CALCIUM SULFATE THRESHOLD AND ADHERENCE STUDIES IN HEATED SYNTHETIC GULF BRINES

Douglas P. Logan and Susan Crnkovich

Calgon Corporation,
P. O. Box 1346,
Pittsburgh, Pennsylvania 15230, U.S.A.

الخلاصـة

يتم وضع مكونات كبرتيات الكلسيوم في المياه ذات التمركز العالي في درجة الملوحة وذلك في درجة حرارة عالية خلال العملية الومضية متعددة المراحل . وفي الإمكان تحقيق وفورات هامة في تكاليف المياه لو أنه تمت زيادة درجة حرارة المياه المالحة أو عنصر التمركز . وقد تم إجراء اختبارات خاصة بالإستخدام والتمسك بهدف دراسة تأثير تمركز ايونات الهيدروجين ودرجة الحرارة وجرعة مانع التفاعل الكيميائي على نصف كبرتيات الكلسيوم والترسب الهيدريدي في مياه البحار الخالية من الكربون والمتمركزة الملوحة . وقد حدث في أول الأمر ترسب للنصف هيدرات في المياه المتمركزة الملوحة غير المعالجة والمفرطة التشبع بنصف الهيدرات وإيدريد كبريتات الكلسيوم بالرغم من أن درجة ذوبان الإيدريد منخفضة .

وفي ظروف مشابهة للملوحة ودرجة تمركز أيونات الهيدروجين ودرجة الحرارة للمياه المالحة غير المعالجة هناك سرعة ترسب الإيدريد في حين لم تتم معالجة ترسب نصف الهيدرات وقد تم تفسير هذه الظاهرة على أساس تمركز أيوني لكل وحدة زمن .

وبالرغم من أن كل كربوكسيلية ومانع التفاعل الكيميائي الفوسفوري قد تم تقويمها على أساس تمركز أيونات الهيدروجين ٧ و٩ وتناقص معالجة نصف الهيدرات في درجة تمركز أيوني عالية فقد تنج خليط من الكربوكسيلية والفوسفور والذي وجد في كلتا حالتي تمركز أيونات الهيدروجين . وكان الناتج ذا فعالية كمانع قلوي للتفاعل الكيميائي . وقد أبرزت الدراسات الخاصة بالحركات الدقيقة الضوئية مدى تأثير كل من مانع التفاعل الكيميائي والمتمركز على هيكل نصف هيدرات كبريتات الكلسيوم المعالجة وغير المعالجة وترسيب الإيدريدات .

وستـؤدي هذه الدراسات إلى إيجاد مفهوم أفضل لتكوينات كبريتات الكلسيوم والتمسك والمعالجة في أنظمة إم . إس . إف .

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ABSTRACT

The potential for calcium sulfate formation currently sets the upper limits of brine concentration and temperature in the multiple stage flash process. Significant water cost savings could be realized if the design top brine temperature or concentration factor can be increased. Threshold inhibition and adherence tests were used to study the influences of pH, temperature, salinity and inhibitor type, and dosage on calcium sulfate hemihydrate and anhydrite precipitation in synthetic, carbonate-free, concentrated, seawater brines. Hemihydrate always precipitated first in concentrated, uninhibited brines supersaturated with respect to both calcium sulfate hemihydrate and anhydrite, even though anhydrite had a lower solubility. Under similar conditions of salinity, pH, and temperature in inhibited brines, anhydrite precipitation was accelerated as hemihydrate precipitation was inhibited. This phenomenon was explained in terms of ion pair concentration per unit time. Although every polycarboxylate and phosphonate inhibitor evaluated at pH 7 and pH 9 exhibited decreased hemihydrate inhibition at the higher pH, a formulated product, containing a polycarboxylate and a phosphonate, exhibited the same inhibition at both pH's. The product was efficacious as an alkaline scale inhibitor, also. Scanning electron photomicrograph studies established the influences of inhibitor type and concentration on the structure of untreated and treated calcium sulfate hemihydrate and anhydrite precipitates. These studies will lead to a better understanding of calcium sulfate scale formation, adherence, and inhibition in MSF systems.

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INTRODUCTION

The multiple stage flash, or MSF, distillation process for the production of fresh water from aqueous solutions accounted for 67% of the world's total desalination capacity in 1981 of more than 7.6 million m^3/d (two billion GPD)[1]. Appreciable savings in the cost of fresh water produced by the MSF process could be realized if plants were designed and operated at higher top brine temperatures or with more concentrated recirculation brines. In one study of MSF design optimization for seawater desalination units, using the three critical cost parameters of electricity, steam, and heat-transfer surface area, the cost of water decreased as the top brine temperature increased. Minimum water costs were obtained between 177 and 204°C (350–400°F)[2]. However, the current maximum brine temperature in operating units is approximately 121°C (250°F)[3]. Fresh water unit cost reductions of 25 to 33% are projected if the maximum brine temperature in MSF evaporators can be increased 55 to 80°C (99–144°F).

The concentration factor, or C. F., of a MSF unit is the ratio of the total dissolved solids (TDS) in the brine blowdown to the TDS in the seawater makeup. Operation of existing units at higher C.F.'s for a fixed top brine temperature would result in reduced seawater makeup and brine blowdown flows for a constant distillate production rate. For example, a unit with a nominal C.F. of 1.5 and a 12000 t/d seawater makeup flow would have a brine blowdown flow of 8000 t/d and a distillate flow of 4000 t/d. If a C.F. of 2.0 could be maintained in the unit with no change in distillate production, the daily mass of makeup would be reduced 33% and the blowdown mass 50% (see Table 1).

Table 1. Mass Flows, t/d

	M_m	M_b	M_d	C.F.
Case I	12 000	8000	4000	1.5
Case II	8 000	4000	4000	2.0

M_m = mass of makeup; M_b = mass of blowdown; M_d = mass of distillate.

In Case II, the reduced makeup and blowdown flows versus Case I will result in lower fresh water costs because of the reduced electrical and chemical pretreatment requirements. The chief impediment to extension of the top brine temperature or brine concentration factor is the formation of mineral scale on heat transfer surfaces[2].

When raw seawater is heated above 77°C (171°F), it becomes unstable with respect to the solubility of various calcium and magnesium compounds[4]. If precipitation and adherence of these compounds occur on heat transfer surfaces, mineral scale formation results. Because mineral scales have much lower thermal conductivity than metals do, their presence on metal surfaces serves as an insulation barrier to the flow of heat energy. If allowed to continue, plant capacity and efficiency can be reduced severely, and the plugging of tubes can render the plant inoperable. Loss of product water is the end result.

The three common scale compounds formed when seawater is concentrated by distillation are calcium sulfate and the 'alkaline' scales, calcium carbonate and magnesium hydroxide (Figures 1–3). The 'alkaline' scales form as a function of pH, temperature, and concentration factor of the brine. On the other hand, calcium sulfate formation does not depend upon the brine pH. The alkaline scales have been successfully controlled in MSF process by many methods[5], but the two common commercial methods are mineral acid injection or the use of 'threshold' scale inhibitors. Numerous authoritative calcium sulfate solubility studies have led to the development of the currently accepted method for control of calcium sulfate scale formation: operation of the unit below the concentration and temperature limits for calcium sulfate hemihydrate precipitation[6–9]. Thus, the overall driving force for the MSF process, which is the temperature difference between the top brine temperature and the brine blowdown temperature, is set by the calcium sulfate scale 'barrier'. The development of a reliable and economical method to control calcium sulfate scale formation on heat transfer surfaces would allow for improved production efficiencies by increasing the driving force for the process. Various methods designed to control calcium sulfate supersaturation include ion exchange, controlled precipitation, or the use of 'threshold' scale inhibitors[10]. Cost and operational considerations favor the development of chemical additives to stifle calcium sulfate scale[2].

Recent studies have focused on the development of laboratory screening methods for the evaluation of

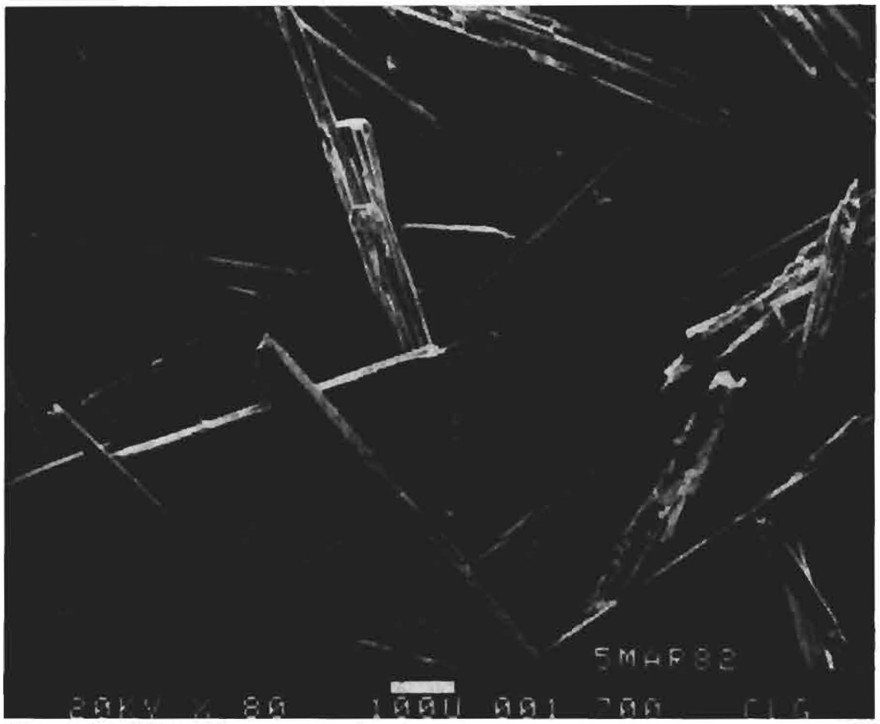

Figure 1. SEM Photomicrograph of Calcium Sulfate Hemihydrate Formed in Concentrated Gulf Seawater at 118°C (245°F). The Magnification is 80 × (8 mm = 100 Microns)

Figure 2. SEM Photomicrograph of Calcium Carbonate (Aragonite) Formed in 1.6 × Gulf Seawater at 116°C (240°F). The Magnification is 20,000 × (1cm = 2 Microns)

Figure 3. SEM Photomicrograph of Magnesium Hydroxide, or Brucite. The Magnification is 5,000 × (6 mm = 1 Micron)

calcium sulfate precipitation and adherence inhibitors in a synthetic brine formulated to represent concentrated Gulf seawater without alkalinity. The effects of various inhibitors on the precipitation and morphology of calcium sulfate have been investigated in a stagnant flask threshold test and a seawater scale adherence simulator, both using concentrated synthetic Gulf seawater heated to 118–121°C (245–250°F). Scanning electron microscopy and energy dispersive X-ray analyses were employed to confirm crystal structures of precipitated species and study crystal morphology differences. These studies will lead to a better understanding of the influence of crystal structure on scale adherence.

EXPERIMENTAL

Threshold Test

A threshold test for $CaSO_4$ inhibition in cycled up Gulf seawater at high temperatures was designed to test the efficacy and efficiency of chemical additives under conditions more stringent than those in a MSF evaporator. Carbonate-free synthetic Gulf seawater stock solution at a cycle factor of 2.50 or 2.75 × was prepared from inorganic salts and used on the same day as testing. The pH of the stock solution was adjusted to either 7.00 ± 0.05 or 9.00 ± 0.05 (with dilute NaOH or HCl), depending upon the test. Next, 200 ml of the stock solution was pipetted into 250 ml Erlenmeyer flasks containing from 0 to 0.6 ml of a 5 g/l solution of chemical additive (adjusted to pH7). A final pH adjustment was then made on each solution. The top of each flask was covered with aluminum foil over which an aluminum weigh pan was wrapped. The flasks were then placed into a preheated vertical steam sterilizer capable of heating the samples without boiling from the ambient up to 135°C at a pressure of 206kPa. After an hour, the desired temperature was reached and time measurement began. Most of the work was done at either 118 or 121°C (245 or 250°F). In the time study of inhibition, time at temperature was varied from 4 to 40 hours. For the standard inhibition series, the test parameters were 4 hours at 118 or 121°C (245 or 250°F), initial pH of 7.00 ± 0.05 or 9.00 ± 0.05, and a concentration factor of 2.75 × carbonate-free Gulf seawater.

Inhibition was based upon loss of calcium in solution. This was determined through Schwarzenbach calcium titrations of aliquots of the stock and final solutions in each flask [11]. Crystal deposits from each flask were collected, when possible, for SEM study, X-ray diffraction analyses and examination under the

Zeiss stereomicroscope. Crystals were prepared for the optical analyses by filtration of the hot solution at 80°C (176°F), followed by air drying them at room temperature.

The Seawater Scale Adherence Simulator, or SWSAS

The SWSAS is designed to heat a feed of synthetic seawater or brine from the ambient temperature up to 121°C (250°F) without boiling the liquid. The unit has a continuous makeup feed and blowdown. Each test is initiated by filling a pyrex test cell with brine, adjusting a nitrogen gas sparge to the desired flow rate, and turning on the steam. The test cell consists of a pyrex cylinder containing an internally steam heated 90/10 cupronickel deposit tube which is totally immersed in the test brine. The continuous nitrogen sparge and blowdown tube insure removal of non-condensable gases and fluid. Brine flows average 0.6–0.8 l/hr during a typical 18 hour test. The long residence time at high temperature for the test brine and the absence of turbulent flow at the deposit tube surface insure the most stringent conditions for scale inhibitor performance evaluations. A deposit rate of scale buildup on the deposit tube is calculated by measuring the total water-insoluble deposit weight and the total brine volume throughput. The degree of scale inhibition is determined by the following relationship:

$$\%\ \text{Inhibition} = \frac{\text{Blank Deposit Rate} - \text{Inhibited Deposit Rate}}{\text{Blank Deposit Rate}} \times 100$$

With a nominal cell liquid volume of 0.5 l, and a brine flow rate of 0.6 l/hr, the brine has an average residence time of 50 min at the cell top brine temperature, typically 116–121°C (240–250°F).

Cupronickel test specimen weights are recorded five times (to the nearest 0.1 mg) during each test run. The clean weight represents the mass of the coupon before exposure to the test solution. The fouled weight is the coupon weight after removal from the test cell, but prior to rinsing the deposit with distilled water. The rinsed weight represents the weight of water-insoluble scale deposited on the cupronickel tube plus the weight of the brine-exposed tube. The acidized weight is the weight of the coupon after the deposit has been removed by chemical or mechanical techniques. Finally, the recleaned weight is the weight of the test specimen after cleaning and polishing recreate a new test surface.

The difference between the fouled weight and the recleaned weight is the total mass accumulated on the coupon, which is air dried by draining the test cell immediately after turning off the steam flow to the unit. The total mass weight represents the quantity of soluble and insoluble compounds on the tube. The mass of soluble salts for each test is determined by the difference between the total mass weight and scale deposit weight, defined below.

The quantity of soluble mass deposited in each run provides a qualitative indication of the bulkiness and packing regime of the scale crystals. Comparison between runs affords chemical formulation changes to optimize additive qualities. A bulky deposit has less tendency to adhere to heat transfer surfaces than does a closely packed solid, especially in flowing systems such as the heat transfer tubes of MSF evaporators. The scale deposit weight in each run is found by subtracting the reclean coupon weight from the rinsed coupon weight. It is used to obtain the scale deposit rate when divided by the total brine throughput during the test.

The scale removed from the deposit tube is examined by methods similar to those used to study the crystals which form in the threshold studies above. SEM and (Zeiss) stereomicroscope photographs of each run's scale enable study of their crystal habits and morphologies, as well as comparison studies between inhibited versus uninhibited runs, and between various inhibitors and formulated commercial additives.

The brine used in all tests was carbonate-free, concentrated synthetic Gulf seawater prepared with analyzed chemical reagents. The compositions of nominal Gulf seawater and the concentrated test brines are given in Table 2.

Table 2. Ionic Composition of Brine Stock Solutions

Ion	Nominal	meq/l			
		1.00 ×	1.50 ×	2.50 ×	2.75 ×
Sodium	575	591	946	1477	1625
Calcium	25	24	38	60	66
Magnesium	129	134	215	335	368
Potassium	N/A	12	19	30	33
Sulfate	68	70	112	175	192
Chloride	659	691	1106	1727	1900
TDS, mg/l	42 110	44 100	70 560	110 250	121 280

The nominal Gulf seawater, chosen as the seawater stock solution composition from which the brine compositions for these tests were prepared, is representative of typical seawater makeup to high temperature MSF units currently operating in Eastern province coastal locations in Saudi Arabia [12].

RESULTS AND DISCUSSIONS

Calcium Sulfate SWSAS Studies

Calcium sulfate scale formation in seawater evaporation processes is a complex phenomenon, because there are at least three forms of calcium sulfate which can occur as a function of brine concentration and temperature. In seawater MSF operations, the prevalent form which occurs first is the hemihydrate, because it does not require as long a nucleation time as the anhydrite before crystallization occurs. The rate of precipitation and subsequent rate of transformation of hemihydrate to anhydrite has been shown to be affected by the molar ratio of calcium to sulfate ions in solution.

There are two crystalline forms, designated α- and β-hemihydrate [10]. Normal seawater, which contains 1.0×10^{-2} M calcium ions and 2.8×10^{-2} M sulfate ions, will form preferentially α-hemihydrate, which converts to anhydrite rapidly above 140°C (284°F). In one study of precipitation of calcium sulfate from seawater at elevated temperatures, the α-hemihydrate always crystallized first, but was replaced by the more thermodynamically stable anhydrite after a time which depended on the temperature. The hemihydrate crystals provided nuclei for the anhydrite to form [13].

The growth of α-hemihydrate from supersaturated solutions is controlled by a surface reaction and is independent of the fluid dynamics of the system. It proceeds at a rate proportional to the square of the relative supersaturation. Dissolution of α-hemihydrate, more rapid than its formation, is a diffusion controlled reaction, however [14]. A series of SWSAS tests in synthetic 1.6 × carbonate-free Gulf seawater established that calcium sulfate hemihydrate is the initial scale deposited below 120°C (248°F) in less than 16 hours. The deposits were identified by microcharacterization and X-ray diffraction.

To establish the effect of time and temperature on the type of scale crystals formed, a special SWSAS test was conducted in Arabian Gulf seawater with a 1.25 × supersaturation with respect to calcium sulfate hemihydrate at 115.6°C (240°F). After 64 hours, the heavily encrusted U-tube was removed from the cell and the extremely tenacious scale scraped off and analyzed by X-ray diffraction. The major portion was hemihydrate, but also included was 15 to 20% anhydrite, and 1 to 4% dihydrate. As expected, the anhydrite form predominated next to the hot tube wall, and the dihydrate was found in the scale crystal samples farthest from the heat source. The final bulk brine temperature was 101.7°C (215°F).

SWAS Inhibitor Evaluations

The relative effectiveness of two formulated inhibitors to prevent calcium sulfate scale was established in a series of SWSAS tests at 115.6°C (240°F) in 1.6 × Arabian Gulf seawater containing no alkalinity (the effect of stoichiometric acid dosing). Sufficient sodium sulfate was added to create a calcium sulfate saturation level of 1.25 ×, with the initial brine pH adjusted to 8.15 ± 0.05. The high saturation level for calcium sulfate insures that laboratory conditions are more severe than MSF conditions. Also, tests were run with long high-temperature residence times to be more rigorous than operating conditions. The intent was to show relative inhibitor effectiveness, so that a choice between two formulations could be made.

EL–X, a phosphonate based product, delayed the onset of scale, achieving a maximum inhibition of 92% at 10 ppm product. In contrast, a formulation containing both phosphonate and polycarboxylate, EL–Y, produced maximum inhibition at 5.0 ppm. Also, the second product maintained high (90%) inhibition at higher dosages, whereas the higher levels of treatment with EL–X resulted in less than maximum inhibition. Figure 4 shows percent inhibition versus dosage curves

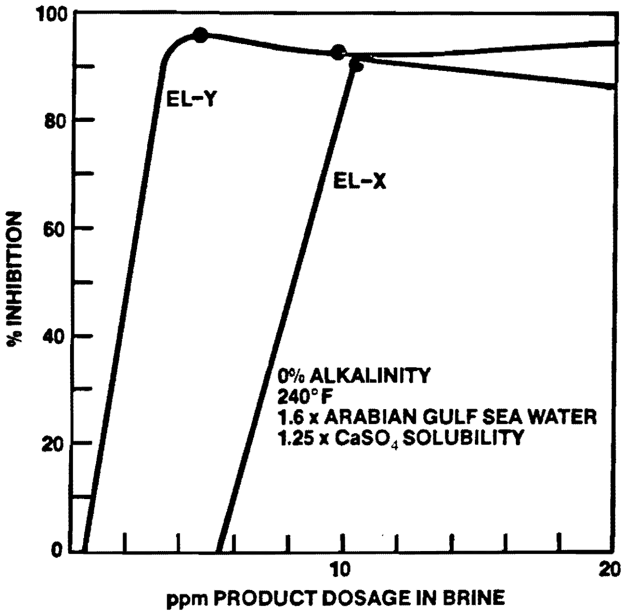

Figure 4. Scale Adherence on Heat Transfer Surface

Figure 5. Zeiss Stereomicroscope Photograph of Uninhibited Calcium Sulfate Scale Formation on a SWSAS Tube (12 × ; 1 cm = 1.2 mm)

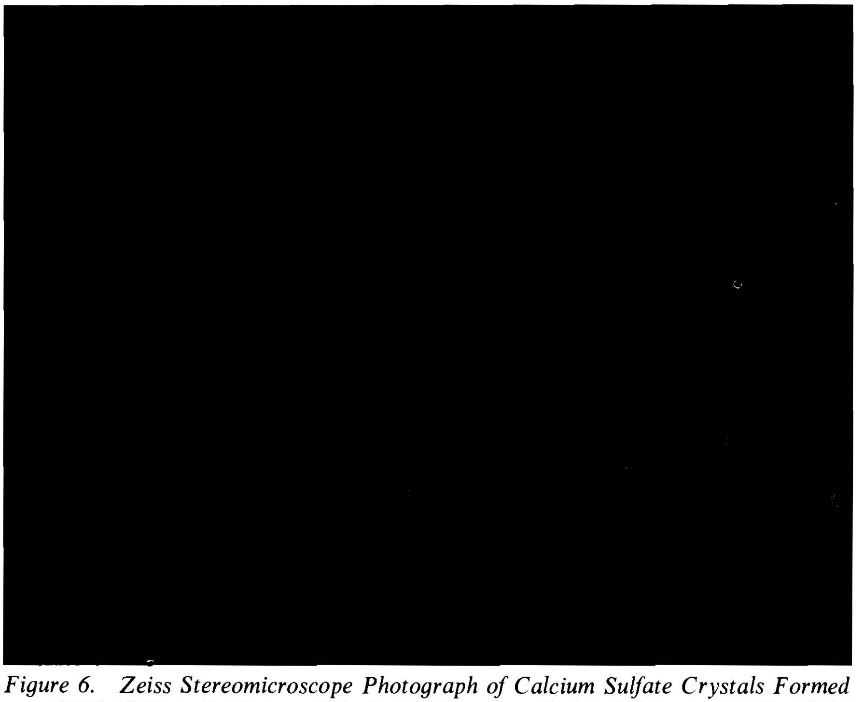

Figure 6. Zeiss Stereomicroscope Photograph of Calcium Sulfate Crystals Formed on a SWSAS Heat Exchanger Tube in the Presence of a Dual Component Threshold Inhibitor (12 × ; 1 cm = 1.2 mm)

for this series. Figure 5 is the typical appearance of a SWSAS tube following a blank run and Figure 6 shows modified crystals from a dual component EL–Y run. Normal velocities found in brine heater tubes would be expected to prevent deposition of these modified crystals on heat transfer surfaces.

Calcium Sulfate Threshold Tests

In addition to tests on heat transfer surfaces in the SWSAS unit, various calcium sulfate 'threshold' studies have been carried out in synthetic concentrated Gulf seawater. The 'threshold' screening method involves commingling of precipitating ions in the presence and absence of inhibitors. The effect of time on the ability of an inhibitor formulation to prevent precipitation of calcium sulfate was investigated in a series of flask tests at 118.3°C (245°F) with 2.5 × synthetic Gulf seawater. The formulation EL–Y contains a phosphonate and a polycarboxylate, both known threshold scale inhibitors. Results appear in Table 3.

Table 3. Effect of Time on $CaSO_4 \cdot 1/2H_2O$ Inhibition

	% Inhibition (EL–Y dosage in mg/l)			
Time, hours	2	5	10	15
9.5	91	93	93	97
17	26	11	0	0

In uninhibited runs of less than 27 hours, hemihydrate was the only identified precipitate. In all runs containing inhibitor, the identified calcium sulfate species was anhydrite. Although results at 9.5 hours showed excellent hemihydrate inhibition, at 17 hours there was little or no inhibition of anhydrite at dosages of 2 to 15 mg/l of EL–Y. This evidence indicates insufficient inhibitor was present to prevent anhydrite precipitation. The extremely severe test conditions relative to MSF operations should be noted in view of the fact the recirculating brine in a typical MSF unit is exposed to high temperatures for seconds, rather than hours. By achieving threshold inhibition for hours at high temperatures the prospects for successful field performance are greatly enhanced.

Interestingly, formation of anhydrite was first observed in treated samples at 4 hours, but not until 27 hours in the blank. The long nucleation time for anhydrite crystals in the absence of threshold agents is well known [13]. We have confirmed that hemihydrate precipitates first in concentrated, uninhibited brines saturated with respect to both calcium sulfate hemihydrate and anhydrite, even though anhydrite has the lower solubility. The phenomenon occurs because anhydrite has a long nucleation time and hemihydrate does not. Nucleation time, the time required for crystal nuclei to form in a supersaturated solution, is a critical step in the formation of mineral scale. Any extension of the nucleation time would *a priori* extend the time for incipient precipitation from a supersaturated solution.

Our studies in concentrated, inhibited brines established that hemihydrate precipitation was retarded timewise, but anhydrite precipitation was accelerated. What causes the acceleration? Calcium sulfate ion pairs, normally reduced in concentration during hemihydrate precipitation, are available in the inhibited solution. If these pairs are involved in the formation of anhydrite, their higher concentration per unit time in the inhibited solution could explain the faster rate of formation of anhydrite in inhibited brines. Experimental design studies can be employed to study the influence of ion pair concentration on the accelerated precipitation of anhydrite from concentrated seawater brines.

Gill and Nancollas [10] reported that phosphonates accelerated the transformation of hemihydrate to anhydrite at higher temperatures but polyacrylate retarded the transformation. In contrast, we found that polycarboxylates, including polyacrylate, also accelerated the formation of anhydrite in concentrated Gulf brines at 121°C (250°F). In 4 hour tests performed at both pH 7 and pH 9, a C.F. of 2.75 × Gulf brine without carbonate, and a temperature of 121°C (250°F), the anhydrite phase was present in deposits from polymaleic acid treatment at dosages ≥ 1.25 mg/l. At dosages > 2 mg/l, the anhydrite phase was the only phase present. Similarly with treatment by polyacrylate, the anhydrite phase was present in deposits when the dosage exceeded 1 mg/l. At dosages of polyacrylate > 2 mg/l, anhydrite was the only phase present. Other polycarboxylates exhibited similar behavior. In all 4 hour test series, the inhibitor dosage at which anhydrite appeared coincided with the dosage required to achieve maximum hemihydrate inhibition. With essentially no hemihydrate precipitating, a maximum $CaSO_4^{\circ}$ ion pair concentration per unit time is available for anhydrite formation. If $CaSO_4^{\circ}$ concentration per unit time is a rate limiting condition in anhydrite formation, we now have an explanation for the accelerated formation of anhydrite in inhibited seawater brines supersaturated with respect to both anhydrite and hemihydrate. Ion pair concentration studies are planned to explore this aspect of calcium sulfate scale formation.

Deposits from various blank and treated samples were photographed using a Zeiss stereomicroscope. Hemihydrate crystals appeared to be needle-like in the blanks (Figure 7). Anhydrite present in the blanks appeared block-like and twinned, orthorombic as expected, and much like those seen in the paper 'Chemical Additives for Calcium Sulfate Scale Control' by Austin and co-workers [13] (Figure 8). Anhydrite in treated samples was highly modified, appearing flower like, with the crystal edges being shaped like a petal, unlike the lamellar blocks of uninhibited anhydrite (Figure 9). Three SEM photomicrographs illustrate the microstructure of modified anhydrite deposits taken from a 31 hour sample treated with 15 mg/l of formulation EL–Y (Figures 10–12). A blank run at 129°C (264°F) produced an anhydrite deposit which was free of hemihydrate. It was used as a reference for the SEM comparisons and structure confirmation by X-ray diffraction.

$CaSO_4$ Threshold Inhibition Versus pH

Threshold inhibition studies established the efficacy and efficiency of various polycarboxylate chemical additives against $CaSO_4$ precipitation at high temperature in cycled up seawater. These were 4 hour tests at 118°C (245°F), pH of 7.00±0.05, and concentration factor of 2.75 × carbonate-free synthetic Gulf seawater. Dosages of additives varied from 1 to 15 mg/l. All exhibited greater than 90% inhibition at a dosage of less than or equal to 2.5 mg/l, indicating they were capable of forming the three-fold helical structure which enables them to adsorb onto Ca^{++} ions in the forming lattice [13].

Several phosphonates were tested under the same conditions as the polycarboxylates. Approximately 7 mg/l of a diphosphonate was required to produce 90% inhibition of $CaSO_4$ hemihydrate precipitation, whereas less than 2.5 mg/l of phosphonate with five active groups was required to produce the same efficiency, because it provided a good fit with active calcium sites in the hemihydrate crystal lattice.

A polymeric sulfonate evidenced $<10\%$ inhibition at dosages ranging from 2.5 to 10 mg/l, indicating that the sulfonate group does not fit the active growth sites on hemihydrate crystals. Also, its large size may contribute to the molecule's ineffectiveness.

The threshold studies at pH 7 represent high temperature MSF plants operating with acid to control alkaline scale. Although these units never operate intentionally at high cycles of concentration, the occurrence of certain events, such as localized corrosion, water-borne deposits or inefficient degassing of makeup seawater, can create localized areas on heat transfer surfaces where the concentration–temperature saturation limit for $CaSO_4$ hemihydrate is exceeded. Often, troublesome calcium sulfate scale occurs. Therefore, it is prudent to use a chemical additive with efficacy against not only the 'alkaline' scales, but also calcium sulfate scale. The additive should contain single or multiple threshold inhibitors effective against both hemihydrate and anhydrite precipitation.

In order to study the inhibition of calcium sulfate precipitation under conditions possible in high temperature MSF plants using chemical additives for scale control, a series of threshold tests were performed in 2.75 × carbonate-free, synthetic Gulf seawater at a pH of 9.00±0.05, temperature of 121°C (250°F), and time of 4 hours.

The polycarboxylates and phosphonates tested at pH 7 exhibited decreased efficiency at pH 9. The polymeric sulfonate was ineffective at the higher pH, also. However, EL–Y, the formulation of polycarboxylate and phosphonate tested in the threshold time study, exhibited the same inhibition at both pH's with greater than 90% inhibition occurring at a dosage of 5 mg/l as product. Earlier SWSAS studies established EL–Y's effectiveness in controlling alkaline scale deposits in seawater brines [15]. A field trial established the product's efficacy in a high temperature MSF unit operating at a top brine temperature of 116 C.

The value of the above formulation as a commercial treatment additive for alkaline scale control in high temperature MSF plants is enhanced by its ability to control calcium sulfate scale.

Crystal Morphology of the Deposits

The deposit form seen in all blanks from the 4 hour threshold inhibition studies in high temperature cycled up seawater was $CaSO_4$ hemihydrate. It appeared needle-like in the Zeiss stereomicroscope at 26 × (Figure 7). An SEM photomicrograph of a blank deposit formed under the conditions of 4 hours at 118°C (245°F) in 2.75 × synthetic carbonate-free Gulf seawater at a pH of 7.00±0.05 appears in Figure 1. The needle-like hemihydrate crystals are hexagonal prisms with extended growth along the *c*-axis.

The deposits formed with typical polycarboxylate

Figure 7. Hemihydrate Formed in 2.75 × Gulf Seawater (Without Carbonate) at 121°C (250°F) and a pH of 9.00 ± 0.05. Note the Needle-like Structure. Magnification is 26 × (1 cm = 2.6 mm)

Figure 8. Anhydrite Formed in 2.50 × Gulf Seawater (Without Carbonate) at 127°C (260°F) and a pH of 7.00 ± 0.05. Note the Blocky Structure and Presence of Twinning. The Magnification is 26 × (1 cm = 2.6 mm)

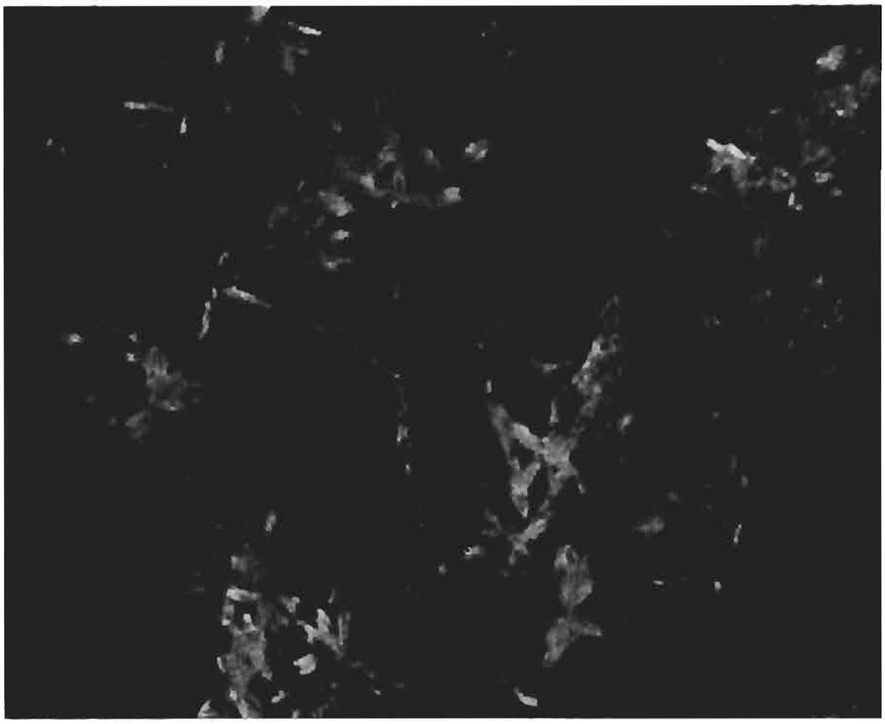

Figure 9. Distorted Anhydrite Formed in Treated 2.50 × Gulf Seawater (Without Carbonate) at 118°C (245°F) and pH of 7.00 ± 0.05 (15 mg/l of a Polycarboxylate–Phosphonate Formulation). Note the Flower-like Appearance, the Edges Being Shaped Like Petals, and Presence of Twinning. The Magnification is 26 × (1 cm = 2.6 mm)

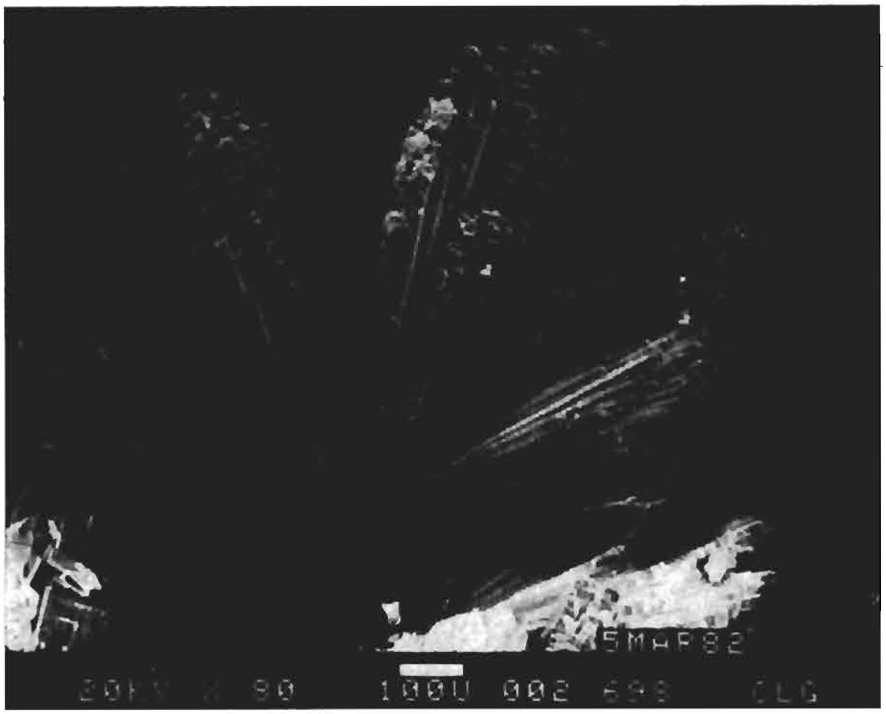

Figure 10. SEM Photomicrograph of Distorted Anhydrite Formed in 2.5 × Gulf Seawater Containing 15 mg/l ELY, after 31 Hours at 121°C (250°F). Note the Growth from a Single Nucleation Site. The Magnification is 80 × (8 mm = 100 Microns)

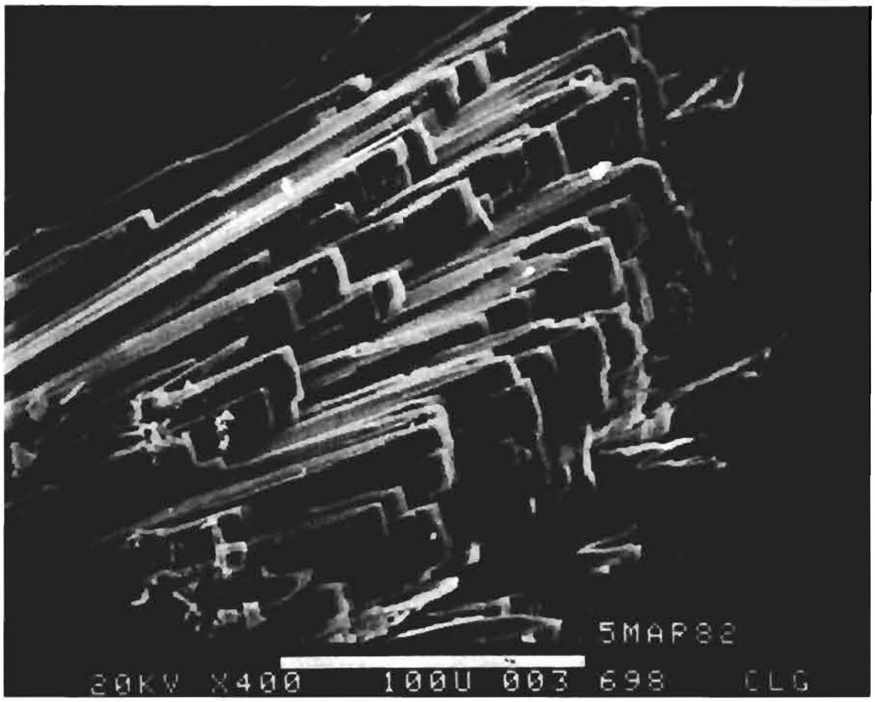

Figure 11. A Close-up of the Crystal From Figure 10 Reveals the Jagged, Irregular Structure of Inhibited Anhydrite. The Magnification is 400 × (4 cm = 100 Microns)

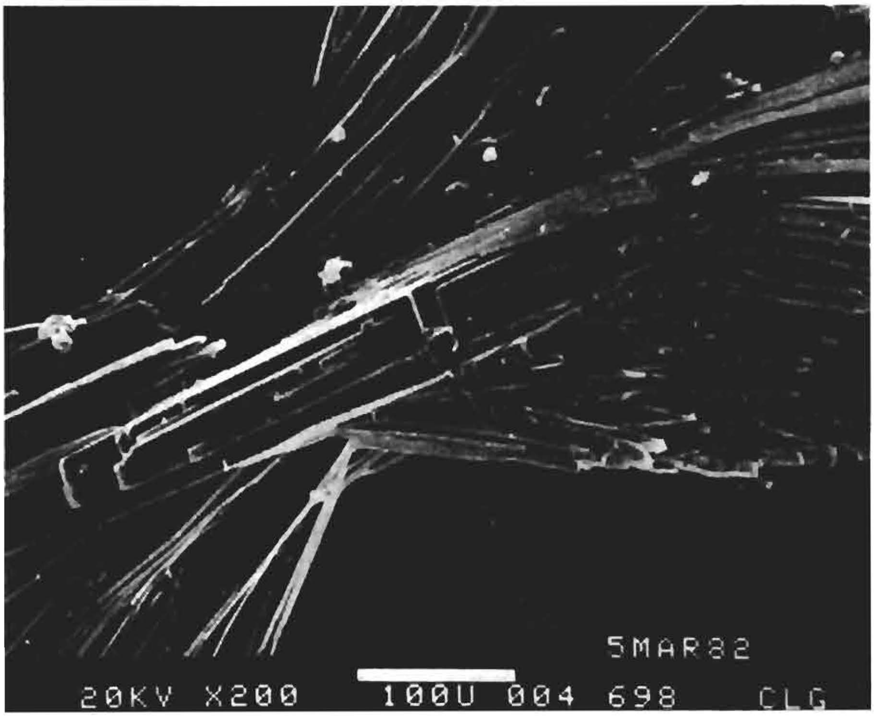

Figure 12. This SEM Photomicrograph Reveals the nature of a Twinned Crystal Nucleation Site. Uncontrolled Growth Began in Opposite Directions, with Highly Modified Anhydrite the Result. Magnification is 200 × (2 cm = 100 Microns)

treatment in 4 hour tests at 121°C (250°F), pH 700 ± 0.05 or 9.00 ± 0.05, and a C.F. of 2,75 Gulf seawater without carbonate, were distorted hemihydrate in samples dosed with less than 1 mg/l (Figure 13). In samples with dosages exceeding 2 mg/l, distorted anhydrite was the major deposit constituent (Figure 10). With some polycarboxylates at higher dosages, distorted hemihydrate was evidenced along with the anhydrite.

CONCLUSIONS/SUMMARY

Calcium sulfate scale formation sets the upper limits of brine concentration and temperature in the MSF process. Significant water cost savings could be realized if the design top brine temperature or concentration factor can be increased. Calcium sulfate scale formation or adherence on heat transfer surfaces can be prevented through the use of threshold chemical additives. The additive of choice should have efficacy against both alkaline and calcium sulfate scales. A new multi-component liquid formulation, EL–Y, exhibits effectiveness against both types of deposits, and is compatible with concurrent addition of acid.

Calcium sulfate threshold studies in synthetic, carbonate-free, concentrated Gulf seawaters at temperatures typically encountered in MSF evaporators have confirmed prior studies which show that the initial deposition phase is hemihydrate. Increasing temperature or residence time increases the tendency toward anhydrite formation. The accelerated precipitation of anhydrite in inhibitor treated supersaturated seawater brines was explained in terms of the increased availability of $CaSO_4^\circ$ ion pairs. Further, at shorter exposure times, precipitation of hemihydrate can be completely eliminated through the addition of various scale inhibitors. However, the additive of choice should prevent, or at least retard, the growth of anhydrite also. A formulation containing a polycarboxylate and a phosphonate evidenced excellent inhibition of calcium sulfate precipitation at low dosages. Future inhibitor studies will define the formulation's thermal, hydrolytic stability and the limits of seawater C.F., temperature, and residence time under which the inhibitor prevents alkaline and calcium sulfate scale formation in commercial units. Tests will include concentrated seawater brines supersaturated with respect to the alkaline scales and cal-

Figure 13. SEM Photomicrograph of Distorted Hemihydrate Formed from 2.75 × Gulf Seawater (Without Carbonate) Treated with ≤ 1.25 mg/l Polycarboxylate under the Threshold Conditions of 4 Hours at 121°C (250°F) and an Initial pH of 9.00 ± 0.05. The Magnification is 79 × (7.6 mm = 100 Microns)

cium sulfate to simulate realistically the evaporator chemistry of inhibitor treated units.

Deposit adherence testing with a seawater scale adherence simulator established the influence of time, temperature, and brine concentration on calcium sulfate precipitation in carbonate-free, synthetic Gulf seawater brines. The Zeiss stereomicroscope and SEM-EDXRA analyses were employed to evaluate the effects of test variables on calcium sulfate crystal morphology, provide data for the formulation of highly effective multi-component scale control additives, and study the influences of crystal structure on scale adherence.

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