

## Effect of Agitation and Molecular Weight on Polymer Adsorption and Deflocculation\*

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### Synopsis

The rates of adsorption of PAM's were measured on calcium phosphate at various intensities of agitation. Vigorous mechanical stirring promotes the adsorption by degrading the flocules, thus providing new surfaces available for further adsorption of polymers. The rising parts of the rate curves correspond to the breaking up of flocs or "deflocculation" by the applied mechanical stirring. The flat portions of the curves in the high stirring time range indicate complete redispersion; no further surfaces are available for the adsorption of polymer flocculants. The effect of the intensity of agitation upon adsorption was investigated. Increasing the number of revolutions of the stirrer causes the adsorption curves to rise more sharply. This suggests that the deflocculation also becomes more rapid. At equimolar initial concentrations the rates of adsorption and deflocculation decrease with increasing molecular weight.

### Introduction

Previous investigations<sup>1-3</sup> on flocculation by polymer have indicated that flocculation is produced by the adsorption of the polymer upon the surface of the particles, whereby the adsorbed polymers bind the particles together. Thus, it is assumed that flocculation occurs by a crosslinking mechanism.

Deflocculation is known as the opposite process of flocculation, and usually it is considered the breaking of the flocs when stirring or shaking is applied.<sup>4</sup> It has been assumed from measurement of filtration rates<sup>4</sup> and settling rates<sup>5</sup> that there is an increasing adsorption of polymers as the flocules are degraded on shaking. However, little is known about the rate of adsorption and, consequently, the rate of deflocculation. Knowledge of the rate of polymer adsorption on particles of flocculated suspensions provides detailed information on the kinetics of deflocculation. Therefore, in this present work, the rate of adsorption on flocculated particles and its dependence upon the intensity of mechanical agitation were investigated. Furthermore, there are given some experimental results on how the mode of mixing a polymer solution with a solid adsorbent and the molecular weight of a polymer influence the rates of adsorption.

\* Abstracted from the Ph.D. dissertation of L. Jankovics, Columbia University, New York, 1961.

### Experimental

The rates of adsorption were investigated with polyacrylamide (PAM) polymers of various molecular weights and calcium phosphate adsorbent. As flocculants, PAM's were used, which are efficient flocculating agents and soluble in water up to very high molecular weight. The PAM-s were supplied by American Cyanamide Company, and their viscosity average molecular weights were: 500,000; 1,000,000; 3,000,000; and 6,000,000. The method of measuring the amount of polymer adsorbed has been described previously.<sup>6</sup>

Calcium phosphate was supplied by Fisher Scientific Company. The samples were certified reagents. This sample of calcium phosphate has a chemical analysis of Ba, 0.01%; Mg, 0.2%; Fe, 0.015%; NH<sub>3</sub>, 0.002%; Cl, 0.008%; NO<sub>3</sub>, 0.02%; CO<sub>3</sub>, 0.03%; SO<sub>4</sub>, 0.06%. For many days the powders were washed repeatedly with distilled water to remove contaminants which could interfere with analyses of the polymers by ultraviolet light absorption. Decantation of the calcium phosphate was followed by evaporating the water at 70°C. and by drying at 110°C. in an oven until constant weight was obtained. The dried cakes were ground in a glass or porcelain mortar and kept in a desiccator. The particle size distribution of calcium phosphate powder was in the 2–16  $\mu$  range.<sup>7</sup>

### Results and Discussion

The influence of rate of stirring upon the rates of adsorption was studied with PAM flocculants and calcium phosphate adsorbent. Calcium phosphate proved to be very suitable for the experiments, since the floc formation is instantaneous on mixing, and the resulting floccules are large and easily observable visually. The purpose was primarily to gain information on the extent of change in adsorption and deflocculation with agitation of various intensities. The rates of stirring in different experiments were the following: 8, 4.5, 3.2, and 2.2 rev./sec. These rates of stirring were determined with a  $3/8 \times 7/8$  in. Pyrex-coated magnetic stirrer in a 100-ml. volumetric flask containing the polymer-calcium phosphate mixture.

In these experiments two different modes of mixing the polymer and the adsorbent were used. The first one is referred to as the "dry" method, since the dilute PAM solution of known concentration was added to dry calcium phosphate powder. (The solid content was 10% w/v.) The other mode of mixing is denoted as the "wet" method since a small calculated amount of concentrated PAM solution was added to an aqueous suspension of calcium phosphate, so that the final solid content was 10% w/v as in all the experiments. The purpose was to see if there is a measurable difference in the rates of adsorption when the dry or wet methods of mixing were used, while the initial polymer concentrations were the same.

Figure 1 shows an experiment on the influence of the rate of stirring. The adsorbed amount of PAM 1,000,000 is plotted versus the time of stirring. The initial concentration was  $100 \times 10^{-10}$  mole PAM/g. calcium phosphate solid.

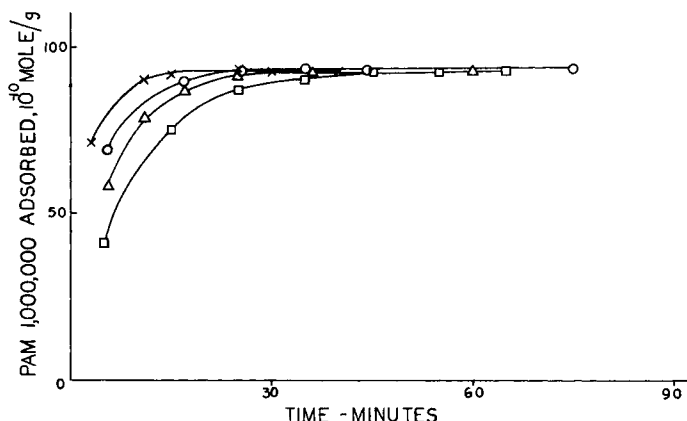


Fig. 1. Adsorbed PAM 1,000,000 at various stirring rates: (X) wet method, 8 rev./sec.; (O) dry method, 8 rev./sec.; (Δ) dry method, 4.5 rev./sec.; (□) dry method 3.2 rev./sec. Initial concentrations:  $100 \times 10^{-10}$  mole/g.

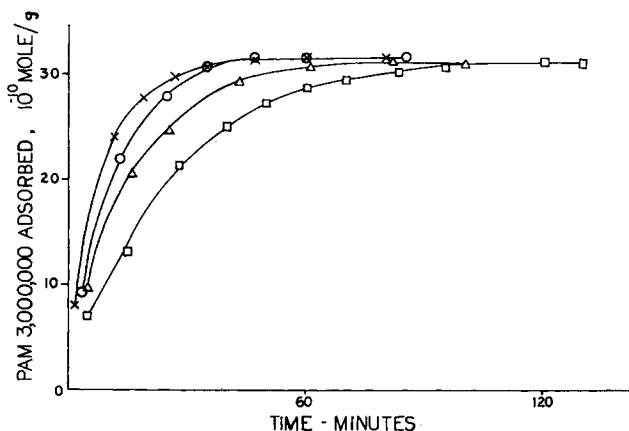


Fig. 2. PAM 3,000,000 adsorption at various stirring rates as a function of time: (X) wet method, 8 rev./sec.; (O) dry method, 8 rev./sec.; (Δ) dry method, 4.5 rev./sec.; (□) dry method, 3.2 rev./sec. Initial concentrations:  $33.3 \times 10^{-10}$  mole/g.

Figure 1 shows how the higher stirring rates increase the rate of adsorption. When the wet method and a stirring rate of 8 rev./sec. are used, equilibrium is reached in 15 min. However, when the dry method is used, the approximate times to attain equilibrium are: 25 min. at 8 rev./sec.; 35 min. at 4.5 rev./sec., and 50 min. at 3.2 rev./sec. As Figure 1 shows, the adsorption is more rapid when the wet method is used. Furthermore, the slower the stirring, the slower is the adsorption and, consequently, the deflocculation.

Figure 2 gives data for a similar experiment with PAM 3,000,000. The initial concentrations were  $33.3 \times 10^{-10}$  mole PAM/g. calcium phosphate. The rate of adsorption was measured at stirring rates of 3.2, 4.5, and 8 rev./

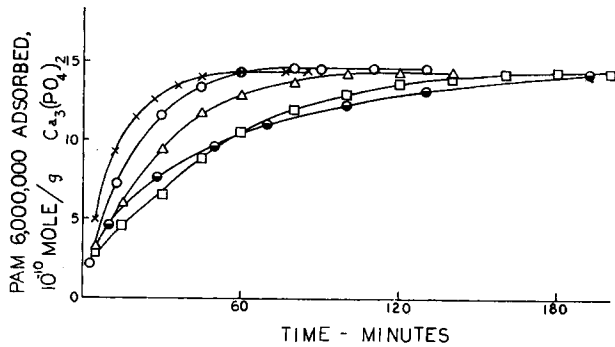


Fig. 3. Adsorbed PAM 6,000,000 at various stirring rates versus time of agitation: (X) wet method, 8 rev./sec., (●) wet method, 2.2 rev./sec.; (O) dry method, 8 rev./sec.; (Δ) dry method, 4.5 rev./sec.; (□) dry method, 3.2 rev./sec. Initial concentrations:  $16.7 \times 10^{-10}$  mole/g.

sec. with the dry method, and at a stirring rate of 8 rev./sec. with the wet method. With increasing stirring rates the rates of adsorption become more rapid. When the dry method is used, the time of reaching equilibrium at stirring rate of 8 rev./sec. is about 50 min.; at 4.5 rev./sec., about 75 min.; and at 3.2 rev./sec., about 2 hr.

Data on the rates of adsorption of PAM 6,000,000 are plotted in Figure 3. We note that the adsorption curves with the wet method rise significantly more steeply in the beginning than the ones obtained with the dry method. Since the adsorption is more rapid, consequently, the breaking up of flocs is faster in the beginning of the experiment. When the wet method was used, a faster degradation of flocs was also observed visually. Immediately after mixing PAM and calcium phosphate, the flocs appeared smaller than the flocs obtained with the dry method, if the initial polymer concentrations were the same. As a probable reason for the higher rate of adsorption, it is assumed that the polymer molecules can adsorb faster if the surface of the solid adsorbent is already wet. (This is the case when small amount of concentrated PAM solution is added to a suspension of calcium phosphate.) On the other hand, when the dry method is used, wetting of a powder may take some time, and this difference may show in the rate of adsorption as well as in the floc size.

The approximate times of reaching equilibrium when the wet method is used are 65 min. at stirring rate of 8 rev./sec. and 230 min. at 2.2 rev./sec.; with the dry method, times to equilibrium are 75 min. at 8 rev./sec., 110 min. at 4.5 rev./sec., and about 170 min. at 3.2 rev./sec. Although the equilibrium is reached more slowly at a stirring rate of 2.2 rev./sec. and the wet method than at a stirring rate of 3.2 rev./sec. and the dry method, the former curve rises more steeply at the beginning.

It was observed in all experiments that the flocculation of calcium phosphate is instantaneous upon mixing with the PAM solutions used. The flocs were large and visually well observable. As the initial steep portions

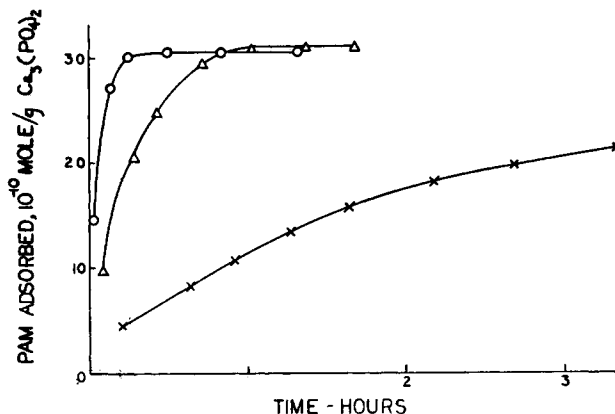


Fig. 4. Adsorption of PAM's of various molecular weights at an initial concentration of  $33.3 \times 10^{-10}$  mole/g. calcium phosphate solid: (O) PAM 1,000,000; ( $\Delta$ ) PAM 3,000,000; ( $\times$ ) PAM 6,000,000. Rate of stirring: 4.5 rev./sec.

of these curves show, the amount of adsorbed polymer increases rapidly in the beginning. However, upon continued stirring, the slopes of adsorption curves become gradually smaller. Furthermore, after a sufficient time period of stirring the amount of polymer adsorbed approaches a constant level. From this finding on the rates of adsorption a mechanism of deflocculation is suggested here for polymer-flocculated calcium phosphate system. Deflocculation is the breaking off of parts of a floc when agitation is applied, and both the mechanical forces and the diffusion of polymer molecules into the interior of flocs are important factors. During the agitation deflocculation occurs, resulting in further adsorption from the bulk solution. In the first period of agitation deflocculation is rapid, and fresh surfaces become exposed, upon which the polymer is rapidly adsorbed. With increasing time of agitation the breaking up of flocs decreases, the exposed surface area and the rate of adsorption decreases exponentially. The amount of adsorbed polymer approaches a constant level at which the particles are uniformly covered with polymers. The values of these constant levels are independent of the rate of stirring; therefore, it can be assumed that the flat parts of the curves indicate complete deflocculation, where the flocs are degraded all the way to primary particles. Further proofs of complete deflocculation are given elsewhere.<sup>6,7</sup>

The above suggested mechanism is in agreement with the effect of increasing agitation upon adsorption and deflocculation, namely, the higher the stirring rates, the more rapid is the breaking up of the flocs in the higher shear field, and the more surface can become available for polymer adsorption. Therefore, the adsorption curves rise more sharply at more intense agitation.

From Figures 1-3 it can be seen that the rate of adsorption decreases with increasing molecular weight. For easier comparison of the rates, Figure 4 shows the adsorption when the initial molar concentrations are the same,

TABLE I  
Molecular Weight Dependence of Adsorption  
(Initial concentration:  $33.3 \times 10^{-10}$  mole/g.)

PAM molecular weight	Stirring rate, rev./sec.	Time, min.	Amt. adsorbed $\times$ $10^{10}$ , mole/g.
500,000	4.5	4	30.1
		10	30.3
		30	30.2
1,000,000	4.5	2	14.5
		8	27.2
		15	30
		30	30.5
		50	30.3
		80	30.3
		3,000,000	4.5
16	20.5		
25.5	24.6		
43	29.5		
61	30.8		
82	31.1		
100	31		
6,000,000	4.5	12	4.5
		38	8.3
		55	10.8
		75	13.7
		98	15.7
		130	18
		160	19.9
		200	21
		240	22.4
		283	23.6
		345	24.7
		420	26.1
		500	27.2
		560	27.9
610	28.3		
1320	29.5		
1380	29.5		

namely,  $33.3 \times 10^{-10}$  mole PAM/g. calcium phosphate adsorbent. The rate of stirring was 4.5 rev./sec. At this stirring rate, PAM 500,000 adsorbed too rapidly for the increase in adsorbed amount to be measured (as the rising portion of curve after mixing the polymer and the adsorbent). Figure 4 shows that PAM 1,000,000 adsorption reaches equilibrium in 15 min., PAM 3,000,000 in 75 min.. With PAM 6,000,000 the time to reach equilibrium adsorption is more than 10 hr. The experimental data summarized in Figure 4 are given in Table I.

An observation was made in the above experiments that the resistance of the flocs to degradation increased with molecular weight. This observation is in agreement with the finding of Linke and Booth<sup>5</sup> that with PAM's

of higher molecular weights the settling rates of silica flocs are more rapid after mechanical mixing than with PAM's of lower molecular weights. We assume that the more resistant the flocs, the slower is the breaking up of flocs, and this slower deflocculation results in a slower adsorption at higher molecular weights.

Figure 4 and Table I indicate that the number of PAM moles adsorbed per gram calcium phosphate is approximately independent of the molecular weight at the tested concentration, if the initial molar concentrations are the same. Consequently, the number of adsorbed molecules per unit area does not depend practically on molecular weight in the 500,000–6,000,000 molecular weight range of PAM. It seems reasonable to assume that, with increasing molecular weight, the free parts of polymer chains increase, more crosslinking occurs and that the flocs therefore grow larger and more resistant to agitation. Consequently, the rate of adsorption becomes smaller with increasing molecular weight.

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### Résumé

On a mesuré les vitesses d'adsorption de PAM's sur du phosphate de calcium à des intensités d'agitation variables. Une agitation mécanique vigoureuse favorise l'adsorption en dégradant les flocules, donc formant de nouvelles surfaces disponibles pour l'adsorption de polymères. Les parties montantes de la courbe correspondent à l'éclatement des flocules ou défloculation sous action de l'agitation mécanique. Les parties plates de la courbe correspondant au temps de haute agitation indiquent une complète redispersion ou réorientation; il n'y a plus de nouvelles surfaces disponibles pour l'adsorption de flocules de polymères. Les effets de l'intensité de l'agitation sur l'adsorption ont été étudiés. En augmentant le nombre de révolutions de l'agitateur, on provoque une ascension plus rapide de la courbe. Ceci suggère que la défloculation aussi devient plus rapide. Pour des concentrations initiales équimoléculaires, les vitesses d'adsorption et de défloculation décroissent avec l'augmentation du poids moléculaire.

### Zusammenfassung

Die Adsorptionsgeschwindigkeit von PAM an Calciumphosphat wurde bei verschiedenen Rührintensitäten gemessen. Heftiges mechanisches Rühren fördert die Adsorption durch Zerkleinerung der Flocken, wodurch neue Oberflächen für weitere Polymeradsorption zugänglich werden. Der ansteigende Teil der Geschwindigkeitskurve ents-

pricht dem Aufbrechen der Flocken oder der "Deflokkulation" durch das angewandte mechanische Rühren. Die flachen Teile der Kurven im Bereich hoher Rührdauern weisen auf eine vollständige Redispersion hin; es werden keine weiteren Oberflächen für die Adsorption von Polymerausflockungen zugänglich gemacht. Der Einfluss der Rührintensität auf die Adsorption wurde untersucht. Eine Erhöhung der Umdrehungszahl des Rührers verursacht einen starken Anstieg der Adsorptionskurve. Das zeigt, dass auch die Deflokkulation beschleunigt wird. Bei äquimolaren Ausgangskonzentrationen nehmen die Geschwindigkeit der Adsorption und der Deflokkulation mit steigenden Molekulargewicht ab.

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