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SULFATE INHIBITOR SELECTION AND USE

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Abstract

Calcium sulfate is the most common impurity in salt. It is found in many forms that must be removed at least in part during brine treating processes to control brine quality and maintain chlorine cell and evaporator equipment. Several types of sulfate inhibitors have been developed that lower the anhydrite form of calcium sulfate at its source. The newest all-organic product—with catalyst—is the most cost effective, having the potential to virtually eliminate calcium sulfate in some brines. Many applications average 75% inhibition rates at very economical dosages under 15 ppm. Sulfate inhibitors are now available for both chlor-alkali and evaporated salt production, meeting FDA/GRAS requirements for food salt.

Successful application of a sulfate inhibitor often begins with a preliminary laboratory report; justifying a more conclusive field evaluation based on cost performance data, potential savings, and brine quality improvements. The duration of a field test is determined by the residence times of individual brine wells and the desired reduction in calcium sulfate. Many solution mining evaluations begin to develop consistently lower sulfate values after just one residence-time displacement, while more definitive progress requires three to five displacements, or more. Evaluations should not be attempted in newly developing brine wells that carry-over undissolved salt—usually lower residence times. Laboratory methods are presented that were developed to utilize either rock salt or drilling core from the plant site, and actual dissolving water. Data is presented in graphic form to clearly show typical product comparisons and resulting cost performance.

Chemical handling is very important and must be considered when selecting a sulfate inhibitor treatment program. As an example, the newest organic inhibitors are viscous concentrations of acidic ingredients that must be handled and used with properly designed equipment. Chemical inhibitors are delivered in bulk via tank truck or ocean container, and in a variety of DOT approved containers and drums. International shipments are typically made in semi-bulk, one-way IBC containers of 1,041 liters (275 gallons) each.

In all cases, reliable chemical metering equipment must be chosen to handle and use the chemical under the most adverse of operating conditions. Particular attention should be paid to cold weather handling, possible contamination and environmental safety.

Sulfate inhibitor performance can be monitored with routine laboratory tests. Once established, daily control of chemical residuals is usually not necessary with the new organic inhibitors. However, it is still important to monitor distribution in multi-well water injection systems and limit wasteful or excessive use. A simple test procedure, adaptable to field office use and employing a unique PHTTT reagent, is presented that accurately measures the most cost effective all-organic inhibitors at very low (ppb) values in both water and brine.

Key words: Sulfate Inhibitors, Calcium Sulfate, Anhydrite, Sulfate Inhibitor Performance, Laboratory Test Method, Chemical Analysis Procedure, Cost Performance.

Introduction

The chlor-alkali industry and food salt producers do not use many specialty chemicals in salt and brine production—or brine treating processes—but sulfate inhibitors have become a valuable economic tool for many companies. Chemicals are generally limited to byproduct and commodity materials: caustic soda, chlorine, acid and soda ash. Specialty chemicals are used to help solve specific problems. These chemicals include sulfate inhibitors, brine treating coagulant aids, biocides, corrosion and scale inhibitors, and flow improvers …generally in that order of use.

Sulfate inhibitors improve overall process efficiency by upgrading brine quality and lowering the cost of brine treating. In the process, they help eliminate tons of hazardous waste, extend the operating life of chlorine cells and improve evaporator efficiency. Other benefits include:

- Lower brine treating costs
- Proportionately less carbonate and caustic brine treating chemicals required
- Reduced sludge handling and disposal
- Reduced salt losses
- Improved chlorine cell (electrical) efficiency
- Prevent scale in vacuum crystallizer tubes
- Improved brine quality to help meet or extend plant design

These products are called *sulfate inhibitors* because they lower the solubility of calcium sulfate at its source, the solution mined brine well or rock salt dissolver. Ordinary brine purification methods remove calcium and magnesium impurities but convert calcium sulfate ($CaSO_4$) to sodium sulfate (Na_2SO_4), a more highly soluble form that finds its way throughout the entire chlor-alkali or evaporator process. Sulfate compounds must eventually be purged or eliminated, accounting for significant loss of salt and processing energy.

Calcium sulfate is one of the most common and abundant impurities in salt formations. U.S. Gulf Coast salt domes are generally very pure, containing less than 3% calcium sulfate and little gypsum, but it is not uncommon in many parts of the world to find up to 10% calcium sulfate in salt. Fortunately, the entire volume of calcium sulfate—regardless of form—does not go into brine solution. Most of it becomes detritus, filling the bottom of solution mined caverns or purged from salt dissolver systems.

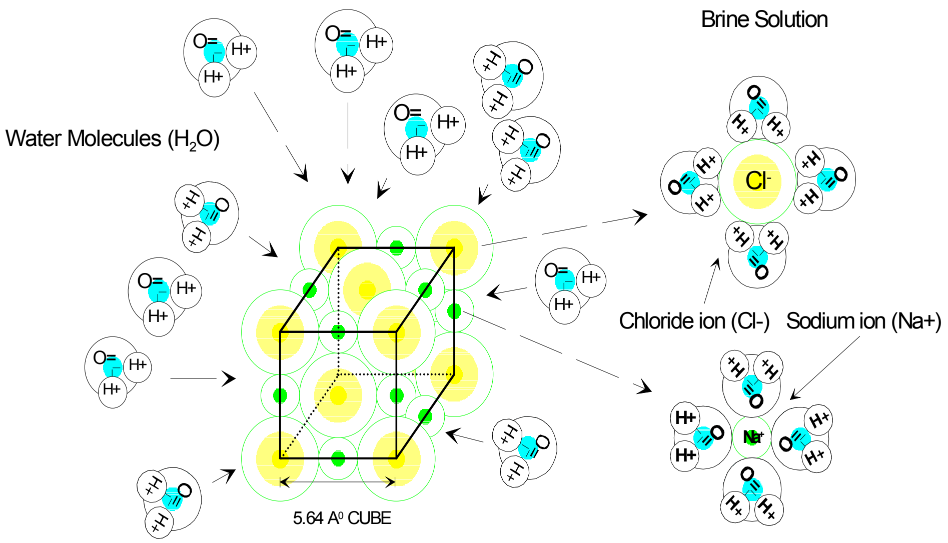
Calcium sulfate may be present as anhydrite ($CaSO_4$), the object of all sulfate inhibitors, or several hydrated sulfate compounds including: gypsum ($CaSO_4 \cdot 2H_20$), hemi-hydrate ($CaSO_4 \cdot ½H_2O$), and polyhalite ($2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$). These mineral forms are not effectively inhibited by chemical treatment because they contain a water pathway. Likewise, calcium sulfate and other minerals already in brine solution (e.g., brine ponds) are not inhibited.

Salt – Impurities

$CaSO_4$ (anhydrite)
$CaSO_4 \cdot 2H_2O$ (gypsum)
$CaCO_3 \cdot$ Mg, Fe, $MnCO_3$ (dolomite)
$CaCl_2$ (calcium chloride)*
$MgCl_2$ (magnesium chloride)*
SiO_2 (quartz)*
Fe_2O_3 (hematite), Fe_2S (pyrite)*
K_2O salts (Potassium)*
Barium and Selenium*
Strontium analogues*
Untreatable: marl, clay, tannin & lignin,
organic waste, H_2S
** <0.5% by weight or trace*

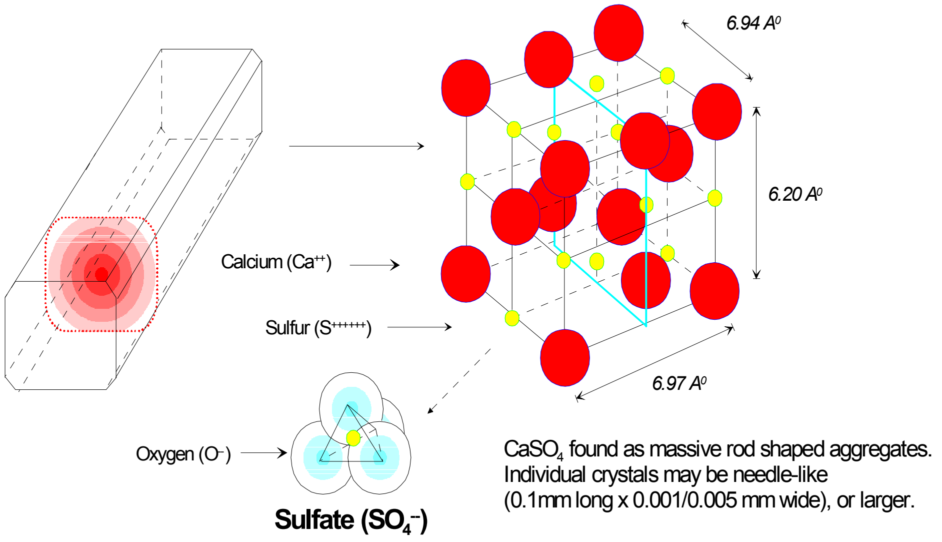
Salt Crystal, NaCl

Salt dissolves when water molecules surround sodium and chloride ions reducing their attraction for eachother. These ions then separate from the salt crystal, which is said to dissolve and form brine. The solubility of salt in water is rapid and increases with temperature: 0^0c = 358 gpl; 20^0c = 360 gpl; 100^0c = 391 gpl
Impurities in salt are released to dissolve or form insoluble compounds. Principal among them is calcium sulfate, $CaSO_4$ (anhydrite). $NaCl + H_2O = Na^{+2}\ Cl^{-1} + H_2O$



Calcium Sulfate Crystal, $CaSO_4$

Anhydrite crystal composition: CaO 41.0%, SO_3 58.8%. Inverted solubility curve (decreases with increasing temperature); decreases with higher pH (7.5 gpl in 10-20% brine; 5.5 gpl in saturated brine). Crystals may contain strontium or barium impurities, replacing calcium. Calcium ions (Ca^{+2}) surrounded by 8 oxygen ions from sulfate groups. Sulfur ions (S^{+6}) located in the centers of oxygen groups of the sulfate molecules.



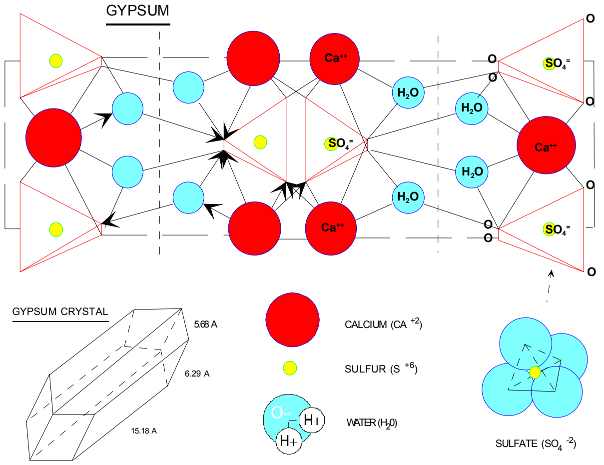
$CaSO_4$ found as massive rod shaped aggregates. Individual crystals may be needle-like (0.1mm long x 0.001/0.005 mm wide), or larger.

Gypsum, $CaSO_4 \cdot 2H_2O$

GYPSUM IS THE MOST COMMON SULFATE MINERAL, NORMALLY THE FIRST SALT DEPOSITED FROM THE EVAPORATION OF SEAWATER, FOLLOWED BY ANHYDRITE ($CASO_4$) AND HALITE (NACL) AS THE SALINITY INCREASES. OTHER HYDRATED SULFATES FOUND WITH HALITE DEPOSITS INCLUDE POLYHALITE [$K_2MGCA_2(SO_4)$. $2H_20$)] AND HEMI-HYDRATE [$CASO_4$. $1/2H_2O$].

GYPSUM HAS A LAMINATED STRUCTURE OF TWO SHEETS OF SULFATE (SO_4^{--}) GROUPS CLOSELY BONDED WITH CALCIUM (CA^{++}) IONS. WATER MOLECULES ARE BETWEEN THESE DOUBLE LAYERS BOUND TOGETHER BY HYDROGEN BONDS. EACH WATER MOLECULE LINKS A CALCIUM ION WITH ONE OXYGEN ION IN THE SAME DOUBLE LAYER, AND WITH ANOTHER OXYGEN ION IN THE ADJACENT LAYER. EACH CALCIUM ION IS SURROUNDED BY 6 OXYGEN IONS FROM THE SULFATE GROUPS AND BY 2 WATER MOLECULES.
CHEMICAL COMPOSITION IS CAO (32.5%), SO_3 (46.6%), AND H_20 (20.9%).

THE SOLUBILITY OF GYPSUM IN WATER @ 68^0F IS 2.583 GPL, DECREASED BY NACL, $CACO_3$, >100^oF AND ACID >75 GPL.
THE LAMINATED CRYSTAL STRUCTURE OF GYPSUM IS FLAT, LATH-LIKE (DIAMETER 0.005-0.010 MM).



Sulfate inhibitors are designed to lower the amount of calcium sulfate in brine to acceptable or economic levels. This level may be different for each company depending on desired product quality and individual equipment, but a typical goal is often <1.5 gpl (1,500 ppm). Some new organic sulfate inhibitors can almost totally eliminate calcium sulfate in raw brine. Each plant must determine the economics of chemical treatment; it is a matter of cost vs. benefits, often driven by current marketing trends. In any case, optimum cost performance should be the goal rather than simply low cost…long term profits vs. short term savings.

The solubility of calcium sulfate is higher in weak brine (10-20% NaCl) than in saturated brine. Maximum solubility in saturated brine is usually taken as 5.5 gpl, while at lower salt concentrations as much as 7.5 gpl is theoretically soluble. Unlike most chemical reactions, the solubility of calcium sulfate varies inversely with temperature; i.e., decreases with increasing temperature. However, like most chemical reactions, maximum solubility develops with increasing time, so the residence time of brine wells or the flow rate through rock salt dissolvers largely determines how much calcium sulfate is solubilized from a given salt source. Typically, smaller brine wells produce lower calcium sulfate values than larger brine wells, and high flow-rate rock salt dissolvers produce lower calcium sulfate values than slower gravity designs.

Sulfate inhibitors are of great economic value in large salt dome caverns where high levels of calcium sulfate develop during long residence times. They are also of significant economic value in salt which contains relatively high levels of calcium sulfate (anhydrite) and naturally produces high levels of soluble calcium sulfate, sometimes very quickly.

Brine Treating

Brine treating processes remove calcium and magnesium impurities, creating a large volume of waste sludge in the process. Filter operation is critical. Lesser impurities can be removed with ion exchange resins if very pure brine is required for evaporated salt or new membrane cells. As shown in the following equations, brine clarification precipitates calcium as a carbonate compound and magnesium as a hydroxide compound. But it also converts calcium sulfate into sodium sulfate which is more soluble in brine than calcium sulfate. To prevent costly losses and maintenance problems, this sulfate must then be purged from the system to prevent over-concentration (crowding out) of the sodium chloride, and eventual scale problems.

Brine Treating

Carbonate Dosage = Stoichiometric + Excess

- $CaSO_4 + NaCO_3 = CaCO_3 + Na_2SO_4$
  (136) (106) (100) (142)…mg/L/mwt.
- Stoichiometry:
  $H(Ca) \times (3.4 \div 136) \times 106 = Na_2CO_3$ (mg/L)
- Excess Na_2CO_3: 360-0.800 gpl
- $CaCl_2$ or $MgSO_4$ not present in brine *if…*
  $[H(Ca) \times 96] \div 40 > SO_4$
- $CaCl_2 + Na_2CO_3 = CaCO_3 + 2\ NaCl$
  (112) (106) (100) 2(58)…mg/L…mwt.

Caustic Dosage = Stoichiometric + Excess + Water Alkalinity

- $MgCl_2 + 2\ NaOH = Mg(OH)_2 + 2\ NaCl$
  (94) 2(40) (58) 2(58)…mg/L / mwt.
- Stoichiometry:
  $H(Mg)(3.92 \div 94) \times 2(40) = NaOH$ mg/L
- Iron in salt is insoluble!
- Soluble iron from water & brine piping
- $FeCl_2 + 2\ NaOH = Fe(OH)_2 + 2\ NaCl$
  (127) 2(40) (90) 2(58)…mg/L / mwt.
- Stoichiometry:
  $Fe_{total} \times (2.27 \div 127) \times 2(40) = NaOH$ mg/L
- Excess NaOH: 0.006 - 0.012 gpl

One increasingly popular practice is to recycle purge streams (including clarifier underflow) and plant effluent from biological oxidation treaters back to the brine wells with new make-up water. This allows highly soluble sodium sulfate to continue increasing—eventually to excessive levels—effecting cell operation and the economics of the entire brine and salt production process. There are limitations and economic problems with this method of plant and process waste disposal that strongly favor calcium sulfate reduction at its source; control the buildup of sodium sulfate…break the *sulfate-cycle*. Some of the problems associated with high sulfates are:

- Salt particle size (smaller)
- Caustic quality degraded
- Diaphragm plugging
- Membrane fouling
- Erosion or oxidation of graphite electrodes

- Scale and/or corrosion
- Salt loss – purge
- Increased sludge disposal cost - treater and filter operation
- Electrical inefficiency – cost
- Ammonia-soda process (Na_2CO_3 production) - deposition of insoluble calcium compounds

Salt Dissolving Water

Carbonate Hardness
$Ca(HCO_3)_2 + 2\ NaOH = CaCO_3 + Na_2CO_3 + 2\ H_2O$
$Mg(HCO_3)_2 + 4\ NaOH = Mg(OH)_2 + 2\ Na_2CO_3 + 2\ H_2O$

Non-Carbonate Hardness
$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$
$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$
$Fe^{++} + 2H_20 = Fe(OH\ )_2 + 2H^+$
$Fe(Cl)_2 + 2NaOH = Fe(OH)_2 + 2\ NaCl$
$CaCl_2 + Na_2CO_3 = CaCO_3 + NaCl$
$MgCl_2 + 2NaOH = Mg(OH)_2 + CaCl_2$
$4Fe(OH)_2 + O_2 = 4Fe(OH)_3 + 2H_2O$

Sources of Dissolving Water
Surface water, well water, sea water
No bayou or waste water

Theoretical Combinations
$Ca^{++} + SO_4^{--} = CaSO_4$
If excess Ca^{++}, then $CaCl_2$
If excess SO_4^{--} then $MgSO_4$ and/or Na_2SO_4
$Mg^{++} + Cl^- = MgCl_2$

Sulfate Inhibitor Performance

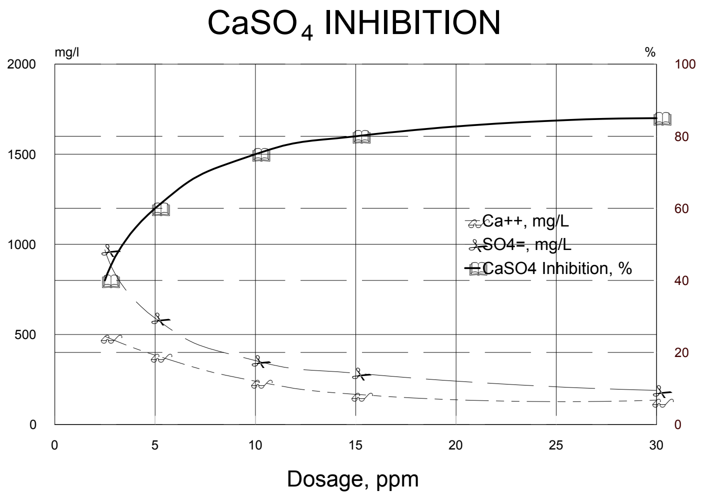
Sulfate inhibitor use began in Europe as early as 1880. Development began in North America about 1950 with readily available inorganic chemicals such as caustic, soda ash and phosphate. But it was not until the introduction of organic inhibitors over 20 years later that high performance products were recognized as money savers by the chlor-alkali industry. The food salt industry is naturally slower to adopt this technology, but new (FDA/GRAS approval) products are becoming available. A partial chronological list of sulfate inhibitor development:

- Bone black ($CaCO_3$), oxidized animal bones
- Calcium chloride ($CaCl_2$)
- Caustic soda, carbonate compounds ($NaOH + Na_2CO_3$ or $CaCO_3$, hydrated lime $Ca(OH)_2$)
- Barium salts ($BaCL_2$ or $BaCO_3$ - reacts with sulfate, precipitating barium sulfate)
- Refrigeration (separates sodium sulfate after normal brine treatment)
- Wash crushed rock salt - separate high sulfate fines
- Centrifuge - separates calcium sulfate hemihydrate at high temperature ($CaSO_4 \cdot 2\ H_2O$ & $CaSO_4 \cdot ½\ H_2O$)
- Solubility-constant. Numerous variations of control, including:
  - Higher temperature and/or higher pH lowers calcium sulfate solubility
  - Supersaturate with additional sulfate
  - Form double salt Glauberite ($Na_2SO_4 \cdot CaSO_4$), then heat to decompose into sodium sulfate decahydrate
- Phosphate compounds: Pyrophosphate ($Na_4P_2O_7$ & $Na_2H_2P_2O_7$), Tripolyphosphate ($Na_5P_3O_{10}$); Tetraphosphate ($Na_6P_4O_{13}$), Hexametaphosphate, a.k.a. meta-phosphate or glassy phosphate [$(NaPO_3)_6$]

  - Scale (tuberculation)/corrosion (Fe^{+2}) protection. Threshold stabilization <5 ppm
  - Sulfate reducer. Sequestering/precipitation 20-50 ppm
    - Polyphosphate plus inorganic alkaline compounds such as calcium chloride, caustic soda, calcium carbonate or sodium carbonate
    - Polyphosphate plus natural organic polymers, dispersants: lignin sulfonates, starch, gum
    - Organo-phosphate compounds (AMP, etc.) plus caustic soda
    - Ion exchange – trace metals (cations); barium, selenium, strontium, etc.
- Surfactants:
  - Solid (flake) surfactant plus phosphate (1950's). Branched-chain DBSA
  - Liquid surfactant (1970's) DBSA/LAS (linear alkylate sulfonate) $[R \bullet C_6H_4\, SO_3^-H^+)$
    Inhibit solubility >5 ppm; No nitrogen or carboxylate materials
  - Liquid surfactant blend (DDBSA/LAS + "builders") (1980's - Proprietary)
  - Food grade (GRAS) liquid surfactant (2001)
  - Food-grade (GRAS) surfactants blend plus "modifiers" (Proprietary - NEW!)

Modified Anionic Surfactants

Surfactants have evolved from hard-to-use, adapted commercial detergents, to liquid formulations that are easily handled and specifically designed to react with anhydrite in brine. They are the most cost effective (and safest) chemicals ever used for the purpose of reducing calcium sulfate in situ.



Anionic surfactant blends perform best at low, non-stoichiometric dosages. Minimum dosage was determined by interfacial tension studies to be 3-5 ppm; e.g. >CMC *critical micelle concentrations.* Maximum recommended dosage is 30 ppm, based on nominal excess; e.g., dissolving water.

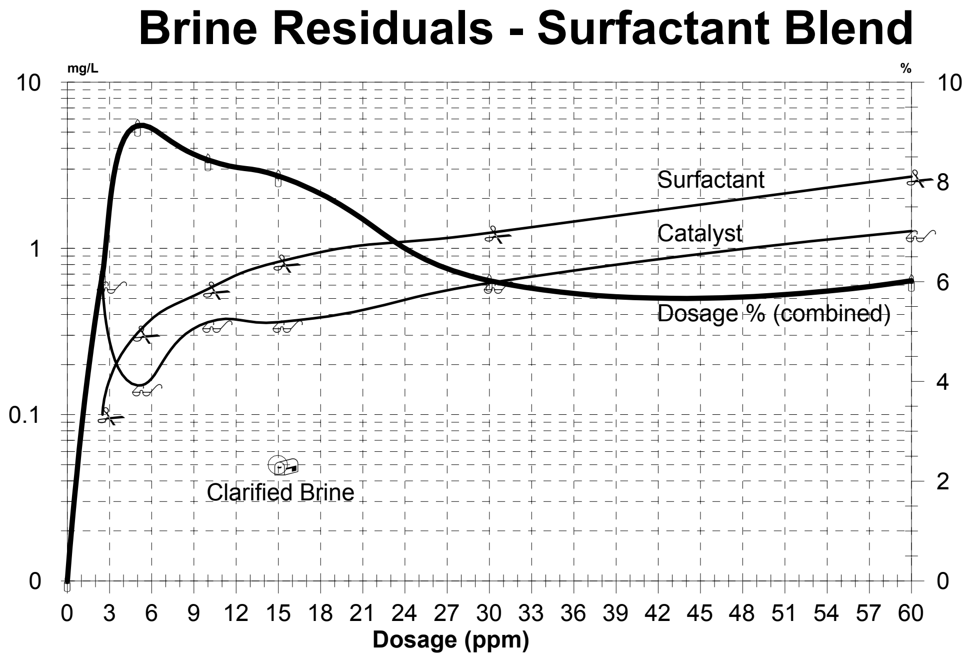
Unlike phosphates, surfactant inhibitors are 100% reactive and do not develop (or require) residuals to "drive" their reaction. Raw brine excess is recommended at less than 1.5 mg/l. As can be seen in the following (simplified) reaction of DDBSA with anhydrous calcium sulfate, sulfate inhibition is actually *anhydrite inhibition*, resulting from chemical and physical absorption on anhydrite crystals.

$$\mathbf{CaSO_4 + 2(RSO_3H) \rightarrow Ca(SO_3R)_2 + H_2SO_4}$$

Absorption onto anhydrite crystals involves complex surfactant chemistry, including ion exchange, interaction of the hydrophobic chains, and complete coverage of the crystal; e.g., micelle colloids. Performance of the newest (proprietary) surfactant product is even more complex—and significantly improved—by adding unique surfactant modifiers that properly balance lyophilic and lyophobic properties.

$$\mathbf{2CaSO_4 + 2(RSO_3H) + (RO)\ PO\ (OH)_2 \rightarrow Ca(RSO_3^-)_2 + Ca((RO)\ PO\ (O^-)_2)_2 + 2H_2SO_4}$$

Inhibited anhydrite crystals remain insoluble in precipitated and filtered sludge; they do not “go” with the brine. Analysis of detritus (“sand” ≈ $CaSO_4$) removed from the bottom of solution mined brine wells after years of use has shown that despite their natural biodegradability and eventually disassociation from precipitated crystals, much of the inhibiting chemical remains…together with the anhydrite. They are <u>not</u> formulated to remain in brine solution beyond brine treating equipment. The following graph presents laboratory data that can be considered a worst case scenario when compared with large solution mined caverns; i.e., more efficient clarification (note clarified brine at <0.1 mg/l).



Brine Laboratory Data. Texas Salt Dome Rock Salt.

PH

Raising the pH of salt dissolving water lowers the solubility of calcium sulfate. PH or temperature adjustments are usually not necessary to get optimum results with the newest surfactant blends. However, phosphate chemistry is more demanding. Note that surfactant inhibitors lower brine pH.

Phosphate Sulfate Inhibitors

Solution mining water treated with inorganic phosphates produces brine that contains phosphate …usually a lot of it; more than needed for dosage control. Phosphate forms a strong complex with calcium that can "slip" through brine treatment in several forms to adversely effect chlorine cells and evaporators. Phosphate is suspect in certain brine filter plugging problems and clarifier inefficiencies, and it is not helpful in ion exchange media and water reuse systems. Another important concern is the nutrient value of phosphate in water systems; microorganisms that cause corrosion and scale feed on it.

High dosages of polyphosphate (20-60 mg/l ≡ 15-40 ppm P_2O_5) are required, generating high residuals in the raw brine. Reactivity may be <50%! This undesirable consequence has been exploited as a dual inhibitor…feed water pipeline scale/corrosion inhibitor *and* calcium sulfate inhibitor. However, brine piping leaks are not prevented and water piping scale and corrosion are not eliminated, although tuberculation may be reduced in some systems. In long-term laboratory studies, sulfate inhibition usually looks good during the first few weeks of testing, only to decline as residence time's increase. This property of polyphosphate—referred to as *reversion*; e.g., time and temperature reversion to ortho-phosphate (reactive $PO4^{-3}$)—requires high feedrates and changes very good initial performance into poor (costly) long-term results. It is better to prevent water pipeline corrosion with anodes, ph control, chlorine, and proprietary biocides, and leave control of sulfate solubility to properly formulated inhibitors.

$$\mathbf{(NaPO_3)_6 + 2CaSO_4 \rightarrow Na_2Ca_2P_6O_{18} + 2Na_2SO_4}$$

In this simplified reaction of sodium hexameta-phosphate with anhydrite, calcium sulfate solubility is not inhibited even though calcium (ions) are sequestered. Sulfate solubility is actually increased! Phosphates do not react with anhydrite crystals like anionic surfactants.

Sulfate Inhibitor Evaluation

Once a decision has been made to improve brine quality by reducing calcium sulfate at its source, and realistic goals have been established (including a preliminary economic review), a series of laboratory tests are required to determine chemical activity, compatibility, and dosage requirements. Successful laboratory work is then followed by a field evaluation to refine cost performance. (A Laboratory procedure is available as a separate hand out.)

The burden of proof is often on technical and R&D personnel to devise laboratory test methods that realistically evaluate numerous samples in simulated plant conditions. Laboratory evaluation is most realistic with samples of salt and dissolving water from actual brine field operations. Either salt core or rock salt may be used, but it should be from a mine or cavern in current production, or at least proposed for development. Old salt samples found lying around the office cannot be used, and it is not possible to develop meaningful results with salt "created" in the laboratory. Local dissolving water is preferred, especially if it is contaminated with chemicals and waste materials that can potentially interfere with inhibitor chemistry. Of course, laboratory jar tests comparing products and demonstrating chemical activity *are* possible without salt and mining water from the site, i.e., from a similar salt mine in the area. However, the influence of water quality can not be under-estimated since surface waters often change dramatically from season to season and transport contaminants that effect sulfate inhibition.

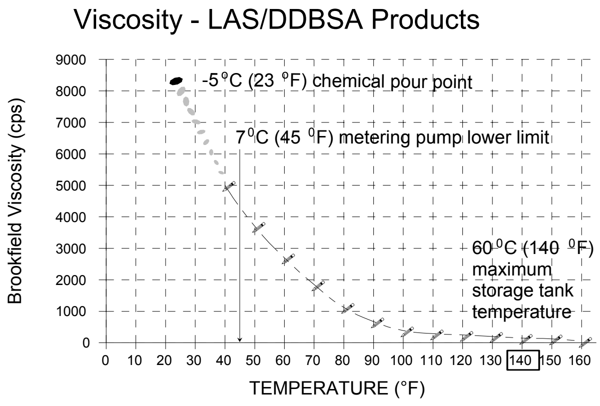
After laboratory tests are successfully completed, a field evaluation is required to translate preliminary data into real numbers. In solution mined brine wells, the duration of this field test must be planned for at least one residence-time turnover, although three or more displacements are necessary to judge magnitude and rate of change. Analysis of current sonar and logging data is required. Calcium sulfate should begin to come down slowly after the first displacement, and then continue at a steady rate of improvement during the next few turnovers, with little practical change after about 5 turnovers. If possible, the cavern should be brined at a steady rate, without work-over or changes in flow direction, to minimize confusing data. In the case of a combined hydrocarbon storage/production cavern, every effort should be made to hold filling or withdrawal rates steady during the test.

Laboratory Test Methods

For surfactant products, a valuable testing tool has been made available for routine plant use, referred to as the "PHTTT" test. This spectrophotometer method uses reagents commonly available in many plant laboratories (plus a special PHTTT reagent) to accurately identify LAS/DDBSA compounds (>30 ppb (0.03 mg/l) with a high quality, multi-beam instrument). There is also a modified procedure for atomic absorption/graphite furnace completion, sensitive to 60 ppb. Less sophisticated (single beam) instruments can be used in brine field offices for routine analysis once an application has been established; e.g., > 0.25 mg/l. The procedure is accurate in both water and brine and should be used instead of the better known methylene blue procedure. (An analysis procedure is available as a separate hand out.)

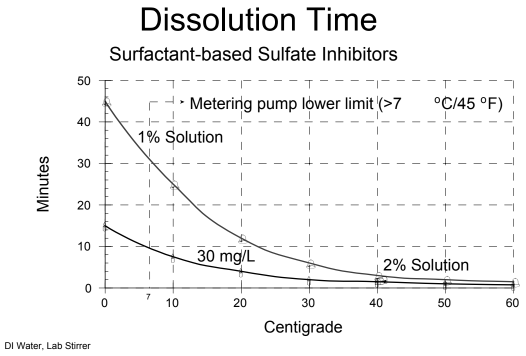
Chemical Handling

As indicated, the most effective new sulfate inhibitors are concentrated liquid blends of proprietary surfactants and catalyst/modifiers. These chemicals are non-viscous liquids that rapidly thicken at low temperatures. In cold climates, storage tanks, IBC's and chemical feed lines should be well insulated and heated to maintain fluidity. Tanks should also be covered to prevent contamination and possible gelling from rain water. Positive displacement metering pumps must be capable of feeding viscous liquids at freezing temperatures. These chemicals are corrosive (especially when diluted with water at the point of feed) so all pump components and feed lines must be resistant to acid corrosion. It is recommended that a corporation stop or injection quill be installed on the chemical feed line where it enters the salt dissolving (injection) water line. The chemical metering pump motor should be powered by the same electrical circuit that controls the water pump, thus protecting the pipe nipple and weld against corrosion from stagnant chemical.



Organic liquid sulfate inhibitors are best handled without dilution—directly from the receiving tank or container. The point of feed must be chosen to allow sufficient time for mixing and complete dissolution in the injection water line *before* contacting the salt. The recommended point of addition in solution mining is before injection water pumps, thus not requiring more-expensive high pressure chemical metering pumps.

If dilution is required, i.e., during a preliminary field test, a 10% (9:1) solution in fresh water has been found to work well. Dissolution is faster in warm water, and product shear from mixer blades is not a problem.



Surfactant-based sulfate inhibitors should not be used in newly developing or small solution mined caverns that are pumped at relatively high rates. Chemical treatment should not begin until the brine well has sufficient residence time to prevent carry-over of undissolved salt and chemical. This is not a function of chemical dosage, which can be initiated at the desired rate (e.g., it is not necessary to work up to the final dosage). Similarly, initiating chemical treatment at higher feedrates to quickly build up inhibitor content is of questionable value.

In almost all cases, it is preferable for the sulfate inhibitor to be metered to the dissolution water as close to the wellhead as practical. If the plant recycles waste streams from chemical plant processes or waste ponds back to the brine field, feed waters from both locations should be tested to determine potential loss of reactivity due to chemicals in the mining water. This test is reviewed in a separate handout.

Cost Performance Data

In the context of sulfate inhibitor selection, cost performance is defined as the net cost of reducing (or inhibiting) calcium sulfate over a broad range of dosages. The goal should be optimum performance—meeting all plant and management requirements—not initial application cost. An optimum dosage depends on the amount of calcium (sodium) sulfate that is acceptable in the raw brine, the net cost of the sulfate inhibitor, and the residual effects of any inhibitor excess. Most importantly, it depends on managements' goals for initiating chemical treatment in the first place.

Clearly Defined Goals

Production management and technical personnel must decide how much sulfate should be removed. Goals depend on how savings are accounted for and the true long term cost of calcium sulfate in the process. For many modern chlor-alkali companies, the market value of caustic and chlorine determines spending to improve brine quality, but all plant areas affected by changes in brine quality should be considered. When the ECU (Electro-Chemical Unit) is high, as it has been recently, it is always a good time to consider additional savings afforded by lowering sulfate (i.e., caustic savings, sludge disposal costs, longer electrode life, less scale cleanup, better salt, etc.).

As an example, test data suggests three ranges of cost performance for one of the newest surfactant blend inhibitors:

1. Low dosages (5-10 ppm) might be expected to reduce calcium sulfate 30-35% … 500 to 600 ppm
2. Medium dosages (10-15 ppm) might be expected to reduce calcium sulfate 70-75% …1200 to 1300 ppm (*an optimum amount*)
3. High dosages (15-30 ppm) might be expected to inhibit even more calcium sulfate (>75 %), but at a long term cost…possibly out of line with performance

Summary

Sulfate inhibitors have evolved to include several types of chemicals that offer excellent cost performance and few problems. The newest surfactant based products described here may be the best choice overall, with the potential to improve brine quality to almost any level of calcium sulfate desired—and now they are available to both chlor-alkali *and* food salt producers. Their selection and use requires clear goals and a comprehensive understanding of cost versus savings and benefits. These are potentially very valuable process chemicals.

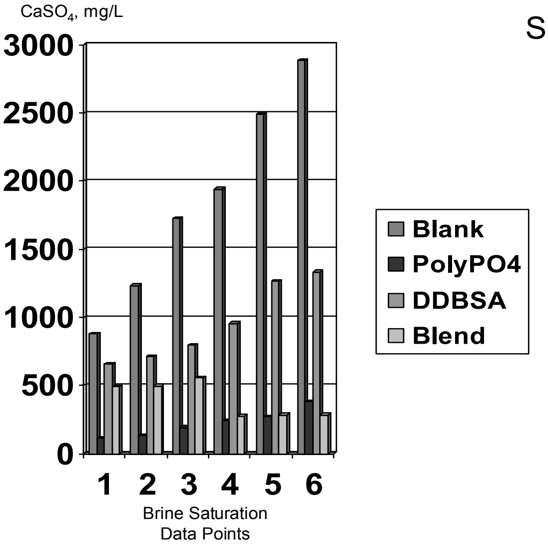
Appendix figures 1-7 present data from a recent laboratory project, and include important data analysis and cost performance calculations usually not shown. Figure 8 reports recent laboratory test results with a new catalyzed food grade (GRAS) surfactant inhibitor.

APPENDIX

Sulfate Inhibitor Comparison - Two-Phase Laboratory Test

Phase 1: Purpose - compare three commercial sulfate inhibitors in salt core samples from a US Gulf coast salt dome, using actual mining water from the site.

Cavern Top, 700m



Salt Core – $CaSO_4$ Reduction

Average 30 Days (#6)

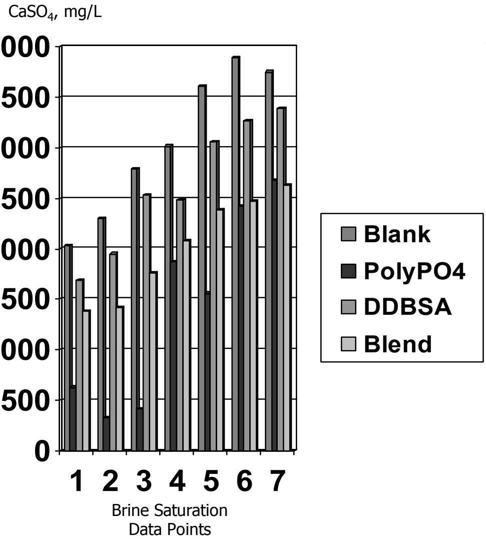
– $PolyPO_4$ 88% 87%
- Dosage = 20 mg/L {69% P_2O_5
- Residual P_2O_5 @ 1 month = 7.5 mg/L

– DDBSA 46% 54%
- Dosage = 10 mg/L {9.6 active
- Residual @ 1 month = 0.39 mg/L

– Proprietary Blend 73% 90%
- Dosage = 10 mg/L {9.7 active
- Residual @ 1 month = 0.37 mg/L
    - P_2O_5 = 0.1 mg/L

Fig. 1

Cavern Mid-span, 900m



Salt Core - $CaSO_4$ Reduction

Average 30 Days (#6)

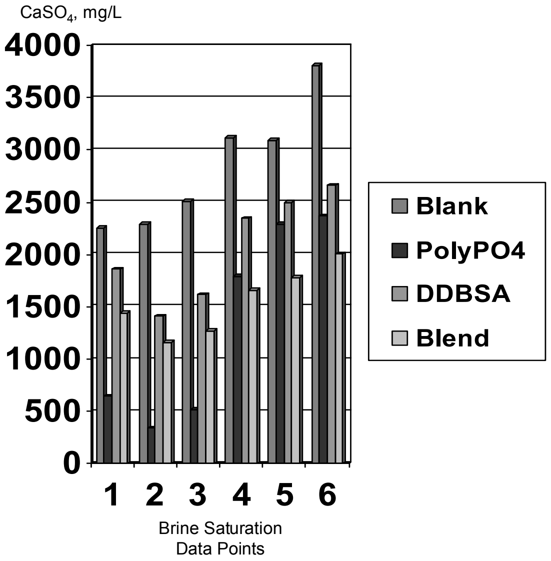
– $PolyPO_4$ 57% 29%
- Dosage = 20 mg/L {69% P_2O_5
- Residual P_2O_5 @ 1 month = 7.35mg/L

– DDBSA 14% 10 %
- Dosage = 10 mg/L {9.6 active
- Residual @ 1 month = 0.31 mg/L

– Proprietary Blend 34% 30%
- Dosage = 10 mg/L {9.7 active
- Residual @ 1 month = 0.37 mg/L
    - P_2O_5 = 0.01 mg/L

Fig. 2

Cavern Bottom, 1200m



Salt Core $CaSO_4$ Reduction

	Average	30 Days (#6)
– $PolyPO_4$	57%	38%
– DDBSA	28%	30%
– Proprietary Blend	45%	47%

– $PolyPO_4$
- Dosage = 20 mg/L {69% P_2O_5
- Residual P_2O_5 @ 1 month = 9.5 mg/L

– DDBSA
- Dosage 10 mg/L {9.6 active
- Residual after 1 month = 0.032 mg/L

– Proprietary Blend
- Dosage 10 mg/L {9.7 active
- Residual after 1 month = 0.030 mg/L
  - – P_2O_5 = 0.01 mg/L

Fig. 3

PHASE 1 CONCLUSIONS

- SALT CORE – mineral differences @ depth; veins
- OVERALL (average) – misleading!

  $PolyPO_4$ – 67% Blend - 51% DDBSA – 29%
- AFTER 30 DAYS – actual improvement

  Blend – 56% $PolyPO_4$ – 51% DDBSA – 31%
- BRINE RESIDUALS – Blend product dosage

  Blend – very low $PolyPO_4$ – high DDBSA – too low
- SHORT TERM VS OPTIMUM BENEFITS – Phase 2

  Extend dosage range and/or contact time of Blend product

Fig. 4

Phase 2: Purpose – (a) determine optimum performance of a new proprietary blend product over a range of dosages; (b) show brine residual (excess) data. Completed with additional Phase 1 core material (composites) and mining water.

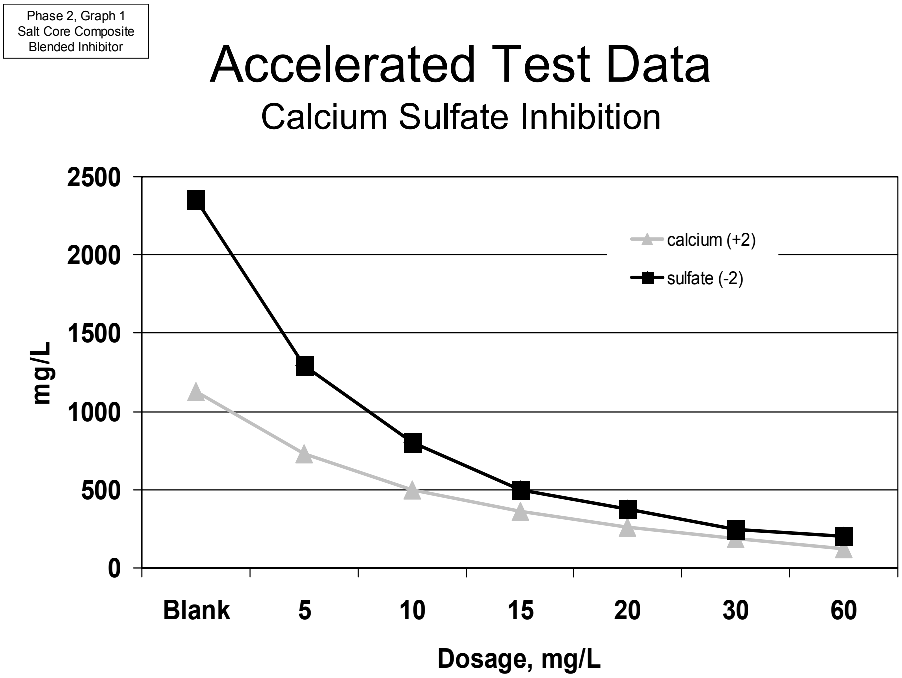


Fig. 5

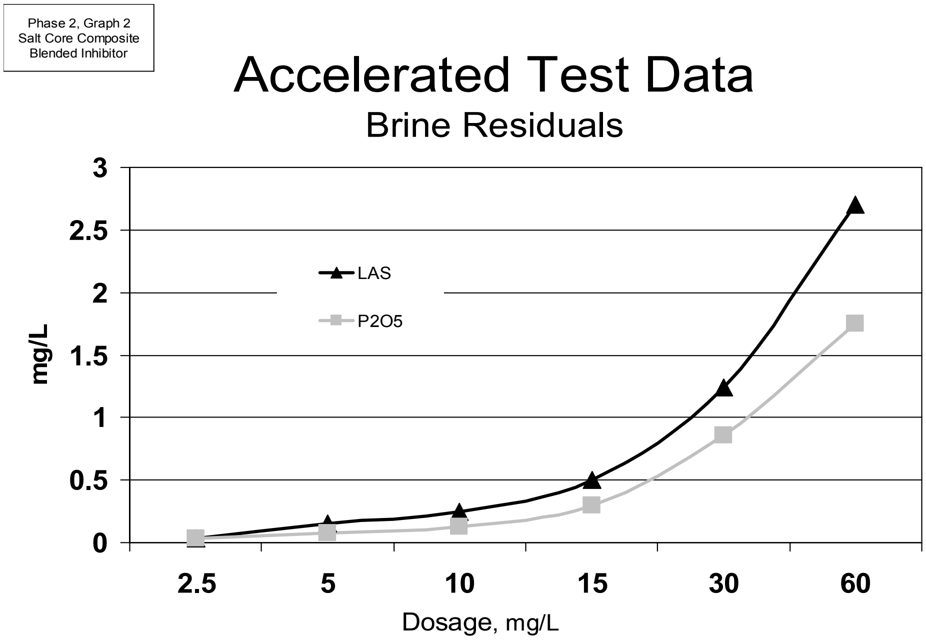


Fig. 6

PHASE 2 CONCLUSIONS: Optimum cost performance of the newest proprietary product was indicated at 15 ppm (71% inhibition) where brine “residual” began increasing. However, the recommended “safe” brine limit excess (1.5 mg/l) was not exceeded until over 30 ppm.

SUMMARY: Sulfate Inhibitor Comparison Project, Phase 1 & Phase 2

Phase 1

Standard jar test Procedure: 30 day average; salt core @ 3 depths; site dissolving water

Proprietary Blend + Catalyst	DDBSA/LAS	Polyphosphate Liquid
51% @ 10 ppm	29% @ 10 ppm	67% @ 20 ppm

Standard jar test Procedure: 30+ days; salt core @ 3 depths; site dissolving water

Proprietary Blend + Catalyst	DDBSA/LAS	Polyphosphate Liquid
56% @ 10 ppm	31% @ 10 ppm	51% @ 20 ppm

Phase 2

Accelerated jar test Procedure: 5-days, composite salt core @ 3 depths; site dissolving water

Proprietary Blend + Catalyst	DDBSA/LAS	Polyphosphate Liquid
57% @ 10 ppm	31%	51%
71% @ 15 ppm (optimum dosage)	DDBSA/LAS and PolyPO_4 dosages > 15 ppm exceed	
75% @ 20 ppm	recommended maximum brine residuals without proportionally	
79% @ 30 ppm	lowering sulfate; e.g., increased cost without increased benefit.	

Product Prices*		
	Proprietary Blend + catalyst	$0.86
	DDBSA/LAS	$0.55-$0.67
	Polyphosphate 33% active solution	$0.65

Product Dosage = Cost

Proprietary Blend + Catalyst	DDBSA/LAS	Polyphosphate Liquid
10 ppm, $0.86 (0.069) = $0.059	$0.55 (0.069) = $0.038	$0.65 (0.069) = $0.449
15 ppm, $0.86 (0.103) = $0.089	$0.55 (0.103) = $0.057	$0.65 (0.103) = $0.067
20 ppm, $0.86 (0.138) = $0.119	$0.55 (0.138) = $0.076	$0.65 (0.138) = $0.090
30 ppm, $0.86 (0.207) = $0.178	$0.55 (0.207) = $0.114	$0.65 (0.207) = $0.135

* Since 2004 when this lab project was completed, chemical prices have increased due to raw materials, energy and transportation. Estimated 2005 prices (bulk/lb.): Blend $1.03; DDBSA/LAS $0.88; Poly$PO_4$ Liquid $0.90

Saturated Brine
(Brine Table, *Sodium Chloride*)

sp. gr. @ 20^0 C/68° F	1.2000
Salometer	99
Weight / gal.	9.99 lb.
Salt, NaCl	25.9%
Salt / gal. Brine	2.59 lb.
Water / gal. Brine	7.41 lb. (0.89 gal.)
Salt / gal. Water	2.906 lb.

Salt & Chemical

Water / ton salt: (2,000 lb. NaCl ÷ 2.906) (0.89) = 612.5 gallons
Brine / ton salt: 612.5 ÷ 0.89 = 688.2 gal.; 688.2 (9.99) = 6,875.1 lb.
Chemical Dosage/ton salt: 1 ppm: 6,875.1 ÷ 10^6 = 0.0069 lb.
10 ppm x 0.0069 = 0.069 lb.
15 ppm x 0.0069 = 0.103 lb.
20 ppm x 0.0069 = 0.138 lb.
30 ppm x 0.0069 = 0.207 lb.

Fig. 7

NEW FOOD GRADE (GRAS) SULFATE INHIBITOR

- Untreated brine
  - $CaSO_4$ 4,800 ppm
- Goal: $CaSO_4$ 1,100 ppm
  - SO_4^{-2} 700 ppm
- Inhibitor 10 ppm
  - Ca^{+2} 52%, SO_4^{-2} 35%
  - $CaSO_4$ 2,700 ppm
- Inhibitor 20 ppm
  - Ca^{+2} 73%, SO_4^{-2} 61%
  - $CaSO_4$ 1,575 ppm
- Inhibitor 30 ppm
  - Ca^{+2} 84%, SO_4^{-2} 70%
  - $CaSO_4$ 1,100 ppm
  - SO_4^{-2} 700 ppm ≈ goal

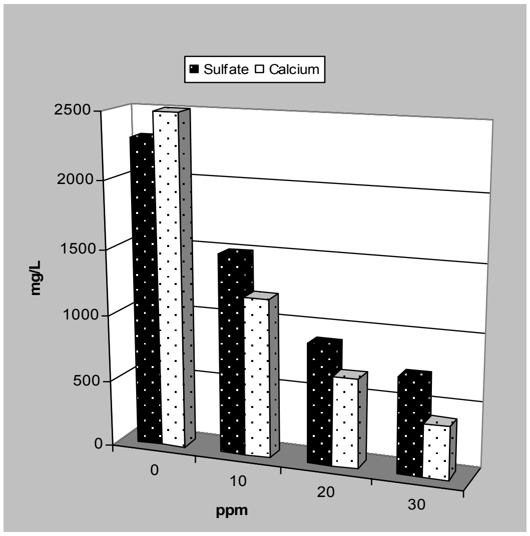
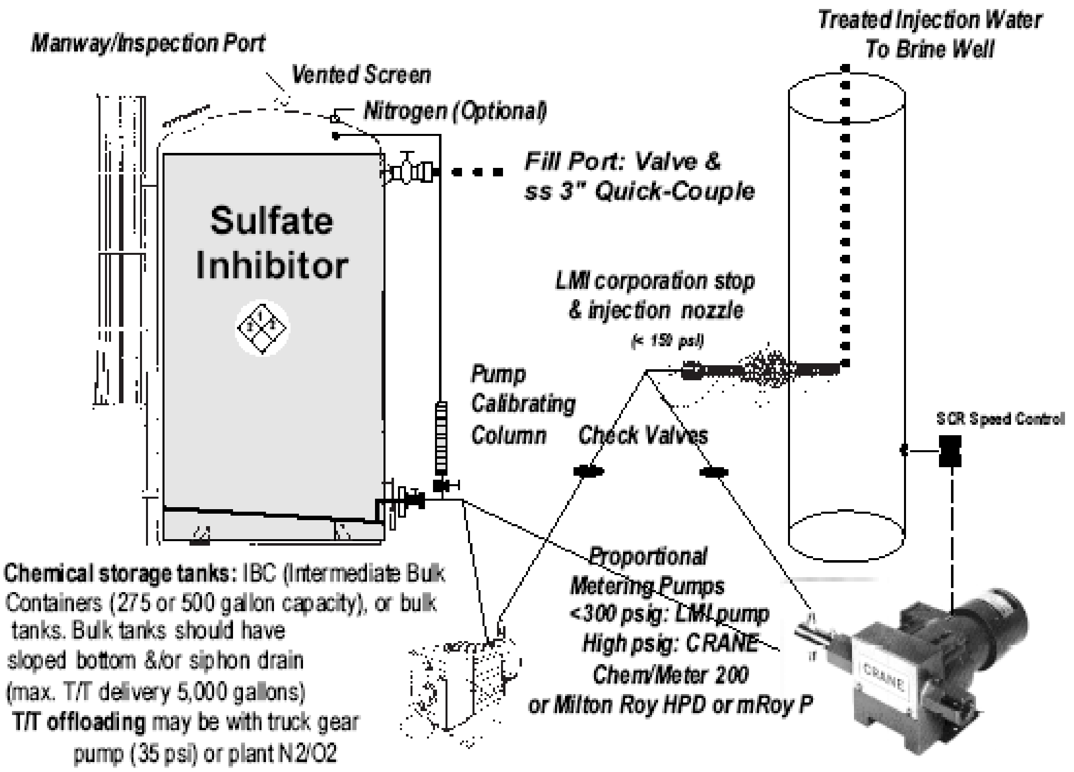


Fig. 8

Chemical Feed Information



Chemical storage tanks: IBC (Intermediate Bulk Containers (275 or 500 gallon capacity), or bulk tanks. Bulk tanks should have sloped bottom &/or siphon drain (max. T/T delivery 5,000 gallons)

T/T offloading may be with truck gear pump (35 psi) or plant N2/O2 pressure (28-75 psi).

Tank insulation and heat tracing *required* if seasonal temperatures below 50°F (10°C).

Chemical feed lines, from the storage tank valve throught the metering pump to the injection water line valve *must be insulated and heat traced* (heat capacity/lb. = 1°F increase per 0.5 btu.).

Storage tank must be covered and vented to prevent water and dirt contamination.

Materials of construction acceptable: FRP (Atlac 400 terephthalalate polyester resin or Atlac 382, 580, 4010 bisphenol-A polyester resin additives), Teflon, PEEK, Viton, Halar (ECTFE), Hypalon, Vinyl, PVC & CPVC (acid compatible/ threaded, teflon), Kynar, Polypropylene, Polyethylene, Methyl Meth-acrylate,Plexiglas, Hastelloy C & D steel, CA-20 steel, and if Product is diluted with water, Inconel 825.

Metering pumps must be positive displacement type, capable of handling viscous, corrosive liquids, approximately 3,500 cps at 45°F (7°C); maximum storage @ 140°F (60°C).

Proportional metering pump recommended; SCR automatically regulates pump speed.

Chemical dilution (10% = 9:1) possible, but not recommended.

Calibration column fills by gravity; 2 ball valves required. Column draw-down timing verifys pump rate (such as Milton Roy #TT-500 for pumps < 20 gallons per hour).

Corporation stop assembly (such as LMI #10741), or high pressure quill, recommended to assure rapid chemical distribution in flowing water. Do *not* pump to 'still' water line.

Special analysis procedures and reagents are available to monitor chemical feed and brine "residuals".

Fig. 9