TECHNICAL NOTE

NEW RAPID TEST FOR EVALUATION OF SCALE INHIBITORS

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Abstract—A new method of evaluation of scale inhibitors efficiency has been developed and tested. This method is based upon solution conductivity measurement. It consists of determining a supersaturation level of any scale forming compound in a given water, at defined conditions, in the presence of a specified amount of scale inhibitor and also without inhibitor. This method allows the stabilizing features of compounds under investigation to be differentiated. With this method the efficiency of preventing CaCO₃ precipitation from aqueous solutions was determined for three phosphonate compounds which are effective as corrosion inhibitors of mild steel in neutral water: 2-phosphonobutane-1,2,4-tricarboxylic acid (TBTC), ethylenediaminetetramethylenephosphonic acid (EDTMP) and phosphono-N-methylenephosphonic derivative of polycaproamide (PMPP). It was ascertained that the above compounds are effective in preventing CaCO₃ crystallization from water. EDTMP showed the best stabilizing properties and PBTC what poorer ones.

Key words—scale inhibitors, water stabilization, phosphonate compounds, conductivity

INTRODUCTION

Precipitation and scale deposition present an important problem in operating water cooling and heating installations. Deposits formed may cause severe crevice corrosion attack, growth of microorganisms and may deteriorate conditions of the heat exchange (Bond, 1990).

Enormous progress in science and technology, made in the area of new technics and apparatus, is often bound up with intensification of heat exchange processes in chemical industries, metallurgy, power industry, etc. Traditional methods of water treatment for industrial purposes (filtration, coagulation, decarbonization, outgassing, ion exchange) have become more and more expensive due to the general degradation of the environment and also are often of low effectiveness. By preventing precipitation and deposition on exchange surfaces intensification of the heat exchange may be obtained. Any effective means of water stabilization would allow the use of natural water of lower quality and/or reused water and would lead to a reduction of water consumption because of the possibility of concentrating it significantly in circulation systems.

At present, research concerning water stabilization which is to lower the tendency to evolve precipitates, focuses on physical and chemical methods. Physical methods include water treatment in magnetic or electric fields and by using sonic waves (Limpert and Raber, 1985). Chemical methods are methods consisting of adding small amounts (i.e. at a level of grams per 1 m³) of agents into water. Those agents are usually composed of organic compounds. Chemical methods are more versatile, as they offer more possibilities for efficient water treatment over a wider variety such as water parameters and technical specifications of operating systems.

Crystallization results from three processes which interact mutually: supersaturation, nucleation and crystal growth. Water stabilizing chemicals (e.g. complexones) may influence each of these processes. There is a lack of references as to the mechanism of crystallization inhibition of sparingly soluble salts by using complexones. In one of the few articles concerning these problems (Tomson and Matly, 1989) nucleation of CaCO₃, CaSO₄ and BaSO₄ under influence of complexone types like phosphonates and polyacrylates were presented. Based on analyses of the diffusion rate into crystal being in the nucleation stage, two ways of affecting crystal nucleation, i.e. increasing supersaturation and decreasing interfacial tension, were presented. A rel-

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The critical degree of supersaturation is most compounds which crystallize from aqueous solution the homogenous nucleation rate is almost zero below this value. For exceeded, i.e. at a critical supersaturation. The critical degree of supersaturation is defined as a ratio of the crystallizing substance concentration to the concentration of saturation (solubility). Although nuclei formation is possible at each super-saturation (S > 1), its rate increases rapidly only when a specific value of the supersaturation is being exceeded, i.e. at a critical supersaturation. The nucleation rate is almost zero below this value. For most compounds which crystallize from aqueous solution the critical degree of supersaturation is very high and reaches a value of 10^2–10^3. The quantity of the critical degree of supersaturation reached is especially important in water systems where the problem of precipitation and deposit forming often exists. Calcium carbonate and sulfate are main scale compounds in most types of usable water. In this paper the influence of chosen phosphonate compounds on the critical degree of supersaturation for only calcium carbonate in water is presented. This new test uses conductivity measurements while calcium carbonate is being precipitated from calcium chloride solution by addition of sodium carbonate.

Based on many tests, it was ascertained that using 0.1 M CaCl₂ as a titrated solution and 0.1 M Na₂CO₃ as the titrating solution was the most convenient set of solutions.

MATERIALS AND METHODS

The test setup, presented in Fig. 1, consists of a test cell thermostated and provided with conductivity sensor and magnetic stirrer. This setup includes also the CC-551 microcomputer conductivity meter (Elmetron) and the U-1 thermostat (MLW Prüfgeräte-Werk).

The tests consisted of putting 60 cm³ of bi-distilled water, 3 cm³ of 0.1 M CaCl₂ and a variable amount of phosphonate compounds in the thermostated vessel of 100 cm³ in volume. Then, the conductivity sensor was installed and after the temperature stabilized at 25 ± 0.1°C, the solution was titrated by using 0.1 M Na₂CO₃. The titrating solution was added in portions of 0.2 cm³ each. The conductivity value was read after 1 min of stabilizing. Solutions being tested were stirred at constant intensity with a magnetic stirrer during measurements. Before each titration the vessel, the sensor and the stirrer were washed with 1 M H₂SO₄ and bi-distilled water to remove all traces of deposits which could become crystal nuclei while the measurements were being carried out. The results obtained are presented as a diagram of the solution conductivity vs the volume of the titrating agent added, from which the initial point of the precipitation was determined.

The following phosphonate compounds were selected to test their abilities to inhibit CaCO₃ precipitation process in aqueous solutions. These compounds are effective in preventing the corrosion of steel in water environment at neutral pH:

- 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTC):
  \[ \text{HOOC–CH₂–CH₂–C(OOH)₃(PO₃H₂)} – \text{CH₂–COOH} \]
- Ethylenediaminetetramethylenephosphonic acid (EDTMP):
  \[ (\text{H₂PO₄})₂–\text{CH₂–N–(CH₂PO₃H₂)}₂ \]
- Phosphono-N-methylene phosphonic derivative of polycaprolactam (PMPP):
  \[ \text{(H₂PO₄)–CH₂–N–(CH₂PO₃H₂)} \]

Fig. 1. Experimental setup for measurement of CaCO₃ supersaturation.
All agents used in the tests were of p.a. purity grade except PMPP which had been synthesized in the laboratory from substrates of p.a. purity grade.

RESULTS AND DISCUSSION

The diagram in Fig. 2 is an example of a titration of the solution containing scale inhibitor. Three linear segments with increasing slope may be distinguished there. At the point of intersection of the straight lines I and II, solution opalescence was usually noticed. However, even after waiting a long time within the second segment (1.4 to 2.8 cm$^3$ 0.1 M Na$_2$CO$_3$) no precipitation occurred. The value of the last point on the straight line II (arrow-marked one, which relates to the value of 2.8 cm$^3$ of 0.1 M Na$_2$CO$_3$) was taken as the boundary concentration of the titrating agent, which caused the initiation of CaCO$_3$ precipitation. At the volume of the titrating agent, represented by the value of 3.0 cm$^3$ on the diagram, a deviation from the linear relationship appears and a rapid precipitation begins, from which a rapid decrease of the conductivity results within a few minutes. Further titration shows a linear relationship to the concentration again but with an increased slope (line III in Fig. 2). The relationship between the solution conductivity and the concentration of the precipitating agent described above only occurs with the presence of complexones. In the case where the solution contains only CaCl$_2$ with no complexones, there is no 2nd segment, which means solution opalescence and precipitation appear simultaneously.

Values for the degree of supersaturation measured for solutions containing phosphonate compounds were compared to the supersaturation obtained at similar conditions but without the addition of the phosphonates. So the values for the degree of supersaturation in the following are relative ones ($S_r$) expressed as a ratio of the supersaturation of CaCO$_3$ in the presence of a phosphonate compound ($S_p$), to the value of the supersaturation under the same conditions for water alone ($S_0$):

$$S_r = \frac{S_p}{S_0}$$

In calculations, both the dilution of phosphonate compounds and deposit forming ion concentrations caused by variable critical values of the titrating agent were taken into account. In the case of the water solution containing 60 cm$^3$ of distilled water and 3 cm$^3$ of 0.1 M CaCl$_2$ and without any additions, 0.6 cm$^3$ of 0.1 M Na$_2$CO$_3$ was consumed before opalescence occurred. So the ionic product of the CaCO$_3$ precipitation at these conditions may be calculated as follows:

- Volume of the solution when turbidity first occurs, $6.36 \times 10^{-2}$ dm$^3$.
- Calcium ion concentration ([Ca$^{2+}$]), $4.71 \times 10^{-3}$ M.
- Carbonate ion concentration ([CO$_3^{2-}$]), $9.43 \times 10^{-4}$ M.

$$[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] = 4.44 \times 10^{-6}$$

From the handbook of physical chemistry the ionic product of CaCO$_3$ at 25°C is $4.8 \times 10^{-9}$, so the value of its supersaturation under test conditions ($S_0$) is 925.

Dependence of the relative degree of supersaturation of CaCO$_3$ in the water solution ($S_r$) on concentrations of the three phosphonate compounds selected is presented in Fig. 3. It appears from Fig. 3 that in the case of EDTMP and PBTC, the relative degree of supersaturation of CaCO$_3$, equal to 3.7, is possible to achieve even at small concentrations of these agents in water (up to 5 $\mu$mol/dm$^3$). A further increase in concentration, however, causes a smaller increase in the relative supersaturation. Better results are obtained using EDTMP than PBTC. The highest supersaturation, 7 times higher than for water alone, was obtained for EDTMP but at a relatively high concentration in water (47 $\mu$mol/
dm$^3$). It is apparent that increasing the EDTMP concentration 10 times, i.e. from 5 to 50 µmol/dm$^3$, only allows the degree of supersaturation to double.

As for PMPP, which is the most effective in preventing corrosion of the mild steel in neutral water, its anti-scale properties are much worse than the other two. So, at the concentration of 10 µmol/dm$^3$, the supersaturation obtained for PMPP is over 2 times lower than for EDTMP and PBTC.

Taking the supersaturation acquired into account and also the costs of using anti-scale compounds, the values of 5 to 10 µmol/dm$^3$ for EDTMP and PBTC, which correspond to 2.2–4.4 and 1.4–2.7 mg/dm$^3$, respectively, are optimal concentrations for gaining a satisfactory stabilizing effect.

CONCLUSIONS

The following conclusions can be drawn from the conducted investigations:

- A new method for evaluation of the effectiveness of scale inhibitors was presented, which allows their stabilizing properties to be distinguished quickly and selectively.
- With this method one may determine a quantitative relationship between scale inhibitor concentration and relative supersaturation of scale forming compounds.
- Small concentrations of EDTMP (2.2 mg/dm$^3$) and of PBTC (1.4 mg/dm$^3$) give a considerable relative supersaturation of CaCO$_3$ in water, 3.7 times, and at higher concentrations of EDTMP (22 mg/dm$^3$) relative supersaturation may exceed 7 times.
- Results obtained with this method have confirmed known and very good anti-scaling properties of EDTMP and PBTC.

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REFERENCES

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