INFLUENCE OF CALCIUM AND SODIUM CONCENTRATION ON THE MICROSTRUCTURE OF BENTONITE AND KAOLIN

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Abstract—The influence of added sodium and calcium nitrate electrolyte on the particle aggregates in the colloid fraction of natural bentonite and kaolin was studied. Clays were flocculated in distilled water and various electrolyte concentrations. Aggregate size was studied by sedimentation analysis; the mean radius of the aggregates was plotted against the concentrations of Na^+ and Ca^{2+}. For bentonite, the mean radii decreased with an increase of Na^+ and Ca^{2+} concentration, reaching a minimum; and further increases in concentration led to an increase of the mean radii of the aggregates. For kaolin, an increase in Na^+ and Ca^{2+} concentration gave rise to an increase in the mean radii of aggregates.

Scanning electron micrographs showed different types of aggregates, depending on the physico-chemical conditions of a sedimentation process. In bentonite and kaolin sediments formed from a distilled water slurry, the dominant aggregate was an edge-face type. The small addition of salts to a bentonite slurry led to the formation of edge-edge-type aggregates; for kaolin edge-face-type aggregates formed, although within the microaggregate face-face associations were observed. The highest concentrations of electrolytes for sediments of both clays led to formation of compact, face-face-type aggregates.

Key Words—Aggregation, Bentonite, Electrolyte, Flocculation, Kaolin, Scanning electron microscopy.

INTRODUCTION

van Olphen's (1956) rheological studies of homo-ionic suspensions of sodium montmorillonite showed significant changes in suspension viscosity as a result of increasing NaCl concentrations. The changes resulted from deflocculation (Michaels and Bolger, 1962; van Olphen, 1951) and aggregation (Granquist, 1959; van Olphen, 1951), which, in turn, resulted from changes in the type of interparticle association. Following van Olphen's (1963, 1964) simplified model, three types of aggregates of plate-like particles of clay mineral may be distinguished: edge-face (E-F), edge-edge (E-E), and face-face (F-F). These types of aggregates apparently result form the state of balance between van der Waals attractive forces and electrostatic repulsive forces that exist between double layers having electric charge of the same sign. Changes of the physico-chemical conditions of the system evoke transitions in the balance of these forces, which result in changes in the type of aggregate (Bennett and Hulbert, 1986). Among different chemical factors, the kind and concentration of electrolyte and the pH exert the greatest influence on the type of microstructure (Swartzen-Allen and Matÿević, 1974). Although van Olphen's aggregate types have not been found in pure forms in natural sediments, a dominance of a certain type has been observed (Moon, 1972).

The evaluation of the type of microstructure has been investigated by numerous researchers. Among others, O'Brien (1971) studied kaolinite and illite floc-cule formation in distilled water and electrolyte solutions. He found that the fabric of kaolinite was dominated by a 3-dimensional network of twisted chains of face-face oriented flakes and that the fabric of illite also consisted of abundant face-face-oriented overlapping flakes. Fitzsimmons *et al.* (1970) studied montmorillonite aggregation at high NaCl and $CaCl_2$ concentrations. Their results indicate that the salt floccules consisted of particles randomly oriented relative to one another. Sides and Barden (1971) studied the influence of $Ca(OH)_2$ on the aggregation of clay minerals and proposed the term turbostratic arrangement for a fabric of domains or stacks. Schofield and Samson (1954) determined rheologically the types of kaolinite association after HCl and NaCl treatments. They obtained three fabrics: deflocculated kaolinite, flocculated kaolinite with particles arranged predominantly face-to-face, or flocculated kaolinite with edge-to-face particles. Tessier and Pedro (1982) examined the influence of NaCl concentration levels and pH on the Na-smectite aggregation by means of scanning and transmission electron microscopy. They failed to find edge-to-face bounds between quasi-crystals.

All the studies mentioned above were concentrated on the determination of microstructure type for the given electrolyte concentration levels. Rand and Melton (1977) and van Olphen (1956), using rheological methods and volume and density measurements, studied the influence of pH and electrolyte addition in a wide range of concentration levels of kaolin and montmorillonite aggregation. Their results, however, were

Figure 1.   Transmission electron micrographs of bentonite.

not confirmed by direct observations, i.e., by scanning electron microscopy (SEM).

It thus seems useful to compare the type of aggregates determined by sedimentation analyses with the direct SEM observation of the microstructure of sediments obtained. The purpose of the present work was therefore to observe the changes of the aggregate structure of some kaolin and bentonite samples in the wide range of salt concentrations.

MATERIALS AND METHODS

Bentonite from Bavaria, Federal Republic of Germany, and kaolin from Pontedra, Spain, were the subject of the present investigations. The mineralogical composition of the <2-μm fraction of these clays was determined by means of X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). XRD studies were conducted on a Philips apparatus using CuKα radiation for: (1) untreated samples, (2) the sample saturated with ethylene glycol, and (3) the sample calcined at 500°C. The results are presented as TEMs (Figures 1 and 2) and XRD patterns (Figures 3 and 4). The bentonite contained about 61% montmorillonite, 30% mica, 5% chlorite, and 4% feldspar. The kaolin contained about 70% kaolinite, 18% mica, and 12% quartz.
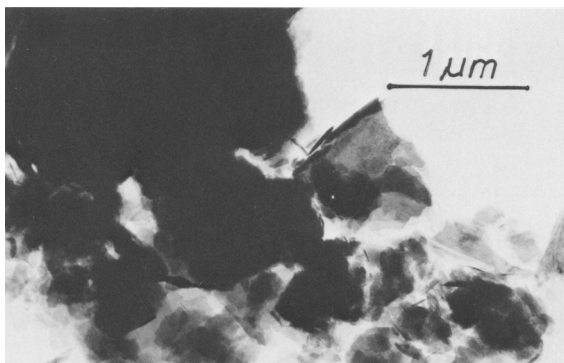

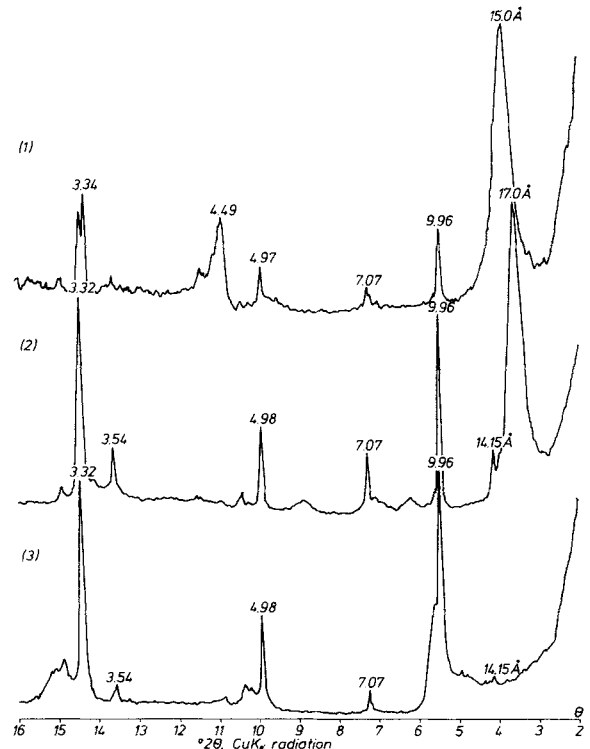Figure 2.   Transmission electron micrographs of kaolin.

Figure 3.   X-ray powder diffraction patterns of bentonite.

For sedimentation and SEM analysis, <2-μm fractions of the minerals were obtained by syphoning. The influence of calcium and sodium salt concentrations on the type and size of aggregates was studied using a Sartorius 4600 sedimentation balance, a detailed description of which was given in Bachmann (1959). The experimentally obtained curves of sedimentation (deposited mass vs. time) were numerically approximated by the equation:

$$m_s = A - A\exp(-bt^c)$$

where m_s is the mass deposited on the balance pan after time t, A is mass deposited on the pan after an infinitely long period of time, and b and c are the curve parameters determined for given experimental points by means of the least squares method. An aggregate distribution function, $\dfrac{dQ}{dr} = f(r)$, where Q is the number of particles of radius r in relation to the total number of particles, was determined from this equation. A mean weighted radius r_m was determined from the aggregate distribution function multiplying the r radius by the integral of $\dfrac{dQ}{dr}$ for r = 0 up to 60 μm. The value of r_m was determined for different concentrations of calcium and sodium nitrate in sedimented suspensions of bentonite and kaolin. The sedimentation curves were de-
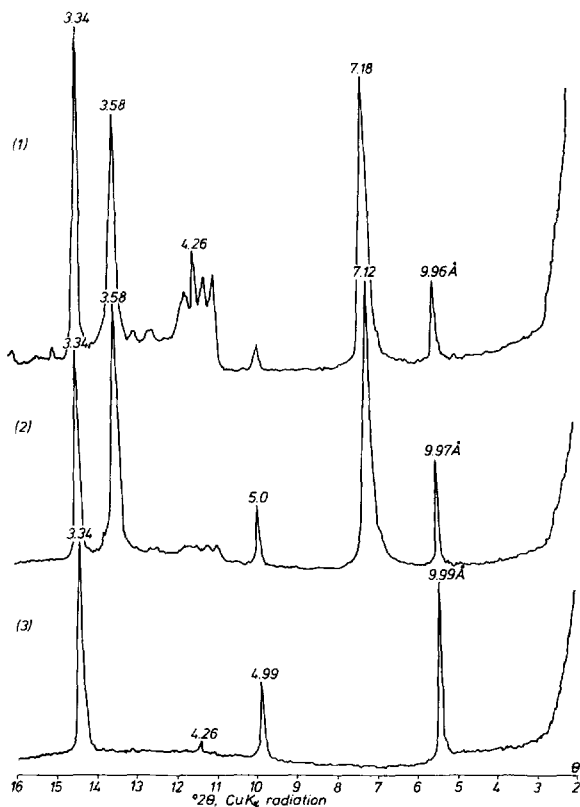
Figure 4.   X-ray powder diffraction patterns of kaolin.

Figure 5.   Relations between the mean associate radius, r_m, and Na^+, Ca^{2+} concentration for bentonite suspensions.

termined for 0.5% suspensions of the minerals in: water, $NaNO_3$ solutions (Na^+ concentrations from 0.1 to 100 meq/dm³ for bentonite and from 0.1 to 1.0 meq/dm³ for kaolin) and $Ca(NO_3)_2$ solutions (Ca^{2+} concentrations from 0.1 to 1.0 meq/dm³ for bentonite and from 0.02 to 1.0 meq/dm³ for kaolin). The dependence of the mean radius of aggregates r_m and Na^+ and Ca^{2+} concentrations determined on the basis of sedimentation analysis are shown in Figures 5 and 6.

To observe the microstructure of the studied sediments resulting from Na^+ and Ca^{2+} additions, SEMs were taken at the chosen concentration levels. Small aliquots of the sedimented deposits were rapidly frozen in liquid nitrogen to fix the microstructure (O'Brien, 1971). The frozen samples were freeze dried at $-30°C$ and 0.1 Pa for 24 hr. The dry samples were coated with gold and examined in the scanning electron microscope.

RESULTS AND DISCUSSION

The relation between the mean aggregate radius, r_m, and Na^+ and Ca^{2+} concentrations are presented in Figure 5 for bentonite and in Figure 6 for kaolin. The dashed lines are extrapolations of the curves to zero concentration. For bentonite, r_m decreased with an in-
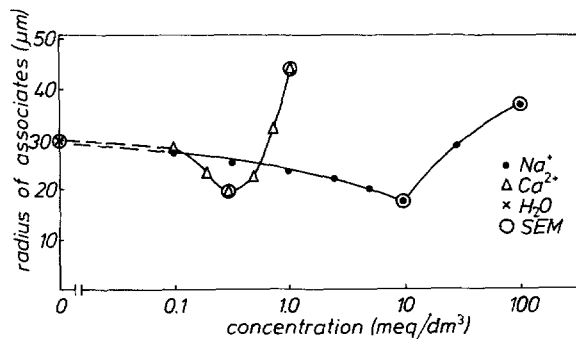
crease of Na^+ and Ca^{2+} concentration, reaching a minimum (~ 20 μm) for both cations at a concentration of 0.3 meq/dm³ for Ca^{2+} and 10 meq/dm³ for Na^+. Further increases in concentration led to an increase of r_m. Because the rate of sedimentation is proportional to the density of the dispersed phase and to the square of particle radius, the sedimentation rate should increase if particle aggregation takes place. Thus, a small increase of salt concentration (according to van Olphen, 1963) should lead to an initial deflocculation of aggregates and then (at less than the minimum value of the mean radius, r_m) to particle aggregation. For bentonite, the above processes took place at the lower concentrations in Ca^{2+} solutions than in Na^+ solutions, probably because of differences in the ability of these cations to compress diffusion double layer (Swartzen-Allen and Matÿević, 1974).

The function $r_m = f(c)$ followed a different course for kaolin (Figure 6). Here, the addition of salt did not lead to a decrease in r_m. The function increased slightly in the beginning and then more sharply. At the highest salt concentration a slight increase of the mean radius r_m was noted. The r_m changes in the kaolin suspension (as in the bentonite suspension modified with Ca^{2+}) took place at lower Ca^{2+} than Na^+ concentrations, and
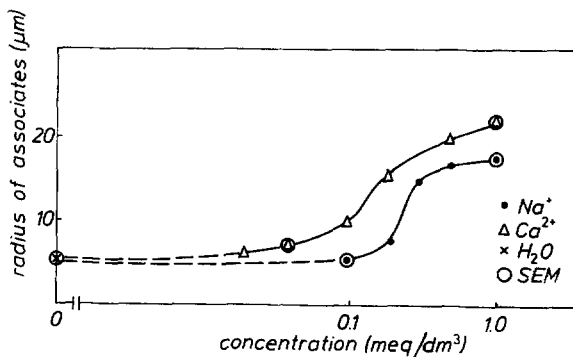

Figure 6.   Relations between the mean associate radius, r_m, and Na^+, Ca^{2+} concentrations for kaolin suspensions.
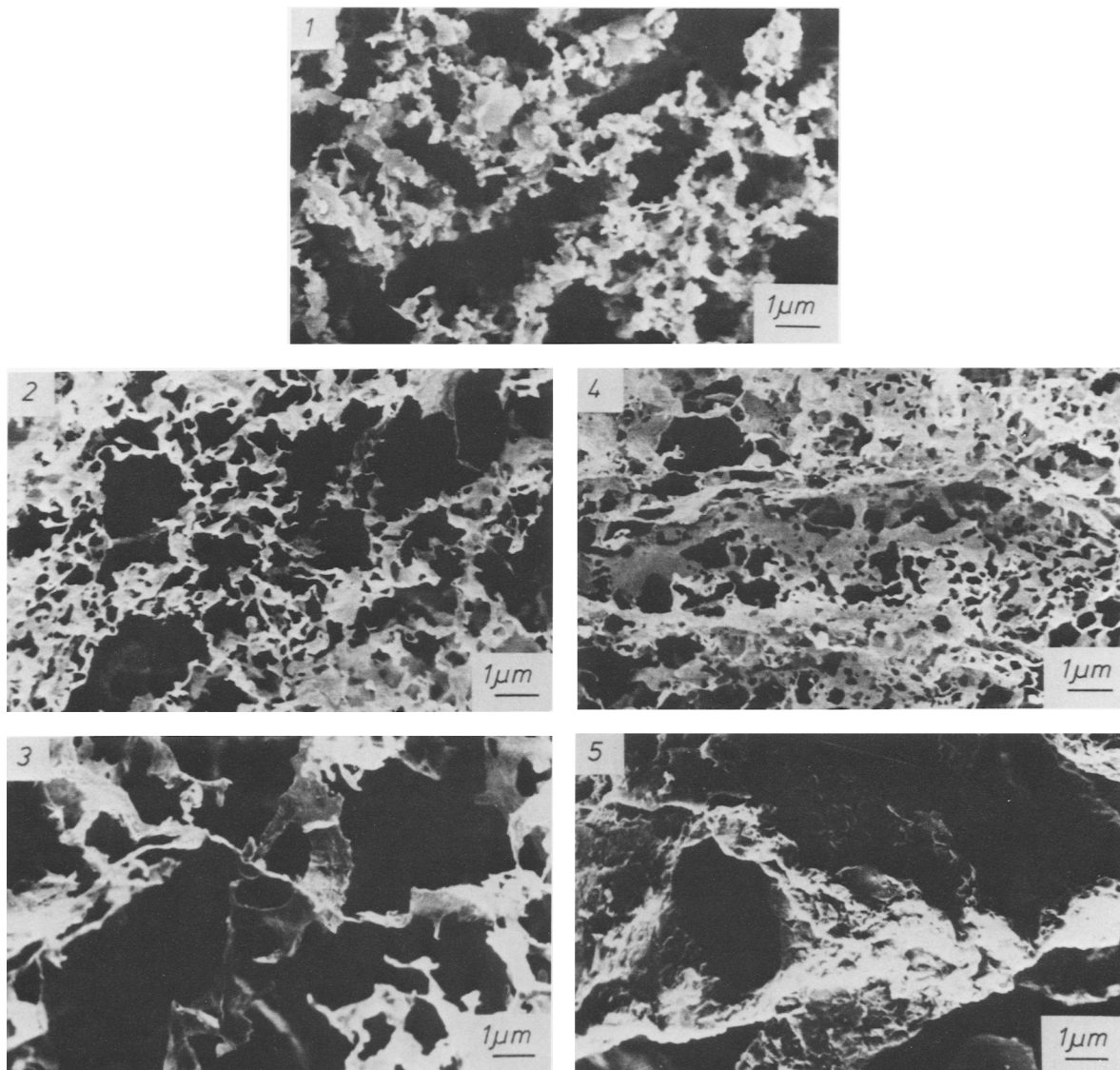
Figure 7. Scanning electron micrographs of bentonite sediments at various concentrations of Na^+ and Ca^{2+} (in meq/dm³). Figure 7.1, 0; Figure 7.2, 10 Na^+; Figure 7.3, 100 Na^+; Figure 7.4, 0.3 Ca^{2+}; Figure 7.5, 1 Ca^{2+}.

r_m values in the whole range of concentrations were higher, if the sample was modified by Na^+. In kaolin suspension, even a small addition of salt led to particle aggregation, in agreement with van Olphen (1963) and Schofield and Samson (1954).

Changes in r_m and the sedimentation rate were probably related to the size, shape, and internal structure of aggregates. SEMs of bentonite at specific Na^+ and Ca^{2+} concentration are shown in Figure 7. Figure 7.1 shows the microstructure of bentonite formed from a water suspension (with no addition of Na^+ or Ca^{2+} ions). The dominant type of aggregation was edge-to-face (E-F), leading to the formation of three-dimen-sional floccules. The addition of sodium salt to a Na^+ concentration of 10 meq/dm³ (Figure 7.2) led to the formation of thin platelets and thread-shape aggregates, with the edge-to-edge (E-E) type being dominant. A ten-fold increase in the Na^+ concentration (Figure 7.3) led to the formation of very compact irregular aggregates having a multi-layer structure of the face-to-face (F-F) type. The structure of bentonite aggregates modified by Ca^{2+} followed a similar course. At a Ca^{2+} concentration of 0.3 meq/dm³ (corresponding to the minimum r_m value), large floccules (of the E-E type) were observed (Figure 7.4). These floccules were larger than for those formed at the same Na^+ concentration.
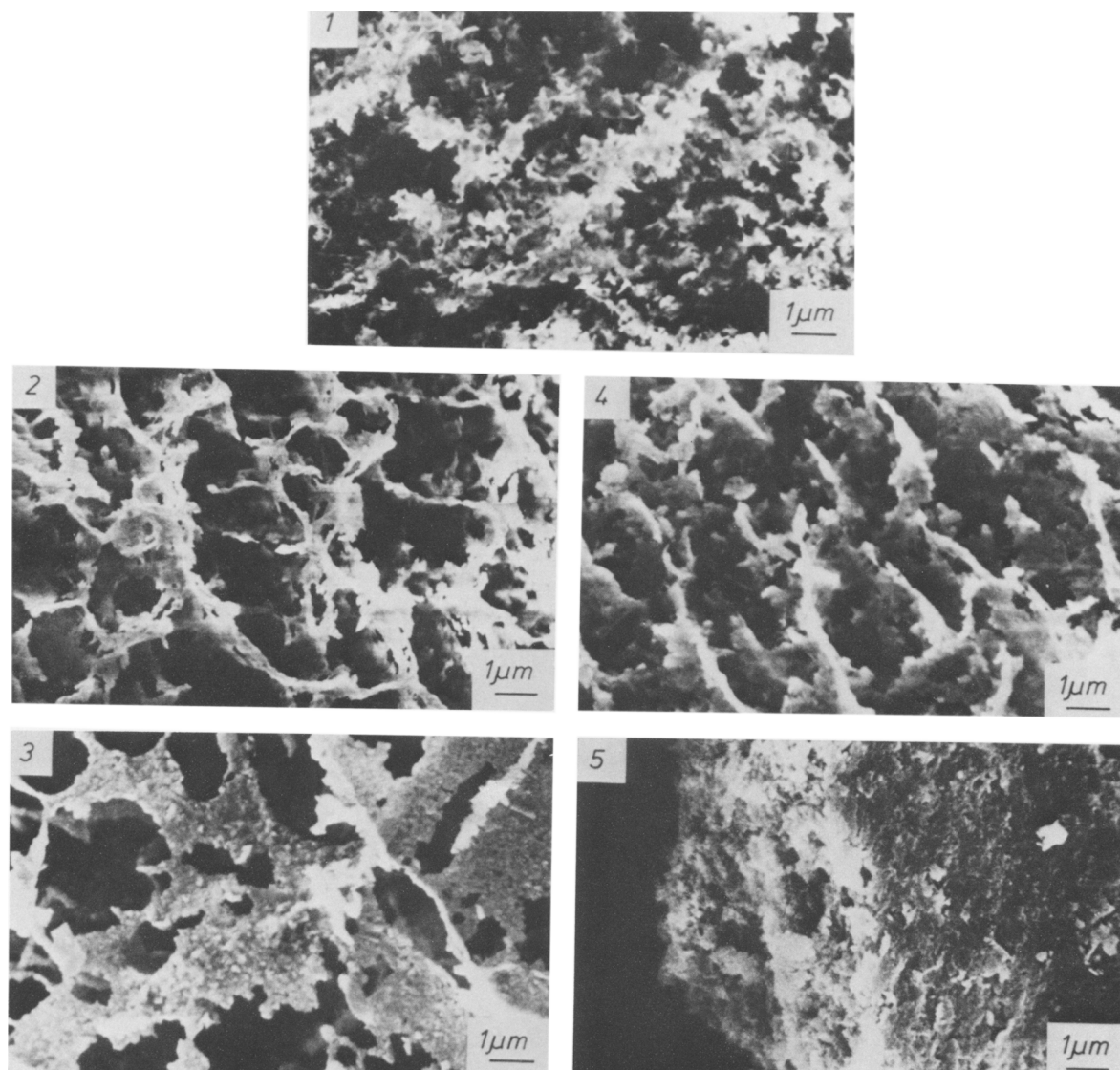
Figure 8.   Scanning electron micrographs of kaolin sediments at various concentrations of Na$^+$ and Ca^{2+} (in meq/dm^3): Figure 8.1, 0; Figure 8.2, 0.1 Na$^+$; Figure 8.3, 1 Na$^+$; Figure 8.4, 0.04 Ca^{2+}; Figure 8.5, 1 Ca^{2+}.

An increase of the Ca^{2+} concentration to 1 meq/dm^3 (Figure 7.5) led to the formation of compact F-F aggregates.

The SEMs of kaolin sediments (Figure 8.1) show the microstructure formed from the suspension with no Na$^+$ and Ca^{2+} additions. Here, E-F floccules dominated in three-dimensional floccules having honeycomb structures. A small addition of sodium salt, to a Na$^+$ concentration of 0.1 meq/dm^3 (Figure 8.2), produced mainly E-F floccules, also in the form of a honeycomb microstructure. Nevertheless, within microaggregates F-F aggregates were observed. Here, stairstep structures were noted inside of microaggregates, probably because of the partial translocation of kaolinite plate-

lets in relation to one another. O'Brien (1971) proved the existence of this type of kaolinite aggregate. A tenfold increase of the sodium salt concentration (Figure 8.3) led to the formation of larger plates, because of the increase in F-F interactions. The honeycomb microstructure (Figure 8.4) was observed in the kaolin sediment modified by Ca^{2+} at the concentration 0.04 meq/dm^3. Here, E-F aggregates (between the microaggregates) and F-F type (within the microaggregates) were dominant. An addition of calcium salt to 1 meq/dm^3 led to the formation of very compact aggregates of the F-F type, leading to the most compacted microstructure at the maximum Ca^{2+} concentration (Figure 8.5).

CONCLUSIONS

On the basis of the studies performed, the sedimentation results agree closely with the direct SEM observations. Different interparticle interaction types were dependent on the salt concentration.

ACKNOWLEDGMENTS

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