

Flocculation of Oxides using Polyethylene Oxide

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SUMMARY

Flocculation of oxides using polyethylene oxide was investigated. Polyethylene oxide adsorbed strongly on and flocculated sodium kaolinite. H-bonding is considered to be the driving force for polyethylene oxide adsorption on kaolinite. The mechanism of adsorption of polyethylene oxide on kaolinite was examined by studying the adsorption/flocculation characteristics of different oxide minerals using the same polymer. Polyethylene oxide flocculated silica gel but did not adsorb on or flocculate hematite and alumina. Quartz was flocculated only below pH 3. Results are examined in terms of the type of surface groups and the degree of hydration of the solids. It is proposed that adsorption of polyethylene oxide on solids requires some optimum hydroxylation of the surface with displaceable water species.

INTRODUCTION

Polyethylene oxide (PEO) has served as an effective flocculant in several systems [1, 2]. However, the exact nature of the mechanism of polyethylene oxide adsorption remains unexplained. Rubio [3] found that polyethylene oxide was an effective flocculant on substances recognized to be hydrophobic but the polymer was ineffective on hydrophilic substrates such as rutile, quartz and copper carbonate. Rubio attributed the specificity of polyethylene oxide flocculation

to H-bonding forces, physical hydrophobic interactions and chemical mechanisms. Tadros [4] examined the adsorption and flocculation properties of silica gel with polyvinyl alcohol and found that maximum flocculation occurred at the point of zero charge of the oxide and also observed an increase in adsorption of PVA upon heat treating the solid up to 700 °C. Tadros examined the mechanism of adsorption based on the degree of hydration of the substrate. Evidently, other than H-bonding, no generic mechanism could be utilized to explain polyethylene oxide adsorption. The U.S. Bureau of Mines has found that polyethylene oxide is an excellent flocculant for clays and red mud [5] and correlated the adsorption of the polymer with the electronegativity index. Polyethylene oxide itself has been a widely used polymer in several systems and its characteristics have been the subject of several reviews [6, 7]. The present work focuses on the adsorption of polyethylene oxide on clay and the constituent minerals of clay. It was the aim to study the adsorption/flocculation behavior of polyethylene oxide on a variety of oxide minerals such as silica gel, quartz, hematite, alumina and kaolinite and utilize the behavior of polyethylene oxide on each mineral to explain its overall flocculation characteristics. The oxides studied vary significantly in their interfacial properties such as point of zero charge (pzc) and degree of hydration.

MATERIALS AND METHODS

Na-kaolinite

A homoionic sample of sodium kaolinite was prepared from a well-crystallized sample of Georgia kaolinite which was obtained from

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the clay repository at the University of Missouri. The surface area of the sample was determined by BET to be 9.4 m²/g. The methodology used for clay preparation has been discussed earlier [8].

Silica gel

Silica gel was purchased from Alfa Products Inc. The surface area of silica gel was 300 m²/g, particle size 70 μm and pore volume 1.6 cm³/g. The characteristics of silica gel were provided by the manufacturer.

Quartz

Natural Brazilian quartz prepared by wet grinding and leaching was used. The surface area of quartz as measured by BET was 0.5 m²/g.

Hematite

Synthetic hematite was obtained from Alfa Products Inc. The surface area of hematite as measured by BET was 7.5 m²/g.

Alumina

Alumina of 0.3 μm size was purchased from Alfa Products.

Polymer

Polyox coagulant obtained from Union Carbide Corporation was used as a flocculant. Polyethylene oxide used in the experiments had an approximate molecular weight of 5 million as determined by the manufacturer. Polyethylene glycol (PEG), molecular weight 8000, was also used in some experiments.

All experiments were conducted in solution made up with triply distilled water.

Adsorption and flocculation experiments

Five grams of the solid were equilibrated with 195 cm³ of triply distilled water or solution of appropriate ionic strength and pH in a 250-cm³ glass beaker using a magnetic stirrer bar for about 2 h. The pH of the suspension was measured after equilibration and taken as the final pH. The beaker was fitted with baffle plates and the suspension stirred using a propeller for 3 min. Five cubic centimetres of the polymer solution at the desired concentration was added dropwise while the suspension was being stirred. As soon as all the polymer was added, the stirring was stopped and the suspension allowed to settle for 15 s.

The top half of the suspension was sucked out using a suction device. About 20 cm³ of the supernatant from the unsettled portion was centrifuged for determination of residual polymer concentration. Both 100-cm³ settled and unsettled portions were filtered separately using filter papers and the residue on the filter paper was dried and weighed. The per cent solid settled was determined from the dry weight of the solid in the settled and unsettled portions.

$$SS\% = \frac{m_s}{m_s + m_{us}}$$

SS% = solid settled per cent

m_s = weight of solid in 100 cm³ of settled portion

m_{us} = weight of solid in 100 cm³ of unsettled portion

Polymer concentration was determined using the method of Attia and Rubio [9].

RESULTS

Effect of conditioning time

The role of conditioning time in determining flocculation was investigated initially at a concentration of 0.5 ppm of polyethylene oxide. The polymer was added dropwise for 55 s at a steady flow rate of 0.1 cm³/s. Conditioning time here refers to the time for which the suspension was further stirred after addition of the polymer. Figure 1 shows that maximum flocculation occurs when the

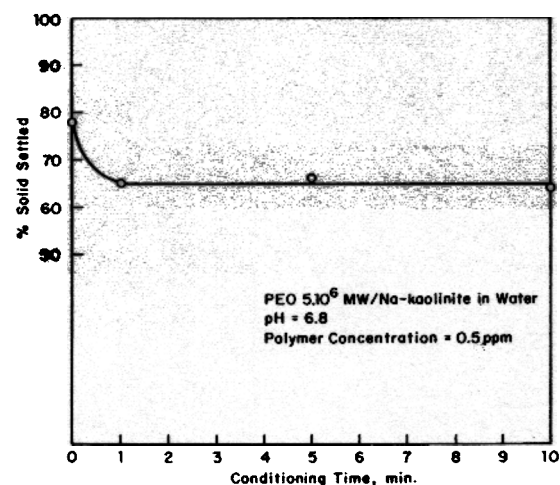


Fig. 1. Flocculation of sodium kaolinite as a function of conditioning time.

stirring is stopped as soon as polymer addition is complete. Per cent solid settled dropped from 78% to 65% in 1 min and did not change significantly beyond that time period. It was also possible to visually observe the floc breakage during conditioning after polymer addition was complete. All flocculation results reported in this work were obtained at zero conditioning time after polymer addition.

Effect of polymer concentration

Figure 2 shows per cent solid settled of sodium kaolinite as a function of initial polymer concentration. It is clear that kaolinite is flocculated by polyethylene oxide even at very low concentrations (1 ppm). Over the concentration range studied, no restabilization occurred. The effect of ionic strength on flocculation is shown in Fig. 3.

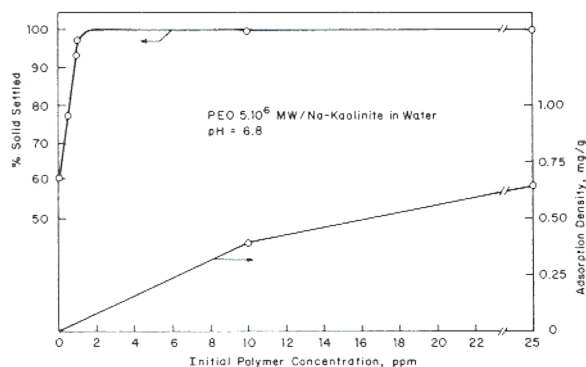


Fig. 2. Flocculation of sodium kaolinite as a function of polyethylene oxide concentration and corresponding polymer adsorption.

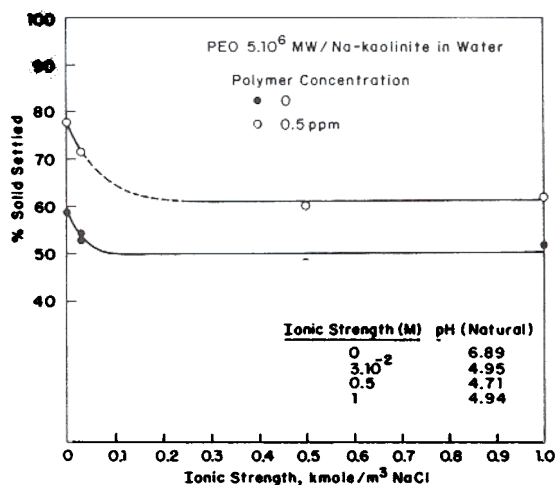


Fig. 3. Effect of ionic strength on the flocculation of sodium kaolinite.

Polymer solutions and suspensions were prepared at the same ionic strength in these experiments. It is clear that maximum flocculation occurs in triply distilled water both in the presence and in the absence of polymer. Addition of salt led to reduction in flocculation and reached a constant value at about $0.1 \text{ kmol/m}^3 \text{ NaCl}$. Figure 4 shows the effect of pH on flocculation of kaolinite. Clearly, flocculation is enhanced at acidic pH conditions. The molecular weight of polyethylene oxide also had a significant role in determining flocculation. Literature data have shown the importance of molecular weight in flocculation of colloidal dispersions. In this study, polyethylene glycol (MW 8000) and polyethylene oxide (MW 5 million) were used. As shown in Fig. 5, the higher molecular

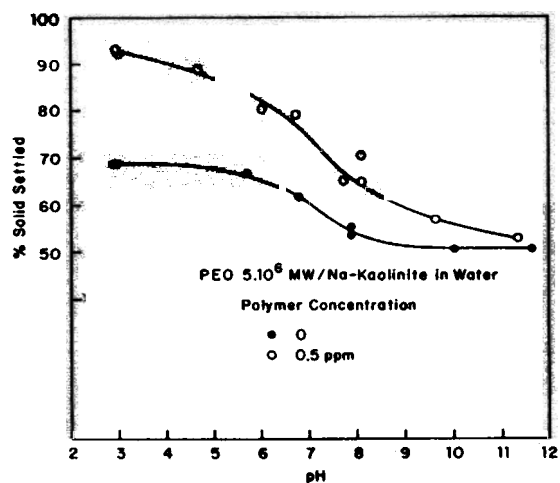


Fig. 4. Effect of pH on the flocculation of sodium kaolinite.

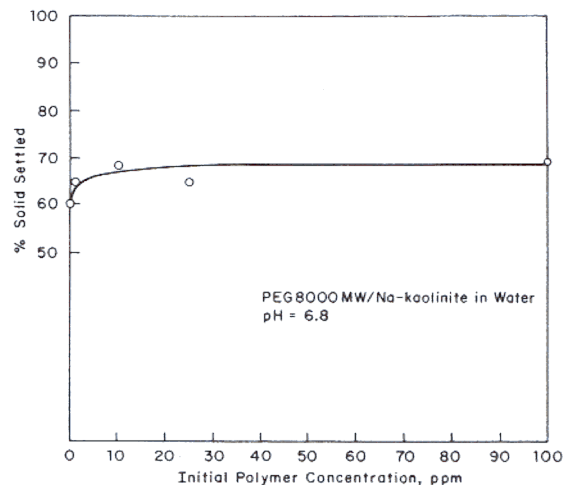


Fig. 5. Flocculation of sodium kaolinite as a function of PEG 8000 concentration.

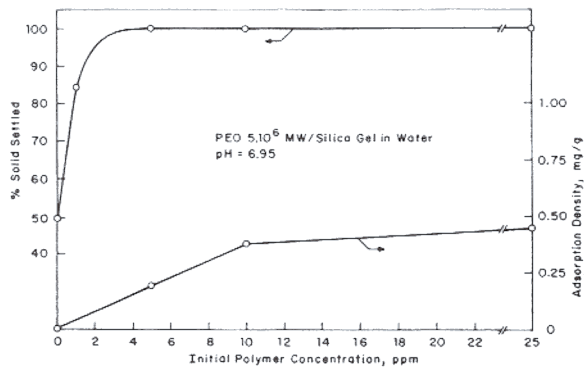


Fig. 6. Flocculation of silica gel as a function of polymer concentration.

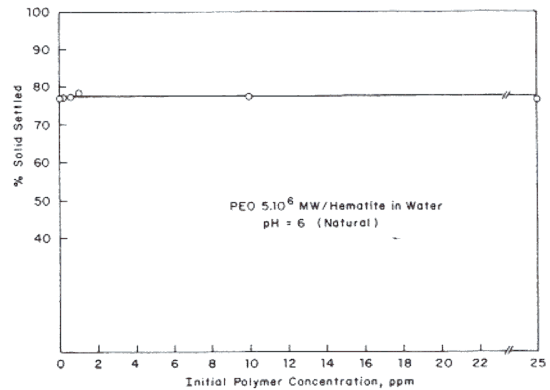


Fig. 8. Flocculation of hematite as a function of polymer concentration.

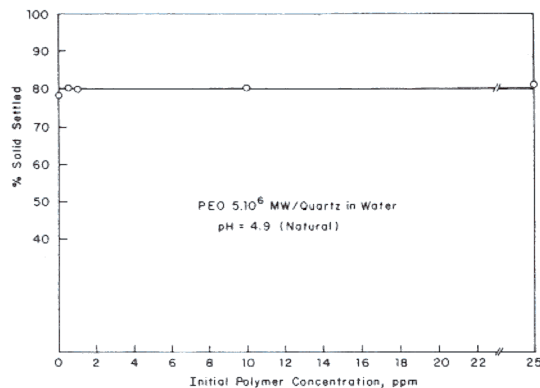


Fig. 7. Flocculation of quartz as a function of polymer concentration.

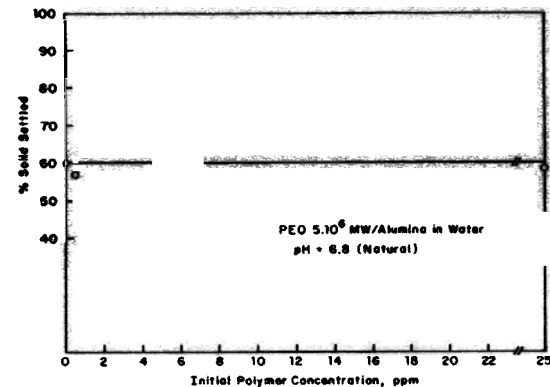


Fig. 9. Flocculation of alumina as a function of polymer concentration.

weight polyethylene oxide is a much better flocculant than polyethylene glycol. This is probably due to the bigger molecule being more amenable to the formation of tails and loops that are favorable for bridging flocculation to occur.

In order to identify the key solid properties responsible for polyethylene oxide adsorption, flocculation of a series of oxide minerals of varying hydration and surface charge characteristics were studied. Figures 6 - 9 show the flocculation of silica, quartz, hematite and alumina along with adsorption densities as a function of polymer concentration. Figures 10 - 12 show the flocculation of these oxide minerals as a function of pH. Silica gel was strongly flocculated by polyethylene oxide at natural pH (around 6.9) but the polymer had little effect on the settling behavior of alumina and hematite over a wide pH range. Quartz in contrast to silica gel was flocculated only at pH 2.5.

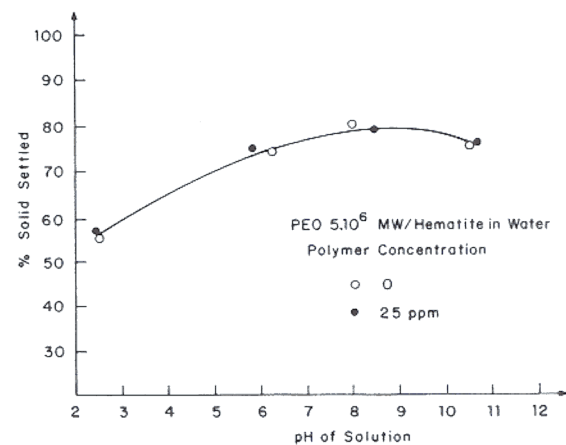


Fig. 10. Effect of pH on the flocculation of hematite.

DISCUSSION

The kinetics of flocculation monitored by stirring the suspension after addition of the polymer show the importance of hydrodynamics in determining flocculation (Fig. 1).

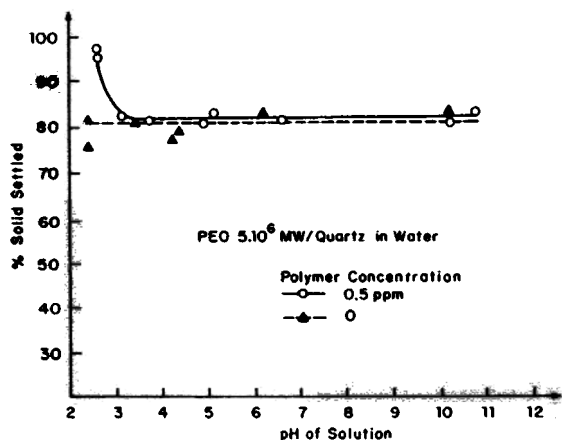


Fig. 11. Effect of pH on the flocculation of quartz.

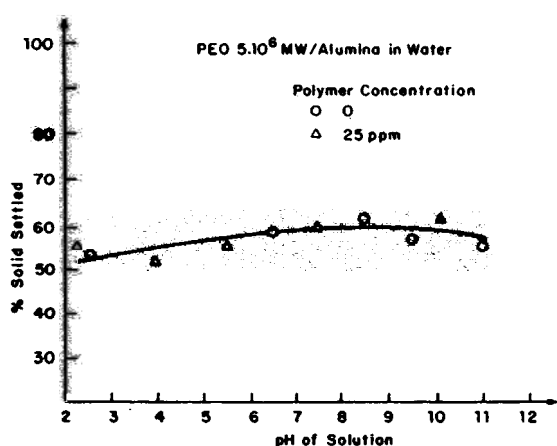


Fig. 12. Effect of pH on the flocculation of alumina.

Prolonged agitation after complete addition of polymer resulted in floc breakage (as observed visually) and thus led to a decrease in per cent solid settled. This is consistent with the observations of Stanley and Scheiner [2] who reported that clay formed strong flocs when polyethylene oxide was used as a flocculant but with time, the flocs disintegrated if the supernatant was not removed. They attribute the floc breakage to the weak interaction between the polymer and the filling water. The hydration water of the clay exists as two different types [10], the hydration shell that is tightly bound and the filling water that is loosely bound to the clay surface. The initial interaction between the clay and the polymer is probably a water bridge involving the filling water molecules which is a weak interaction that is broken up upon rigorous stirring.

The role of polymer concentration and ionic strength (Figs. 2 and 3) indicates that over the concentration range studied restabilization does not occur. Most interestingly, increasing ionic strength led to a decrease in flocculation. The general effect of adding an electrolyte to a dispersion is to lower its stability by compressing the electrical double layer. The double layer compression in conjunction with bridging by polymer normally leads to an increase in flocculation, unlike what is seen in the clay/polyethylene oxide system in this study. This is possibly due to the complex crystal and electrical double layer structure of clay. Depending on solution pH, clay crystals expose two different surfaces, a negatively charged layer surface and a positive or negatively charged edge surface. Consequently, due to oppositely charged double layers, the edge of one clay particle could be associated with the surface of another resulting in mutual coagulation of clay [11 - 13]. In the absence of an indifferent electrolyte, both double layers are sufficiently well developed for edge/face internal mutual coagulation to occur, causing relatively high solid per cent settled in the presence and absence of polymer. With increasing electrolyte concentration, both double layers are compressed and their effective charge will be reduced, leading to a reduction in edge/face flocculation.

The effect of pH on flocculation as shown in Fig. 4 is consistent with this explanation. The flocculation was enhanced at acidic pH, but in the presence and in the absence of polymer. In the absence of polymer, high solid settled per cent in acidic pH can result from internal mutual coagulation. At acidic pH, the flat surfaces still possess a negative charge, whereas the edge surfaces carry a positive charge, leading to mutual coagulation. However, at alkaline pH, the positive charge is reversed and electrostatic repulsion prevents coagulation. The effect of polymer in determining flocculation as a function of pH suggests that conformational aspects may be playing a role in enhancing flocculation at acidic pH. As polymer concentrations used in the study were very low, it was not possible to obtain quantitative information on adsorption using the analytical technique of Attia and Rubio [9]. Flocculation results, however, suggest that bridging is more effective at

acidic pH. One reason for this is the attraction between the negative charge on the ether oxygen of the polymer being able to attach to the positive sites of clay at acidic pH. Thus, at acidic pH, there are more sites for the polymer to anchor on clay.

Solid per cent settled in the presence of polymer increased at all pH values, suggesting polymer adsorption over the entire pH range. (Depletion flocculation at these polymer concentrations is not expected in this system.)

The results on the adsorption and flocculation behavior of the oxides silica gel, quartz, hematite and alumina (Figs. 6 to 12) reveal the importance of the solid surface properties that influence polyethylene oxide adsorption on minerals. Silica gel was strongly flocculated at its natural pH, whereas quartz was flocculated only at pH 2.5. Most interestingly, polyethylene oxide did not adsorb or flocculate hematite and alumina over the entire pH range.

Hydrogen bonding has often been proposed to be the driving force for the adsorption of nonionic polymers on oxides. In the case of polyethylene oxide, the hydrogen bond occurs between the ether oxygen of the polymer and the surface hydroxyls. At alkaline pH values, the negative MO^- site is not favorable for H-bonding. The behavior of silica gel and quartz can be explained using the H-bonding mechanism. The zeta potential measurement of silica gel and quartz is shown in Fig. 13. At any given pH level above 3, quartz is more negative than silica gel. Quartz being a stronger proton donor has more negative sites, which are not favorable for H-bonding with the ether oxygen. At very low pH, quartz is flocculated by polyethylene oxide due to an increase in SiOH sites and a decrease in the negative sites ($H_3SiO_4^-$). The zeta potential results also suggest that the

number of negative sites on silica gel are less than on quartz throughout the entire pH range, permitting polyethylene oxide adsorption on silica gel and flocculation under all pH conditions.

The necessity for neutral or positive sites on the solid surface cannot explain the inertness of polyethylene oxide for alumina and hematite throughout the entire pH range studied. In addition to H-bonding, entropy changes also contribute to adsorption of polymers. The release of water molecules, the loss of water from the polymer and the entropy of dilution of bulk phase are important favorable factors for polymer adsorption. Of all the above factors, release of the water molecules from the solid surface upon adsorption is perhaps the most significant and is expected to govern the overall effect of entropy. The replacement of water molecules during the adsorption process is related to the concentration of the hydroxyl groups on the surface, since these species provide the sites for the initiation of multilayer adsorption of water molecules [14]. For example, a partially hydrated surface was found to be the best for H-bonding with polymer, whereas a completely hydrated surface (densely covered with OH groups) preferred water to polymer [1, 15, 16]. The concentration of surface hydroxyl groups on oxides has been determined by several investigators [14, 17]. The Table shows the hydration of oxides in terms of the number of OH groups per 100 \AA^2 . It is clear that alumina and hematite are strongly hydrated in contrast to silica gel. The absence of adsorption of polyethylene oxide on hematite and alumina is therefore attributed to the inability of the polymer to displace the strongly H-bonded water molecules associated with the surfaces.

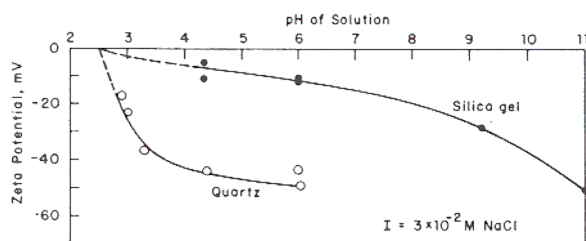


Fig. 13. Zeta potential of quartz and silica gel.

TABLE

Concentration of surface hydroxyl groups

Oxide	Number of OH/100 \AA^2
Silica (amorphous)	4.2 - 5.1
Titania (anatase)	4.9 - 6.2
Titania (rutile)	2.7 - 8.5
α -Hematite	4.6 - 9.1
α -Alumina	15
τ -Alumina	10

CONCLUSIONS

The flocculation behavior of several oxides — kaolinite, alumina, hematite, silica gel and quartz — with polyethylene oxide was investigated. The flocculation of clay was strongly affected by system variables such as conditioning time, ionic strength and pH. Increasing the conditioning time after polymer addition led to floc breakage. Flocculation of kaolinite was enhanced in the absence of indifferent electrolyte due to electrostatic attraction between the oppositely charged clay surfaces, leading to mutual coagulation.

The adsorption of polyethylene oxide on oxide minerals was governed primarily by the H-bonding characteristics and the degree of hydration of the substrate. Silica gel was strongly flocculated by polyethylene oxide with the silanol sites serving as the principal adsorption sites. Quartz was not flocculated by the polymer above pH 3 due to the predominance of negative species on the surface. Alumina and hematite were inert to the polymer due to their strong hydration and the polymer's inability to displace the bound water.

ACKNOWLEDGMENT

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