



Calcium sulfate precipitation studies with scale inhibitors for reverse osmosis desalination



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HIGHLIGHTS

- Development and performance evaluation of scale inhibitors for brackish water reverse osmosis desalination plant.
- Precipitation and inhibition studies of calcium sulfate (gypsum) scale.
- Characterization of gypsum scale.

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ABSTRACT

This study is focused on precipitation and inhibition studies of calcium sulfate (gypsum) scale in reverse osmosis (RO) desalination plants. The temperature and concentration range encountered in brackish water RO desalination process has been considered in conducting precipitation and inhibition experiments. Initial screening of a number of additives has been carried out. Formation of gypsum scale has been verified by XRD and SEM analysis. Successful additives were evaluated by measuring induction times using conductivity of solutions and their performance was compared with that of blank supersaturated calcium sulfate solution. The induction time of STD100, SHMP, STD101 was found to be 70, 690 and 1200 min respectively at dose level of 10 ppm, whereas a blended formulation FM101 (10 ppm) did not show any precipitation till 3000 min. The SEM micrographs of precipitate collected when FM101 was added as a scale inhibitor with that of a blank solution and other inhibitors indicate that, the formulation FM101 has significantly modified the crystal morphology and is probably responsible for increased induction time.

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1. Introduction

Precipitation and scale deposition is one of the major problems in reverse osmosis (RO) desalination plants and other water treatment installations. In the RO process, the dissolved salts in the feed water are concentrated. If supersaturation occurs and their solubility limits are exceeded, precipitation or scaling will occur. Currently acceptable methods of preventing scale formation utilize chemicals, which are generically known as threshold agents. It is well known that the addition of less than stoichiometric quantities of certain polyphosphates to supersaturated solutions of various salts, would prevent precipitation for substantial periods of time [4,25].

The specific mechanism of threshold activity is not clearly understood but it is believed that a common feature of threshold agents is sequestration or the capability of forming stable complexes with polyvalent cations. Threshold treated solutions are evidently stabilized in

some manner involving alteration in crystal morphology at the time of nucleation and subsequent inhibition in growth rate [27].

At Research Institute, several research studies have been conducted related to the fundamental knowledge about scale formation phenomena [13,15] and methods for predicting scaling in water treatment systems and oil wells [13,28]. Assessment of scale control techniques in MSF desalination plants [14] and comparative evaluation of commercially available scale control additives to control scaling in RO plants [6,7] have also been carried out. Each system has its own water composition, temperature, pressure and hydrodynamics. Having developed comprehensive understanding about scale formation, its prediction methods and control techniques in wide variety of systems, it was felt necessary to initiate a research program to develop antiscalant formulations to control scaling in desalination plants, cooling towers, oil wells and other water treatment systems.

This paper discusses the preliminary work started on the development of antiscalant formulations to control calcium sulfate (gypsum) scaling in brackish water RO desalination plants. Several scale control chemicals available in the market along with blended formulations were investigated and the results are reported.

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2. Calcium sulfate scale inhibition studies

The early work on the threshold agents have been extensively reviewed by Elliot [9]. The mode of action of these threshold agents have not yet been fully explained but would appear to be due to adsorption of the additive on the growing crystal nuclei which inhibits growth at the preferred nucleation sites and results in the formation of irregular, distorted crystals. Leung and Nancollas [17] reported the results of adsorption of nitrilotrimethylenephosphonic acid on barium sulfate crystals and concluded that only 5% surface coverage is necessary for complete inhibition of crystal growth. Busch [5] developed a formulation to control scale build-up on metallic surfaces. Principle components of the formulation include a chelant, polymeric conditioners, a gluconate, a triazole and sodium sulfate. Addadi et al. [1] noticed that the required dosages of these additives vary from 5 wt. % in solution for the objective of habit modification up to 10 wt.% for total inhibition. In the water treatment industry these additives have been used successfully to control carbonate as well as sulfate scales.

According to Logan and Walker [19] additives may act to stifle scale formation by one of several possible routes. They may change the precipitating salt's chemical potential by affecting complex formation and adsorption, and be adsorbed onto the precipitating ions for inhibiting scale nucleation, or be adsorbed onto growing crystals for distorting and/or inhibiting further crystal formation. It is likely that the effective inhibitors function through more than one of the above routes. But it is well established that once supersaturation has occurred in any real system, *precipitation is inevitable*, regardless of the merits of any known or conceivable threshold inhibitor.

Davey [8] presented an excellent review on the role of additives in precipitation processes. He pointed out that most of the literature available is regarding the precipitation inhibition of sparingly soluble inorganic substances. He classified the various additives studied into the following 4 groups: (i) low molecular weight organic substances, e.g. citric, succinic, tartaric acids, nitrilotrimethylene phosphonic acid, (ii) low molecular weight inorganic materials, such as sodium triphosphate and sodium pyrophosphate, (iii) long chain polymeric materials with acidic and hydroxylic side groups e.g. polyacrylic acid (PAA) and polyglutamic acid (PGA), and (iv) proteinaceous materials, e.g. gelatin, statherin, phosphoproteins, and polyribonucleotides. He reviewed the effect of various additives (PAA, sodium triphosphate, polymethacrylic acid, sodium pyrophosphate) on the precipitation behaviour of different supersaturated solutions (strontium sulfate, gypsum, calcium oxalate) and concluded that the active additives invariably extend the induction time. He explains that the presence of active additive in the system may result in adsorption onto embryos that reduce the speed at which they pass through the critical size barrier and thus reduces the rate of nucleation.

Harris [12] (in Porteous [29]) discussed the effect of various additives in retarding the precipitation of alkaline scale (e.g. calcium carbonate, magnesium hydroxide) and sulfate scale in desalination plants. He mentioned that the use of threshold quantities of polyphosphates could prevent or reduce the formation of calcium carbonate scale. However, the polyphosphates are susceptible to hydrolysis, and the rate of hydrolysis increases with temperature. Polymaleic acid was found to overcome the disadvantage of polyphosphate and has the ability to withstand high temperatures and prevents the formation of alkaline scales. Harris believes that the only additive which appears to be in commercial use to retard calcium sulfate, strontium sulfate or barium sulfate scale formation is polyphosphate, although investigations have shown that many chemicals can affect the rate of crystallization of calcium sulfate.

Reitz [24] developed a broad spectrum antiscalant for RO desalination plants. The additive (FLOCON 100) was designed specifically to control calcium sulfate, calcium carbonate, and strontium sulfate scaling. He presented operating data from RO plant and showed that FLOCON 100 performed better than SHMP.

Amjad [2] presented the influence of various antiscalants on crystallization of gypsum at 25 °C. The antiscalants investigated were, polyphosphates, phosphonates, polystyrene sulfonate, polyacrylamide, polyacrylate and formulated polyelectrolytes. He concluded that inhibition of gypsum growth for limited periods was observed in supersaturated solutions containing low levels of polyelectrolytes such as polyacrylates, sodium hexametaphosphate, and formulated polyelectrolyte. In addition, he found that the effect of antiscalant dosage on duration of the induction period is significant.

Gill and Varsanik [11] pointed out that a close comparison between the inhibitors and the inhibited or regulated minerals shows some structural correlation. Various inhibitors have differing degrees of effectiveness even for different hydration forms of the same scale. Two crystallographic forms of calcium sulfate, dihydrate and hemihydrate have been shown to have markedly distinct interactions with inhibitors like polyvinyl sulfonate (PVS) and PGA with respect to change of the crystal habit. PGA is more effective than PVS for dihydrate phase while the reverse is true for the hemihydrate phase. They attributed the changes in morphologies and inhibition to the close association of the negatively charged groups on the inhibitor and positively charged calcium ions in the crystal lattice of calcium sulfate hemihydrate/dihydrate.

Polycarboxyl type antiscalants in general have a tendency to become less effective in the presence of multi-valent metal ions such as Ca^{++} and Mg^{++} in sea water. Fukumoto et al. [10] developed a new antiscalant "AQUAKREEN KC-550" by the copolymerization technology and has much higher stability against such multi-valent ions.

Rahman [23] investigated number of antiscalants and developed additive formulations to inhibit vanadium sulfate scaling in supersaturated vanadium solutions. Some of the formulations investigated for the vanadium sulfate system were felt suitable for the calcium sulfate (gypsum) inhibition studies in the initial stages of this work. More formulations are developed and are being evaluated in the present study.

Oner et al. [21] discussed the inhibitory effect of polyelectrolyte architecture on calcium sulfate dihydrate crystal growth. They investigated the influence of acrylic and methacrylate polymers by varying polyelectrolyte charge, structure and molecular weight. They found that the acrylates were more effective than equivalent methacrylates and the higher inhibitory efficiency was attributed to the maximum surface charge density due to the adsorbed polymer. They determined the effectiveness of the polymers on the rate of precipitation of gypsum by measuring the conductivity of the supersaturated solution prepared by mixing 0.008 M CaCl_2 and Na_2SO_4 solutions at 30 °C. Gouellec and Elimelech [16] studied the effect of hydrodynamics and antiscalant dosage on inhibition of gypsum scaling in nanofiltration system. They investigated the inhibition effect of PAA against gypsum precipitation. They reported that PAA dosage has strong effect on inhibition of gypsum formation and it does not vary simply with the number of nuclei formed in a linear manner but, rather prevents the gypsum crystal growth by other more complex phenomena. Five commercial antiscalants were ranked by Shih et al. [26] based on the crystallization induction time experiments performed in a well-mixed crystallization vessel with a back-light scattering turbidity meter to monitor gypsum formation. It was found that the presence of aluminum, even at trace levels (up to 100 $\mu\text{g}/\text{L}$), significantly reduced the crystallization induction time, thereby reducing antiscalant effectiveness. Based on RO scaling studies with brackish water from the California San Joaquin Valley (~10 000 mg/L total dissolved solids), Rahardianto [22] discovered that membrane gypsum scaling was increasingly retarded with rising bicarbonate concentrations. Amjad [3] examined the inhibition of gypsum precipitation by homo- and copolymers in aqueous solution. He reported that the polymer performance as gypsum inhibitor depends upon polymer architecture and concludes that compared to polymers, surfactants perform poorly as gypsum inhibitors.

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