

The Role of Edge Surfaces in Flocculation of 2:1 Clay Minerals

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ABSTRACT

The effect of pH on the flocculation, settling rate, and gel volume of pyrophyllite in dilute suspension was studied in solutions of various NaNO_3 concentrations to evaluate the role of the edge surfaces in particle-particle interaction. The critical flocculation concentration (CFC) increased with increasing pH, being 1.6×10^{-4} , 4×10^{-4} , 1.5×10^{-3} , 9.5×10^{-3} , 1.6×10^{-2} , and $0.1 \text{ mol}_c \text{ L}^{-1}$ at pH 3.2, 4.4, 5.3, 6.0, 7.4, 8.5, and 10.2, respectively. The CFC increased significantly in the presence of small amounts of sodium hexametaphosphate in the suspension. The changes in CFC from low values in the absence of the polymer to higher values in the presence of it support the hypothesis that the edge surfaces are involved in particle-particle interactions. The settling rate of the clay particles at pH 8.5 increased as the electrolyte concentration was decreased. The effect of electrolyte concentration on settling rate was explained by the presence of an electrical field associated with the edge surfaces. The gel volume, after reaching a stable volume, increased with the increasing of electrolyte concentration. This increase in water content, indicating an open structure of clay platelets, also supports the hypothesis that edge surfaces are associated with clay flocculation. The electrical field associated with the edge surface also has an effect on the gel volume.

MONTMORILLONITE PLATELETS in aqueous suspension may flocculate in three possible modes of particle association (Van Olphen, 1977): (i) association between siloxane planes of two parallel platelets (FF), (ii) association between edge surfaces of neighboring particles (EE), and (iii) association between an edge surface and a siloxane planar surface (EF). In the presence of electrolyte (e.g., NaCl) at low concentration, the double layers on the Na-montmorillonite particles are well developed and osmotic repulsion prevents particle association. Thus, a stable suspension of individual platelets is obtained (Van Olphen, 1977). As the concentration of NaCl in the suspension increases, double layers at both the planar and the edge surfaces are compressed, and at the CFC, both EF and EE association can occur. As the electrolyte concentration increases further, the FF mode of particle association occurs, and "oriented aggregates" are formed. Although the van der Waals attraction energy between two plates is independent of the charge density of the plate, the repulsion energy depends on it along with the composition and concentration of the electrolyte in suspension (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948; Pashley, 1981). Thus, the CFC of 2:1 clay minerals should decrease with the surface electrical potential (ψ_0). The CFC values for Na-montmorillonite range from 7 to 24 $\text{mmol}_c \text{ L}^{-1}$ NaCl (Arora and Coleman, 1979; Goldberg and Foster, 1990;

Keren et al., 1988; Oster et al., 1980), whereas for illite, the CFC has ranged from 55 $\text{mmol}_c \text{ L}^{-1}$ NaCl (Oster et al., 1980) to 90 $\text{mmol}_c \text{ L}^{-1}$ NaCl (Goldberg and Foster, 1990), depending on pH. Recent investigations have related the CFC of montmorillonite and illite to suspension pH (Goldberg and Foster, 1990; Hesterberg and Page, 1990; Keren et al., 1988). For example, at pH 9.8 (a value that is well above the PZC of the edge surfaces), the CFC of Na-montmorillonite is 44 $\text{mmol}_c \text{ L}^{-1}$ NaCl (Keren et al., 1988). At such a high pH, however, an EE or EF association is not likely to occur. Moreover, at 44 $\text{mmol}_c \text{ L}^{-1}$ NaCl, the repulsion energy due to the double layer at distances $>0.25 \text{ nm}$ from the clay surface exceeds the attraction energy, despite the fact that at this NaCl concentration and pH, the clay flocculates. Keren et al. (1988) suggested that FF association between two platelets takes place at surface regions that have lower specific charge density than the average value of the entire montmorillonite surface (0.117 C m^{-2}).

As mentioned above, the CFC of 2:1 clay minerals decreases as the specific charge density decreases. Thus, clay that has an electrostatic charge close to zero may flocculate regardless of the electrolyte concentration in suspension, unless the edge surfaces are involved in this system. This hypothesis is tested in this study.

Pyrophyllite, in contrast to montmorillonite, shows little deviation from the ideal formula. The dioctahedral structure of this clay mineral consists of essentially neutral tetrahedral-octahedral-tetrahedral layers and is the prototype of the structure of montmorillonite and illite groups. The platelets are held together by van der Waals forces, which are comparatively weak with respect to the primary valence forces that hold the atoms in the unit layers together. Consequently, cleavage parallel to the unit layers is relatively easy, and the mineral occurs in the form of flakes (Van Olphen, 1977). Despite the lack of a charged planar layer, the edge surface properties are similar to those of the rest of the phyllosilicates. The lack of electrical field associated with the planar surfaces may allow the evaluation of the edge surface reactivity in clay particle interaction. The purposes of this study were to determine the influence of pH and Na-hexametaphosphate on CFC and the effect of electrolyte concentration on the gel water content.

MATERIALS AND METHODS

Clay Preparation

Pyrophyllite [$\text{Al}_2 \text{Si}_4 \text{O}_{10} (\text{OH})_2$], a 2:1 type clay from Robbins, NC (Ward's Natural Science Establishment, Rochester, NY), was used in this study. A ball mill (Norton, Akron, OH) was used to increase the proportion of the $<2\text{-}\mu\text{m}$ particle-

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Abbreviations: CFC, critical flocculation concentration; FF, face-to-face; EE, edge-to-edge; EF, edge-to-face; PZC, point of zero charge; PZSE, point of zero salt effect.

size fraction of the clay. Five-hundred grams of air-dried powdered clay were transferred to a hollow rotating cylinder filled with hard ball-shaped, wear-resistant media (Zirconia) and ground for 30 h.

The <2- μm clay fraction was obtained by allowing the larger particles to settle out of a suspension and then decanting the upper suspension containing the <2- μm clay particles. The clay was saturated with Na by washing three times with 0.5 M NaNO_3 . The clay was then washed with distilled water and separated in a high-speed centrifuge until the electrical conductance of the equilibrium solution was <10 $\mu\text{S cm}^{-1}$. A stock suspension at a concentration of 0.13 g mL^{-1} was used for the flocculation experiments.

The clay particle-size distribution in suspension was determined by using a Sedigraph 5000D particle-size analyzer (Micromeritics Instrument Co., Norcross, GA).

Flocculation Experiments

These experiments were conducted by introducing the clay into a series of test tubes and adding various proportions of distilled water and NaNO_3 solution. In this way, the total dilution of the clay particles was held constant while different amounts of NaNO_3 were added to each tube. The clay concentration in the suspension of each tube was 0.1%. The pH was adjusted by adding a small volume (<0.15 mL) of either 0.1 M NaOH or HNO_3 to the 0.1% suspensions prior to settling. The amount of Na used in pH adjustment was included in the CFC determinations. Similarly, another series of test tubes was prepared, with the exception that sodium hexametaphosphate [$(\text{NaPO}_3)_6$] was added to the suspensions at a final concentration of 100 mg L^{-1} .

A series of glass tubes (20 cm long and 0.484 cm in diameter) was used for the gel volume measurements. Three and one-half milliliters of 10 g kg^{-1} pyrophyllite suspension, at pH 8.5 and a given NaNO_3 concentration, were added to each of the tubes, and the clay was allowed to settle under gravity. Following flocculation, a sharp boundary existed between the gel and the clear solution. Even though the individual particles were not visible, the boundary was visible, and the velocity of settling of the boundary was assumed to be equal to the velocity of settling of the flocculi. The settling rate was determined by measuring the height of the gel at selected time intervals.

Computations

The Nernst relationship (Parks, 1965) was used to calculate the clay edge surface electric potential, ψ_0 , at a given pH_i ,

$$\psi_0 = \frac{2.302RT}{F} (\text{pH}_{\text{PZC}} - \text{pH}_i) \quad [1]$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, and pH_{PZC} is the pH of the equilibrium solution when the sum of all positive and negative charges on the clay surface is zero.

The electric potential, $\psi_{(x)}$, changes with distance from the edge surface was calculated by the following equation (Babcock, 1963):

$$y_{(x)} = 2 \ln \{ [e^{kx} + \tanh(Y_0/4)] [e^{kx} - \tanh(Y_0/4)]^{-1} \} \quad [2]$$

where the parameters

$$Y_{(x)} = \frac{|Z_i|e\psi_{(x)}}{kT} \quad [3]$$

$$Y_0 = \frac{|Z_i|e\psi_0}{kT} \quad [4]$$

$$\kappa' = \left(\frac{8\pi Z_i^2 e^2 n_0}{DkT} \right)^{1/2} \quad [5]$$

and where Z_i is the ion valence, e is the electron charge, k is the Boltzmann constant, T is the absolute temperature, D is the dielectric constant, n_0 is the electrolyte concentration in solution (number of ions per cubic centimeter solution), and x is the distance perpendicular to the edge surface of the clay.

RESULTS AND DISCUSSION

The effect of pH on the CFC of pyrophyllite in the absence and presence of $(\text{NaPO}_3)_6$ is shown in Fig. 1. In general, the CFC increased with pH. Similar behavior was observed for Na-montmorillonite (Keren et al., 1988), but the values were higher than those obtained for pyrophyllite. The CFC for Na-pyrophyllite at pH 5.3, for example, was 0.4 mmol L^{-1} , whereas, the value for Na-montmorillonite was 10 mmol L^{-1} at the same pH. Similar to Na-montmorillonite, the CFC increased sharply above pH 7.

The van der Waals attraction energy, V_A , between two semi-infinite plates such as for a 2:1 clay mineral is given by

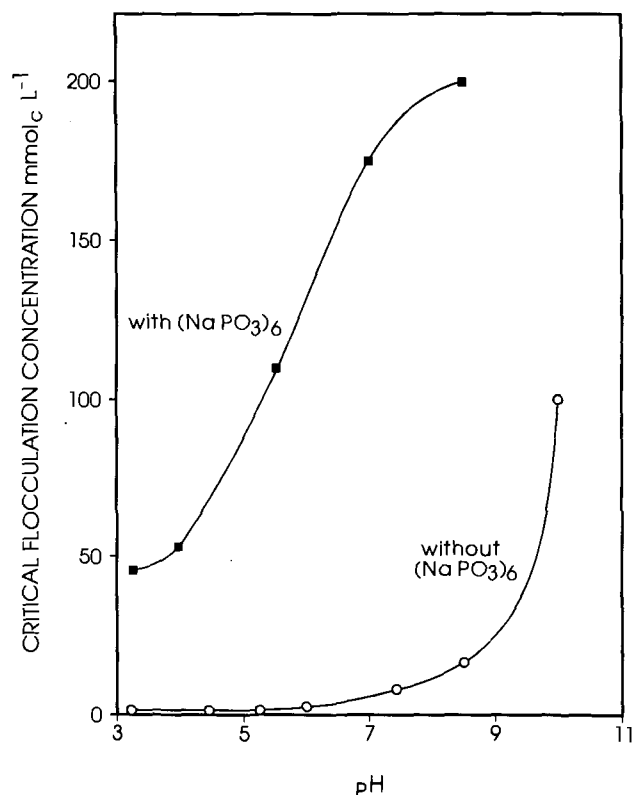


Fig. 1. The critical flocculation concentration of pyrophyllite in NaNO_3 solution with sodium hexametaphosphate (0.16 mol kg^{-1} clay) and without it as affected by suspension pH (the clay concentration was 0.1% and the apparent size of the particles was <2 μm).

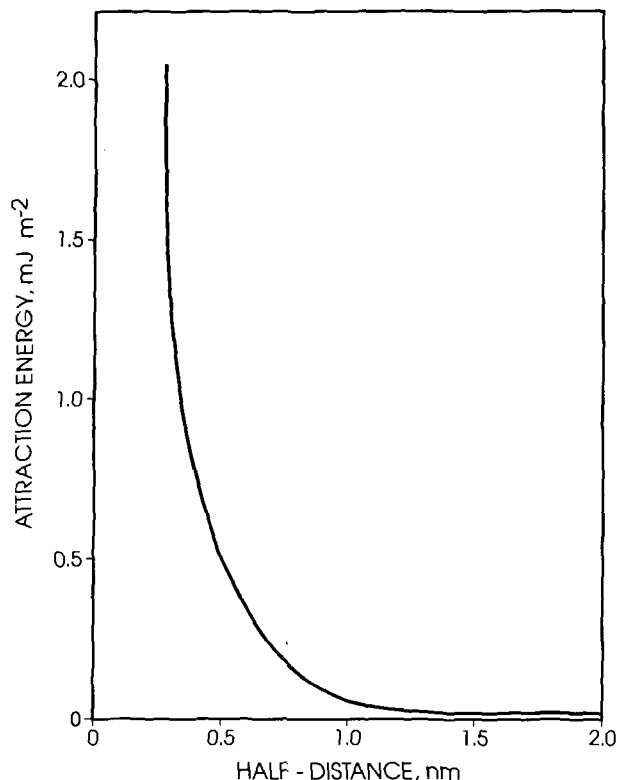


Fig. 2. The attraction energy between two Na-montmorillonite platelets as a function of the distance from clay surface.

$$V_A = -\frac{A}{12\pi} \left(\frac{1}{h^2} + \frac{1}{(h+2t)^2} - \frac{1}{(h+t)^2} \right) \quad [6]$$

where A is the Hamaker constant (2.2×10^{-20} J; Israelachvili and Adams, 1978), h is the distance between the surfaces of the plates, and t is the thickness of the clay plate.

The van der Waals attraction energy as a function of the distance from the clay surface is presented in Fig. 2. The attraction forces are independent of the surface charge density of the clay and the composition and con-

centration of electrolyte in the suspension. The curve in Fig. 2 represents montmorillonite clay using $t = 9.6 \text{ \AA}$. For pyrophyllite, the van der Waals attraction forces are even larger since the thickness of the clay particles is greater than that of Na-montmorillonite (Keren et al., 1994).

The repulsion energy $V_R(d)$ between two clay platelets can be computed from the diffuse double layer theory (Lyklema, 1982) using Eq. [7]:

$$V_R(d) = \frac{64nkT}{\kappa} \left[\tanh\left(\frac{Ze\psi_s}{4kT}\right) \right]^2 e^{-2\kappa d} \quad [7]$$

where n is the number of cations per unit volume, k is the Boltzmann constant, T is the temperature, Z is the cation valence, ψ_s is the Stern layer potential, d is the distance from the clay surface to the midway plane between two parallel platelets, e is the electron charge, and κ is the Debye-Hückel parameter, which for a symmetric electrolyte is given by

$$\kappa = \left(\frac{2e^2nZ^2}{DkT} \right)^{1/2} \quad [8]$$

where D is the dielectric constant of the medium.

The Derjaguin, Landau, Verwey, and Overbeek theory of colloid stability assumes that the dispersed particles are not hydrated and hence do not have an additional repulsive force when two particle surfaces approach one another in aqueous solution.

The structure of pyrophyllite is the prototype structure of the three-layer clay minerals of the montmorillonite and illite groups. The dioctahedral structure of this clay mineral consists of essentially neutral tetrahedral-octahedral-tetrahedral layers. Under such conditions, $V_R \rightarrow 0$ (since $\psi_s \rightarrow 0$, Eq. [7]) and only van der Waals forces are acting between clay platelets if only the planar surfaces are associated with flocculation. Under these circumstances, pyrophyllite should flocculate regardless of the electrolyte concentration in the suspension. The results presented in Fig. 1, however, indicate that the

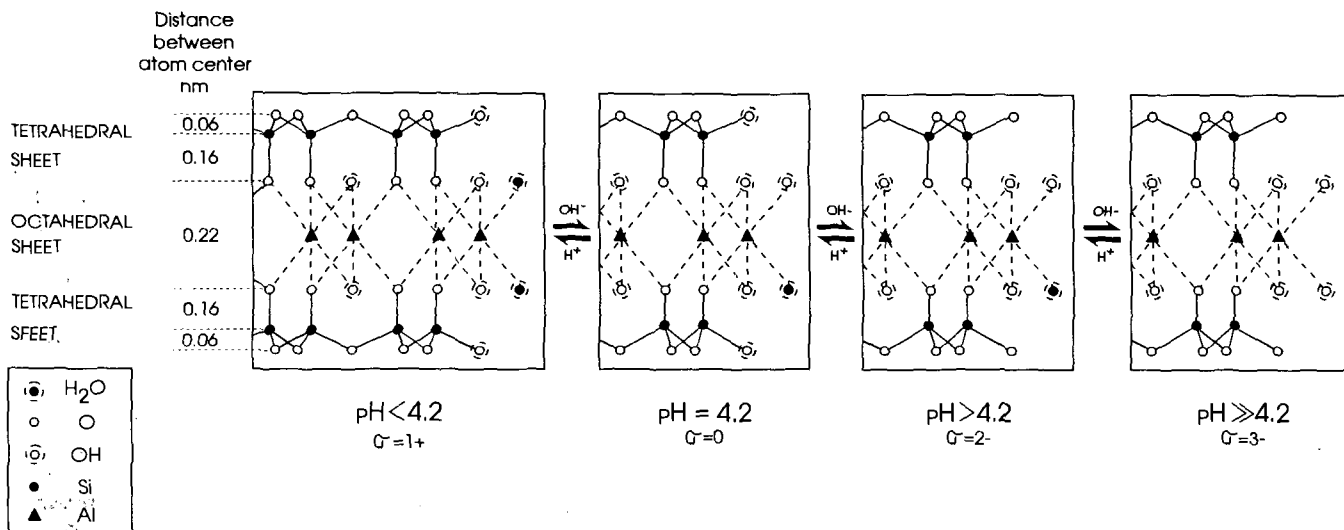


Fig. 3. Atomic arrangement in the unit cell of pyrophyllite.

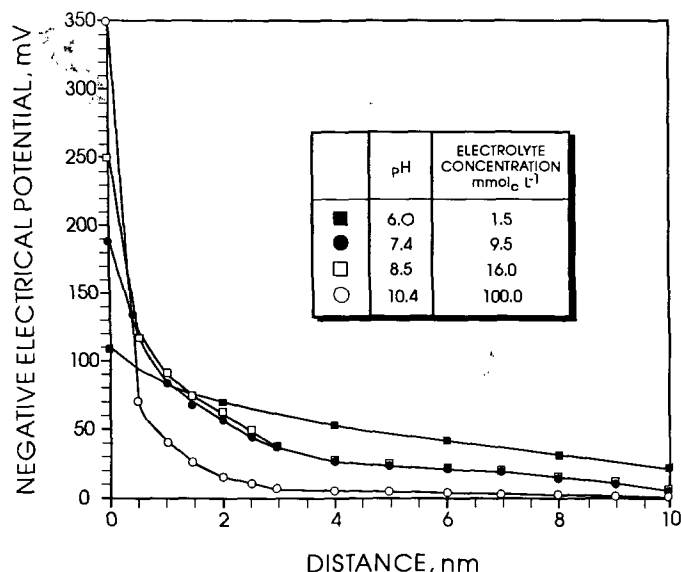


Fig. 4. Electrical potential charges as a function of distance from the edge surfaces of pyrophyllite at various pH and NaNO_3 concentrations.

suspensions remained stable below the CFC values at pH above 5 (the effect of pH on CFC will be discussed below). These results indicate that the edge surfaces may play a major role in flocculation and settling of pyrophyllite in aqueous media.

The most reactive surface functional group on the edge surfaces is the hydroxyl exposed on the periphery of the clay mineral. This functional group is associated with

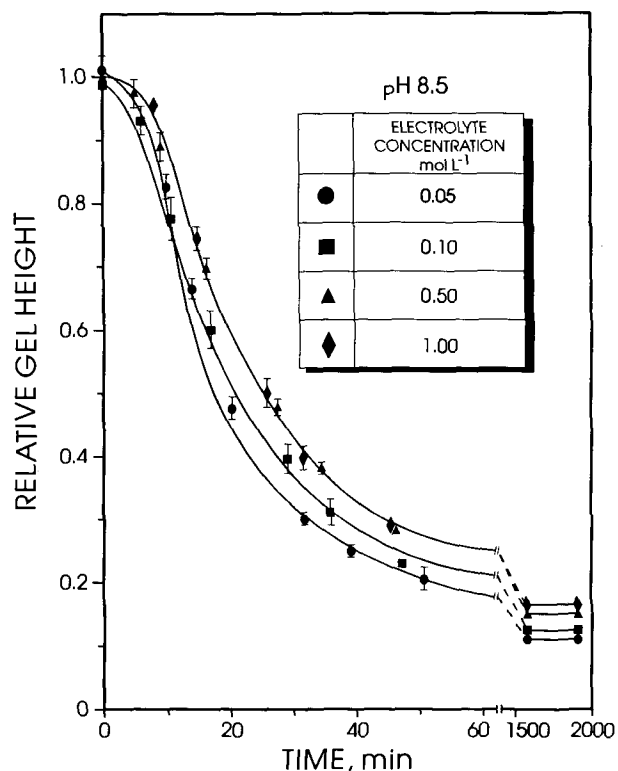


Fig. 5. Relative gel height in pyrophyllite gel at pH 8.5 as a function of time and NaNO_3 concentration.

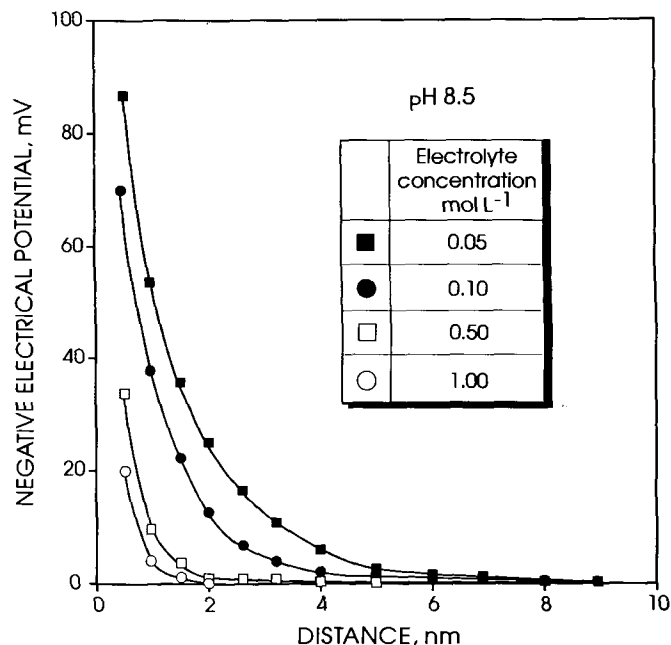


Fig. 6. Electrical potential charges as a function of distance from the edge surface and NaNO_3 concentration for pyrophyllite suspension at pH 8.5.

the structural cations Al(III) and Si(IV) , which are located in the octahedral and tetrahedral sheets, respectively. The atomic arrangement on the edge surface of a unit cell of a 2:1 clay mineral (e.g., pyrophyllite) is presented in Fig. 3. At the edge of the octahedral sheet, the Al(III)·OH is a Bronsted acid site. The hydroxyl group associated with this site can interact with a proton at low pH values. At the edge of the tetrahedral sheet, hydroxyl groups are singly coordinated to Si^{4+} cations.

The potentiometric titrations of pyrophyllite suspensions at various indifferent electrolyte concentrations indicate that the PZSE of the edge surfaces of 4.2 (data not shown) is close to the value suggested by Rand et al. (1980). Thus, the density of the negative electrical charge on the edge surfaces increases with pH at $\text{pH} > \text{PZSE}$. The negative electrical potentials associated with the edge surfaces at several pHs above the PZSE, as a function of distance from the clay surface, are given in Fig. 4. The electrical potentials were calculated using the electrolyte concentrations equal to the CFC value for each pH. The absolute value of the surface electrical potential increases with pH, and the absolute value of the electrical potential decreases with distance. At pH 8.5, for example, the absolute value of the electrical potential associated with the edge surfaces dropped from 350 mV at $x = 0$ nm to about 70 mV at $x = 0.5$ nm, whereas a less sharp drop was observed at pH 6. The absolute value of the electrical potential dropped from about 110 mV at the clay surface to 95 mV at a distance of 0.5 nm from the surface at NaNO_3 solution concentration of 1.5×10^{-3} mol L⁻¹. Flocculation occurred when the absolute value of the electrical potential at the distance of 0.5 nm from the clay surface dropped to ≈ 100 mV (Fig. 4), where all the lines in Fig. 4 are approximately crossing each other.

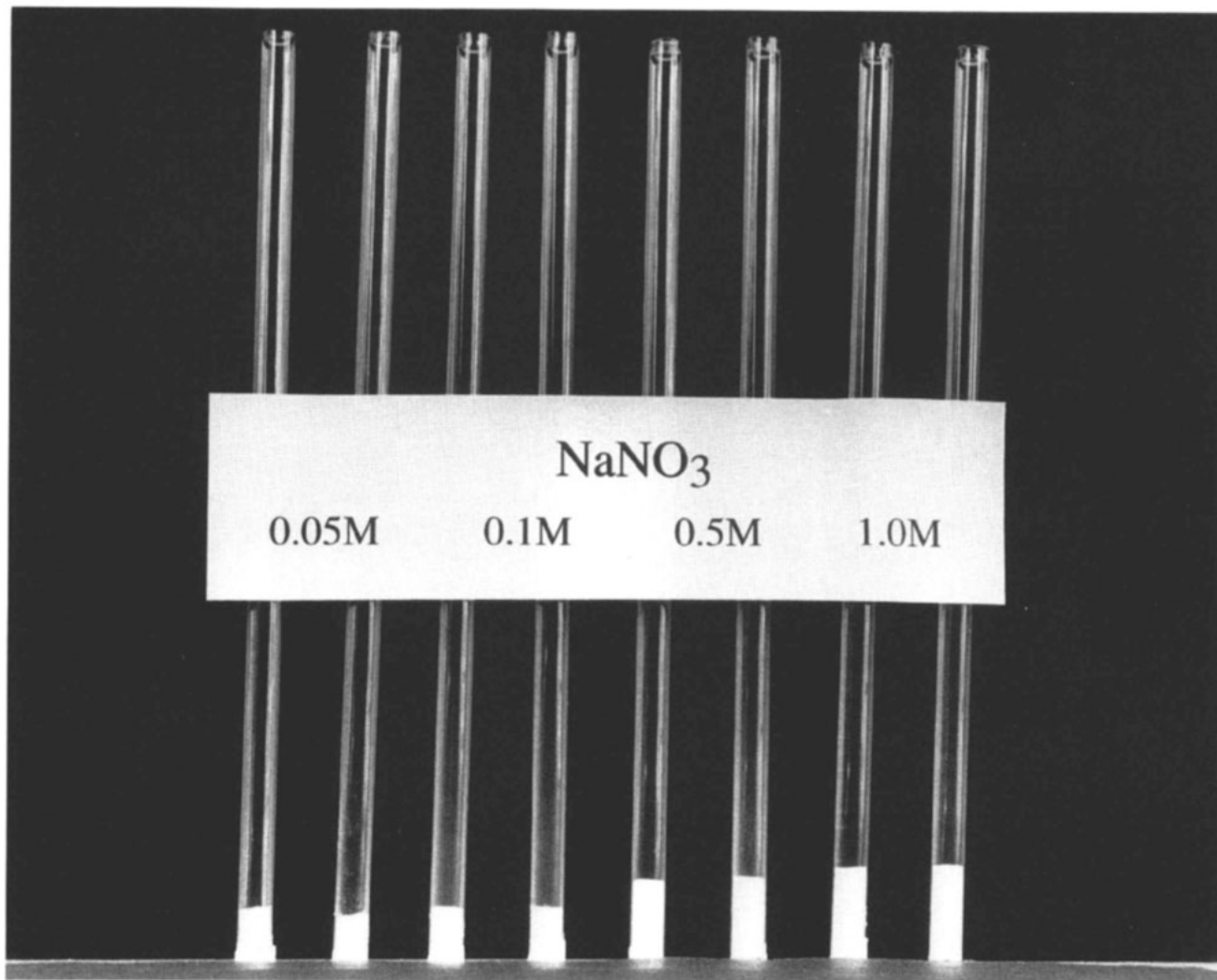


Fig. 7. Final gel height of pyrophyllite under gravitation forces at pH 8.5 as a function of NaNO_3 concentration.

The role of the edge surfaces in pyrophyllite flocculation was evaluated by introducing sodium hexametaphosphate to the clay suspension. The effect of the adsorbed polymer on flocculation is shown in Fig. 1. The presence of a small amount of polymer (0.16 mol kg^{-1} clay) affected the CFC significantly. For example, the CFC at pH 7 increased from about $5 \text{ mmol NaNO}_3 \text{ L}^{-1}$ in the absence of the polymer to 175 mmol L^{-1} in the presence of it. Its effect was pronounced even at the low pH range, whereas only a small pH effect was observed in the absence of the polymer.

Van Olphen (1977) suggested that anions are chemisorbed at the edge surfaces of the clay platelets by reacting with the exposed Al, and the charge of the edge surfaces becomes more negative. The presence of sodium hexametaphosphate on clay surfaces increases the absolute value of the electrical potential associated with the edge surfaces; therefore, a higher electrolyte concentration was needed to allow for clay particle association. The role of the edge surfaces in particle-particle interaction was also shown by Keren (1988) for montmorillonite. It was suggested that the edge surfaces were involved

in linkages between clay platelets and were responsible for the pseudoplastic characteristics of the clay suspension. In studies of the effect of NaCl on the rheological behavior of Na-montmorillonite suspensions at different pH values, Rand et al. (1980) concluded that for dilute suspensions at NaCl concentrations above $5 \times 10^{-3} \text{ mol L}^{-1}$, there was no evidence for EF interactions in the pH range of 4 to 11, and the coagulation produced by NaCl additions ($<0.3 \text{ mol L}^{-1}$) was considered to be initially a result of EE particle interactions. They based their conclusion on the assumption that the edge surface isoelectric point lies at a pH value below 4. The changes in CFC from low values in the absence of the polymer to higher values in the presence of it support the hypothesis that edge surfaces are involved in particle-particle interactions.

The relative pyrophyllite gel height at pH 8.5 as a function of time and NaNO_3 concentration (all concentrations were above the CFC) is given in Fig. 5. During the first 50 min after mixing, the clay settled and the relative gel height was $\approx 20\%$ of its original height. The gel height remained stable under gravitational forces

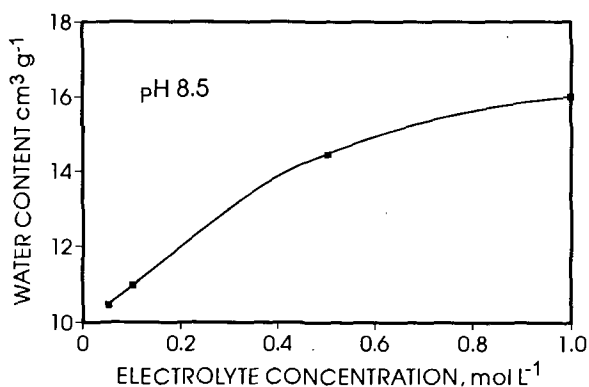


Fig. 8. Water content in pyrophyllite gel at pH 8.5 as a function of NaNO_3 concentration.

after 25 h. The rate of settling increased as the electrolyte concentration was decreased. The effect of electrolyte concentration on settling rate can be explained by the presence of electrical fields associated with the edge surfaces. The electrical potentials as a function of distance from the clay surface and electrolyte concentration are presented in Fig. 6. The absolute value of the electrical potential dropped sharply at a short distance from the surface, and this rate of drop increased as the electrolyte concentration was increased. This sharp drop in the absolute value of the electrical potential led to a stronger interaction between clay platelets (Keren et al., 1988). Since the suspension viscosity increases under these conditions (Keren, 1988; Rand et al., 1980), the rate of settling decreased.

The aqueous gel volume after formation of a stable gel increased with the increasing of electrolyte concentration (Fig. 7), and the water content increased from $10.5 \text{ cm}^3 \text{ g}^{-1}$ clay at 0.05 M NaNO_3 to $16 \text{ cm}^3 \text{ g}^{-1}$ at 1.0 M NaNO_3 . The gel volume for pyrophyllite was between 30 and 45 times smaller than that observed for Na-montmorillonite at the same pH (Keren et al., 1988). This smaller volume is probably due to the existence of a smaller number of pyrophyllite particles than for the Na-montmorillonite at a given suspension concentration and volume. The Na-montmorillonite at low ionic strength exists in suspension as single platelets, and the distance between them is determined by the diffuse double-layer forces and the clay concentration in suspension. On the contrary, pyrophyllite exists in thicker particles (Keren et al., 1994) since the platelets are held together by van der Waals forces while no repulsion forces exist due to the absence of planar electrical charge. The increase in water content with electrolyte concentration (Fig. 8) may also support the hypothesis that edges

are associated with clay flocculation. The decrease of the negative electrical potential with distance from edge surfaces becomes steeper as the electrolyte concentration in suspension increases. Thus, the strength of the EE bonds increases with electrolyte concentration, and as a result, a higher stable gel volume could be formed.

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