

# Theory of Scale Formation and Prevention

## Scale Formation and Prevention

Most commercial water contains alkaline earth metal cations such as magnesium, calcium and barium, and anions such as carbonate, bicarbonate, sulfate, silicate, oxalate, phosphate, etc. Different combinations of these anions and cations will give rise to potentially scalant systems, such as calcium carbonate, calcium silicate, calcium sulfate, calcium oxalate, barium sulfate, magnesium sulfate, etc. Thus when combinations of these anions and cations are present in concentrations which exceed the solubility of their reaction products, precipitates form until their product solubility concentrations are no longer exceeded. For instance, when the concentrations of the calcium ions and carbonate ions exceed the solubility of calcium carbonate, reaction product will precipitate out. As various precipitates accumulate, they form scale; scale is a serious problem because it prevents effective heat transfer, interferes with fluid flow, enhances corrosion and invites bacteria. Scale is an expensive problem in many industrial systems, causing delays and shut-downs for cleaning and removal. This is most prominent in the pulp and paper industries, where scale causes major problems in digesters, evaporators, liquor heaters, deinking and bleach plants as well as headbox, felts, screens, etc. In order to understand the relationship between scale formation and/or scale prevention, we need to visit the following phenomena:

### **Threshold Effect and Scale Inhibition:**

The phenomenon of threshold effect was discovered in the late 1930's when sodium hexametaphosphate at 1-10 ppm concentration was found to retard or inhibit the precipitation of supersaturated solutions of calcium carbonate. Because of the low concentration (sub-stoichiometric) required, the term "threshold treatment" was applied. Thus when a precipitation inhibitor is present in a potentially scale forming system at a markedly lower concentration than that required for sequestering or chelating the scale forming metal cation, it is said to be present in threshold amounts and the precipitation inhibitor (such as sodium hexametaphosphate) is said to exhibit a threshold effect.

ATMP is one of the best threshold scale inhibitors around and is superior to inorganic polyphosphates, phosphate esters and polyacrylates. It has been possible to keep in solution 6500 ppm of calcium carbonate with 2 ppm of ATMP (ca. 1 mole ATMP to 10,000 moles  $\text{CaCO}_3$ ) and 5000 ppm of calcium carbonate with 2 ppm of ATMP (ca. 1 mole ATMP to 5500 moles  $\text{CaSO}_4$ ) at pH 7.0 and 25°C over a period of 100 hours.<sup>1-6</sup> On the other hand, aminocarboxylates (NTA, EDTA, DTPA, etc.) and  $\alpha$ -hydroxycarboxylic acids (gluconates and

glucoheptonates), though very effective chelating agents, they do not exhibit threshold activities.

Present mechanistic theories postulate that the threshold agent is adsorbed on the growth sites of the scalant crystallite during the process of crystallization. This adsorption alters the growth pattern so that the resultant scalant crystals are formed more slowly and are highly distorted.

### **Crystal Growth Modification:**

The process of crystallization is one of ordering, wherein randomly arranged ions in solution take up regular positions in the solid state. The initial stage in the process of crystallization is nucleation. Once formed, the nuclei grow by deposition on the crystalline faces. This process may be considered to be a dynamic equilibrium between particles in the fluid phase and those in the solid. Stated differently, the formation of scale is caused by crystalline deposition of selective cations and anions from saturated solutions. These crystalline deposits harden up to a tightly close-packed arrangement due to the formation of symmetrical crystals that fit together tightly by inter-crystal bonding forces.

Organophosphonates inhibit the formation of hard scale by preventing the formation of symmetrical crystals. The mechanism of inhibition involves covering the growing faces of crystal nuclei by the adsorbed organic phosphonate molecule-ions. Thus the mushy and soft scale formed involves modified, distorted and amorphous crystals. The precipitate (scale) never has the chance to form into a tightly closed-packed arrangement where the inter-crystalline bonding forces never are generated to form an orderly hard and dense deposit. Organophosphonates have a concentrated charge that is very efficient in distorting the growing crystal matrix. In this case, the solubility of the growing crystal is increased by altering its growing pattern. The modified crystal is thus less adherent and more easily dispersed.<sup>2,5,6</sup>

In the case of polymers, such as low molecular weight polyacrylates, as well as many other polymers on the market, low polymer dosages can distort, albeit to a much lesser extent than the phosphonates, the crystal lattice structure of scale-forming minerals. The resulting crystals are soft and do not adhere well to heat transfer surfaces. It is this most important property which has the most influence on the sludge conditioning properties of polyacrylates and other polymers.

## Calcium Carbonate Stabilization:

Crystal growth inhibition process influences the morphology of the growing crystals. The effect of the chemical treatment is to increase the average particle size and to change the gross size of the  $\text{CaCO}_3$  crystal from orthorhombic to highly jagged and irregular.

In a potentially scalant system where calcium carbonate ( $\text{CaCO}_3$ ) crystals are forming, relatively small but highly charged organophosphorus compounds (such as ATMP, HEDP, PBTC, etc.) can become strongly absorbed and then partially absorbed onto the growing  $\text{CaCO}_3$  crystal nuclei. This strong adsorption results from the strong electrostatic interaction (which also involved coordinate-covalent bonding as well as Van der Waals forces) between the highly and negatively charged organophosphonate anions and the positively charged calcium ions. This highly charged atmosphere, i.e., phosphonate-calcium interaction, creates a very intense but local and sharply defined charge differential that results in extreme crystal distortion and/or inhibition. Moreover, since the charge is highly intense and localized, charge repulsion characteristics that are necessary for dispersancy characteristics are minimal or none existent in some cases. This explains why phosphonates are powerful sequestrates, i.e., crystal modifiers and scale inhibitors but weak dispersants.

On the other hand, in the case of polymers, such as low molecular weight polyacrylates, the much longer polymer chain (30 to 70 monomer units) with its diffused and extended charge network (charges are spread over the charge network) cannot get in as close to the  $\text{CaCO}_3$  nuclei because of steric hindrance (the negative charges on the carboxyl groups are far apart and spread into (3) dimensional space, i.e., the negative buckering and steric effects. The negative charges on the polymers can interact with calcium cations and thus be absorbed to various degrees but not absorbed. Thus, the charge density that is induced by the polymer onto the  $\text{CaCO}_3$  nuclei is not intense and local (less concentrated) but diffused and extended into space. The net effect of the polymers charge on the growing nucleus, while not as intense as phosphonates, is to interfere with the growth pattern of the  $\text{CaCO}_3$  crystal. This results in a system that promotes repulsion and dispersancy but has minimum effect as a sequestrate.<sup>2,4,5,6,7</sup> The fact that a dispersant can exhibit a capacity to modify crystal morphology is incidental to its function as a dispersant. However, dispersant action does not require crystal modification as a prerequisite to dispersion activity. This phenomenon is quite evident in the use of polyacrylates in Kaoline clay dispersion.

## References:

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