

A New Look at the Scale Inhibition Mechanisms and Some Refinement of the Scale Inhibition Theory

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ABSTRACT

The data on scale inhibition mechanisms are critically analyzed with the emphasis on the published data disparity and controversy. On the grounds of three independent approaches it is demonstrated that foreign background "nanodust" particles have a dramatic impact on antiscalant efficacy. These approaches include: (i) a direct nanoparticle counter application in stock solutions; (ii) a novel DLS special technique, based on the standard nanoparticles injection into the supersaturated inorganic salt solution during the induction period; and (iii) an application of fluorescent-tagged antiscalants for the direct visualization of a scale inhibitor during scale formation.

It is demonstrated, that foreign solid nanoparticles ("nanodust") appear to be inevitable component of any process in aqueous phase. A non-conventional mechanism of scale inhibition is proposed. It states, that a pre-nucleation step of inorganic scale formation in the bulk aqueous phase takes place not so much as a spontaneous homogeneous ion pairs or clusters formation, but as a heterogeneous formation on a "nanodust" particles surface. Thus an antiscalant destabilizes this process by "nanodust" particles surface blockage instead of unclear impact on homogenous clusters spontaneous formation. In this sense a "nanodust" approach provides a different look at the threshold effect and at its mechanism. It is shown that the visualization of antiscalant is a very promising and universal tool for reagent traceability, and for industrial equipment fouling diagnostics.

Key words: Scale inhibition; mechanisms; fluorescent-tagged antiscalants; "nanodust", gypsum, barite

INTRODUCTION

Precipitation and scale deposition is one of the major problems in power plants, boilers, cooling water facilities, evaporation plants, oilfields, reverse osmosis (RO) and nanofiltration (NF)

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desalination plants and other water treatment installations.¹⁻⁸ Currently acceptable methods of preventing scale formation utilize chemicals, which are known as threshold agents (antiscalants): phosphates, phosphonates and polycarboxylates, Table 1. An addition of less than stoichiometric quantities of certain antiscalant to supersaturated solutions of sparingly soluble salts (calcite, gypsum, barite, etc), postpones their precipitation for substantial periods of time.^{6,9-12} This retardation of scaling appeared to be highly beneficial economically for numerous industrial applications. Recently the world market of antiscalants represents hundreds of trademarks, thousands tones of reagents and an annual turnover ranging from 4 to 5 billions of US dollars.¹³

Irrespective of long-lasting, broad and successful application of antiscalants in industry, and of intensive research, the specific mechanisms of threshold activity is so far not clearly understood. Since early works of Elliot.¹⁴ Nancollas¹⁵ and Amjad¹⁶ till now days¹⁷⁻²⁴ these issues are the matter of discussions. However there is a general agreement that scale inhibitors may act by one of several possible routes. They may (i) change the precipitating salt's chemical potential by complex formation (masking such cations as Ca^{2+} and Ba^{2+}); (ii) be adsorbed onto sparingly soluble salt embryos (this reduces the speed at which embryos pass through the critical size barrier and thus diminishes the rate of scale nucleation); (iii) impart a significant electrostatic charge to the scale nuclei and thus retard their aggregation due to electrostatic repulsion of sparingly soluble salt colloids; and (iv) be adsorbed onto growing crystals, distorting and/or inhibiting further crystal growth. It is likely that the effective inhibitors function through more than one of the above routes. But once a supersaturation has occurred in any real system, precipitation becomes inevitable, regardless of the merits of any known threshold inhibitor.²⁵

Table 1.
Antiscalants, Commonly Used in Industry and in R&D

Short Name	Name	Short Name	Name
Polyphosphates		Polyelectrolytes	
TPP	tripolyphosphate	PA	polyacrylate
HMP	hexametaphosphate	PASP	polyaspartate
Organophosphonates		PESA	polyepoxysuccinate
PBTC	2-phosphonobutane 1,2,4-tricarboxylic acid	PCS	polycarboxysulfonate
EDTPH	ethylenediaminetetra(methylenephosphonic acid)	PMA	polymaleate
ATMP	aminotris(methylenephosphonic acid)	MA-AA	copolymer of maleic and acrylic acid
HEDP	1-hydroxyethane-1,1-bis(phosphonic acid)		

However, our research group being involved over the past five years in the routine tests of the industrially manufactured antiscalant relative efficacy following NACE Protocol,²⁶ came across the facts that conflict most of aforementioned scale inhibition mechanisms. First of all we have noticed that there is a large discrepancy of the efficacy sequences for one and the same set of reagents in different publications.^{27,28} For example, different research groups report for CaCO_3 deposits the reversed antiscalant efficacy sequences. Particularly for the traditional reagents HEDP and PA, as well as for the novel PESA and PMA, one group presents a ranking: HEDP > PESA (1,500 Da) > PMA (600 Da) > PA (1,800 Da), while another one reports: PA (1,800 Da) > PMA (600 Da) > PESA (1,500 Da). Meanwhile for the pair HEDP/PA, the diversity of CaCO_3 antiscaling efficiency estimations is ranging from HEDP >> PA (1,800 Da) to PA (2,000 Da) ~ HEDP, and even to HEDP < PA (2,000 Da). A similar inconsistency is observed for HEDP and ATMP: ATMP >> HEDP; ATMP ~ HEDP and ATMP << HEDP.²⁷

In the same way for gypsum scaling one research group reports that PMA (600 Da) > PA (1800 Da) > PESA (1500 Da), while another one presets PESA (1500Da) ≥ PA (1800 Da) ≥ PMA (600

Da).²⁸ Only part of these data disagreements can be explained by the differences in measurement technique or in scale formation conditions. Thus, there exists some important experimental peculiarity, that is neglected by most of researchers, but which appears to be of key importance for the final experimental result.

The second evident disagreement with theory we have found in our NACE protocol tests of gypsum scaling in presence of several phosphonates and polycarboxylates. We got the following efficacy sequence: MA-AA ~ ATMP > PESA (400–1500Da) > PASP (1000–5000 Da) > PAAS (3000–5000 Da) ~ HEDP~PBTC.²⁸ However, the scanning electron microscopy (SEM) of corresponding sediments indicated clearly, the gypsum crystal morphology is changed not by the “best” antiscalants (ATMP, PESA), but by the least effective PBTC,²⁸ Figure 1.

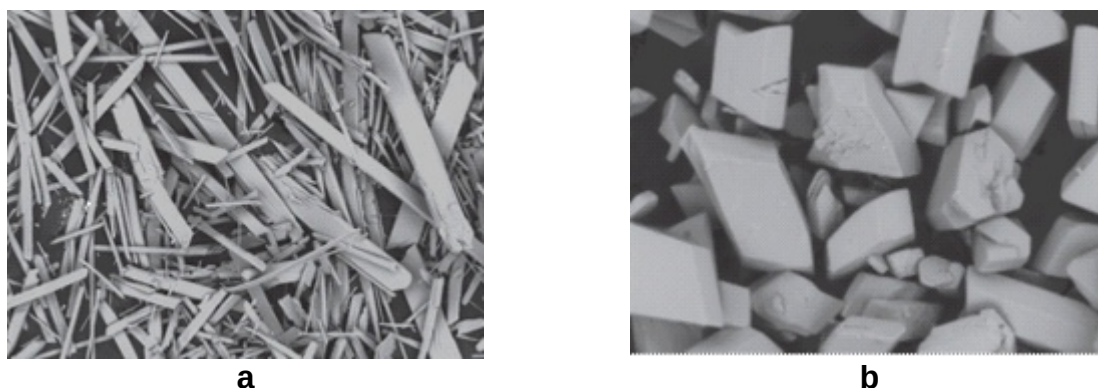


Figure 1: SEM images (x100) of gypsum crystals isolated from gypsum brines in a blank experiment (a) and in the presence of $0.5 \text{ mg} \cdot \text{dm}^{-3}$ PBTC (b).²⁸

If a distortion of a crystal is recognized as a sign (or as a proof) of scale formation process inhibition via crystal growth centers blockage by antiscalant molecules, then it is reasonable to expect that the “strongest” reagents would cause the major distortion, while the “weakest” – the minor one, if any. Otherwise it is not a proof. In our case we have demonstrated the lack of direct correlation between antiscalant efficacy and the scale crystals distortion. This result does not deny the retardation of crystals growth by the antiscalant sorption onto their surface. At the same time it indicates, that at least in some cases this distortion is not the rate determining factor in scale inhibition process. The third controversy with theoretical grounds is associated with electrostatic repulsion. In both experimental runs with CaCO_3 ²⁷ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ²⁸ we have found the zeta-potentials for all antiscalants about $0 > \zeta > -15 \text{ mV}$, while for the colloid solution stabilization one needs $-30 \text{ mV} > \zeta$.²⁹ At the same time there was also a lack of correlation between zeta-potential and inhibition efficacy.^{27,28} Thus an electrostatic factor does not seem to influence retardation of scaling process at least in the beaker tests.

Complex formation between antiscalant and a scale forming cation (Ca^{2+} , Ba^{2+}) really takes place. However, this one is unable to impact the total Ca^{2+} or Ba^{2+} concentration due to substoichiometry: 1 mol of antiscalant is usually taken for 1000 moles of an alkaline earth cation. Meanwhile it may become critical for an antiscalant itself. Some phosphonates like ATMP, HEDP are known to form insoluble calcium and barium salts.^{30,31,32} Thus these antiscalants are very sensitive to the alkaline earth cations excess. This property may cause certain disagreements in their relative efficacy evaluations, and will be considered further. The last, but not least controversy was registered in our comparative study of phosphonate and phosphorus-free antiscalant efficiency by static and dynamic methods.³³ Therefore, a lot of work is still needed to elaborate a system of laboratory tests for antiscalants in order to provide reliable assessment and selection on their way from laboratory to industry. All the aforementioned controversies reveal evident gaps in understanding of scale inhibition process and forced us to look for some novel nonconventional mechanisms of scale inhibition in the bulk supersaturated aqueous solutions of sparingly soluble salts. One of such gaps in our opinion is represented by the role of foreign suspended particles (“nanodust”)

always present in any aqueous medium. Surprisingly, their possible participation in scale formation process is usually either completely neglected, or underestimated in a recent water treatment R&D.

RESEARCH APPROACHES USED

In our studies the three novel independent approaches have been used: (i) a direct application of a particle counter for “nanodust” quantitative content evaluation in the stock solutions used for antiscalant efficacy measurements; (ii) a semi-quantitative determination of the scale nuclei along the induction time period by a modified dynamic light scattering (DLS) technique; and (iii) an application of fluorescent-tagged antiscalants for the direct visualization of a scale inhibitor during scale formation process. As far as we know none of these approaches was used previously in water treatment R&D.

A novel DLS special technique used by us is based on the standard Ag nanoparticles (or silica nanoparticles) injection into the supersaturated gypsum solution. These nanoparticles act as an internal indifferent light scattering intensity reference, and provide a semiquantitative measurement of a relative gypsum particles content in a blank solution and in the system treated with antiscalants.^{32,34} For the direct visualization of a scale inhibitor a novel fluorescent-tagged bisphosphonate scale inhibitor 1-hydroxy-7-(6-methoxy-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)heptane-1,1-diyl-di(phosphonic acid), (HEDP-F) was synthesized and used for fluorescent microscope visualization of gypsum³⁵ and barite³⁶ crystal formation in supersaturated aqueous solutions as well as in reverse osmosis facility tests,³⁷ Figure 2. Actually, HEDP-F is a structural analogue of HEDP. Recently two novel fluorescent-tagged polyacrylates are also synthesized Figure 3³⁸, and are tested for visualization of carbonate membrane fouling visualization.³⁹

RESULTS AND DISCUSSION

Particle Counter Analysis

In all our laboratory experiments the stock solutions (prepared with analytically grade purity reagents and then filtered through 220 nm filters), appeared to contain a significant amount of micro- and nanoparticles, detected by a particle counter SLS-1100, see for example the data for barite studies,³⁶ Table 2. Notably, the recent particle counters do not detect quantitatively the fractions with sizes <100 nm. However, looking at the trend of a relative foreign particles abundance in different fractions, Table 2, it would be not a big error to suppose that the concentration of particles with sizes <100 nm exceeds that one of those with a size >100 nm. Meanwhile, particularly these solid impurities should serve as barite, gypsum or calcite nucleation centers.

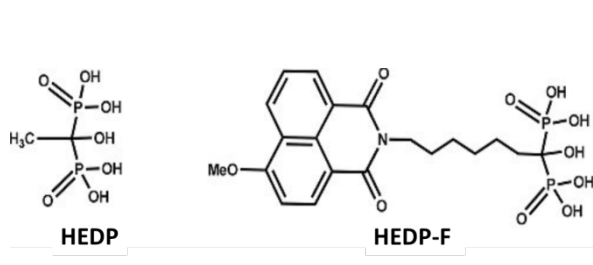


Figure 2: HEDP and HEDP-F molecular structure

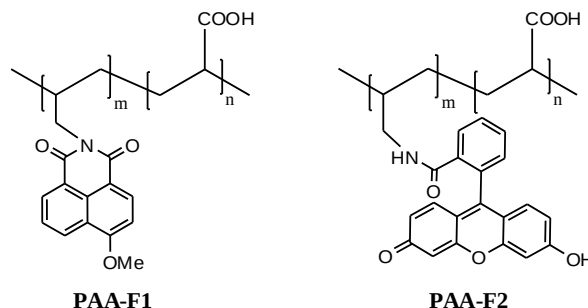


Figure 3: Fluorescent-tagged polyacrylate PAA-F1 and PAA-F2 molecular structures

We have done a demo study of a water treatment R&D microfiltration procedure results for the high purity reagents used for the brines preparation. These data indicate a presence of substantial