

AUXILIARY REAGENTS

DEVELOPMENT OF AN EFFECTIVE SCALE INHIBITOR BASED ON ORGANOPHOSPHONIC COMPOUNDS IN AN AQUEOUS-ALCOHOL SOLVENT

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We have studied the effect of the ratio of hydroxyethylidene diphosphonic acid and nitrilotri(methylphosphonic acid) and also polyaminopolyether methylenephosphonate chelating agent additives on scale inhibition in simulated formation water. We show that replacing the water with an aqueous-alcohol solvent lowers considerably the pour point of the reagent without having an appreciable effect on its effectiveness. We have developed a composition that exhibits high effectiveness of scale inhibition for scale composed of calcium carbonate and also calcium and barium sulfates when added at 10-20 mg/L.

Keywords: *scale inhibitor, organophosphonic acids, polyaminopolyether methylenephosphonate, calcium carbonate, calcium sulfate, barium sulfate.*

A complication with well drilling and crude oil recovery and processing is scale formation in the bottom-hole stratum, on well equipment, and in ground-based pipes for collecting and transporting crude oil [1]. This complicates seriously the processing and leads to breakdowns in costly equipment and labor-intensive repairs, and, eventually, to a significant reduction in the volume of recovered crude oil [2]. Typical scales contain mainly calcium carbonate and calcium and barium sulfates in addition to other salts [2, 3]. The most effective and technical method of those known today for battling scale is to prevent it

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from forming by using scale inhibitors [1-5]. Deposition of inorganic salts through the whole system of well production from bottom hole to oil and water preparation points can be avoided by selecting correctly the inhibitors and the technique for using them. Therefore, the use of highly effective scale inhibitors would decrease significantly production interruptions and equipment outages.

Currently, various chemicals [4-7] are used as inhibitor bases. Among these, the most common are organophosphonic acids, in particular, hydroxyethylidenediphosphonic acid (HEDP) and nitrilotri(methylphosphonic acid) (NTP) [8-10]. These reagents exhibit good inhibitor properties with respect to calcium carbonate and sulfate scales [8-10]. However, high concentrations of the active ingredient are required in order to achieve a high level of inhibition. Polyaminopolyether methylenephosphonate (PAPEMP) exhibits high inhibiting ability with respect to calcium carbonate and calcium and barium sulfates [11]. However, it is rather costly so that this reagent cannot be used as the principal component for manufacturing scale inhibitors.

The present work focused on the development of a new complex reagent containing organophosphonic acids neutralized by monoethanolamine in addition to a chelating complexant in aqueous MeOH solution.

The scale inhibitors were prepared using HEDP and NTP, monoethanolamine (MEA), PAPEMP, and mixtures of doubly distilled H₂O and technical MeOH as the solvents.

Scale inhibitors were prepared by mixing the components as follows. A container equipped with a stirrer was charged with the required amount of solvent (H₂O + MeOH mixture). The mixture was stirred and treated in portions with the organophosphonic components at intervals necessary for complete dissolution. Then, MEA was added with stirring so that the temperature in the container did not rise above 40°C. The amount of added MEA was sufficient to neutralize the phosphonic acids. A MeOH content of 30 mass% ensured that the inhibitor freezing temperature was below -50°C [12]. Several scale inhibitor compositions were prepared by this method (Table 1). Compositions (SI1-SI5) with various HEDP and NTP ratios without PAPEMP were prepared first. These compositions also contained MEA (16 mass%), MeOH (30 mass%), and H₂O (39 mass%). Scale inhibitors (SI6-SI9) with added PAPEMP were also prepared. After all components were added, the compositions were stirred again to form a homogeneous solution. The resulting reagents (SI1-SI9) were light-brown liquids of density 1160-1200 kg/m³ and freezing temperatures below -30°C.

Table 1

Reagent	Active ingredient composition, mass %		
	HEDP	NTP	PAPEMP
SI1	3.7	11.3	-
SI2	5.0	10.0	-
SI3	7.5	7.5	-
SI4	10.0	5.0	-
SI5	11.3	3.7	-
SI6	3.7	11.3	0.4
SI7	3.7	11.3	1.2
SI8	3.7	11.3	2.0
SI9	3.7	11.3	4.0

Note. Content in all reagents of MEA, 16 mass%; MeOH, 30 mass %.

The effectiveness of the prepared compositions was determined chemically using methods developed at NIIneftpromkhim Corp. Tests were conducted with reagent concentrations 10 and 20 mg/L. The compositions were tested for effectiveness of preventing carbonate and sulfate scales under high mineralization conditions. The test medium was model formation water corresponding to the formation water composition of Bereзов section of Romashkino field at Tatneft Corp. Solution A, which contained precipitating cations (Ca^{2+} or Ba^{2+}), and solution B, which contained precipitating anions (HCO_3^- or SO_4^{2-}), were prepared separately. Model formation water was prepared by mixing solutions A and B and adding scale inhibitor beforehand. The resulting supersaturated solution was mixed, heated to 90°C , and stored for 4 h.

The effectiveness of the scale inhibitors was determined from the concentrations of Ca^{2+} and Ba^{2+} in the freshly prepared solution and in that after heating with and without scale inhibitor. The concentration of Ca^{2+} was calculated using complexometric titration by EDTA. The titrant for Ba^{2+} was a standard MgSO_4 solution.

The degree of calcium sulfate and carbonate scale prevention (DSP, %) was calculated using the formula:

$$SPR = 100 (C_{inhib} - C_{cont}) / (C_{init} - C_{cont})$$

where C_{inhib} is the Ca^{2+} concentration in the solution with inhibitor after heating; C_{cont} , the Ca^{2+} concentration in the solution without inhibitor after heating; and C_{init} , the Ca^{2+} concentration in the solution without inhibitor before heating.

The DSP of barium sulfate was calculated using the formula:

$$SPR = 100 C_{inhib} / C_{init}$$

where C_{inhib} is the Ba^{2+} concentration in the solution with inhibitor after heating; C_{init} , the Ba^{2+} concentration in the solution without inhibitor before heating.

The influence of the HEDP:NTP ratio on the effectiveness of scale prevention was studied. It is well known that these P-containing complexants prevent nucleus formation in supersaturated solutions and can

Table 2

Reagent	Degree of scale inhibition, %		
	CaCO_3	CaSO_4	BaSO_4
SI1	76.5 / 85.4	85.1 / 92.5	75.4 / 83.7
SI2	68.0 / 80.4	80.0 / 90.1	71.8 / 79.2
SI3	68.2 / 82.2	83.5 / 89.1	70.3 / 76.7
SI4	74.1 / 82.8	78.7 / 88.4	69.3 / 72.3
SI5	75.9 / 83.2	74.3 / 85.7	66.2 / 69.9
SI6	85.3 / 93.2	94.2 / 95.8	87.5 / 89.2
SI7	89.0 / 94.5	96.7 / 96.7	90.5 / 91.5
SI8	87.1 / 96.9	95.0 / 96.5	91.4 / 92.5
SI9	89.9 / 98.3	96.8 / 97.2	90.3 / 91.6

Note. Values for inhibitor dose 10 mg/L in the numerator; 20 mg/L, in the denominator

effectively inhibit scale formation. Test results for reagent concentration 20 mg/L (Table 2) showed that the optimum HEDP:NTP ratio was 1:3. The maximum DSP for SI1-SI5 was 85.4, 92.5, and 83.7% for calcium carbonate and calcium and barium sulfates, respectively. This was a satisfactory result although the issue of improving the reagent composition remained.

PAPEMP was used as an additional component in order to increase the scale-inhibition effectiveness because the chelate structure of this compound effectively prevented the growth of sulfate and carbonate crystals [11]. Table 2 shows that a PAPEMP content from 2 to 4 mass% gave the highest DSP. Increasing the SI6-SI9 inhibitor concentration from 10 to 20 mg/L increased the inhibition for calcium carbonate although the inhibition for the sulfates was practically unchanged.

Compositions SI8 and SI9 under high formation-water mineralization conditions and at small reagent concentrations prevented highly effectively sulfate (97.2% for calcium sulfate and 92.5% for barium sulfate) and carbonate (98.3% for calcium carbonate) scales.

The developed scale inhibitors could be recommended for application in various industrial sectors for preventing calcite and barite scales. The low freezing temperatures of the proposed compositions allowed them to be used in cold climates.

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