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Flocculants Prepared from Mixtures of Fatty Amines with Colloidal Chrysotile Asbestos

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SUMMARY

The flocculating effectiveness of mixtures of various fatty amines with colloidal chrysotile asbestos was studied to determine the extent to which the amine and the asbestos act in concert as polycations. Tallow 1,3-propylene diamine was the principal amine studied, although other fatty amines showed similar properties. Aqueous solutions of the amine defibrillate the chrysotile into primary tubules about 250 Å in diameter and several microns in length. It is believed that the amine molecules adsorb on the surface of the chrysotile tubules, promoting their defibrillation and the high stability of the resultant dispersion. The flocculating effectiveness of the amine/asbestos mixtures was determined on several neutral or anionic mineral suspensions including titania and kaolin by measuring sedimentation rate and volume. The flocculating effectiveness was also determined on a suspension of hydrophilic organic matter, partially digested diluted municipal waste, by measuring filtration rate. The amine/asbestos mixtures are more effective flocculants than either the amine or the asbestos alone. Moreover, in contrast to behavior frequently observed with conventional polymeric flocculants, the mixtures show little tendency to restabilize the suspended matter at higher than optimum concentrations.

INTRODUCTION

The two basic attributes of high molecular weight polymers that enable them to flocculate suspensions of mineral particles are believed to be 1) their large effective length, permitting each molecule to bridge two or more particles, and 2) their substantivity to the surfaces of the particles. Other materials that possess these two attributes of length and substantivity, which are not considered polymeric in the conventional sense, might also be expected to be effective flocculants at low concentrations.

This paper presents the results of a brief investigation of the flocculating power of mixtures of two materials, one of which is selected to provide the length or bridging capacity and the other of which is selected to provide the substantivity. The two materials chosen for this study, based on some preliminary evidence of their ability to work in concert, were colloidal chrysotile asbestos and tallow diamine (tallow 1,3-propylene diamine). The ability of the individual components (both of which are cationic) and mixtures in various proportions to flocculate anionic silica suspensions was determined.

Natural colloidal chrysotile consists of bundles of primary tubules which are about 250-300 Å in diameter and 1-10 μ in length. The bundles can be separated into individual tubules having a slight net positive charge when the chrysotile is dispersed in water containing a small amount of acetic acid (pH 4.5 to 5.0). Complete separation of the tubules is evidenced by a characteristic shimmering pearlescence upon gently agitating the dispersion.

Tallow diamine also dissolves in dilute acetic acid at pH 4.5 to 5. Like the asbestos, it is cationic but obviously of much higher charge per unit mass.

EXPERIMENTAL

Stock 0.5 wt% asbestos dispersions were freshly prepared each day by adding Union Carbide High Purity Asbestos (obtained from the New Idria serpentinite formation of central California) to 0.25% acetic acid in distilled water. The slurries were agitated in a Waring Blendor for about 1 min to yield the characteristic pearlescent dispersions.

A stock 5% tallow diamine solution was prepared by adding Armour Duomeen T as received to approximately 4% acetic acid in distilled water.

Suspensions of Williams Super White amorphous silica (approx. 90 wt% < 25 μ diam, 50 wt% < 7 μ, 10 wt% < 1 μ) were prepared at 0.1% concentration by adding 1 g to 1 liter of distilled water in a Waring Blendor and agitating for 30 sec. The suspensions showed only slight evidence of settling after standing several days.

Flocculation tests were performed by adding the desired number of milliliters of either or both stock solutions to the silica suspension and inverting several times. The floccules were always observed to settle to the bottom of the cylinder between 1 and 6 hr after addition of the reagents, with little or no further clarification of the supernatant taking place in the next few days. Consequently a convenient settling time of 18 hr was chosen, whereupon 50 ml of supernatant was withdrawn at the 500-ml mark on the cylinder. Optical density, as determined at 450 mμ in a 1-cm path length cell was used as a measure of turbidity.

RESULTS AND DISCUSSION

The flocculating effectiveness of the asbestos alone after 18 hr settling is shown in Fig. 1. Below a concentration of about 3 or 4 ppm (0.3-0.4% on the weight of silica) the asbestos has little flocculating effect. The silica appears to be fully flocculated at asbestos concentrations of 8 to 10 ppm or higher. The asbestos-induced flocs are large and settle rapidly to collect as a voluminous sediment, which is characteristic or bridging-type flocculation.

The flocculating effectiveness of tallow diamine alone is also shown in Fig. 1. The minimum in the curve at 2 ppm is presumably the point of charge reversal. Taking the cation equivalent weight of tallow diamine to be 180, 1.8 ppm corresponds to 1.0 meq/100 g of silica, a reasonable base exchange capacity for silica. The flocculation of the silica suspension at its zero point of charge is probably aided by the oleophilic nature of the long alkyl portion of the adsorbed tallow diamine molecules. Collisions between silica particles have a greater chance of being effective since the oleophilic groups tend to associate. This is supported by the observation that many of the tallow diamine-induced flocs tend to stick to the walls of the cylinder; in addition, the ones that settle form a very dense sediment. The oleophilic nature of the silica surface at this point no doubt facilitates charge reversal at higher concentrations of tallow diamine by providing oleophilic sites for adsorption.

The flocculating effectiveness of mixtures of tallow diamine with 0, 1, 3, and 5 ppm asbestos is shown in Fig. 2. Note the expanded concentration

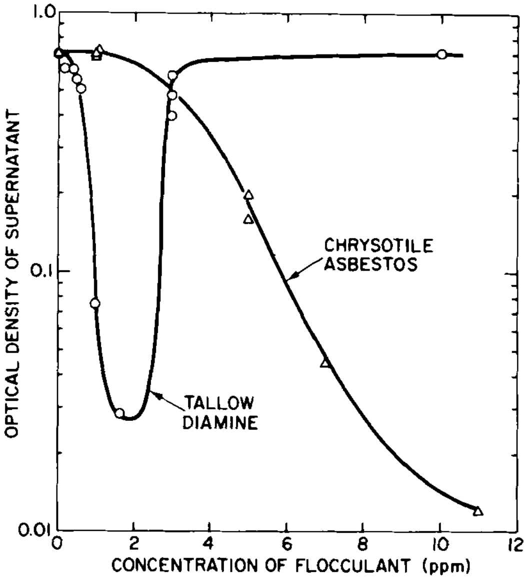

Fig. 1. Flocculation of silica with asbestos and tallow diamine separately.

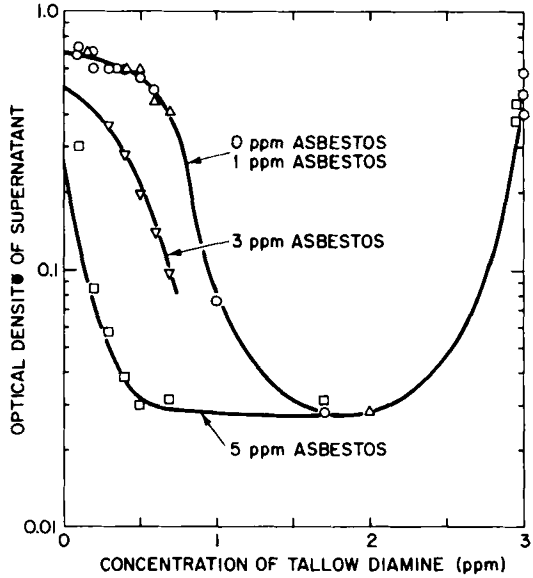

Fig. 2. Flocculation of silica with mixtures of tallow diamine and asbestos.

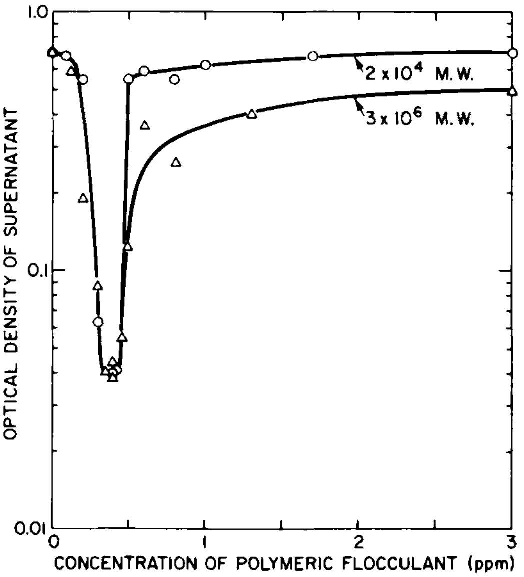

Fig. 3. Flocculation of silica with cationic polymers.

scale. Apparently, 1 ppm asbestos does not alter the flocculation effectiveness of the tallow diamine. At 3 ppm asbestos some enhancement is shown. The most pronounced effect is at 5 ppm asbestos where only 0.5 ppm tallow diamine is necessary to achieve the same degree of flocculation as the 2 ppm of tallow diamine in the absence of asbestos.

Charge reversal and redispersion of the silica takes place at approximately the same concentration of tallow diamine as in the absence of asbestos. This identity in the concentrations of tallow diamine necessary to redisperse the silica indicates that the asbestos contributes a negligible number of cation equivalents to the flocs; this is consistent with the absence of any redispersion effect for the asbestos alone at high concentrations. The identity in tallow diamine concentrations also indicates that the interparticle repulsion caused by the tallow diamine in excess of 2 ppm completely overwhelms the bridging by the asbestos. Above 2 ppm, the tallow diamine most likely simply displaces the weakly attached asbestos tubules from the silica particles.

Mixtures of asbestos and tallow diamine at asbestos concentrations higher than 5 ppm were not evaluated, since 8 ppm of asbestos alone flocculates the silica as effectively as the optimum amount of tallow diamine alone.

The flocculating effectiveness of two cationic polymers of approximate molecular weights 2×10^4 and 3×10^6 is shown in Fig. 3 for comparison.

Note the extremely narrow concentration range of effective flocculation for both polymers. The silica is dispersed at polymer concentrations only slightly above or below its zero point of charge. Any bridging effect by the polymer is apparently overwhelmed by the electrostatic repulsion between the silica particles when they possess a net positive or negative charge.

In contrast, the mixtures of 5 ppm asbestos with tallow diamine show a much broader range of effective flocculation. The bridging effect of the asbestos below the zero point of charge (which is taken to be 2 ppm for tallow diamine) is presumably responsible. Although the extended chain length of the 3×10^6 molecular weight polymer is similar to the length of the primary asbestos tubules, it is possible for the flexible polymer chains to lay down on the surface of the silica particles without appreciable bridging between particles. The stiff asbestos tubules, however, are more likely to contact several silica particles.

Note also that the tallow diamine alone shows a wider concentration range of effective flocculation than the polymers. The oleophilic nature of the adsorbed tallow diamine molecules probably can cause particles to stick together even in the presence of a mild electrostatic repulsive force.

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