but varying greatly in size. And even denser structures exist, usually of smaller dimensions. Obviously such kernels provide excellent starting conditions for production of observable sources of x-ray emission, with magnetic compressions.

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 - $\overline{p} = [66 \times 10^{-10} \text{ (gauss)}^2 (\text{Gev})^2]$
 - erg/sec per electron $\nu_c = [6 \times 10^{12} \text{ (gauss) Gev}^2] \text{ sec}^{-1}$

For a source cell having volume V, density of 10-kev electrons = $\alpha^2 N_1$, and magnetic fluid $\alpha^2 N_1$, distant from Earth by d, the intensity received on Earth would be

 $\frac{V(\alpha^2 N_1)}{2} \quad \frac{\overline{p}}{2} \quad \cong 10^{-30}$ $4 \pi d^2$

m² • (cy/sec) Vo Thus both Coulomb and magnetic brems-strahlung intensities are far below threshold sensitivity for radio telescopes. A second mechanism of x-ray emission in these regions namely synchrotron emission by the electron component of primary cosmic rays traversing the enhanced magnetic fields—is likewise of small intensity.

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 $\alpha^3 \exp(-h\nu/kT_2) \sim \alpha^3$ for $h\nu < kT$

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Flocculation Mechanism: Charge Neutralization and Bridging

Abstract. Electrophoresis measurements and electron-microscope observations with two model colloids and a polymeric flocculant show zeta-potential changes and details of floc structure. Fibers of the flocculant extend radially from the particle surface and vary in thickness from 20 to 300 angstroms. Both charge neutralization and bridging may function simultaneously.

The mechanism of flocculation is under study principally because of the current importance of removing colloidal contaminants from water. Such contaminants may be responsible for turbidity, they may carry odor and taste components on their surfaces, they may be difficult to remove, and most importantly they interfere with many tertiary or advanced waste-water treatments such as adsorption, filtration, and various membrane techniques. The relative importance of charge neutralization and bridging by polymeric flocculants is a highly controversial subject (1). Evidence for both mechanisms has now been obtained by electrophoresis measurements and electron-microscope observations on two widely different materials, a finely divided silica and a polystyrene latex.

Minusil No. 5 silica from the Pennsylvania Glass Sand Corporation has a particle diameter of about 1 μ and a ζ potential of -27 ± 2 mv, and has been used as a standard in electrophoresis studies in this and other laboratories. Dow LS-052 Å polystyrene latex has a particle size of 1260 Å and a ζ of -50 mv, and has been used as a standard in electron-microscope studies. The cationic polymeric flocculant, a polyamine sulfate (C-7) of high molecular weight, was obtained from Rohm & Haas. Water was twice distilled in quartz.

Electrophoretic mobilities were determined directly with a Zeta Meter which measures particle velocities in both directions by reversing polarity

(2). The ζ potential was calculated from particle velocity by means of the Helmholtz-Smoluchowski equation, $\zeta = 4\pi u_{\eta}/D$, in which u is the electrophoretic mobility, and η and D are, respectively, the viscosity and the dielectric constants of the liquid in the boundary layer.

Samples were prepared for the electron microscope by direct deposition of the colloidal solutions onto collodion supports. Some were shadowcast (3) to improve visibility. This is often necessary, because even relatively thick structures of organic polymers and certainly their thin fibers are transparent to the electron beam. Moreover, shadowcasting provides the third dimension.

Calculation of "equivalent monolayers" of adsorbed flocculant involves several assumptions and simply provides a tentative basis for mechanism considerations. An approximate surface area of the colloidal silica is based on particle-size measurements on the electron microscope as well as on observations made in the Zeta Meter. The indicated particle size of about 1 μ is equivalent to a surface area of approximately $1 \text{ m}^2/\text{g}$. The surface area of the horizontally oriented polymer is assumed to be about 1000 m²/g, based on considerable thin-film work with polar polymers (3). Minimum coiling or folding of adsorbed polymer and an approach to complete adsorption are assumed.

Concentrations, calculated "equivalent monolayers" [(parts per million of flocculant \times 1000)/(parts per million of colloid)], electrophoretic mobilities, and ζ values for colloidal silica with the C-7 flocculant are listed in Table 1. The ζ of the original particles,

Table 1. Zeta potential of colloidal silica on the addition of a cationic polymeric flocculant.* Abbreviation: ppm, parts per million.

Cationic polymeric flocculant		Electro- phoretic	Zeta poten-
ppm	("Mono- layers")	$(\mu/\text{sec per volt/cm})$	tial (mv)
0	0	2.1	-27
0.01	0.1	2.2	-28
0.05	0.5	0.88	-11
0.075	0.75	(0)	(0) †
0.10	1.0	0.66	+ 9
1.0	10	2.0	+26
10	100	2.1	+27
50	500	2.0	+26
100	1000	2.0	+26

* 100 ppm Minusil No. 5 colloidal silica with the C-7 floculant. \dagger Athough most particles are motionless ($\zeta = \text{zero}$), some show a small negative ζ.



Fig. 1. Electron micrographs of colloidal silica and a cationic polymeric flocculant. (A) Silica blank; (B) silica plus flocculant; (C) silica plus flocculant (shadowcast); (D) silica plus flocculant at higher magnification (shadowcast). Fig. 2. Electron micrograph of polystyrene latex and a cationic polymeric flocculant. Markers in all figures indicate 1 micron.

-27 mv, is not significantly affected by 0.1 monolayer. However, a remarkably close approach to zero ζ is observed in the monolayer region. An addition of 0.5 monolayer gives a ζ of -11 mv, 1.0 monolayer gives +9 mv, and the intermediate 0.75 monolayer gives effectively zero. In the latter case, most of the particles are motionless under the applied potential; a few move very slowly.

A plateau at a ζ of +26 mv is shown in the broad range of 10 to 1000 monolayers. This may indicate that there is a leveling off (equilibrium) in flocculant adsorption, possibly because of charge reversal and repulsion, or that, because of particle geometry or the nature of the adsorption, thickness of the flocculant film does not change ζ . Electron microscopy provides some support for the latter effect-thick films of low-density material, presumably the polymer, surround some of the silica particles.

Examinations by electron microscope further clarified the flocculation effects. Many micrographs of the silica, as shown in Fig. 1A, indicate discrete particles whose diameters are predominantly in the $1-\mu$ range. No flocs of any significance are observed. Probably because of the method of sample preparation small aggregates containing a few particles are found in all systems.

Figure 1B shows a typical floc formed when 0.75 monolayer of flocculant

has been introduced. Figure 1C shows a shadowcast sample obtained at the same magnification as that of Fig. 1B. Shadows appear as light areas and the direction of shadowcasting is indicated by arrows on the micrographs. Tight packing is again apparent. Most striking in this and in a number of other samples are the threadlike or fiberlike structures that extend radially from some of the particle surfaces. These fibers, which are presumably the polymeric flocculant material, appear to be reaching out to capture and bind neighboring particles. Bridging between particles is clearly observed here as well as in other samples.

Figure 1D, at a greater magnification, shows considerably more detail. Shadow widths indicate that some fibers are 200 to 300 Å, whereas others appear to be 20 to 30 Å in diameter. The latter values approach the expected diameter for a single polymer chain with some branching or perhaps some folding or coiling. Thickness of the radially oriented fibers decreases with distance from the silica surface. Fiber formation clearly lessens the material available for adsorption.

Figure 2 is a micrograph of latex spheres in the presence of excess flocculant. Many flocs remain in spite of charge reversal (-50 to +24 mv). Part of a large, dense aggregate appears in the upper left portion of the micrograph. Most striking, however, are the well-defined fibers that connect the remaining latex spheres. Not only do all of these latex particles appear to be attached to fibers (none is in the "open" area), but they apparently prefer the thicker portions of the fibers and in many cases the points of branching. Electrical attraction plus van der Waals forces are undoubtedly responsible for such attachments. The shadows again indicate that fiber thickness covers a broad range, 20 to 300 Å.

Thus electrophoresis and electronmicroscope studies of model colloids in the presence of a polymeric flocculant provide evidence that charge neutralization and bridging may function simultaneously.

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