Study on sodium and potassium salts of polyacrylic acid as corrosion inhibitors

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Received 04 February 2005; accepted 05 July 2005

The effect of sodium and potassium (20-100 ppm) salts of polyacrylic acid (PAA) was determined on mild steel (MS) and copper (Cu) metals by immersing in Jalgaon ground water for 4-24 h in reflux condition (100 °C) and from 5-30 days in ambient condition. The salt deposition on MS and Cu plates was compared with and without polymer addition in water. The salt deposition on MS and Cu increases with increase in time in hot and cold water without addition of polymer. On addition of polymer, with increase in concentration in water, the salt deposition decreases. In cold water on MS, salt deposition is more than Cu, while in hot water it is vice-versa. With increase in the reflux time (4-24 h), salt deposition on Cu and MS increases up to 6 h of reflux time for all concentrations of K salt of PAA and further it decreases from 12 to 24 h. For Na salt of PAA, deposition increases for the lower concentrations (up to 40 ppm), up to 12 h of reflux time and further the deposition decreases for both MS and Cu. At higher concentrations (100 ppm), Na salt of PAA in water is more effective than K salt as the deposition becomes negligible on Cu.

Keywords: Polyacrylic acid, Mild steel, Copper, Sodium, Potassium, Salt deposition

IPC Code: D21H21/38

Introduction

The water-soluble polymers (biopolymers as well as synthetic macromolecules) that play an important role as antiflocculants and flocculating agents used in various industrial fields inhibit the hindrances occurred due to salts dissolved in water as well as impurities present in water. Synthetic water-soluble polymers have a large group of commercially useful products such as modified cellulose, polyethylene glycol, polyvinylalcohol, polyacrylic acid (PAA), polyacrylamide (PAM), polymethylacrylic acid and their cationic and anionic derivatives.

The effect of aminotris methylene phosphonic acid (ATMP) on calcium sulfate dihydrate crystallization indicated that the crystal growth and crystal size decrease with addition of ATMP. Although mechanism of scale formation has been investigated yet examination of this phenomenon from the angle of rate of deposition and variables influencing the kinetics has not been carried out so far. A lot of differences are being observed with reference to characterization or method of detection of scale formation. A comparative study of PAM and homopolymer of acrylonitrile (PAN) as antiscalant agents showed that with increase in the amount of polymers concentration in water, the salt deposition on vessel decreases. PAN gives more effective results over PAM for longer time. The formation of calcium sulphate and carbonate scale has been prevented by using acrylonitrile-acrylic acid (AN-AA) and acrylonitrile-methacrylic acid (AN-MAA) copolymers between 50-80°C at different pHs (7.0-8.5). The amount of scale deposition increased with increase in temperature and pH. The polymers acted as good antiscalants at low temperature and pH ranges. The effect of PAA as an antiscalant agent on heat exchanger was also studied. Salt deposition decreases with increase in concentration of PAA and time. No effects on heat transfer coefficients and heat transfer rate of shell and tube heat exchanger was observed using PAA (100 ppm) in hot and cold water.

The objective of present work is to determine the effect of K and Na derivatives of PAA on formation of crystals on Cu and MS metals, which are used in fabrication of heat exchangers. The comparison of effectiveness as antiscalant agents of PAA-K and PAA-Na was done.

Materials and Methods

Synthesis of Polyacrylic Acid (PAA) and its Salts

Acrylic acid (15 ml) was poured in toluene (150 ml) containing round bottom three-neck flask, fitted with condenser and mechanical stirrer. A 35 ml
solution of benzoyl peroxide (4 %) was added drop by drop in toluene until the polymerization reaction at 110° C for 90 min. The polymer obtained (90 %) was filtered and dried at 50°C.

KOH (5.1 g) was dissolved in ethyl alcohol (100 ml) and solution was transferred to the two neck round bottom flask fitted with mechanical stirrer. PAA (10g) was added slowly in alcoholic KOH with constant stirring for 30 min at room temperature. The product was filtered and washed with ethanol to remove the excess KOH and dried at 40-50°C. The sodium salt of PAA was also synthesized by the same method.

**Molecular Weight Determination**

The molecular weight of PAA was determined by viscosity method using Ostwald7,9 viscometer. PAA was dissolved in 1, 4-dioxane and very dilute solutions with polymer (0.1, 0.2, 0.3, 0.4 and 0.5 % w/v) were prepared. The K and α values of PAA for 1,4 dioxane are 76 x 10^{-3} and 0.50 respectively. The molecular weight of PAA was observed to be 6761.66 ± 150.

**Determination of Hardness**

Jalgaon water sample has following characteristics: total hardness, 300-446; permanent hardness, 136-246; dissolved solids, 576-735; iron, 0.2-0.8; fluoride, 0.31-0.50; chloride, 59.0-108.0; and nitrates, 2.5-2.9 ppm; pH, 7.2-8.0. The hardness of water caused by calcium and magnesium was determined (pH 10) by simple complexometric titration method using EDTA, which forms complex with the metallic salts in water. Using Erichrome Black –T indicator, the titrant value of water sample corresponded to the total hardness present. Value of temporary hardness was determined by the same method, only difference being that the water sample used was boiled for 30 min. Difference between total hardness value and permanent hardness value determined the value of permanent hardness of water sample. The hardness was: permanent, 136; temporary, 184; and total hardness, 320 ppm. The dissolved solid contents were 858 ppm.

**Determination of Scale Deposition on Metal Strips**

Metal strips (3.8 cm x 1.5 cm x 0.165 cm) of Cu and MS were kept in the different concentration of PAA-K and PAA-Na (20, 40, 60, 80 & 100 ppm) of Jalgaon ground water in round bottom flask (500 ml). The said prepared water samples (250 ml) were used for these tests for (i) 4-24 h under the refluxing condition and (ii) for 5-30 days. The deposition of salt on strips was measured at (i) 5-h interval and (ii) 5-day interval by measuring the gain in weight of the strips. The same study was done for no addition of PAA-K and PAA-Na in water maintaining the same conditions.

**Results and Discussion**

**Effect of PAA-K on Deposition of Salts on MS and Cu**

The effect of PAA-K was observed with varying its concentration (0-100 ppm) for 4-24 h in reflux condition on MS. Salt deposition increases with time from 6.5 mg at 4 h to 9.5 mg at 24 h in control (without PAA-K). On increase in PAA-K concentration (20-100 ppm), salt deposition decreases for all the time periods. On comparing with increase in time for individual concentration for PAA-K, unlike control, the salt deposition decreases with increase in time. However, at 6 h, it shows increment in salt deposition on MS sheet and further it declines. This behavior is observed up to 80 ppm concentration of PAA-K in water. PAA-K shows constant salt deposition up to 6 h (6 mg at 100 ppm) and thereafter (6-12 h), it shows sharp declination like in other concentrations.

The salt deposition on Cu increases with increase in reflux time in control (without PAA-K in water) and on addition of PAA-K, it decreases with increase in the concentration of PAA-K (0-100 ppm) for an individual time period. The same behavior is also observed for an individual concentration of PAA-K with increase in the reflux time. The salt deposition in control is more on Cu than the MS for all the reflux times. But on addition of PAA-K for the respective concentrations, the deposition of salt is less on Cu than MS for all respective time periods. Being higher reactivity of Cu in comparison to the MS, the salt deposition in control is observed more, while with PAA-K it is observed less, as the non-polar part of polymer comes over the surface. Moreover, PAA-K reacts with salts dissolved in water. Hence, the degree of deposition is less.

**Effect of PAA-Na on Deposition of Salts on MS and Cu**

On 20 ppm concentration of PAA-Na in water, the salt deposition increases with increase in time, while from 40 to 100 ppm, it increases up to 6 h and thereafter, it decreases up to 24 h of reflux time (Fig. 1). The salt deposition decreases with increase in the PAA-Na concentration (0-100 ppm). However, the salt deposition on MS is recorded more in PAA-K
than PAA-Na for all the concentrations up to 6 h of reflux time. But the salt deposition drastically reduces from 12-24 h in PAA-K in comparison to PAA-Na containing water.

The salt deposition on Cu increases with increase in time for 20 ppm and 40 ppm concentration of PAA-Na in water. At lower concentration and higher reflux time, the salt deposition is more while at higher concentration and higher reflux time, the salt deposition decreases, and at 100 ppm for 18 to 24 h, the salt deposition is negligible (Fig. 2). However, on MS, it shows more deposition for the respective concentration and time of reflux (Fig. 1). On comparing with PAA-K for respective concentration and reflux time, it shows the reverse trend up to 40 ppm, and at 100 ppm concentration and higher reflux time, it is more effective than PAA-K.

Salt Deposition on MS and Cu using PAA-K and PAA-Na in Water at Ambient Condition

The deposition of salt decreases with increase in PAA-K concentration (0-100 ppm), but with increase in time (5-30 days), there is increment in deposition of salt on MS (Fig. 3). On Cu, salt deposition decreases with increase in the retention time (5-30 days). However, with increase in concentration, the deposition decreases (Fig. 4). The depositions of salt on MS increases with increase in time, however, the deposition decreases with increase in concentration of PAA-Na in water for the respective time periods (Fig. 5). At higher concentration (60 ppm of PAA-Na) and at higher retention time (20 days) onwards, the deposition becomes negligible on Cu (Fig. 6).

The salts deposited on MS and Cu without addition of polymers (PAA-K and PAA-Na) are in compact form, which shows the chemical reaction with metals. In the case of PAA-K and PAA-Na added in water,
the deposition observed on the metal plates is broken after drying and is of very light weight. It means the polymer encapsulates these plates instead of salt deposition. There is less deposition of salt. It is due to the non-polar nature of the polymer, which is getting reacted, with polar part of the metals. Hence, the salts are not able to react with the metal surface. That's why, the permanent coating of the salts does not occur like that obtained without PAA-K and PAA-Na in water. The less deposition on Cu in comparison to MS in PAA-K and PAA-Na added in water for the reflux condition and at room temperature is due to the higher reactivity of the Cu which forms a thin layer of the polymers more efficiently than the MS. Hence, it shows less deposition on Cu.

Conclusions

The salt deposition increases with increase in time in water while the addition of PAA-K and PAA-Na inhibits the salt deposition on MS and Cu both in reflux condition as well as at room temperature. But the inhibition is more in reflux condition. At higher concentration (100 ppm), PAA-Na inhibits more than PAA-K for Cu. PAA-K shows better results on MS at this concentration and higher reflux time. The less deposition of salts on Cu in presence of polymers is due to its greater reactivity than MS. The salts dissolved in water react with polymer to substitute Na and K. Moreover, the polymer dissolved in water encapsulates the metal, and inhibits the scaling reaction.

Acknowledgment

Authors are thankful to the University Grants Commission, New Delhi, for providing financial assistance.

References

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