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## EFFECTS OF ENVIRONMENTAL FACTORS ON THE DISPERSION BEHAVIOR OF IRON OXIDE IN AQUEOUS SOLUTIONS WITH POLY ACRYLIC ACID

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After preparing aqueous suspensions from magnetite particles with a poly-acrylic acid, we investigated the effects of several experimental parameters. We characterized the stability of the suspensions using visual inspection, sedimentation, adsorption, and thermal stability of the dispersant. The dispersion stability is affected by the solution pH, the concentrations of magnetite particles, the molecular weight, the concentration of the dispersants, and the temperature. The stability of the suspensions increased as the concentration of the dispersant and the temperature increased. In terms of the molecular weights of the dispersant, the suspensions with dispersant of low-molecular weight (1800) were more stable than those of high-molecular weight (250000) at room temperature. However, at high temperature the suspensions with high-molecular weight showed stability. The adsorption efficiency of the dispersant was very low. The dispersant of high-molecular weight showed a higher thermal integrity than that of low-molecular weight. From this work, we obtained the optimum conditions for stable aqueous suspensions of magnetite particles.

*Keywords:* Poly-acrylic acid, dispersion stability, magnetite, nanoparticles, suspension

### 1. Introduction

Corrosion products and other impurities in the secondary side of pressurized-water reactors (PWRs) can deposit onto steam generator (SG) tubes and internal surfaces. Accumulation of these deposits can result in the formation of occluded regions where impurities concentrate, creating highly corrosive environments that can lead to corrosion, fouling, flow-accelerated corrosion, and stress corrosion cracking [1]. In order to improve the performance of the SGs, failed tubes are removed and plugged. For many years, utilities have made significant efforts to reduce the quantity of corrosion products in SGs by using advanced amines and mechanical methods. However, it was not possible to inhibit the deposition of corrosion products onto the SGs surfaces even when iron concentrations in inlets of the SGs were reduced. Even a low level of deposits has a profound impact on the secondary systems of PWR plants, thus making this a crucial issue for utilities. Another approach is to use dispersants. They are used in the preparation of stable suspensions, preventing the deposition of metal particles. In an aqueous solution, functional groups of the dispersants become negatively charged due to the release of hydrogen ions [2, 3]. These charged groups adsorb onto metal particle surfaces, maintaining them in suspension. The stable suspensions enhance the removal of corrosion products and other impurities from the SGs via blowdown.

The most well-known type of dispersant for metal oxides is a poly-acrylic acid (PAA). PAA has one carboxyl group (COOH) per monomer and dissociates in water in order to form a negatively charged carboxylate group (COO<sup>-</sup>) leading to an increase in pH. The degree of dissociation affects both the pH of the solutions and the absorption efficiency of PAA. This technique has been employed at fossil fuel plants to inhibit corrosion-product deposition for many years [1, 4]. In ceramic industries, PAA has been used for the preparation of stable aqueous suspensions of many materials, such as TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> [5, 6]. However, PAA has not been used in PWRs due to the presence of impurities. Recently, a high-purity PAA has been developed for nuclear applications [7].

This paper presents the influence of pH, molecular weight, and concentration of PAA, as well as the temperature, on the stability of magnetite suspensions. In order to characterize the suspensions, visual observation, sedimentation, and adsorption methods of dispersants onto particles were measured. From these data, optimum conditions for stable suspensions are discussed.

### 2. Materials and methods

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) (SIGMA-ALDRICH, USA) was chosen because it is a major corrosion product in the sec-

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ondary side of PWRs. These species range in size from 20 nm to 30 nm; their specific surface area is  $>60$  m<sup>2</sup>/g. PAA (SIGMA-ALDRICH, USA) samples with different weight-average molecular weights of 1800 and 250000 (g/mol) were used without any additional purification. For convenience, one PAA (Mw = 1800) is denoted in this paper as PAA18, while the other PAA (Mw = 250000) is represented by PAA25. The solution pH was adjusted with reagent-grade hydrochloric acid (HCl) or ethanalamine (H<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OH, ETA).

In order to obtain wt% of magnetite particles needed to prepare the suspensions, 0.005, 0.01, and 0.1 wt% of magnetite particles, respectively, were added to polymeric solutions with adjusted pH of 8.96. After one-day equilibrium, the pH values of the suspensions changed from 8.96 to 8.6, 8.55, and 7.78, respectively. Moreover, the concentrations of PAA affect the pH of the solutions. When 0.1, 1, 2, and 5 mg of PAA18 was added in 1 ℓ solutions of pH 8.98, the pH values of the solutions changed to 8.98, 8.90, 8.84, and 8.17, respectively. As a result, the optimum concentrations of magnetite particles and PAA should be chosen for the following tests.

All experiments were performed at room temperature using suspensions with 100 ml of deionized water contained in 100 ml capped-vials [8]. For sedimentation tests, we prepared suspensions as follows. The pH of 100 ml of deionized water ( $>17$  MΩ · cm) was adjusted using either 0.01 M HCl or 0.01 M ETA solutions; then, either 1 ppm of PAA18 or 1 ppm of PAA25 was added to the pH-adjusted solutions. Premixed solutions were magnetically stirred for 1 h and allowed to stand for 24 h in order for equilibrium to be reached. Upon adding the optimum amount of magnetite particles, the suspensions were dispersed with sonication for 15 min and were then allowed to stand for 1 h to let the large particles settle. We poured 20 ml of each suspension into vials to measure the transmittance using a dispersion stability analyzer (Turbiscan Lab, Formulacion, France); we left all suspensions in 100 ml mess cylinders for long visual inspections [9]. After 300 days, we decanted the supernatant fluid in the mess cylinders in order to measure the concentration of Fe with an inductively coupled plasma atomic emission spectrometer (ICP-AES). X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to measure the filtered solids and the supernatant fluid, respectively.

For adsorption measurements, suspensions of 0.003 wt% of magnetite particles were prepared with varying dispersant concentrations. After 24 h equilibrium, centrifugation at 15000 rpm for 15 min was conducted to separate the supernatant fluid and the solids. We filtered the supernatant fluid several times using a 0.1 μm membrane filter to remove the remaining

particles [2]. The non-adsorbed fraction of PAA18 was measured using a total organic carbon (TOC) analyzer (TOC-V, SHIMADZU). Thermal analyses of the suspensions were performed using a differential scanning calorimeter (DSC, Netzsch, Germany), which determined the integrity of the dispersant with increasing temperature.

### 3. Results and discussion

Sedimentation tests by visual observations were used to determine the qualitative stability of the suspensions. For this, we prepared suspensions of 0.015 wt% of magnetite particles and 1 ppm of PAA over a pH range of 3.2 ~ 9.6. Figure 1 shows the behaviors of the magnetite suspensions with 1 ppm of PAA18 as a function of pH. The suspensions initially were turbid; however, they became transparent depending on the suspension pH values. At pH 3.2, most of the particles agglomerated and then settled to the bottom after 5 h; the supernatant fluid was almost transparent after 24 h. According to previously reported results, PAA is uncharged at pH 3.2 [2, 10]. However, in this work, the magnetite particles were suspended in the suspension for more than 5 h. This is because undissociated COOH groups adsorb onto the particle surfaces by hydrogen bonding between the COOH groups and surface hydroxyls [8, 10]. Suspensions of pH 6.9, 7.8, and 9.0 showed similar phase behaviors in visual inspections. In this pH range, most of the COOH groups in PAA are ionized into COO<sup>-</sup> groups; the dissociated COO<sup>-</sup> groups adsorb onto the particle surfaces, forming complexations by chelation or chemical bonds [2, 8]. As a result, the suspensions maintained the stability for a long time. All of the COOH groups in PAA 18 were ionized at pH 9.6; however, most of the particles settled down in the course of one day. This is because during the one-day equilibrium, many ionized COO<sup>-</sup> groups bonded with NH<sub>3</sub><sup>+</sup> groups in the ETA before adsorbing onto the magnetite particle surfaces. Hence the adsorption efficiency of the dispersant nearly disappeared. After 300 days, we measured the suspended particles in the supernatant fluid using ICP-AES. The iron contents of the suspensions at pH 3.2, 6.9, 7.8, 9.0, and 9.6 was 1.1, 7.0, 7.2, 7.3, and 1.0 ppm, respectively, which is in good agreement with the results of visual investigations. The XRD measurement of the filtered solids revealed in the formation of a maghemite (Fe<sub>2</sub>O<sub>3</sub>) due to the oxidation of the magnetite particles in solution. At pH 6.9, 7.8, and 9.0, the suspensions with PAA18 were stable for more than 300 days, whereas the suspensions with PAA25 settled down in less than 20 days.

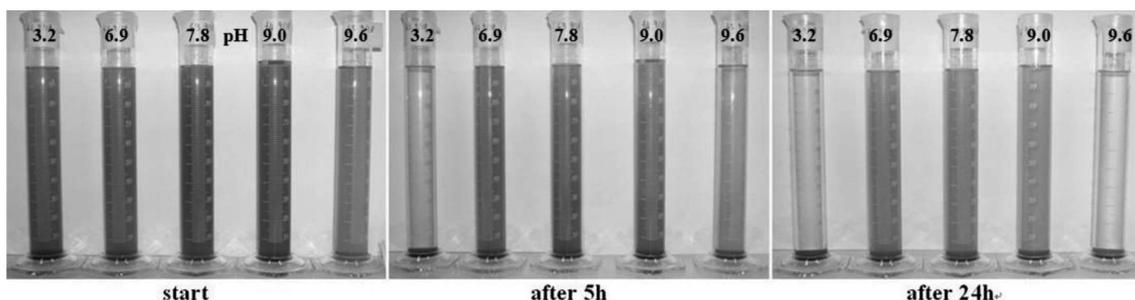


Fig. 1. Behaviors of suspensions with 0.015 wt% of magnetite particles and 1 ppm of PAA 18 as a function of pH

Figure 2 (a) shows the morphology of dispersed particles in the suspension with 1 ppm of PAA18 at pH 9.0; it also shows the polymers adsorbed onto the particle surfaces. The results shown here indicate that the particles coalesced to a single large particle before being absorbed by PAA18. The TEM image in Fig. 2 (b) shows the magnetite particles in the re-dispersed suspension, which was prepared from the suspension of pH 3.2 by adding 1 Mℓ 0.1 M of ETA. This suspension remained stable for 300 days. This confirmed that a flocculation phenomenon occurred in the suspension of pH 3.2. Figure 2 (c) provides a TEM image of the dispersed particles in the suspension prepared with PAA18 at pH 9.0 after 300 days. Most of the particles coalesced, which resulted in an increase in the size of the particles and a change in particle size from 50 nm to 250 nm. In this dispersed state, discrete particles of different sizes exist in the suspension; and they repel one another upon approach [11]. As a result, this suspension was stable for 300 days. A TEM image of the particles in the suspension prepared with PAA25 at pH 9.0 after 210 days is shown in Fig. 2 (d). Based on visual observations, all of the particles are seen to have been aggregated and deposited. However, a few dispersed particles were observed by TEM. The size of the particles was found to be between 50 and 100 nm, which was smaller than the particles shown in Fig. 2 (c). The particles in the above suspensions formed a bridging flocculation between 3 and 4 particles, which keeps the particles suspended. The results suggest that PAA18 is useful in suspending particles for a long time, whereas PAA25 is applicable to systems where suspensions are removed continuously for a short period of time.

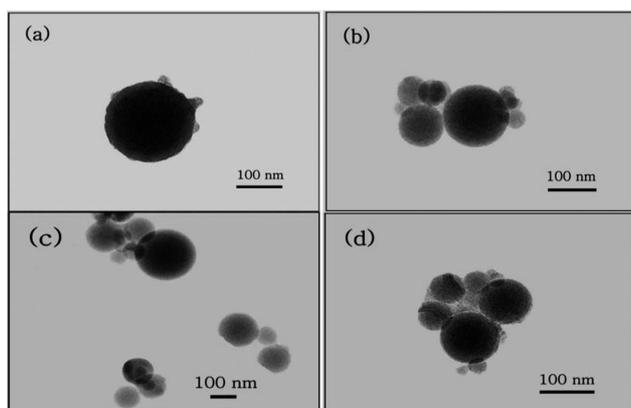


Fig. 2. TEM images of magnetite particles obtained for suspensions with 0.015 wt% of magnetite particles and 1 ppm of (a) PAA18 (after 20 days), (b) PAA18 (re-dispersed and then after 300 days), (c) PAA18 (after 300 days), and (d) PAA25 (after 210 days) at pH 9.0

We used Turbiscan LAB to quantify the stability of the suspensions while varying the pH and PAA concentration. 0.005 wt% of magnetite particles and 1 ppm of PAA were adopted to prepare the suspensions for the following tests. The suspensions were allowed to stand for 1 h to allow the large particles to settle; suspensions were then analyzed for one day. In order to evaluate the stability of the dispersions, we used the transmission profiles produced by Turbiscan LAB, which are related to particle migration and to the increase in particle size [12, 13]. The transmittance of the suspensions increases with increasing instability of the suspensions. Figure 3

shows the calculated mean value kinetics for each transmission profile between 10 mm and 30 mm of the vials as a function of time. The transmittance increases with an increase in pH, indicating instability of the suspension. As the pH of the solutions increases,  $\text{NH}_3^+$  groups in ETA increase. As most of the  $\text{COOH}$  groups in PAA dissociate into  $\text{COO}^-$  groups for the tested solutions, the amount of  $\text{COO}^-$  groups in the suspensions is the same. During one-day equilibrium, many  $\text{COO}^-$  groups bond with the  $\text{NH}_3^+$  groups; remaining  $\text{COO}^-$  groups then join in adsorbing onto the magnetite surfaces. As a result, the adsorption efficiency of PAA decreases with an increase in pH. The difference in the dispersion stability of the suspensions of PAA18 and PAA25 is due to their molecular weights. PAA18 with low-molecular-weight has a fully stretched rod-like conformation, and the  $\text{COO}^-$  groups consequently repel each other. Owing to this phenomenon, PAA18 is more effective than PAA25 with high-molecular-weight [14]. An increase in particle size due to coalescence and flocculation enhanced the transmittance and finally allowed particles to deposit, which resulted in a decrease in suspension stability [12, 13].

Figure 4 shows the stability of suspensions prepared from 0.005 wt% of magnetite particles at pH 9 as a function of the concentration PAA18. The stability of the suspensions increases as the concentration of PAA18 increases from 0.01 to 2 ppm. At very low concentrations, the amount of dispersant is not sufficient to adsorb onto the particles. Sharing of the charged groups with many particles causes a macroscopic precipitation due to bridging flocculation. At very high concentration, depletion flocculation occurs due to excess of the dispersant [12]. Figure 5 shows the effect of temperature on the dispersion stability of the suspensions, indicating that the stability of the suspensions increases with increasing temperature and molecular weight of the dispersant. As the temperature increases, tangled polymer chains change to a stretched conformation, which will improve the performance of the dispersant with high molecular weight.

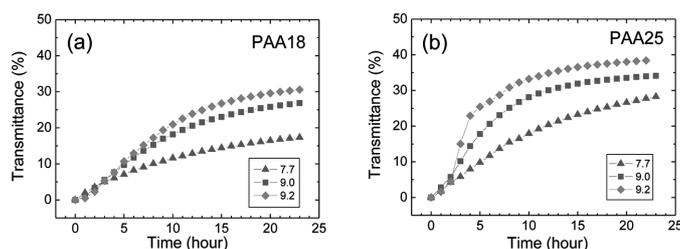


Fig. 3. Variation of the % transmittance measured for suspensions with 0.005 wt% of magnetite particles and 1 ppm of (a) PAA18 and (b) PAA25 at different pHs

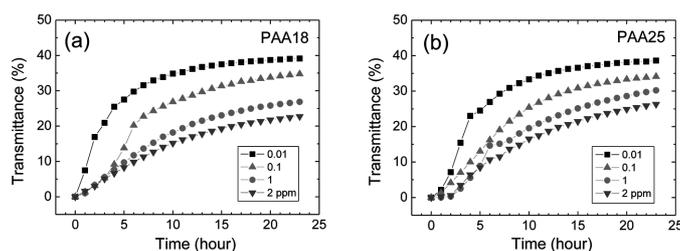


Fig. 4. Variation of the % transmittance measured for suspensions with 0.005 wt% of magnetite particles and 0.01, 0.1, 1, and 2 ppm of (a) PAA18 and (b) PAA25 at different concentrations

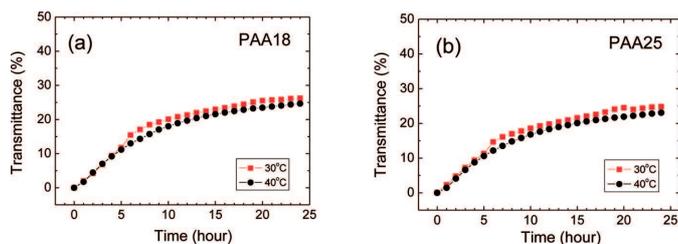


Fig. 5. Variation of the % transmittance measured for suspensions with 0.005 wt% of magnetite particles and 1 ppm of (a) PAA18 and (b) PAA25 at pH 9 and at different temperatures

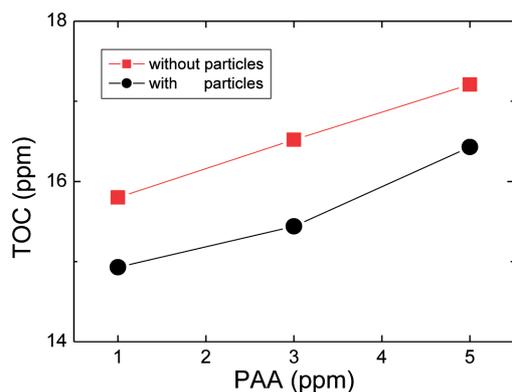


Fig. 6. TOC of the suspensions with 0.003 wt% of magnetite particles at different concentrations of PAA18

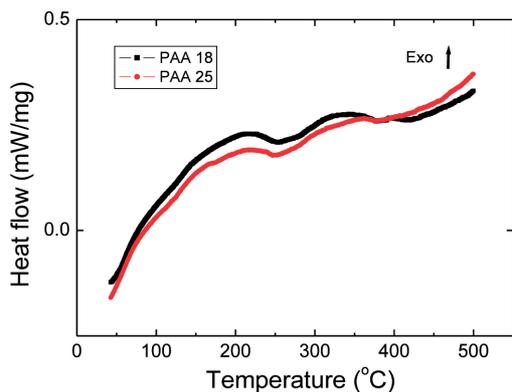


Fig. 7. DSC curves of precipitates containing PAA at different temperatures

Adsorption studies of PAA18 were performed using 0.003 wt% of magnetite particles. Non-adsorbed dispersants remaining in the supernatant fluid are shown in Fig. 6. The adsorbed amount increases until 3 ppm of PAA18 and thereafter decreases. As can be seen in Fig. 6, most of the polymers were not adsorbed onto the particles. This may be due to the loosely bonded complexes made of particles and polymers, as well as to other parameters that affected the efficiency of the dispersants. Changing the order of adding the dispersant and magnetite particles can improve the adsorption efficiency of the dispersant because of the preferential adsorption of the charged particles onto the particle surfaces. In order to assess the dispersant integrity of PAA18 and PAA25 at high temperature, the precipitates were measured using DSC from

room temperature to 550°, as shown in Fig. 7. PAA25 presents higher thermal stability than that of PAA18, indicating less thermal decomposition.

#### 4. Conclusions

The interaction of magnetite nanoparticles with PAA was systematically studied by conducting sedimentation, adsorption, and thermal analyses. The prepared suspensions were characterized by visual inspection, Turbiscan LAB, ICP-AES, XRD, TEM, TOC, and DSC measurements. The results showed that the suspensions were stable in a range of pH 7.7 to pH 9.2. The suspension stability increased with increasing concentrations of PAA from 0.01 to 2 ppm and with increasing temperature from 30° to 40°. The adsorption of PAA onto the surface of particles was very low. The integrity of PAA25 was higher than that of PAA18 at high temperatures. For stable suspensions, the optimal pH and concentration at 25° were pH 7.7 and less than 1 ppm, respectively. PAA18 is recommended for applications at room temperature, whereas PAA25 is recommended at high temperature.

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#### REFERENCES

- [1] K. Fruzzetti, M. Kreider, A. Miller, J. Jevic, P. King, *Int. Conf. Water Chem. NRC*, (San Francisco, 2004).
- [2] A. Degan, M.Kosed, *J. Am. Ceram. Soc.* **86**, 2001 (2003).
- [3] D.A. Skoog, D.M. West, F.J. Holler, *Fundamentals of Analytical Chemistry*, 6<sup>th</sup> Ed. (Harcourt Brace Jovanovich, New York, 1992), 118-145.
- [4] J.M. Jevic, P.J. King, K. Fruzzetti, *Proc. 11<sup>th</sup> Int. Symp. on Environ. Degrad. of Mater. in Nucl. Power Syst.-Water React.* (Stevenson, 2003).
- [5] J. Cesarano III, I.A. Aksay, *J. Am. Ceram. Soc.* **71**, 250 (1988).
- [6] A. Sehgal, Y. Lalatonne, J.F. Berret, M. Morvan, *Langmuir* **21**, 9359 (2005).
- [7] R. Crovetto, C.J. McDonough, *Proc. 10<sup>th</sup> Int. Symp. on Environ. Degrad. of Mater. in Nucl. Power Syst.-Water React.* (Stevenson, 2001).
- [8] A.A. Zaman, R. Tsuchiya, B.M. Moudgil, *J. Colloid and Interface. Sci.* **256**, 73 (2002).
- [9] N. Azema, *Powder Technol.* **165**, 133 (2006).
- [10] G.H. Kirby, D.J. Harris, Q. Li, J.A. Lewis, *J. Am. Ceram. Soc.* **87**, 181 (2004).
- [11] J.A. Lewis, *J. Am. Ceram. Soc.* **83**, 2341 (2000).
- [12] H. Buron, O. Mengual, G. Meunier, I. Cayre, P. Snabre, *Poly. Int.* **53**, 1205 (2004).
- [13] E.H. Lee, M.K. Lee, C.K. Rhee, *Mater. Sci. and Eng.* **A449-451**, 765 (2007).
- [14] P. Munk, T.M. Aminabhavi, *Introduction to Macromolecular Science*, (John Wiley and Sons, New York, 2002), 57-70.