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## MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

# Polyacrylic Acid and Formulations Based on It as Inhibitors of Deposit Formation in Water-Recycling Systems

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**Abstract**—The performance of polyacrylic acid of various molecular weights and of its formulations with sodium tripolyphosphate and Na2EDTA as inhibitors of deposit formation and as dispersants was examined..

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To mitigate the detrimental effect of industry on the environment, industrial enterprises should utilize natural waters with maximal efficiency. One of the main ways to meet this requirement is reuse of water in the production, which makes it necessary to provide water recycling with cooling of technical water that has been heated in the industrial process. As a rule, water is cooled by evaporation in cooling towers. Evaporation leads to concentration of soluble and insoluble impurities present in water, and conditions arise for deposition of hardness salts in heat exchangers, which decreases the efficiency of heat transfer, causes increased power consumption, and makes it necessary to interrupt the production process to perform expensive and time-consuming operations of equipment cleaning. Furthermore, deposit formation stimulates subsurface corrosion leading to premature wear of the equipment.

One of efficient solutions of the problem of deposit formation in water-recycling systems is the use of special chemical reagents inhibiting scale formation. Among such reagents, the most widely used are phosphates, phosphorus-containing complexones (phosphonates), and polyelectrolytes [1, 2]. Inhibitors affect the formation, growth, and structure of scale crystals [2, 3]. Polyelectrolytes, in particular, those based on polyacrylic, polymethacrylic, and polymaleic acids and on polyacrylamide find growing use today. The mechanism of the inhibiting effect of reagents of this group differs from that of phosphorus-containing compounds and is yet poorly understood.

It should be noted that, to reliably eliminate scale formation, the reagent should exhibit good dispersing properties toward a series of substances: microcrystals of hardness salts and their agglomerates, corrosion products, clay particles, so as to stabilize the precipitate of insoluble impurities in the suspended form for a long time [4].

In this study we examined the performance of polyacrylic acid (PA) and its formulations with sodium tripolyphosphate and $Na_2EDTA$ as scale formation inhibitors and dispersants.

## EXPERIMENTAL

As inhibitors of deposit formation we used polyacrylic acid samples with MW 1000, 2100, 3000, 5000, and 78 000 ($PA_1$, $PA_2$, $PA_3$, $PA_5$, $PA_{78}$) purchased from Aldrich, sodium tripolyphosphate [STPP, GOST (State Standard) 13493–86], and disodium dihydrogen ethylenediaminetetraacetate, $Na_2EDTA$ (GOST 10652–73). Solutions of calcium and magnesium chlorides and of sodium hydrogen carbonate were prepared in distilled water from chemically pure grade chemicals.

To evaluate the performance of the inhibitors, we used a PMAC SCL-30P-2A laboratory installation (the United Kingdom) simulating the deposit formation under real conditions. The principle of its operation consists in dynamic measurement of the differential pressure in a metallic capillary, increasing as a result of scale formation, at variable or fixed experimental parameters.

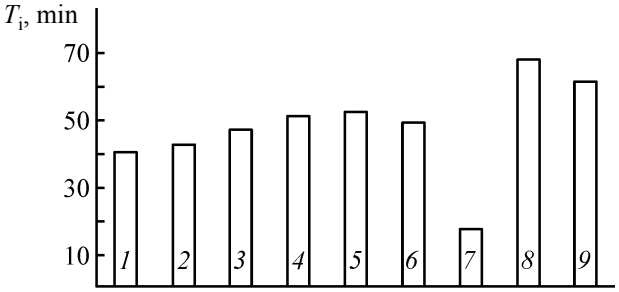



**Fig. 1.** Time of the change in the differential pressure in the system in the presence of inhibitors. ($T_i$) Inhibition time. Inhibitor: (*1*) $Na_2EDTA$, (*2*) STPP, (*3*) $PA_1$, (*4*) $PA_2$, (*5*) $PA_3$, (*6*) $PA_5$, (*7*) $PA_{78}$, and (*8*) formulation of $PA_5$ with $Na_2EDTA$, and (*9*) formulation of $PA_5$ with STPP (dosage of reagents and formulations 0.2 ppm; the parameter for the uninhibited system 23 min).

Model solutions of preset concentration (solutions of calcium chloride, magnesium chloride, sodium hydrogen carbonate) are pumped into the capillary of the device in a constant volume at a constant flow rate. The scale formation inhibitor is fed separately. After mixing and heating the solutions to 90°C, a deposit of calcium carbonate is formed on internal walls of the capillary, which leads to an increase in the differential pressure along the capillary.

As a characteristic of the performance of deposit formation inhibitors, we used a relative parameter, time interval $T_i$ in which a scale layer formed in the capillary leads to an increase in the differential pressure from zero to a certain level equal in all the experiments (in our case, to 13.8 kPa). The solution feed rate, water hardness, pH, and temperature were kept constant.

We used a photometric method for determining the relative dispersion capacity (RDC) for kaolin. The experimental RDC value characterizes the percentage of kaolin in the suspended form in 5 h at pH 8. The higher the dispersion capacity of the inhibitor, the better are kaolin particles retained in the suspended state in an aqueous dispersion and the higher is the optical density.

To obtain a control suspension sample, kaolin was finely ground, a fraction with a particle size of 0.05 mm was taken, and, after drying at 250 ± 5°C and cooling, this fraction was placed in a solution containing a mixture of calcium chloride, magnesium chloride, and sodium hydrogen carbonate and left to swell for 12 h. The test sample of kaolin suspension containing an inhibitor was prepared similarly. The control and test samples of kaolin suspension were placed in cells, and the optical density at the chosen wavelength was measured in 5 h. The RDC (%) was found by the formula

$$\mathrm{RDC} = \frac{D_t}{D_c} \times 100$$

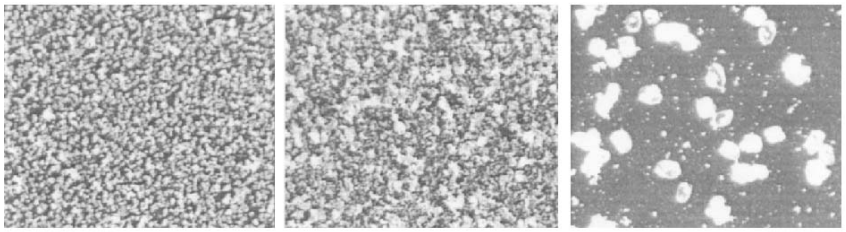
where $D_t$ and $D_c$ are the optical densities of the test and control samples of kaolin suspension, respectively.

The results of studying the inhibiting performance of STPP, complexone ($Na_2EDTA$), and polyacrylic acid show that addition of any of these reagents leads to an increase in the time interval preceding the deposit formation in the system. The parameter characterizing the inhibiting performance of the reagents toward deposit formation, $T_i$, for PA is somewhat higher than for STPP and $Na_2EDTA$ (Fig. 1). For PA samples of relatively low MW (1000–5000), $T_i$ is in the range 46.9–52.1 min, and in going to high-MW PA ($PA_{78}$) it drastically decreases. In the latter case, the lack of the inhibiting effect is due to flocculation of the precipitate particles (Fig. 2c).

The mechanism of the inhibiting effect is based on adsorption of inhibitor molecules on the surface of growing crystals of calcium carbonate, which inhibits the crystal growth, favors stabilization of metastable phases of calcium carbonate, and leads to formation of finer crystals of irregular shape [4, 5]. In the case of PA, carboxy groups of the polymer are sorbed on cations of the mineral salt or substitute anionic components of the crystal on the surface. The layer of polymer molecules covering the surface complicates formation of the next layer and prevents growth of the regular three-dimensional crystal lattice of calcite [4]. The forming amorphous crystals of irregular shape are incapable of forming a stable deposit (coating) and can be readily removed from the system.

The results of an X-ray phase analysis of precipitates of calcium and magnesium carbonates obtained in the absence (control) and in the presence of PA show that the polyelectrolyte significantly affects the crystal formation of calcium carbonate and the morphology and size of its particles. The structure of crystals in the presence of the inhibitor is deformed, becomes more amorphous and loose.

Comparison of the photographs of the precipitate (Fig. 2) confirms changes in the size and shape of calcium carbonate crystals on adding the polymer: The precipitate obtained in the presence of $PA_5$ (Fig. 2b) consists of flake-like particles differing from those of the control sample



(a) (b) (c)

**Fig. 2.** Photograph of the precipitate (×2) obtained (a) without inhibitor, (b) in the presence of $PA_5$, and (c) in the presence of $PA_{78}$.

particles by the larger size and amorphous structure.

It is known that scale formation in water-supply systems is caused by formation of insoluble calcium carbonate in decomposition of calcium bicarbonate [4]. In the examined model solutions without inhibitor (control) and with additions of STPP, $Na_2EDTA$, and PA, after circulation in the PMAC laboratory installation we determined the content of $HCO_3^-$ and $CO_3^{2-}$ ions. We found that, in the presence of the same amount of reagents, the content of bicarbonate ions with all the examined reagents is approximately the same and is 2.6–2.8 times higher than in the control sample, whereas the amount of carbonate ions is 3.2–3.3 times lower. Apparently, the presence of an inhibitor in the system prevents formation of insoluble carbonate particles. As a result, the solution remains stable (with a high content of bicarbonates), and mineral deposits (carbonates) are not formed.

The quantity RDC characterizing the capability of the reagent to stabilize the dispersion system and prevent agglomeration of insoluble particles occurring in water in the suspended state (kaolin in our case) for all the examined reagents is lower than the control level and for PA is higher than for STPP and $Na_2EDTA$ (Fig. 3).

A decrease in the optical density of the dispersion system containing kaolin particles is due to removal of the precipitate from the zone being analyzed. The smaller the change in the optical density of the system, the higher is the dispersing power of the additive. As seen from Fig. 4, the optical density of the kaolin dispersion containing $PA_5$ decreases to a lesser extent, compared to the polymers of the lower MW.

The use of $PA_5$ in combination with $Na_2EDTA$ or STPP enhances the inhibiting and dispersing effect, compared to the reagents taken separately: $T_i$ (time of deposit formation inhibition) for the system with $PA_5$ + $Na_2EDTA$ increases by a factor of 1.4 and 1.7 (Fig. 1); RDC of $PA_5$ + STPP is 1.5 and 1.7 times higher than those of the reagents taken separately (Fig. 3).

## CONCLUSIONS

(1) Polyacrylic acid, sodium tripolyphosphate, and $Na_2EDTA$ inhibit crystallization of calcium and magnesium carbonates, affect the particle size and

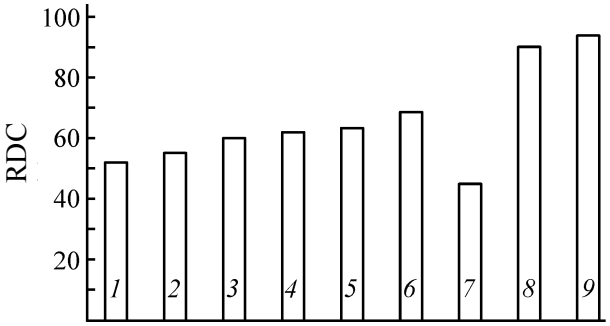



**Fig. 3.** Relative dispersion capacity RDC of (*1*) $Na_2EDTA$, (*2*) STPP, (*3*) $PA_1$, (*4*) $PA_2$, (*5*) $PA_3$, (*6*) $PA_5$, (*7*) $PA_{78}$, (*8*) formulation of $PA_5$ with $Na_2EDTA$, and (*9*) formulation of $PA_5$ with STPP for kaolin. Reagent dosage 0.2 ppm. RDC for the system without inhibitor is taken as 100%.

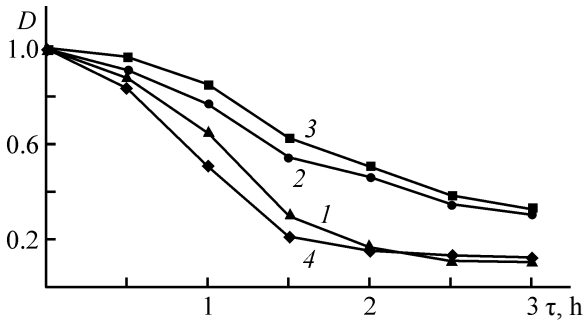



**Fig. 4.** Variation of the optical density *D* of a mixture of salt solutions (*1*) without inhibitor and in the presence of (*2*) $PA_2$, (*3*) $PA_5$, and (*4*) $PA_{78}$. (τ) Time.

structure of crystals, and exert a stabilizing effect on the kaolin dispersion.

(2) Binary formulations based on polyacrylic acid (MW 5000), $Na_2EDTA$, and sodium tripolyphosphate exhibit synergism in the inhibiting and dispersing effect.

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