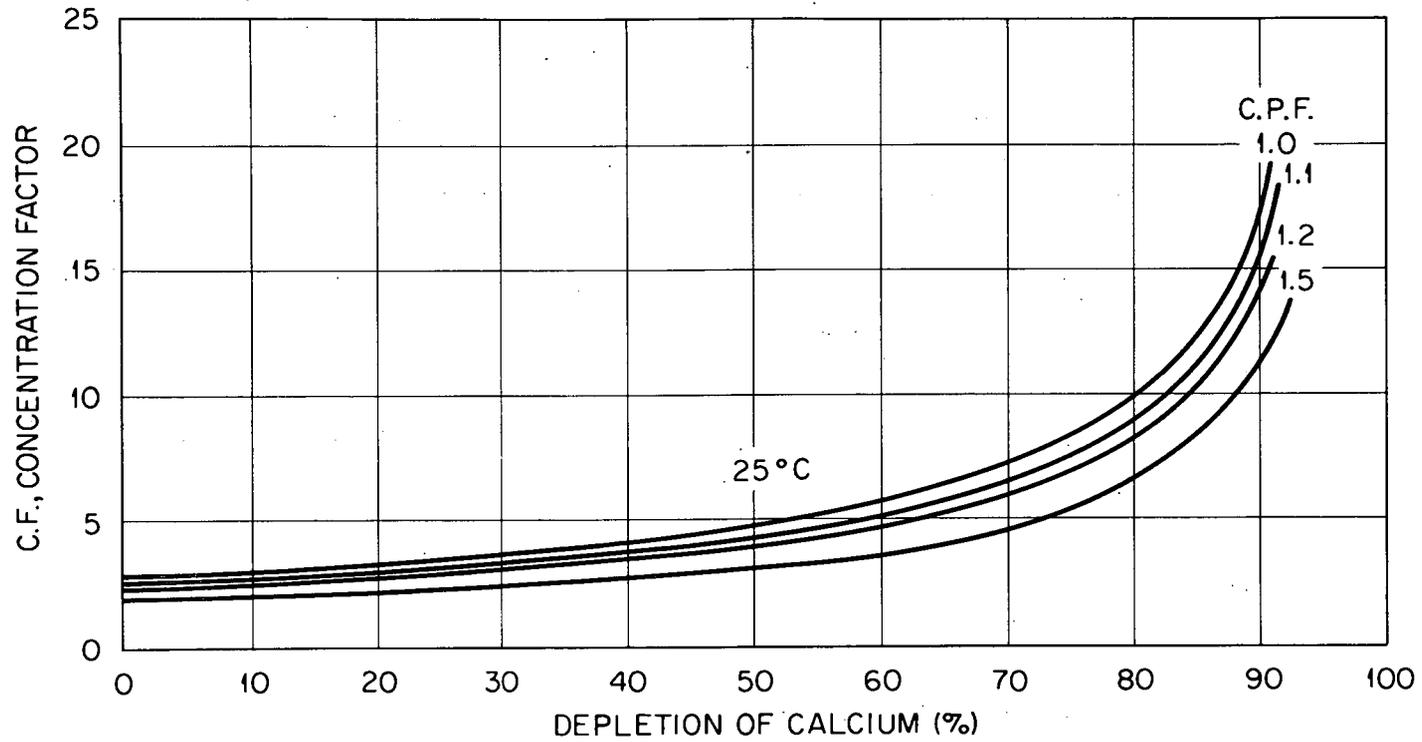


Figure 17 The Effect of Removing Calcium from Wellton-Mohawk Ariz., Water upon the Saturation Concentration Factor at Various Concentration Polarization Factors (C.P.F.) and 25°C.

calcium depletion is constant (see Table XIII A). When no calcium is removed from this post-irrigation water, the maximum water recovery decreases from ~64% to ~46% as the C.P.F. value increases from 1.0 to 1.5. At 50% calcium depletion, the corresponding maximum water recoveries are ~79% and ~69%, respectively.

#### 4. CONCLUSIONS

The results of this study on the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  in two brackish well waters and in a post-irrigation water show that the formal solubility product quotients ( $Q_{\text{fsp}}$ ) at constant ionic strength are only slightly greater than those obtained in  $\text{NaCl-H}_2\text{O}$  solutions. The slightly higher solubilities in these waters are attributed to the presence of magnesium which forms  $\text{MgSO}_4^0$  neutral molecules (ion pairs), requiring further dissolution of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to satisfy the actual solubility product quotient.<sup>1,8</sup>

The agreement under various conditions between the values for the saturation concentration factor (or maximum water recovery) obtained from the experimental results and those calculated using a computer program (Table XIII A and Ref.1) indicate that the calculational method is certainly adequate for use in the field. Only where an exact value for the saturation concentration factor is required is the experimental approach necessary or justified.

The addition of Calgon at the level of 5 ppm and 20 ppm to each of the three brackish waters under study showed that the solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  apparently are increased somewhat by Calgon. However, the increased solubilities do not appear to be an exact, or even regular, function of the Calgon concentration. That is, increasing the concentration of Calgon by a factor of 4 times (4X) does not result in a 4X increase in solubility. Furthermore,

most of the experimental results were erratic in behavior. It is proposed therefore, that the Calgon (polyphosphate) may peptize some of the excess powdered particles of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to form a stable colloid,<sup>9</sup> thereby apparently raising the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Later, hydrolysis of Calgon may destroy this power of peptization, and thus the saline water concentration of  $\text{CaSO}_4$  approaches closely the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in the absence of added Calgon. However, in reverse osmosis plant operations where a saturating solid  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is not yet present, Calgon may be considered to act also as an inhibitor of crystal nucleation, thereby allowing supersaturation to occur.

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APPENDIX



Table IA. Composition of the Three Waters Used at 25°C in Studies  
of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  Solubilities

Component	Brackish Well Water				Post-irrigation Water
	Webster, S. Dak.		Gillette, Wy.		Wellton-Mohawk, Ariz.
	On-site (ppm)	ORNL (ppm)	On-site (ppm)	ORNL (ppm)	On-site (ppm)
Na	106	108	52.4	103	945
K	16	10	14	9.2	16
Ca	140	190	429	338	244
Mg	105	83	213	116	88
Fe	~0.3	~0.08	~3.8	~0.04	0
Mn	1.1	-	0	-	0
B	-	-	-	-	1.7
Cl	10	14.5	9.9	<5	1210
$\text{SO}_4$	900	990	1536	1290	982
$\text{SiO}_2$	33	39	~85	20	28
$\text{HCO}_3$	~300	(~17)	486	236	355
$\text{NO}_3$	-	-	-	-	8
F	-	-	0.95	-	2
$\text{PO}_4$	-	-	-	-	2.7
TDS*	~1600	1630	2828	2230	~3900
pH**	7.1	7.33	6.8	7.96	-

\*Total dissolved solids.

\*\*This is the pH at the site, prior to acidification to pH = 5.5 for the solubility studies.

Table IIA. Solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Aqueous NaCl Solution at 25°C

NaCl (m)	$\text{CaSO}_4$ (m)	$Q_{\text{fsp}}^*$	$I^{**}$	$I^{1/2}/(1+1.5I^{1/2})$
		(molal units)		
0	0.0153	$2.35 \times 10^{-4}$	0.0613	0.181
0.0100	0.0165	2.71	0.0759	0.195
0.0251	0.0176	3.09	0.0955	0.211
0.0502	0.0194	3.75	0.128	0.233
0.0905	0.0219	4.79	0.178	0.258
0.201	0.0267	7.13	0.308	0.303
0.404	0.0334	11.2	0.538	0.349
0.814	0.0423	17.9	0.983	0.399
1.55	0.0516	26.7	1.75	0.443
3.20	0.0565	31.9	3.43	0.490

\* $Q_{\text{fsp}}$  = formal solubility product quotient = total calcium molality  
x total sulfate molality

\*\* $I$  = ionic strength =  $4 \cdot m_{\text{CaSO}_4} + m_{\text{NaCl}}$

Table IIIA. Solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Aqueous  $\text{Na}_2\text{SO}_4$  Solutions at 25°C

$\text{Na}_2\text{SO}_4$ (m)	$\text{CaSO}_4$ (m)	$Q_{\text{fsp}}^*$	$I^{**}$ (molal units)	$I^{1/2}/(1+1.5I^{1/2})$
0	0.0153	$2.33 \times 10^{-4}$	0.0611	0.180
0.0100	0.0128	$2.92 \times 10^{-4}$	0.0812	0.200
0.0251	0.0112	$4.06 \times 10^{-4}$	0.120	0.228
0.0501	0.0104	$6.26 \times 10^{-4}$	0.192	0.264
0.100	0.0101	$1.12 \times 10^{-3}$	0.341	0.331
0.251	0.0108	$2.83 \times 10^{-3}$	0.796	0.382
0.506	0.0127	$6.57 \times 10^{-3}$	1.57	0.435
1.027	0.0157	$1.64 \times 10^{-2}$	3.14	0.485
1.563	0.0177	$2.80 \times 10^{-2}$	4.76	0.511
2.014	0.0186	$3.78 \times 10^{-2}$	6.12	0.525

\* $Q_{\text{fsp}}$  = formal solubility product quotient = total calcium x total sulfate

$$** I = 4 \cdot m_{\text{CaSO}_4} + 3 \cdot m_{\text{Na}_2\text{SO}_4}$$

Table IVA. Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  in Acidified, Synthetic Gillette, Wy., Brackish Well Water and Its Concentrates with Calgon Present

Concentration Factor	$\text{CaSO}_4$ (m)	$\text{SO}_4$ (total) (m)	$Q_{\text{fsp}}^*$	$I^{**}$	$I^{1/2}/(1+1.5I^{1/2})$ (molal units)	Initial Calgon (ppm)
1. Calgon added; phases equilibrated overnight (17 hr) by rocking, and samples analyzed.						
1	0.0140	0.0244	$3.40 \times 10^{-4}$	0.0964	0.212	5
2	0.0130	0.0338	4.39	0.133	0.236	10
4	0.0137	0.0554	7.60	0.216	0.274	20
6	0.0114	0.0739	8.39	0.287	0.294	30
$\text{H}_2\text{O}$	0.0155	0.0155	2.40	0.0620	0.181	5
2. Equilibrated phases in part 1 (above) stood for 12 days, "re-equilibrated" by rocking overnight (19 hr), and samples analyzed.						
1	0.0132	0.0236	$3.11 \times 10^{-4}$	0.0927	0.209	5
2	0.0123	0.0331	4.07	0.130	0.234	10
2(repeat)	0.0122	0.0330	4.03	0.130	0.234	10
4	0.0113	0.0530	5.99	0.208	0.271	20
6	0.0102	0.0727	7.42	0.285	0.296	30
$\text{H}_2\text{O}$	0.0152	0.0152	2.31	0.0608	0.180	5
$\text{H}_2\text{O}$	0.0152	0.0152	2.31	0.0608	0.180	0

\* $Q_{\text{fsp}}$  = formal solubility product quotient = total calcium molality x total sulfate molality

\*\*I = ionic strength

Table VA. Calculated Saturation Concentration Factors (C.F.) at 25°C for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Acidified Gillette, Wy., Brackish Well Water upon Depleting Calcium or Calcium and Magnesium.

Calcium Depletion (%)	C.F.	Calcium and Magnesium Depletion*	C.F.
0	1.22	0	1.22
10	1.31	10	1.30
20	1.43	20	1.39
30	1.56	30	1.51
40	1.75	40	1.67
50	1.99	50	1.89
60	2.35	60	2.21
70	2.93	70	2.72
80	4.00	80	3.69
90	6.97	90	6.38

\*The values indicate the percentage of calcium and of magnesium removed from the original water

Table VIA. Calculated Saturation Concentration Factors at 25°C and Various Concentration Polarization Factors (C.P.F.) for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Acidified Gillette, Wy., Brackish Well Water after Calcium Depletion of Varying Degrees

Calcium Depletion (%)	C.P.F.*	C.F.	Calcium Depletion (%)	C.P.F.*	C.F.
0	1.0	1.22	60	1.0	2.35
	1.1	1.11		1.1	2.14
	1.2	1.02		1.2	1.96
	1.5	0.82		1.5	1.57
10	1.0	1.31	70	1.0	2.93
	1.1	1.19		1.1	2.67
	1.2	1.10		1.2	2.44
	1.5	0.88		1.5	1.95
20	1.0	1.43	80	1.0	4.00
	1.1	1.30		1.1	3.63
	1.2	1.21		1.2	3.34
	1.5	0.95		1.5	2.67
30	1.0	1.56	90	1.0	6.97
	1.1	1.42		1.1	6.32
	1.2	1.30		1.2	5.78
	1.5	1.05		1.5	4.65
40	1.0	1.75			
	1.1	1.59			
	1.2	1.46			
	1.5	1.17			
50	1.0	1.99			
	1.1	1.81			
	1.2	1.66			
	1.5	1.33			

\*Membrane surface to bulk water ratio of ionic concentrations.

Table VIIA. Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25°C in Acidified, Synthetic Webster, S. Dak., Brackish Well Water and Its Concentrates with

Calgon Present						
Concentration Factors	$\text{CaSO}_4$ (m)	$\text{SO}_4$ (total) (m)	$Q_{\text{fsp}}^*$	$I^{**}$	$I^{1/2}/(1+1.5I^{1/2})$	Calgon (ppm)
1. Phases equilibrated by rocking overnight (16 hr)						
1	0.0141	0.0211	$2.97 \times 10^{-4}$	0.0827	0.201	5
1.5	0.0135	0.0239	3.22	0.0933	0.209	7.5
2	0.0143	0.0283	4.05	0.110	0.221	10
3	0.0130	0.0340	4.41	0.131	0.235	15
4	0.0125	0.0404	5.05	0.155	0.248	20
5	0.0122	0.0473	5.78	0.181	0.260	25
6	0.0124	0.0544	6.76	0.208	0.271	30
7	0.0126	0.0616	7.74	0.235	0.282	35
1	0.0140	0.0210	$2.94 \times 10^{-4}$	0.0823	0.201	5
1.5	0.0135	0.0240	3.24	0.0936	0.210	7.5
2	0.0142	0.0282	4.02	0.110	0.221	10
3	0.0130	0.0339	4.41	0.131	0.234	15
4	0.0122	0.0402	4.90	0.154	0.247	20
5	0.0123	0.0472	5.81	0.181	0.260	25
6	0.0125	0.0544	6.79	0.208	0.271	30
7	0.0129	0.0619	7.95	0.236	0.281	35
8	0.0131	0.0690	9.00	0.263	0.290	40
H <sub>2</sub> O	0.0154	0.0154	2.36	0.0615	0.181	5
1	0.0154	0.0224	$3.45 \times 10^{-4}$	0.0880	0.205	20
1.5	0.0192	0.0297	5.69	0.116	0.266	30
2	0.0141	0.0281	3.96	0.109	0.221	40
3	0.0140	0.0427	5.97	0.135	0.237	60
5	0.0142	0.0491	6.98	0.188	0.262	100
7	0.0133	0.0622	8.29	0.238	0.282	140
8	0.0135	0.0693	9.33	0.264	0.290	160
H <sub>2</sub> O	0.0191	0.0191	3.66	0.0765	0.195	20
2. Phases equilibrated by stirring for 1 hr.						
1	0.0142	0.0212	$3.01 \times 10^{-4}$	0.0832	0.201	20
1.5	0.0146	0.0251	3.68	0.0981	0.213	30
2	0.0154	0.0294	4.53	0.114	0.224	40
3	0.0186	0.0396	7.35	0.153	0.247	60
4	0.0140	0.0419	5.85	0.161	0.251	80
5	0.0135	0.0485	6.55	0.186	0.262	100
6	0.0144	0.0563	8.11	0.215	0.274	120
7	0.0142	0.0631	8.94	0.241	0.283	140
8	0.0130	0.0690	8.95	0.263	0.290	160
H <sub>2</sub> O	0.0157	0.0157	2.47	0.0629	0.182	20

\* $Q_{\text{fsp}}$  = formal solubility product quotient = total calcium molality x total sulfate molality.

\*\* I = ionic strength

Table VIII A. Calculated Saturation Concentration Factors at 25°C for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Acidified Webster, S. Dak., Brackish Well Water upon Depleting Calcium or Calcium and Magnesium

Calcium Depletion %	C.F.	Calcium and Magnesium Depletion*	C.F.
0	3.32	0	3.32
10	3.57	10	3.54
20	3.90	20	3.82
30	4.30	30	4.17
40	4.83	40	4.62
50	5.56	50	5.28
60	6.59	60	6.20
70	8.25	70	7.69
80	11.4	80	10.6
90	20.0	90	18.4

\*The values indicate the percentage of calcium and of magnesium removed from the original water.

Table IXA. Calculated Saturation Concentration Factors at 25°C and Various Concentration Polarization Factors (C.P.F.) for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Acidified Webster, S. Dak., Brackish Well Water after Calcium Depletion of Varying Degrees

Calcium Depletion (%)	C.P.F.*	C.F.	Calcium Depletion (%)	C.P.F.*	C.F.
0	1.0	3.32	60	1.0	6.59
	1.1	3.02		1.1	6.00
	1.2	2.76		1.2	5.51
	1.5	2.21		1.5	4.38
10	1.0	3.57	70	1.0	8.25
	1.1	3.25		1.1	7.45
	1.2	2.97		1.2	6.90
	1.5	2.38		1.5	5.50
20	1.0	3.90	80	1.0	11.4
	1.1	3.55		1.1	10.4
	1.2	3.26		1.2	9.53
	1.5	2.60		1.5	7.61
30	1.0	4.30	90	1.0	20.0
	1.1	3.91		1.1	18.2
	1.2	3.60		1.2	16.7
	1.5	2.86		1.5	13.3
40	1.0	4.83			
	1.1	4.40			
	1.2	4.03			
	1.5	3.22			
50	1.0	5.56			
	1.1	5.04			
	1.2	4.64			
	1.5	3.71			

\*Membrane surface to bulk water ratio of ionic concentrations.

Table XA. Solubilities of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  in Acidified, Synthetic Wellton-Mohawk, Ariz., Post-irrigation Water and Its Concentrates with Calgon Present

Concentration Factor	$\text{CaSO}_4$ (m)	$\text{SO}_4$ (total) (m)	$Q_{\text{fsp}}^*$	$I^{**}$ (molal units)	$I^{1/2}/(1+1.5I^{1/2})$	Calgon (ppm)
1)						
1	0.0167	0.0235	$3.93 \times 10^{-4}$	0.126	0.232	5
1.5	0.0166	0.0266	4.41	0.151	0.245	7.5
2	0.0180	0.0314	5.64	0.190	0.263	10
3	0.0184	0.0386	7.09	0.250	0.286	15
4	0.0194	0.0462	8.96	0.313	0.304	20
5	0.0177	0.0513	9.07	0.366	0.317	25
6	0.0186	0.0590	11.0	0.429	0.330	30
7	0.0176	0.0648	11.4	0.484	0.340	35
8	0.0184	0.0724	13.4	0.547	0.351	40
$\text{H}_2\text{O}$	0.0154	0.0154	2.37	0.0615	0.181	5
2)						
1	0.0182	0.0249	$4.55 \times 10^{-4}$	0.132	0.235	20
1.5	0.0174	0.0275	4.77	0.158	0.249	30
2	0.0188	0.0322	6.05	0.193	0.265	40
3	0.0174	0.0376	6.54	0.246	0.284	60
4	0.0183	0.0452	8.26	0.309	0.303	80
5	0.0180	0.0516	9.27	0.366	0.317	100
6	0.0180	0.0588	10.6	0.425	0.323	120
7	0.0181	0.0654	11.9	0.485	0.341	140
8	0.0185	0.0724	13.4	0.545	0.350	160
$\text{H}_2\text{O}$	0.0190	0.0190	36.2	0.0761	0.195	20

\* $Q_{\text{fsp}}$  = formal solubility product quotient = total calcium molality x total sulfate molality

\*\*I = ionic strength

Table XIA. Calculated Saturation Concentration Factors (C.F.) at 25°C  
for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Acidified Wellton-Mohawk, Ariz., Post-irrigation  
Water upon Depleting Calcium or Calcium and Magnesium

Calcium Depletion (%)	C.F.	Calcium and Magnesium Depletion*	C.F.
0	2.79	0	2.79
10	3.03	10	3.01
20	3.32	20	3.28
30	3.69	30	3.62
40	4.16	40	4.05
50	4.81	50	4.65
60	5.74	60	5.63
70	7.22	70	6.91
80	10.0	80	9.56
90	17.2	90	16.3

\*The values indicate the percentage of calcium and of magnesium removed from the original water.

Table XIII A. Calculated Saturation Concentration Factors at 25°C and Various Concentration Polarization Factors (C.P.F.) for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in Acidified Wellton-Mohawk, Ariz., Post-irrigation Water after Calcium Depletion of Varying Degrees

Calcium Depletion (%)	C.P.F.*	C.F.	Calcium Depletion (%)	C.P.F.*	C.F.
0	1.0	2.79	60	1.0	5.74
	1.1	2.54		1.1	5.20
	1.2	2.33		1.2	4.78
	1.5	1.86		1.5	3.82
10	1.0	3.03	70	1.0	7.22
	1.1	2.76		1.1	6.59
	1.2	2.53		1.2	6.01
	1.5	2.02		1.5	4.82
20	1.0	3.32	80	1.0	10.0
	1.1	3.02		1.1	9.16
	1.2	2.77		1.2	8.41
	1.5	2.21		1.5	6.70
30	1.0	3.69	90	1.0	17.2
	1.1	3.35		1.1	15.6
	1.2	3.07		1.2	14.3
	1.5	2.46		1.5	11.5
40	1.0	4.16			
	1.1	3.78			
	1.2	3.46			
	1.5	2.77			
50	1.0	4.81			
	1.1	4.36			
	1.2	4.01			
	1.5	3.21			

\*Membrane surface to bulk water ratio of ionic concentrations.

## Table XIII A Computer Program

Computer Program for Calculating Saturation Concentration Factors (CF) to Avoid Precipitation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum) from Brackish Waters. [Program written in FORTRAN IV) (International Business Machines Co.) For Interpretation and use, a basic knowledge of the FORTRAN languages is necessary.]

## The READ Values:

- NST = No. of separate temperatures for evaluation; maximum value of subscript,  $\underline{I}$ .
- TEMP = temperature ( $^{\circ}\text{C}$ ).
- DHS = limiting Debye-Hückel slope [ $\times$ (density of  $\text{H}_2\text{O}$ ) $^{1/2}$ ] for 1-1 electrolyte.
- A =  $A_{\text{sp}}$  parameter.
- B =  $B_{\text{G}}$  parameter for solubility product calculations for gypsum.
- C =  $C_{\text{G}}$  parameter for solubility product calculations for gypsum. (Above quantities are read in once for  $\underline{I} = 1$  to NST for evaluation of all saline water compositions.)
- TITLE = title for the particular saline water composition.
- A11 = molal ionic strength of the saline water.
- CAL1 = molal concentration of calcium in the saline water.
- R = molal ratio,  $\text{SO}_4/\text{Ca}$ , in the saline water.
- TMG1 = total molality of magnesium in saline water. (Calculations are repeated for each additional TITLE card and different values of A11, CAL1, R, and TMG1.)

## The WRITE Values:

- A. TITLE, A11, CAL1, R, TMG1, the A parameter used for the variation of  $K_{\text{d}}^{\text{O}}(\text{MgSO}_4)$ .
- B. For each solid: TEMP, concentration factors (CF) on molal, molar, and weight fraction bases, ionic strengths at saturation,  $K_{\text{sp}}^{\text{O}}$ 's and number of iterative calculations (NIT) to obtain values of CF.
- C. Some particular constants used to obtain values of CF: DHS,  $K_{\text{d}}^{\text{O}}(\text{MgSO}_4)$ ,  $A_{\text{sp}}$  parameters for  $K_{\text{sp}}$  variations with ionic strength, and A, B, and C parameters for gypsum.

An Alternate Equation to Substitute into Program for Specific Use with Sea water:

$$\text{WF1/A11} = 0.04790 - 0.002194 * \text{A11} + 0.00006900 * \text{A11}^{**2}$$

(= wt. fraction/ionic strength)

In this present paper, K's are replaced by Q's, and  $K_{\text{sp}}^{\text{O}}$  by  $K_{\text{fsp}}$ .

FORTRAN IV Computer Program for Calculating Temperature-Solubility Limits of Calcium Sulfate Dihydrate in Saline or Brackish Waters and Their Concentrates.

Table XIII A Continued

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C L.B.YEATTS AND W.L.MARSHALL--NOV.10,1972
C CALCN,TEMP-SOLY LIMITS(CASO4 DIHYDRATE IN BRACKISH WATERS),YEATTS+MARSHALL
C L.B.YEATTS AND W.L.MARSHALL(1972)-OAK RIDGE NATL.LAB.,TENN.,U.S.A.
C PROGRAM IN FORTRAN IV LANGUAGE(READ IN TAPE 5,READ OUT TAPE 6),(1972)
ODIMENSION TITLE(10),DHS(100),TEMP(100),TA(100),A(100),B(100),
1C(100),JJ(100),XKDISO(100),SOLPO(100),AIF(100),CFML(100),CFMR(100),
2CFWF(100)
READ(5,1)NST
1 FORMAT(110)
OREAD(5,2)(TEMP(I),DHS(I),A(I),B(I),C(I),I=1,NST)
2 FORMAT(5E10.0)
DO21 I=1,NST
TA(I)=TEMP(I)+273.16
OSOLPC(I)=10.**((390.9619-152.6246*ALOG10(TA(I))
1-12545.6/TA(I)+0.0818493*TA(I))
210XKDISO(I)=10.**((-158.540+62.160*ALOG10(TA(I))
1+4810.6/TA(I)-0.046298*TA(I))
22 READ(5,3)TITLE,A11,CAL1,R,TMG1
3 FORMAT(10A4,4E10.0)
SOLP1=R*CAL1**2
WF1=A11*(0.05838-0.003260*A11+0.00012489*A11**2)
FMR1=A11*(0.9970-0.01883*A11)
DO 25 I=1,NST
ASSMG=0.0
CFML(I)=1.
DO 23 J=1,100
CAL=CAL1*CFML(I)
TMG=TMG1*CFML(I)
AI=A11*CFML(I)-4.*ASSMG
OSOLP=SOLPO(I)*10.**((8.*DHS(I)*SQRT(AI)/(1.+A(I)*SQRT(AI))
1+B(I)*AI-C(I)*AI**2)
XKDIS=XKDISO(I)*10.**((8.*DHS(I)*SQRT(AI)/(1.+SQRT(AI)))
ASSMG=TMG*SOLP/(XKDIS*CAL+SOLP)
X=SQRT((SOLP+ASSMG*CAL)/SOLP1)
IF(ABS(X-CFML(I))/X-.001)24,24,23
23 CFML(I)=X
24 JJ(I)=J
AIF(I)=CFML(I)*A11
OCFWF(I)=AIF(I)*(0.05838-0.003260*AIF(I)+0.00012489*
1AIF(I)**2)/WF1
25 CFMR(I)=AIF(I)*(0.9970-0.01883*AIF(I))/FMR1
WRITE(6,4)TITLE
4 FORMAT(11H1,10A4)
WRITE(6,5)A11
5 FORMAT(27HOIONIC STR OF SALINE WATER=E12.4)
WRITE(6,6)CAL1
6 FORMAT(26H INITIAL CONC N OF CALCIUM=E12.4)
WRITE(6,7)R
7 FORMAT(20H MOLAL RATIO SO4/CA=E12.4)
WRITE(6,8)TMG1
8 FORMAT(28H INITIAL CONC N OF MAGNESIUM=E12.4)
WRITE(6,9)
9 FORMAT(29H A PAR FOR KDISS(MGSO4)= 1.0)
WRITE(6,10)
100FORMAT( 65HOCONC N FACTORS FOR CASO4 DIHYDRATE),CF=CONC N(SATD)/CONC

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Table XIII A Continued

```

IN(INITIAL))
WRITE(6,11)
110FORMAT(113HO TEMP(C)      CF(MOLAL)      CF(MOLAR)      CF(WT
1 FRACT)      ION STR(MCLAL-SATD)      SCLY PD(ZERC)      NO. ITER)
OWRITE(6,12)(TEMP(I),CFML(I),CFMR(I),CFWF(I),AIF(I),
1 SOLPD(I),JJ(I),I=1,NST)
12 FORMAT(1H ,F6.0,5E18.3,I12)
WRITE(6,13)
13 FORMAT(52HOPARTICULAR CONSTANTS USED IN THE ABOVE CALCULATIONS)
WRITE(6,14)
140FORMAT( 74HO TEMP(C)      D H SLOPE      K-DIS(O)(MGSC4)      A PARA
1 B(GYPS)      C(GYPS))
OWRITE(6,15)(TEMP(I),DHS(I),XKDISO(I),A(I),B(I),
1 C(I),I=1,NST)
15 FORMAT(1H ,F6.0,F13.4,E20.3,F13.3,2F11.4)
GO TO 22
END

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Table XIII Continued

## WELLTON-MOHAWK CHANNEL WATER (CA=1X)

IONIC STR OF SALINE WATER= 0.8380E-01

INITIAL CCNCN OF CALCIUM= 0.6120E-02

MOLAL RATIO SO4/CA= 0.2108E 01

INITIAL CONCEN OF MAGNESIUM= 0.3640E-02

A PAR FOR KDISS(MGSO4)= 1.0

## CCNCN FACTORS FOR CaSO4 DIHYDRATE), CF=CCNCN(SATD)/CCNCN(INITIAL)

TEMP (C)	CF (MOLAL)	CF (MCLAR)	CF (WT FRACT)	ION STR (MOLAL-SATD)	SCLY ED (ZFKC)
0.	0.225E 01	0.225E 01	0.224E 01	0.189E 00	0.343E-04
10.	0.253E 01	0.252E 01	0.251E 01	0.212E 00	0.351E-04
25.	0.279E 01	0.279E 01	0.277E 01	0.234E 00	0.424E-04
40.	0.287E 01	0.286E 01	0.284E 01	0.240E 00	0.414E-04
50.	0.284E 01	0.283E 01	0.282E 01	0.236E 00	0.391E-04
60.	0.278E 01	0.277E 01	0.276E 01	0.233E 00	0.355E-04
70.	0.268E 01	0.267E 01	0.266E 01	0.225E 00	0.324E-04
80.	0.256E 01	0.255E 01	0.254E 01	0.215E 00	0.285E-04
90.	0.244E 01	0.244E 01	0.243E 01	0.205E 00	0.255E-04
100.	0.232E 01	0.232E 01	0.231E 01	0.195E 00	0.224E-04

## PARTICULAR CONSTANTS USED IN THE ABOVE CALCULATIONS

TEMP (C)	D H SLOPE	K-DIS (0) (MGSO4)	A PARA	B (GYPS)	C (GYPS)
0.	0.4875	0.744E-02	1.450	0.0880	0.0234
10.	0.4943	0.572E-02	1.468	0.0474	0.0182
25.	0.5080	0.400E-02	1.500	0.0194	0.0134
40.	0.5229	0.288E-02	1.530	0.0022	0.0120
50.	0.5337	0.234E-02	1.544	0.0	0.0108
60.	0.5459	0.192E-02	1.558	0.0	0.0096
70.	0.5585	0.158E-02	1.570	0.0	0.0082
80.	0.5715	0.130E-02	1.580	0.0	0.0064
90.	0.5860	0.107E-02	1.588	0.0	0.0042
100.	0.6008	0.879E-03	1.554	0.0	0.0020

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