Mechanism of gypsification*

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Abstract—Petrographic studies have shown that many gypsum deposits have been formed by the hydration of anhydrite, but the mechanism for hydration has not been fully explained. Gypsum has been produced experimentally by the agitation of anhydrite in pure water, a reaction that is accelerated by certain acids, bases, and salts, particularly alkali sulphates.

Phase investigations and reaction velocity studies indicate that accelerated hydration of anhydrite takes place through the medium of transient surface complexes in dilute solution. Concentrated solutions may precipitate double salts.

Contrary to recent hypotheses of gypsum dehydration by concentrated salt solutions, double salts and/or gypsum are stable phases below a temperature of 42°C. Above 42°C double salts may replace anhydrite as the stable phase. Gypsum, however, may remain a metastable phase indefinitely in its saturated solution below the hemihydrate transition temperature (98°C).

Experimental data indicate that precipitation of anhydrite from sea water is unlikely.

Introduction

Hydration of the mineral anhydrite ($CaSO_4$) to gypsum ($CaSO_4 \cdot 2H_2O$) has been a well-known phenomenon for many years. Although the hydration of anhydrite by pure water is extremely slow, it is accelerated in the presence of certain salts, alkalis and acids. The mechanism whereby this acceleration takes place has never been fully understood. This paper attempts to shed new light on the mechanism by which activation of anhydrite takes place.

Previous Work

Farnsworth (1925) carried out hydration experiments using very finely ground anhydrite agitated in pure water. Several weeks were required for complete conversion. This reaction has been demonstrated by Posnjak (1940) to take place via solution phase. His results are based on solubility data for calcium sulphate phases in water which show gypsum to be the least soluble phase below 42°C.

Thermodynamic studies by MacDonald (1953) show that hydrostatic pressure assists hydration by driving the components of the following reaction to a state of lesser volume.

(A) $\qquad CaSO_4 \text{ (anhydrite)} + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O \text{ (gypsum)}$
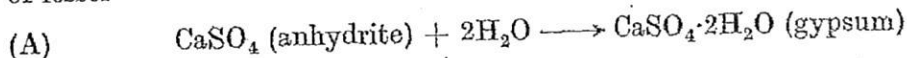
However, when the lithostatic pressure exceeds the hydrostatic pressure, and confined water is allowed to escape, the equilibrium temperature for the above reaction is lowered. MacDonald theorized that when pressure differential exists, gypsum in pure water could exist only at depths less than about 2500 ft.

Several investigators have also postulated that certain salt solutions decrease the solubility of anhydrite relative to gypsum to the point that anhydrite is the stable phase at temperatures well below 42°C. This change in solubility is based

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on the thermodynamic considerations of vapour pressure relationships by MAC-DONALD and POSNJAK and also KELLEY, SOUTHARD and ANDERSON (1941). MACDONALD proposed that concentrated saline solutions, as evaporating bodies of sea water, precipitate anhydrite at temperatures as low as 7°C.

POSNJAK (1940) demonstrated the persistence of gypsum as a metastable phase up to 98°C (hemihydrate transition temperature) and this has been substantiated in the present investigation. Finely ground gypsum in contact with saturated NaCl solution remained unchanged at room temperature over a period of 6 months. Anhydrite nuclei added to this mixture were subsequently transformed to gypsum. Upon elevation of the solution temperature to 60°C, no alteration to anhydrite took place after 3 weeks. Other similar experiments with saturated solutions of sea water, $MgCl_2$, $CaCl_2$ and Na_2SO_4 over more extended periods of time gave the same results. Precipitated calcium sulphate formed by the following reaction occurs as gypsum up to about 70°C:

(B) $$CaCO_3 + 2H^+ + SO_4^= \xrightarrow{H_2O} CO_2\uparrow + Ca^{++}SO_4^= \longrightarrow ppt.$$
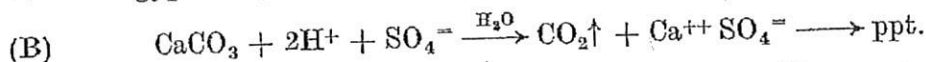
At higher temperatures hemihydrate precipitates and readily reverts to gypsum in water below 70°C. Hence, it may be concluded that the following reaction under standard conditions of temperature and pressure proceeds with extreme slowness, if at all:

(C) $$CaSO_4 \cdot 2H_2O(G) \xrightarrow[soln.]{satd.\ salt} CaSO_4(A) + 2H_2O$$
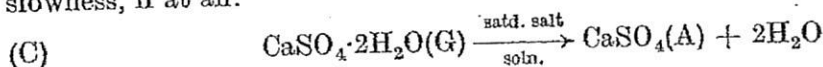
In contrast to the work of POSNJAK and MACDONALD showing that in certain salt solutions the gypsum–anhydrite transition temperature is lowered, several workers have demonstrated that these salts activate rather than inhibit hydration. This activation occurs even under conditions theoretically favouring anhydrite.

HENNICKE (1923) introduced in Germany a mortar-forming process which utilized solutions of "alkali salts, acids and bases" with ground anhydrite. These solutions accelerated the hydration process. Further investigations of acceleration processes have been carried out by RANDEL (1933), OTTEMAN (1950), and GELMROTH (1953).

Recent experiments (LEININGER, CONLEY and BUNDY, 1957) conducted to determine the relative effectiveness of activators yielded the following qualitative series:

$$K^+ \gg Na^+ \gg NH_4^+ > Mg^{++} > Fe^{++} > H^+ > Al^{+++} > Ca^{++}$$
$$\text{and } SO_4^= \gg Cl^- > OH^-$$
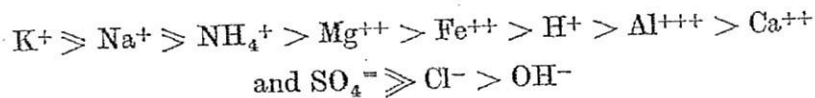
Although other ions may promote conversion, only these were studied because of their industrial and geochemical application. Potassium and sodium sulphate were investigated in detail because of their efficiency in activation and presence in natural waters.

DOUBLE SALT FORMATION

The reaction for the conversion of anhydrite to gypsum with activator solutions:

(D) $$CaSO_4(A) \xrightarrow{act.}{H_2O} Ca^{++} + SO_4^= \xrightarrow{H_2O} CaSO_4 \cdot 2H_2O\ (G)$$
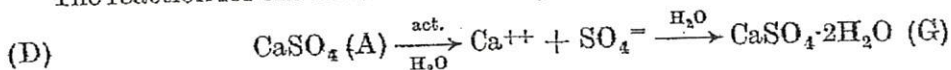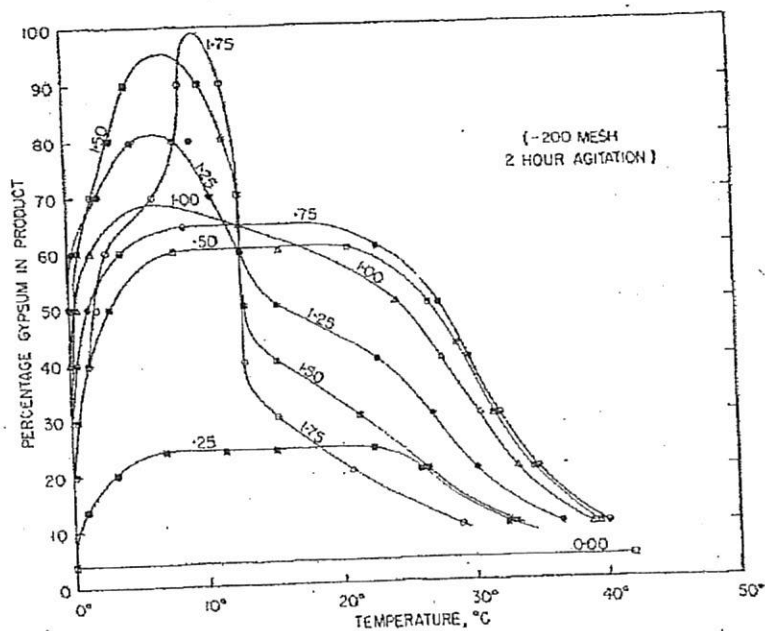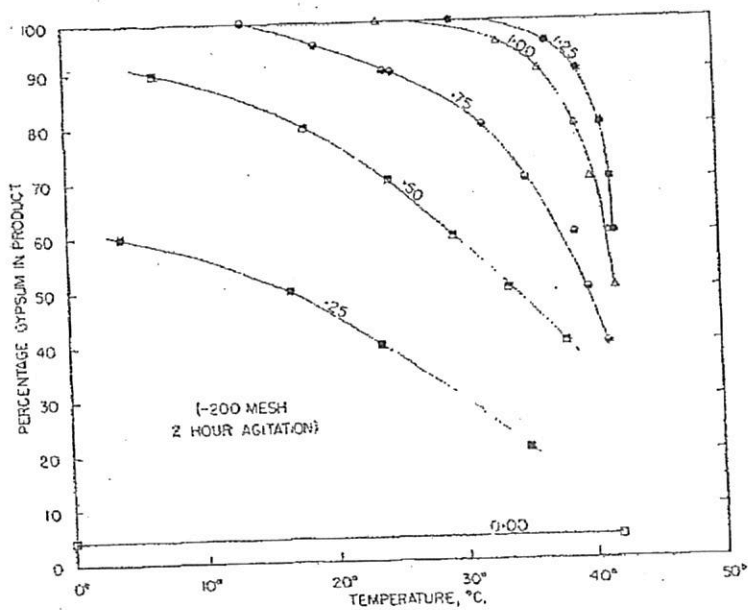
Fig. 1. Sodium sulphate isomolarity curves.

Fig. 2. Potassium sulphate isomolarity curves.

is primarily dependent upon solution temperature and concentration. Figs. 1 and 2 illustrate the effects of these parameters when sodium sulphate and potassium sulphate are used as activators and the product is removed and washed free of activator.* In this process gypsum results from decomposition of any double salt that has been formed. In Fig. 1 it is apparent that anomalous conversion to gypsum occurs at temperatures below 13°C and concentrations above 0·75M

* Gypsum content determined by standard A.S.T.M. gravimetric method.

Na_2SO_4. Experiments conducted within this field give rise to the formation of a stable double salt which subsequently decomposes upon washing. This double salt appears identical in composition with the sodium hemicalcium sulphate salt, $2Na_2SO_4 \cdot CaSO_4 \cdot 2H_2O$, designated as labile salt, and synthesized by HILL and WILLS (1938) by the following method:

A slight excess of gypsum is placed in a solution of sodium sulphate, 24·2 to 29·0 per cent by weight. The mixture is maintained in a sealed container at 75°C for 72 hr.

Table 1. Chemical analyses of labile salt

Component	Labile salt (theory)	Synthetic (HILL and WILLS)	Synthetic (CONLEY and BUNDY)
Na_2SO_4	62·27	61·6	69·4*
$CaSO_4$	29·83	29·7	23·8
H_2O	7·90	8·7	7·7
	100·00	100·0	100·9

* High sodium content due to activator contamination.

Table 1 includes chemical analyses of the double salt obtained from a solution at 6·5°C, the salt synthesized by HILL and WILLS, and the stoichiometric composition of labile salt. X-ray spectrometer data of the synthesized salts are shown in Fig. 3.
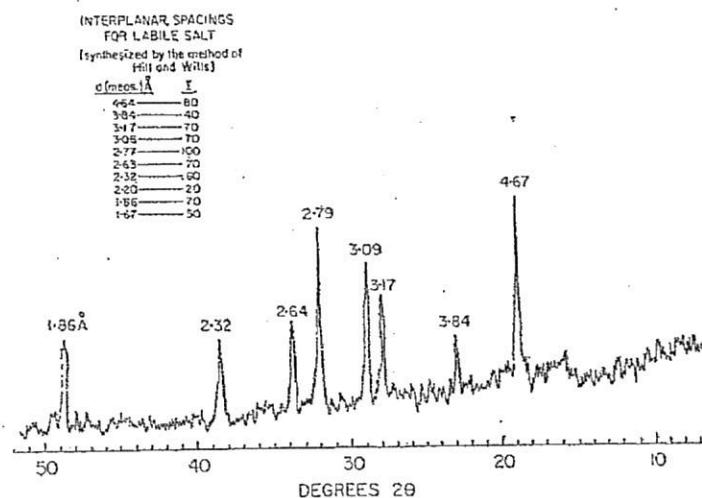

Fig. 3. X-ray spectrometer trace and interplane spacings for labile salt.

Fig. 2 shows that conversion is largely dependent upon K_2SO_4 concentration, and no critical temperature is observed below 42°C. Throughout the operating range 0–42°C and 0·25–1·25 M K_2SO_4 a double salt which corresponds to the mineral syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, is obtained. Chemical analyses for the double salt obtained in these experiments and the stoichiometric composition of

syngenite are given in Table 2. An X-ray spectrometric trace of the double salt is shown in Fig. 4. Although this pattern is not in complete accord with the A.S.T.M. data listed for syngenite,† it is believed that chemical and X-ray data are adequate to conclude that syngenite is present.
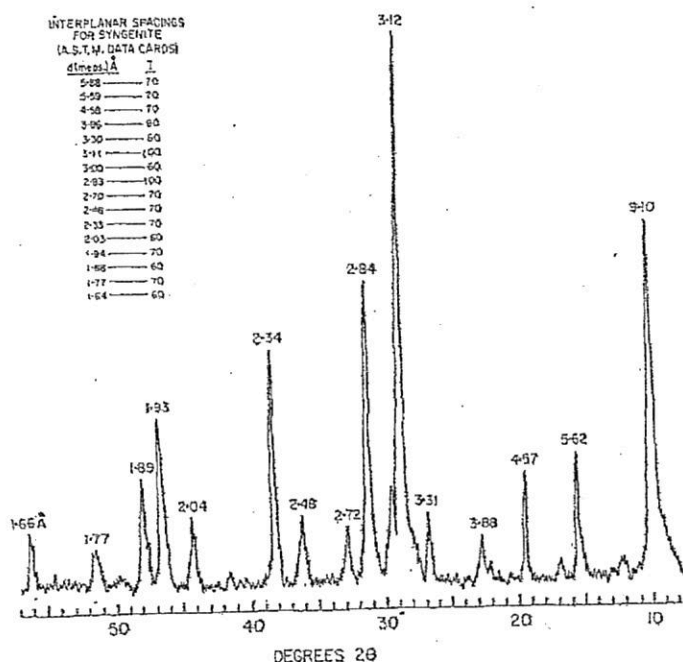

Fig. 4. X-ray spectrometer trace and interplane spacings for syngenite.

PHASE STUDIES

Ternary phase diagrams for the systems $CaSO_4$–Na_2SO_4–H_2O and $CaSO_4$–K_2SO_4–H_2O have been constructed in order to obtain a better understanding of phase equilibria. HILL and WILLS (1938) collected data for the former in the range 25°–100°C and HILL (1934) for the latter from 40°–100°C. These workers

Table 2. Chemical analyses of syngenite

Component	Syngenite (theory)	Synthetic (CONLEY and BUNDY)
$CaSO_4$	41·46	41·0
K_2SO_4	53·06	53·5
H_2O	5·48	5·5
	100·00	100·0

† All the lines on the diagram that are within the range of those recorded on the A.S.T.M. card check to within 0·02 Å. The one line on the card that does not show up on the diagram (5·88 Å) is also missing from the syngenite pattern on file at the U.S. Geological Survey, so it is possible that it was due to an impurity in the material from which the pattern summarized on the A.S.T.M. card was made. Ed.

have demonstrated the stability of various double salts above 42°C. It was necessary to supplement these data with information obtained in the range 0–25°C.

For this purpose a warming-curve method modified after Tammann cooling-curves (1903) was employed. Fig. 5(a) shows the temperature change with time
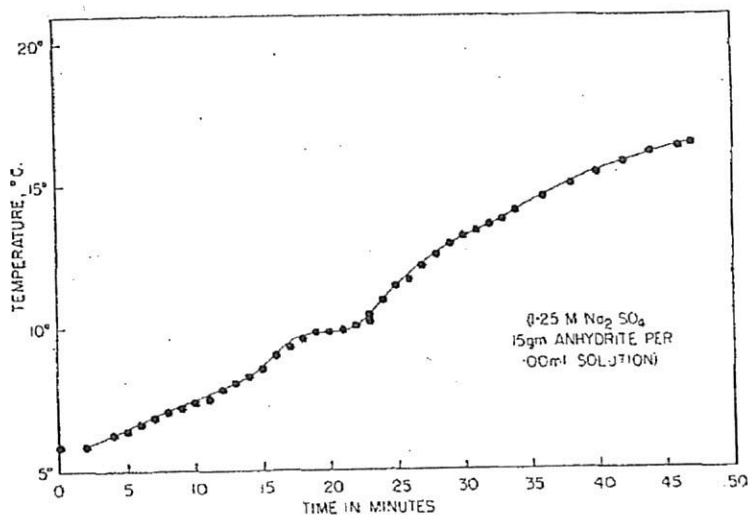

Fig. 5(a) Warming curve for the system Na_2SO_4–$CaSO_4$–H_2O.
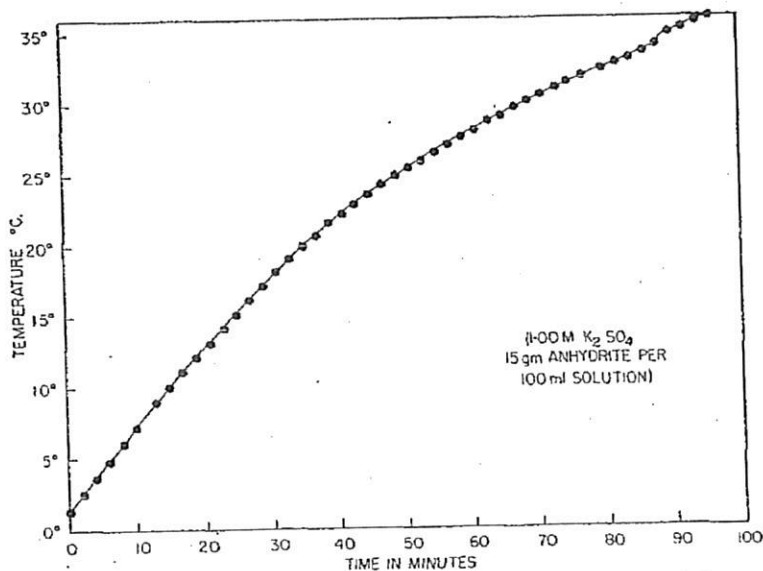
Fig. 5(b). Warming curve for the system K_2SO_4–$CaSO_4$–H_2O.

of a Na_2SO_4 activated suspension of anhydrite. The composition of this mixture was selected from the field of complex salt stability in Fig. 1. The mixture was agitated for 6 hr in a 2°C bath to obtain maximum double salt formation. The resulting mixture was removed from the bath and allowed to warm in air at room temperature. Temperature measurements of the warming solution were determined periodically with an N.B.S. calibrated thermometer graduated in 0·1°C.

A well-defined plateau in Fig. 5(a), originating from an endothermic reaction, is observed at 9·8°C. The change of slope above this temperature indicates the formation of a new phase. Results of X-ray analysis show that below 9·8°C labile
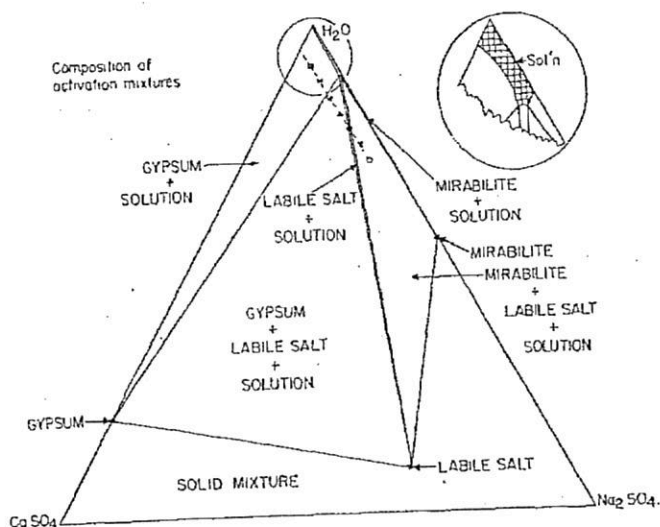
Fig. 6(a). Weight (%) ternary diagram of Na_2SO_4–$CaSO_4$–H_2O at 9°C.
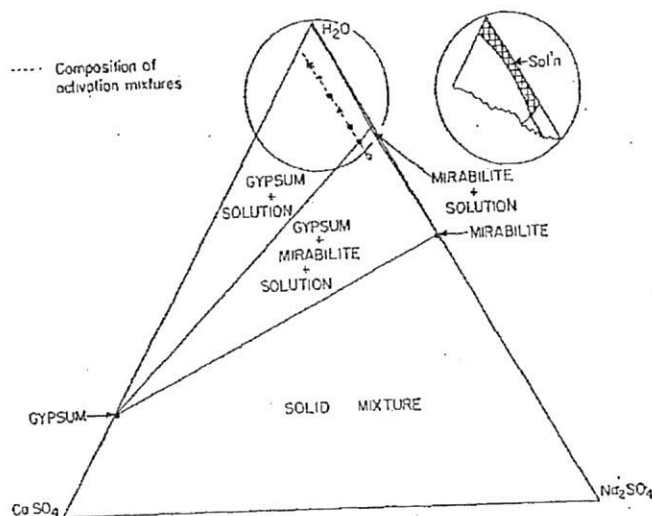
Fig. 6(b). Weight (%) ternary diagram of Na_2SO_4–$CaSO_4$–H_2O at 25°C.

salt and small quantities of gypsum exist as stable phases but above this temperature gypsum and mirabilite, $Na_2SO_4 \cdot 10H_2O$, are stable. Therefore, 9·8°C is the temperature at which labile salt begins to dissociate into gypsum and mirabilite (the solubility of labile salt equals the solubility of gypsum). It should be noted that the transition temperature 13°C apparent in Fig. 1, probably represents

63

equilibrium between the solubilities of the two metastable phases, labile salt and anhydrite. In Fig. 5(a) a very small break occurs at about 13°C. At this point equilibrium is believed to exist between metastable labile salt and the very small
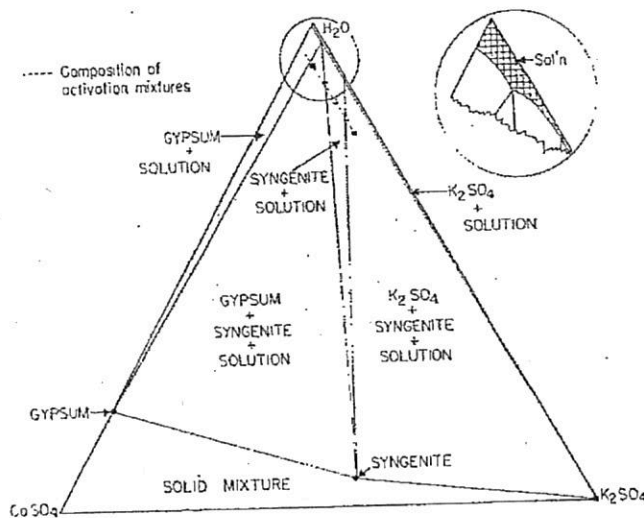
Fig. 6(c). Weight (%) ternary diagram of K_2SO_4–$CaSO_4$–H_2O at 25°C.
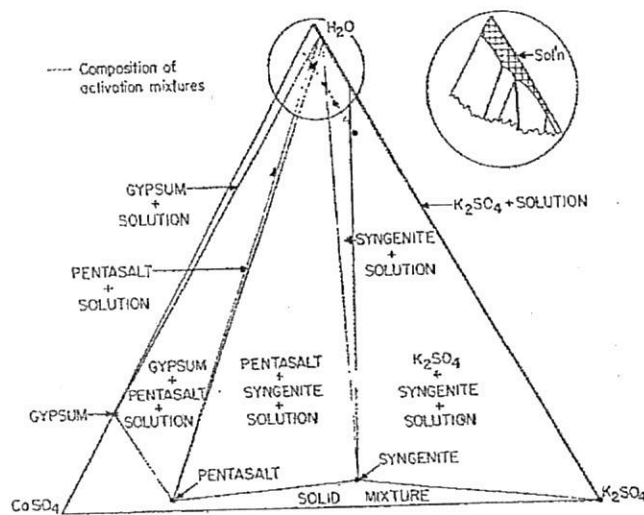
Fig. 6(d). Weight (%) ternary diagram of K_2SO_4–$CaSO_4$–H_2O at 40°C.

quantity of anhydrite remaining in the mixture. Other warming-curve data taken from an automatic recorder and plotted as the second derivative, d^2T/dt^2, support this interpretation.

The discontinuity occurring at a temperature lower than 9°C could not be interpreted with present phase information. A new phase region may be indicated by this break.

From the above determinations, along with $CaSO_4 \cdot 2H_2O$ and $Na_2SO_4 \cdot 10H_2O$ solubility data, the ternary diagram [Fig. 6(a)] was constructed. The extreme narrowness of the field, labile salt + solution, inhibits precise determination of the phase boundary, labile salt + solution/solution. The diagram was drawn in accordance with the general principles reviewed by MARSH (1935) and RIVETT (1923). A similar ternary phase diagram [Fig. 6(b)] was constructed from 25°C data to show the shift of the various stability fields.

A second warming curve [Fig. 5(b)] was obtained by using a K_2SO_4 activated suspension of anhydrite. The methods employed were similar to those used in obtaining the Na_2SO_4 warming curve. An exothermic reaction was obtained at about 34·5°C. This represents the equilibrium temperature between the fields of syngenite + gypsum and syngenite + pentasalt $[(CaSO_4)_5K_2SO_4 \cdot H_2O]$. No other phase changes were observed up to the terminal temperature, 60°C. These phases are substantiated by X-ray analysis, and the results are in agreement with conclusions of HILL (1934). Figs. 6(c) and 6(d) are two ternary phase diagrams constructed from 25°C and 40°C data. The greater efficiency of K_2SO_4 over Na_2SO_4 activation may be expected to result from the greater stability range of the K–Ca double salts. X-ray determinations and warming-curve data show syngenite to be stable throughout the temperature range in Fig. 5(b).

MECHANISM OF DOUBLE SALT FORMATION

The transition from anhydrite to a double salt and the decomposition of the double salt to gypsum by washing were observed to be relatively rapid processes. Transformation of anhydrite to gypsum by means of stable double salt formation and decomposition can therefore be readily understood. Comparison of Fig. 1 with Figs. 6(a) and (b) and Fig. 2 with Figs. 6(c) and (d) indicates that relatively rapid conversion also occurs outside the double salt stability fields. The reactions within these areas of complex salt instability require a more thorough explanation.

OTTEMAN suggested the formation of transient double salts as a possible mechanism of transformation. He further postulated that the increased solubility of anhydrite in concentrated Na_2SO_4 solution is a primary factor in this transformation process. Results of the present investigation are in agreement with OTTEMAN's "transient double salt" postulation; however, the writers do not believe that the slight increase in anhydrite solubility contributes significantly to the conversion process. The negligible effect of this solubility increase is shown in Fig. 7. Fig. 8 shows that after 2 hr of agitation in pure water 0·2 per cent of anhydrite is converted to gypsum, whereas under the same conditions with 0·75 M Na_2SO_4 in saturated $CaSO_4$ solution about 60 per cent of anhydrite is converted. The reaction rate is increased 300-fold, but the solubility-differential between anhydrite and gypsum for these two solutions shows only a slight increase.

This relation is further demonstrated by an analysis of the effects produced by NaCl activation. The solubility of calcium sulphate in 0·5 M sodium chloride solution is approximately three times greater than in an equivalent sodium sulphate solution (COMEY and HAHN, 1921). Conversely, the activating efficiency of the Na_2SO_4 is about fifty times greater than that of NaCl. It is concluded that both the cation and anion enter into an activation complex.
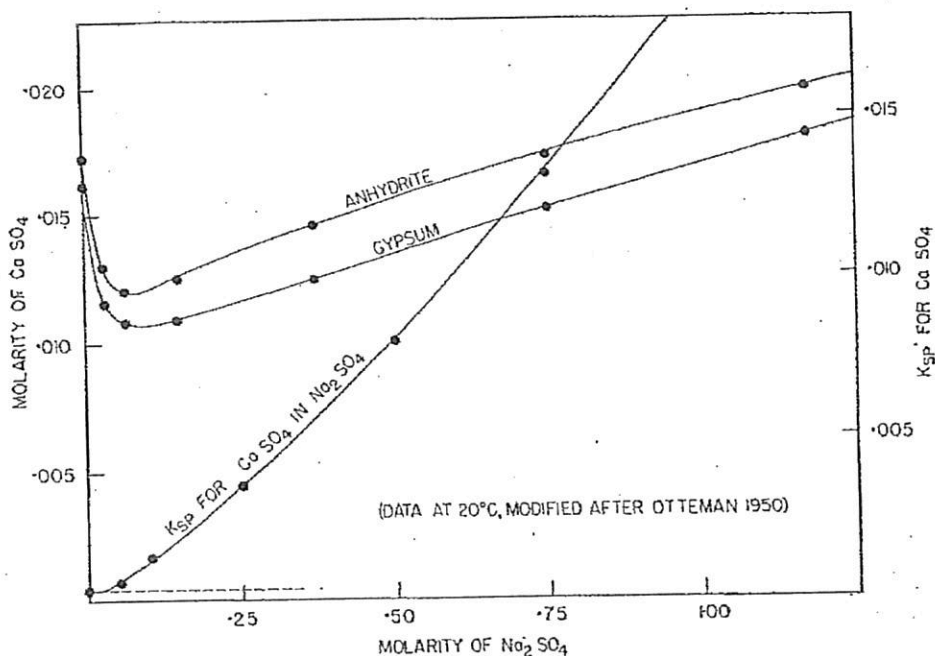
Fig. 7. Solubility and solubility product relationship of CaSO₄ in Na₂SO₄ solutions.
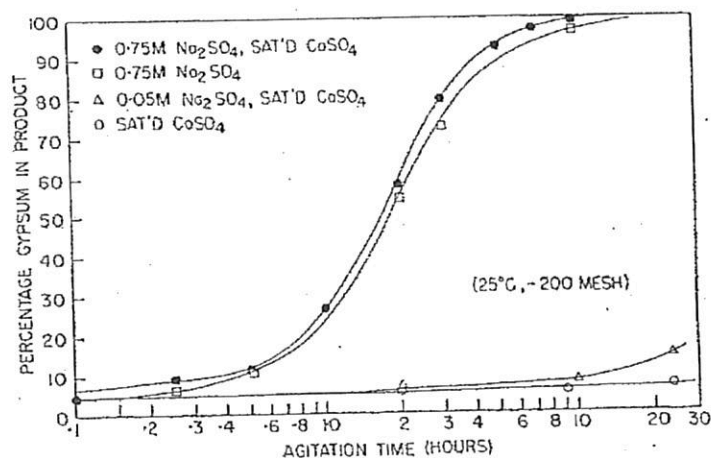
Fig. 8. Rate of gypsum formation in activating solutions.

Experimental work (LEININGER, CONLEY and BUNDY, 1957) indicates that sulphate salts are more effective activators than foreign anion salts. To comprehend better the effect of the anion upon activation, the following theoretical treatment is given. The surface of anhydrite* is considered as a network of alternating Ca^{++} and $SO_4^=$ ions. When this surface is in contact with a saturated

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* Microscopic observations of anhydrite undergoing hydration by an activating solution show that the 100 plane is most susceptible to this attack (OTTEMAN, 1950).

66

calcium sulphate solution, the following transitions take place and approach equilibrium:

	Interfacial ion		Solvated ion
(E)	(Ca^{++})	$\longleftrightarrow$	Ca^{++}
(F)	$(SO_4^=)$	$\longleftrightarrow$	$SO_4^=$
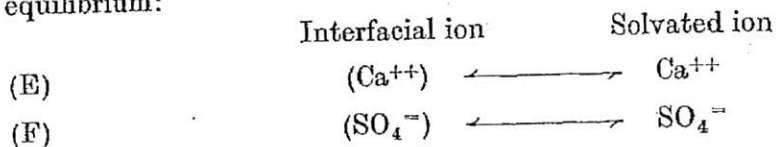
This exchange process is shifted slightly to the solution phase below 42°C and results in very slow rate of gypsum precipitation.

If the anhydrite surface is in contact with a calcium sulphate solution which contains a dissolved salt $M^{+a}X^{-b}$ of a given concentration, the following transitions can occur:

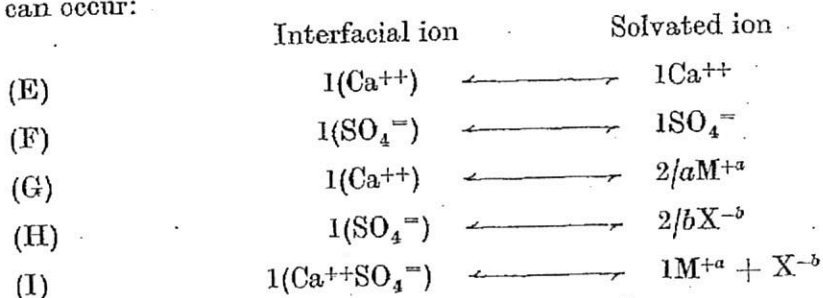|	Interfacial ion		Solvated ion
(E)	$1(Ca^{++})$	$\longleftrightarrow$	$1Ca^{++}$
(F)	$1(SO_4^=)$	$\longleftrightarrow$	$1SO_4^=$
(G)	$1(Ca^{++})$	$\longleftrightarrow$	$2/a M^{+a}$
(H)	$1(SO_4^=)$	$\longleftrightarrow$	$2/b X^{-b}$
(I)	$1(Ca^{++}SO_4^=)$	$\longleftrightarrow$	$1M^{+a} + X^{-b}$

Only these ionic transitions permit the net surface charge to remain electro-statically unaltered. If the molar concentration of the salt $M^{+a}X^{-b}$ is large with respect to the concentration of calcium sulphate, transitions (G), (H) and I predominate.

It is apparent that when X^{-b} is the sulphate ion, the statistical probability of a surface transient complex formation is considerably higher than when X^{-b} is Cl^-, etc. Many investigators have reported double sulphate salts of Ca^{++} and cation M^{+a}, but relatively few complex salts which have a composition of the general type MX·NY (different cations and different anions) are known. The increased quantity of $SO_4^=$ ions in solution also increases the precipitation rate of gypsum by virtue of a greater number of Ca^{++}–$SO_4^=$ collisions in the solution phase.

The formation of surface transient complexes may then be considered as a statistical replacement process whereby M^{+a} ions are substituted randomly for Ca^{++} ions or adsorbed on the calcium sulphate surface. The adsorption of these foreign ions in localized areas produces surface deformities and reduces the surface energy. Because of surface energy reduction, more Ca^{++} and $SO_4^=$ ions are released per unit time. These, in turn, precipitate as gypsum from the already saturated calcium sulphate solution. The increased rate of gypsum formation is produced, therefore, by making the anhydrite more readily soluble.

If a double salt is the least soluble species under the conditions of the system, a double salt crystallite will be formed. Growth will occur upon the crystallite surface by depletion of Ca^{++}, M^{+a} and $SO_4^=$ ions from the surrounding solution. The solution is replenished by dissolution of the more soluble anhydrite and, if present, solid phase $M_{2/a}SO_4$. This process of precipitation may result in the inclusion of the anhydrite grain by peripheral double salt growth. Microscopic observations show this type of inclusion to occur.

Nuclei for double salt formation also may be provided by direct precipitation from solution. This type of nuclei formation can be observed during the interaction of saturated calcium sulphate solution with potassium sulphate solutions above approximately 0·2 M and concentrated NaSO₄ solutions below 9·8°C.

If the solubility of the double salt is greater than that of gypsum (the double salt is unstable under the conditions of the system), dissolution of the crystallite surface will occur and supersaturate the solution with resepct to $CaSO_4 \cdot 2H_2O$. Precipitation of $CaSO_4 \cdot 2H_2O$ then will occur either on the surface of existing nuclei or by spontaneous nucleation. Depletion of the solid phase anhydrite will be most rapid when the ratio of anhydrite to gypsum is large. As greater quantities of gypsum form, a competing reaction due to foreign cation adsorption on the gypsum surface will then decrease the anhydrite dissolution rate and, consequently, the gypsum formation rate. Therefore, an inflexion in the hydration rate curve would theoretically be obtained when the surface area (or surface activity) of calcium sulphate in the anhydrite phase is equal to that of the calcium sulphate in the gypsum phase. It is apparent from Fig. 8 that the data show a maximum for the rate change at about 50 per cent yield.

The precipitation of gypsum from a saturated calcium sulphate solution may then be considered as a two-stage process: (1) formation of incipient nuclei, and (2) crystal growth of these nuclei. The overall reaction may be represented by the following equation:

(J) $$nCa^{++} + nSO_4^{=} + 2nH_2O \longrightarrow nCaSO_4 \cdot 2H_2O.$$
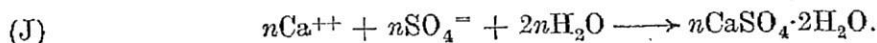
If the mole fraction of water is large relative to the concentration of calcium and sulphate ions, the precipitation of gypsum will be limited primarily by the Ca^{++} and $SO_4^{=}$ ion concentrations. Crystallite formation is dependent upon the total number of anion–cation collisions which in turn are a function of the anion and cation concentrations. The rate of formation of nuclei is proportional to $[(Ca^{++})(SO_4^{=})]^{p/2}$ where p is the number of monomers, or ion members of a nucleus, required to sustain the crystalloid (O'ROURKE and JOHNSON, 1955). With regard to nucleation, it must be pointed out that natural anhydrite may contain intrinsic gypsum and also may provide simultaneous growth planes (SPANGENBERG and NEUHAUS, 1930; TURNBULL and VONNEGUT, 1952) for gypsum. Both of these processes would circumvent the necessity of incipient nuclei formation.

The precipitation rate of gypsum by crystal growth of nuclei is represented by the following solution equation:

(K) $$-\frac{dC}{dt} = k(C - C_s)^q$$

where C = concentration of monomers

C_s = concentration at saturation

q = number of monomers in the growth nucleus

Simply stated, the driving force for precipitation is a function of the concentration

68

of calcium and sulphate ions above the saturation concentration. The equation can be transformed to:

$$(L) \qquad -\frac{dC}{dt} = k\left\{\sqrt{([Ca^{++}][SO_4^{=}])} - \sqrt{([Ca^{++}]_s[SO_4^{=}]_s)}\right\}^q.$$

The value $\sqrt{([Ca^{++}]_s[SO_4^{=}]_s)}$ can be equilibrated with the $(K_{sp})^{1/2}$ for calcium sulphate. As Fig. 7 shows, the K_{sp} varies strongly with $SO_4^{=}$ concentration. The growth order, q, and nucleation order, p, for the reactions are assigned the value of 4 based on the similar barium sulphate kinetic study by JOHNSON and O'ROURKE (1954). Hence, it is concluded that the rate of precipitation is $\alpha([Ca^{++}][SO_4^{=}])^2$ for nucleation and $\alpha\{\sqrt{([Ca^{++}][SO_4^{=}])} - \sqrt{K_{sp}}\}^4$ for growth.

The above treatment of solution kinetics has been incorporated to show that a sulphate activator provides greater precipitation rate for gypsum than other anion activators do. These kinetics also indicate that very dilute activator solutions. even in the range where calcium sulphate solubility is sharply depressed, are more efficient in producing hydration (as $[M_{2/a}SO_4] \to 0$) than water alone. This is substantiated by the 0·05M Na_2SO_4 data appearing in Fig. 8.

GEOLOGICAL APPLICATION

Gypsification of secondary anhydrite is believed to take place primarily by the action of activating cations. This concept of natural activation is supported both by the prevalence of saline solutions associated with gypsum–anhydrite deposits and by laboratory evidence.

The salinity of ground water associated with evaporite deposits is largely dependent upon beds of the more soluble K, Mg and Na salts. The prevalence of these salts in the Stassfurt evaporite deposits of Germany should result in the formation of concentrated salt solutions. It can be assumed, therefore, that activation of anhydrite through the formation of both stable and unstable double salts is a significant process in these deposits. Some of the complex salts which occur in the Stassfurt deposits and which may be related to activation processes (CLARKE, 1924) are:

Glauberite	$CaSO_4 \cdot Na_2SO_4$
Polyhalite	$2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$
Krugite	$4CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$
	(polyhalite admixed with anhydrite (FORD, 1947))
Syngenite	$CaSO_4 \cdot K_2SO_4 \cdot H_2O$

Obviously, the stable double salts persist only as long as their environments lie within their fields of stability. Dilution of the salt solutions and, with some salts. change of temperature result in their decomposition and subsequent precipitation of calcium sulphate as gypsum.

In contrast to the Stassfurt deposits the evaporites occurring in south-western Indiana (McGREGOR, 1954) are limited to anhydrite and gypsum. The ground water associated with these deposits contains relatively little solute. Chemical

analyses of water samples from the National Gypsum Co. and United States Gypsum Co. mines near Shoals, Ind., show a salinity of less than 20 parts per thousand. The following analysis (Table 3) of a sample taken from the National Gypsum Co. mine indicates the dilute character of the subsurface water:

Table 3. Analysis of mine water (National Gypsum Co., Shoals, Ind.)

Constituent	Concentration (%)
Na	0·56
Ca+Mg	<0·1
Cl	0·59
SO$_4$	0·43
B	trace
Fe	trace
K	trace
Li	trace
Sr	trace
S (as sulphide)	trace
Total dissolved solids	1·78
pH	8·0

The constituents of these subsurface waters may have been derived from any of the following sources:

(1) Connate water. Occurs as liquid inclusions in mineral grains and pore fluids within rock strata.

(2) Disseminated salts. Minute crystals included in the anhydrite–gypsum beds.

(3) Adsorbed ions. On clay structures by ion exchange.

(4) Previous salt deposits. Although petrographic evidence does not indicate the presence of soluble K, Na and Mg salts, these may have been removed by the action of ground water.

The relative rate of hydration produced by dilute solutions is illustrated in Fig. 8. The amount of conversion obtained by using a 0·75M Na$_2$SO$_4$ activator solution is shown by the upper two curves. The time lag between these two curves indicates the necessity of calcium sulphate saturation before gypsum precipitation can occur. At 0·75M sodium sulphate concentration the anhydrite solubility is noticeably increased with respect to dilute Na$_2$SO$_4$ solutions (see Fig. 7). The curve obtained with 0·05M Na$_2$SO$_4$, where anhydrite solubility is depressed, shows that activation occurs even in very dilute solutions. Although dilute solutions do not greatly accelerate hydration, the slight rate increase over pure water is significant when geologic time is considered. This observation becomes important when applied to geologic conditions in which the number of nuclei and amount of reaction surface are comparatively small.

On the assumption that crystallites of anhydrite form in sea water, as postulated by earlier workers, the present investigation indicates that activating constituents

contained therein would bring about almost immediate conversion to gypsum and/or double salts. Gypsum formation requires that temperatures during precipitation do not greatly exceed 42°C. The activating effect of sea water is shown in Fig. 9.* A second curve of activation by NaCl is included for comparison. The greater efficiency of sea water activation can be accounted for by the presence of small quantities of sulphate ion in sea water. It can be seen that above 214 parts per thousand salinity for sea water and 196 parts per thousand for NaCl, anhydrite is still converted to gypsum. Above these concentrations, theoretical vapour
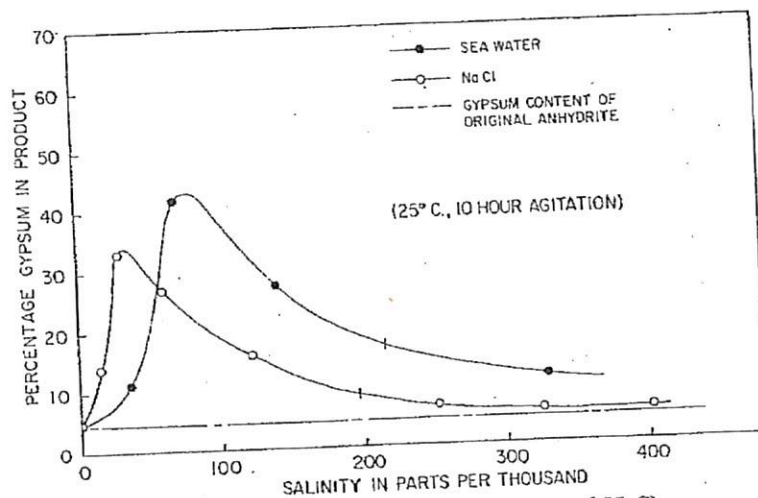

Fig. 9. Activation effect of sea water and NaCl.

pressure calculations indicate that at 25°C only anhydrite can be precipitated from solution. It must be concluded, therefore, that former thermodynamic applications based on vapour pressure relationships, which predict the formation of anhydrite from gypsum in concentrated salt solutions are incomplete. These applications do not incorporate the lattice alterations and intermediate calcium sulphate–activator complexes which influence the reaction kinetics.

It appears more reasonable to assume that anhydrite is formed, given sufficient time, only after burial when gypsum is subjected to directed stresses and increased temperatures.

SUMMARY

(1) The hydration of anhydrite is accelerated by certain acids, bases, and salts. Alkali sulphates are the most effective of these activators.

(2) In dilute activating solutions hydration proceeds via transient complexes. Depending upon temperature, double salts can be stable in concentrated activator media. The formation of complexes is believed to be a surface ionic transfer process and is a function of probability.

(3) Hydration of anhydrite in nature is believed to take place primarily by action of the activating cations occurring in ground water.

(4) Primary precipitation of anhydrite from sea water is improbable. The

* ROBERT F. CONLEY (1957) Unpublished manuscript.

relative ease of crystallization of metastable gypsum within the anhydrite stability field prevents sufficient supersaturation for nucleation of anhydrite. Abundant activating cations present in sea water further inhibit the formation of anhydrite.

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Attachment B-11