

Improving Evaporator Efficiency By Controlling Scale Formation

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Abstract

In the phosphate industry, scale build-up in evaporators is a constant problem, which necessitates periodic shut-downs for descaling. Descaling is a time consuming and labor intensive process and can result in an evaporator unit being idle for hours to days at a time.

An investigation was conducted to evaluate the efficiency of various chemical reagents in controlling and reducing the formation of scale. The primary objectives of the investigation were to (1) prolong the evaporator production cycle (2) to reduce scale formation, and (3) improve acid quality.

This paper provides details of the preliminary laboratory investigation along with the results of a limited plant trial. The paper also discusses some fundamental aspects of scale formation.

Introduction

Due to their highly acidic environment, phosphoric acid plants exhibit unique scaling tendencies. The large number of impurities found in the product acid (often supersaturated), contributes to significant scaling throughout the reaction, filtration, storage, and evaporation steps. Specifically, high fluorine, sodium, and silicon levels, present in the phosphate rock fed to the reactors, cause sodium fluosilicate (Na_2SiF_6) scale to accumulate on the agitator shafts, reactor walls and especially in 30% P_2O_5 lines because of the vacuum stress on the system. For a 1,000 ton per day P_2O_5 plant, as much

as 50 to 75 tons of material may precipitate out of solution. Although much of this material leaves the system with the by-product gypsum cake, a considerable fraction remains solubilized and recycles with the weak acid filtrate. Removal of deposits must be performed mechanically, due to the lack of an economically viable chemical solution. Filter piping may require weekly descaling by running a flush cycle, in which water is used for cleaning. Rock feed compartments and other vessels are cleaned annually in the same manner, or with high pressure water jets. Evaporators also require periodic time consuming and labor intensive shutdowns for descaling. The evaporator units are idled for hours, or sometimes days.

Chemical and x-ray diffraction analysis of evaporator scale indicates that it is primarily made up of fluosilicates (Na_2SiF_6) with a smaller proportion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and other trace contaminants, depending on whether hemihydrate or dihydrate gypsum is being produced. This scale is hard and densely compacted, although some evidence of porosity is observable. The descaling operation uses steam, high pressure condensate or combinations thereof.

At the suggestion of certain phosphoric acid producers, Nalco Chemical Company initiated an investigation into the efficacy of various chemical reagents in inhibiting the formation of scale during the evaporation stage of the manufacture of phosphoric acid. This two part study involved preliminary investigation in the laboratory followed by a limited plant test. Further plant evaluation is planned to determine the commercial feasibility of this program.

Quantifying Scaling Conditions ^(1, 2)

Before combating a known or unknown scaling situation, it is necessary to evaluate a water's scaling potential, including the specific types of scale that are expected to form. A complete water analysis, including pH, hardness, total alkalinity, and total dissolved solids is the logical starting point. Based on these values, various methods exist for predicting carbonate scale formation. While carbonate scale formation is of interest in several industrial applications, this instance which exhibits high calcium and sulfate levels indicate the potential for the formation of gypsum scale. In general, for these types of systems, for a precipitate A_xB_y , a saturation ratio may be computed as follows:

$$\text{Saturation Ratio} = \frac{(\text{A})_x (\text{B})_y}{(\text{A}_0)_x (\text{B}_0)_y}$$

where, A_0 , B_0 are saturation concentrations and A and B are actual concentrations. Thus for a saturated solution, the Saturation Ratio = 1. Values for A_0 and B_0 may be determined for water systems of any pH, temperature, and alkalinity.

Since the use of such a ratio would be somewhat tedious if computed for several potential scaling agents, A_xB_y , deposit analysis is of considerably greater value and has been used extensively for this study. Once collected from the cross section of a pipe or from the impeller of a pump, for example, a scale's chemical composition may be identified readily through x-ray diffraction. This technique pays additional dividends when a complex precipitate is discovered, since chemical treatment for the prevention of a mixed deposit may be different than for the prevention of its component parts independently.

Controlling Scale Formation ^(1, 2)

There are two classes of scale inhibitors, those which function by a stoichiometric relationship and those which are sub-stoichiometric. The former mechanism is known as chelation and involves the formation of a soluble complex from one of the chelant molecules plus a cation. This type of scale inhibition is only of mild interest for obvious cost reasons. The second mechanism of scale inhibition is referred to as threshold inhibition -- a small amount of inhibitor is able to stabilize large quantities of potential scaling agents. Organophosphate compounds, inorganic phosphates and polymers all work via this "threshold effect."

The threshold effect itself is comprised of several independent processes for inhibition, the most important of which are stabilization and dispersancy. Stabilization is a crystal growth inhibition process. Since scale formation involves the processes of nucleation, crystal growth and deposition, by altering the rate of any one of these three, scale formation may be reduced or eliminated.

Stabilization actually increases the solubility of the scaling species by affecting the net rate of crystal growth. Some inhibitors may be absorbed into the crystal structure and, in this manner, distort its morphology. Other inhibitors function by adsorbing on active growth sites, thus "stunting" crystal growth in certain directions.

Another functional mechanism is dispersancy. This mechanism is one of charge repulsion, modifying the electrical double layers surrounding the fine particulates. Dispersants impart a de-localized charge to the particles by specific adsorption through their extended charge networks. An increased surface concentration of anions will alter both the charge and potential distributions in the diffused layer. A dispersant is rated by its ability to prevent adherence of a particle to any surface (including other particles), to keep solids suspended and minimize settling or deposition.

Laboratory Investigation ⁽³⁾

This investigation used a step-wise approach. The first phase involved the collection of field data and laboratory experiments to simulate the feed to the evaporator. The simulated feeds were then used to carry out scale tests.

Samples of the scale from 28% acid evaporators were obtained from a phosphoric acid producer in Florida. These samples were analyzed and a typical assay obtained from several samples that were collected is shown in the table below.

Table I: Analysis of Scale Sample From Evaporator Steam Chest

Sample: Evaporator Steam Chest
Physical Appearance: Black Chunk

Inorganic Analysis
(Scaled to 100%)

Potassium (K ₂ O)	19
Silicon (SiO ₂)	19
Sulfur (SO ₃)	18
Calcium (CaO)	17
Phosphorus (P ₂ O ₅)	13
Sodium (Na ₂ O)	9
Magnesium (MgO)	2
Iron (Fe ₂ O ₃)	1
Chromium (Cr ₂ O ₃)	1
Other	1
<hr/>	
Loss at 800 C (%)	42

SEM Analysis

The following elements were not detected:

Al Cl Ti V Mn Cd Ni Cu Zn Sr Sn Ba Pb

X-ray diffraction indicates evidence of the following:

Sodium Fluosilicate	Na ₂ SiF ₆
Bassanite	2CaO.2SO ₃ .H ₂ O or CaSO ₄ .0.5H ₂ O
Calcium Fluophosphate	Ca ₅ (PO ₄) ₃ (OH,F)

The analysis indicated that the deposits were mainly sodium fluosilicate and was evident in every sample analyzed.

Since all laboratory testing was being conducted in Nalco's Naperville, Illinois research facility it was necessary to synthesize a typical evaporator feed. The objective of this simulation was to eliminate the problem of feed sample aging, and yield a consistent

material for all tests. Several feed samples were analyzed. A typical analysis of the components of the feed to the evaporator is given below.

Table II: Analysis of Evaporator Feed

Water Analysis

CATIONS	Total ppm	Ratio per 1000 ppm
Sodium (Na)	390	8.9
Calcium (Ca)	1100	25.0
Magnesium (Mg)	1000	22.7
Aluminum (Al)	2000	45.5
Chromium (Cr)	19	0.4
Iron (Fe)	2300	52.3
Potassium (K)	270	6.1
Manganese (Mn)	64	1.5
Molybdenum (Mo)	3	0.1
Nickel (Ni)	4	0.1
Strontium (Ni)	13	0.3
Titanium (Ti)	49	1.1
Vanadium (V)	32	0.7
Zinc (Zn)	14	0.3
Zirconium (Zr)	6	0.1
ANIONS		
Boron (B)	8	0.2
Phosphorus (P)	44000	1000.0
Silica (Si)	4400	100.0
Sulfur (S)	3100	70.5

Using typical analyses such as this, a synthetic feed to the evaporator was formulated. The synthetic formulation was 28.0% P_2O_5 content.

In order to simulate the operation of the evaporator in increasing acid strength from 28.0% to 40.0% P_2O_5 , 150 grams of the synthetic feed were placed in an inert bottle. Graphite coupons were also inserted in these bottles and 53.3 grams of an 85% acid H_3PO_4 was added to the bottle, bringing the acid strength up to 40%. The bottles were placed in a water bath and the temperature was maintained at 175 degrees F for a 24 hour period. The coupons were then removed, dried and the weight of the scale formed was determined. Follow-up tests were conducted on-site using feed to the evaporator instead of the synthetic feed. The rest of the procedure remained the same.

Evaporator liner degradation tests were also conducted to assess the effect of the proposed scale control agents. The table below shows that these agents are not likely to cause degradation.

Table III: Evaporator Liner Degradation Tests

Testing Medium	% Weight Change				
	Blank	TX 10170		TX 10172	
	0 ppm	10 ppm	20 ppm	10 ppm	20 ppm
D. I. Water	0	0.46	0.33	0.51	0.56
28% P ₂ O ₅	- 0.9	0.01	0.03	0.015	0.018
40% P ₂ O ₅	-0.3	- 0.23	- 0.25	0.1	0.14

The next section provides details of the experimental results and a brief discussion.

Results and Discussion ^(3,4)

Synthetic Feed

Several reagents were tested to determine their efficacy in preventing the formation of scale on test coupons. Figure 1 gives details of some of the tests that were conducted.

These results indicate that Nalco TX 10170 and Nalco TX 10172 gave the best scale inhibition, so it was decided to site test these reagents using actual feed to the evaporator. However, the procedure used to simulate the evaporator remained the same. Figure 2 gives details of the on-site tests.

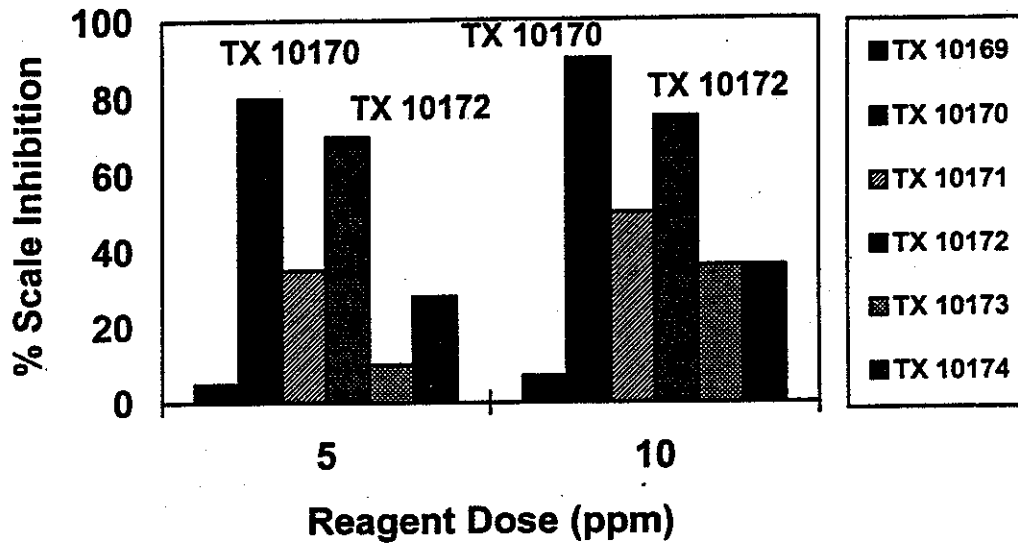


Figure 1: Scale Inhibitor Tests Using Synthetic Evaporator Feed

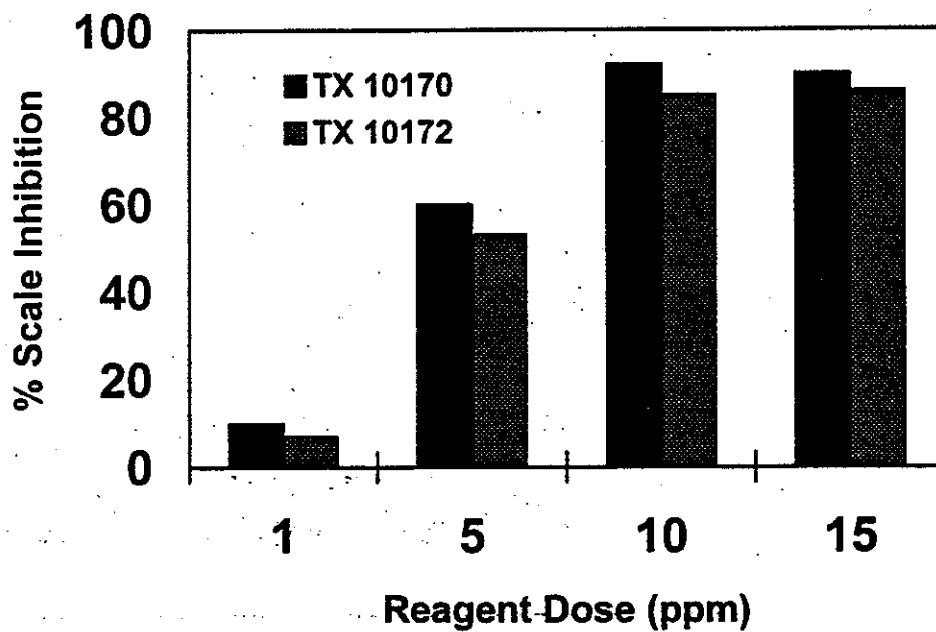


Figure 2: On-Site Scale Inhibition Tests Using Evaporator Feed

Based on these confirmatory results, it was decided to evaluate TX 10170 in the plant.

Plant Evaluation ^(3,4)

The plant evaluation was conducted over a two week period. Nalco TX 10170 was introduced into the feed tank of the 28% acid evaporator. The dose was maintained at a constant 10 ppm (volume basis) and the reagent was fed at a constant strength of 2%. A sample of scale formed without the addition of Nalco TX 10170 was collected during the prior cleaning cycle.

Unfortunately, unrelated mechanical problems caused disruption of the tests and prevented collection of detailed information as to evaporator pressures, length between cleaning, etc., could not be obtained. However, a sample of the scale was obtained and this along with the sample of scale prior to the addition of Nalco TX 10170 was analyzed by scanning electron microscopy. These SEM photographs are presented below in Figures 3 and 4.

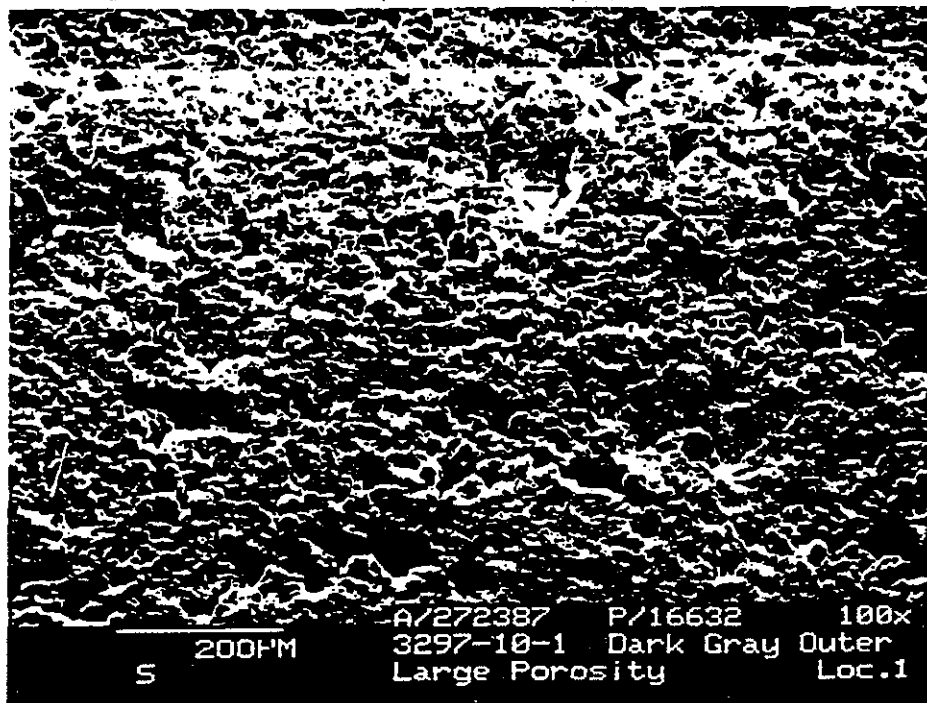


Figure 3: Scanning Electromicrograph of Scale (100X) without Nalco TX 10170 Treatment



Figure 4: Scanning Electromicrograph (100X) of Scale with Nalco TX 10170 Treatment

It is clear from these two figures that Nalco TX 10170 causes a coarsening of the scale formed. Furthermore, the particle edges are more rounded after its treatment. The coarsening and the rounding of the edges would be expected to lead to considerable scale inhibition and less, or easier to break, deposits. Nalco Chemical Company intends to test this again in future plant tests.

Conclusions

- Laboratory studies indicate that Nalco TX 10170 is an effective scale inhibitor
- The scale particles formed when using Nalco TX 10170 are larger and porous
- Nalco TX 10170 will not affect the rubber lining at the required dosages and solution strengths at which it is used.
- The limited plant trial indicated that Nalco TX 10170 offers the potential of being an effective evaporator scale control agent

Summary

This investigation indicates that Nalco Chemical Company's scale control technology is a possible method of improving evaporator cycle length thus improving productivity and reducing maintenance costs. The crystals formed after treatment are larger, more rounded and more porous making it easier to clean. This in turn should decrease maintenance costs and evaporator down-time. However, more plant data must be gathered prior to commercial application. Nalco is in the process of soliciting an industry partner to evaluate this promising technology.

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