# EFFECT OF SALT ON THE FLOCCULATION BEHAVIOR OF NANO PARTICLES IN OIL SANDS FINE TAILINGS

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**Abstract**—Currently, two commercial plants, operating in the Athabasca region of Alberta, produce approximately 20 percent of Canada's petroleum requirements from oil sands. Surface mined oil sand is treated in a water based separation process that yields large volumes of clay tailings with poor settling and compaction characteristics. Clay particles, suspended in the pond water, interact with salts, dissolved from the oil sands ore, to produce mature fine tailings (MFT) containing only 20 to 50 w/w% solids. As a result, large sedimentation ponds are required to produce enough process water to recycle for the plant. Tailings pond dykes can only be constructed during a short summer season. Consequently, the capability to predict production rate and final volume of MFT is essential for mine planning and tailings disposal operations.

Previous research has demonstrated that a small fraction of nano sized clay particles (20 to 300 nm) effectively controls the bulk properties of MFT. These particles are present in the original ore and become mobilized into the water phase during the oil separation process. In this work, the nano sized particles have been separated from the bulk tailings and subjected to a fundamental study of their flocculation behavior in model tailings water.

Photon correlation spectroscopy and a deuterium NMR method were used to follow particle flocculation and gelation processes. These results were correlated with particle settling data measured under the same conditions. It was determined that the nano particles form fractal flocs that eventually interact to give a thixotropic gel. The ultimate sediment volume produced is almost entirely dependent on the original concentration of nano particles while the rate of water release is governed primarily by electrolyte concentration.

**Key Words**—Fine Tailings, Flocculation, Gelation, $^2$H NMR, Nano Particles, Oil Sands.

## INTRODUCTION

The Athabasca oil sands deposit in Alberta contains about $5 \times 10^9$ m³ of bitumen accessible by surface mining. Currently, two commercial plants are operating to produce approximately 20 percent of Canada's petroleum requirements. Bitumen is extracted from oil sands using the hot water extraction process (HWEP). Mined oil sands are mixed with steam and hot water to which a small amount of sodium hydroxide was added. After gravity separation of bitumen, the remaining aqueous slurry of sand and clay is transported to sedimentation basins where the solid particles are settled out to separate "clean" water to recycle for the extraction process. Coarser solids are used to form the containment dykes while the remainder of the tailings is discharged to the pond over a beach. Approximately one-half of the silt and clay and almost all of the residual bitumen remain in suspension and flow to the center of the pond. Eventually, mature fine tailings (MFT), having a characteristically low compaction rate form as a distinct layer in the pond. Tailings toxicity, loss of bitumen, diluent naphtha and process water are among the problems associated with the build-up of these fine tailings (Camp 1977).

The gelling, evident in the formation of MFT in the field, has been attributed to the presence of nano-sized, inorganic particles found in all oil sands ores (Kotlyar et al. 1992a, 1992b, 1993). This fraction comprises delaminated aluminosilicate clays only a few layers thick. Particle sizes are in the range of 20 to 300 nm. During processing, the ores are subjected to mechanical dispersion forces which result in mobilization, or liberation, of these nano particles into the process water. Even though these particles are present in only minor amounts they are capable of forming thixotropic gels, ultimately producing fine tailings with a high water holding capacity. Consequently, large sedimentation ponds are needed to provide adequate fine tailings storage capacity and process water for recycling. Tailings pond dykes can only be constructed during a short summer season. Therefore, the capability to predict production rate and final volume of MFT is essential for mine planning and tailings disposal operations.

The degree of nano particle flocculation and gelation and hence, the rate of MFT formation, is dependent on several factors. One of the most important is the amount and type of electrolytes in the process water. Sodium chloride, or common salt, is the major electrolyte component in tailings water and is the dominant contributor to the aggregation of nano-sized clay particles present in the tailings. This salt is extracted from oil sands ore during processing. Because water

is constantly recycled the salt concentration is continually increasing. Also, future mine expansion will encounter new ore bodies containing higher salt concentrations than those found in the currently mined ore. The objective of predicting, and possibly mitigating, MFT formation therefore requires an understanding of the behavior of nano particle clays suspended in salt solutions covering the range of concentrations likely to be encountered in existing and future tailings pond water.

In recent years, photon correlation spectroscopy (PCS) has been commonly used to study aggregation processes in model colloid systems at low solids concentration (Weitz et al. 1991; Cametti et al. 1989; Hoekstra et al. 1992). This technique provides information on floc structure in terms of self-similarity and corresponding fractal dimension. In this work, we use this same kinetic approach to study the flocculation of nano particles from oil sands fine tailings in model process water containing different concentrations of salt. These results were correlated with settling data for the same suspensions.

We also examined the effect of salt concentration on gel formation of more concentrated (0.4 to 3.1 vol.%) suspensions of nano particles by a $^2$H NMR method recently developed in our laboratory (Ripmeester et al. 1993). In the latter tests, nano particle concentrations were more typical of those found in actual MFT samples. A gelation index, calculated from the NMR data, provides an insight into the progression of the structure forming process. These suspensions, still in their NMR tubes, were also used to determine sediment volumes as a function of time.

Our results are discussed in terms of the influence of salt concentration on MFT properties such as: settling rate, differential settling and final sediment volumes or equivalent solids' content. This information is expected to provide predictability for tailings formation based on a knowledge of pond water quality and processed ore type.

### EXPERIMENTAL MATERIALS AND METHODS

#### Materials

Mature fine tailings (20 L) was supplied by Suncor Inc. After mixing, the sample was sub-divided. The composition of the sub-samples ranged from 26 to 31 wt.% solids and 1 to 2 wt.% bitumen, the remainder was water.

Deuterated water, containing 99.9 atomic % deuterium ($^2$H) was supplied by MSD Isotopes.

#### Separation of Nano-Sized Clay Particles from Bulk MFT

For this work, nano particles were selectively separated from MFT by a technique described by Kotlyar (1992a). MFT samples were subjected to vigorous me-

chanical agitation followed by mild centrifugation for two h at a relative centrifugal force (RCF) of 500 gravities. This treatment resulted in layering of the MFT into several components, each with distinct properties. Nano-sized clay particles ($\leq$200 nm) separate as an aqueous suspension, which can easily be removed from the remaining solids by decantation.

In MFT, nano-sized clay particles exist in two forms. Most of the particles exhibit hydrophilic surface properties, however, about 20 wt.% display some hydrophobic characteristics. In the latter case the particles collect at oil-water interfaces, indicating biwettable characteristics. These biwetted particles are known to accelerate the flocculation and gelation process (Kotlyar et al. 1994).

In order to prepare reproducible test samples, the suspended particles were deflocculated by replacing the pond water with distilled water in a series of sequential washing and centrifuging steps (Kotlyar et al. 1992b). A concentrated suspension, containing 3.1 vol.% of dispersed solids, was prepared by decanting off the supernatant water after high speed ultra-centrifugation. This sample was used as a stock suspension for both light scattering and $^2$H NMR experiments.

#### Light Scattering Measurements

Dynamic light scattering experiments were performed using a Malvern 4700 PCS system, utilizing a 15 mW 633nm He-Ne laser. Measurements of scattered light were made at a scattering angle of 90° using a 64 channel autocorrelator. The autocorrelation functions were analyzed by the method of cumulants (Berne and Pecora 1976). The first cumulant, $\Gamma_1$ of the correlation function was used to obtain the translational diffusion coefficient D, from:

$$D = \Gamma_1/q^2 \qquad [1]$$

where q is a scattering vector. Knowing D and the Stokes-Einstein relationship allows the mean hydrodynamic radius, $R$, to be calculated from the following equation:

$$D = k_b T/6\pi\eta R \qquad [2]$$

where $\eta$ is liquid viscosity, T is absolute temperature and $k_b$ is Boltzmann's constant.

The dilute colloidal suspensions for these tests were prepared from the stock suspension by addition of appropriate volumes of salt solution with the desired concentration. Final solids concentration was 0.06 vol.%. The value of $R$ was determined at intervals of two to three minutes over a period of several hours. For sedimentation studies, the nano particle concentrate was also diluted to 0.06 vol.% with the same salt solutions. The resulting suspensions were allowed to settle in 100 mL cylinders for several months.
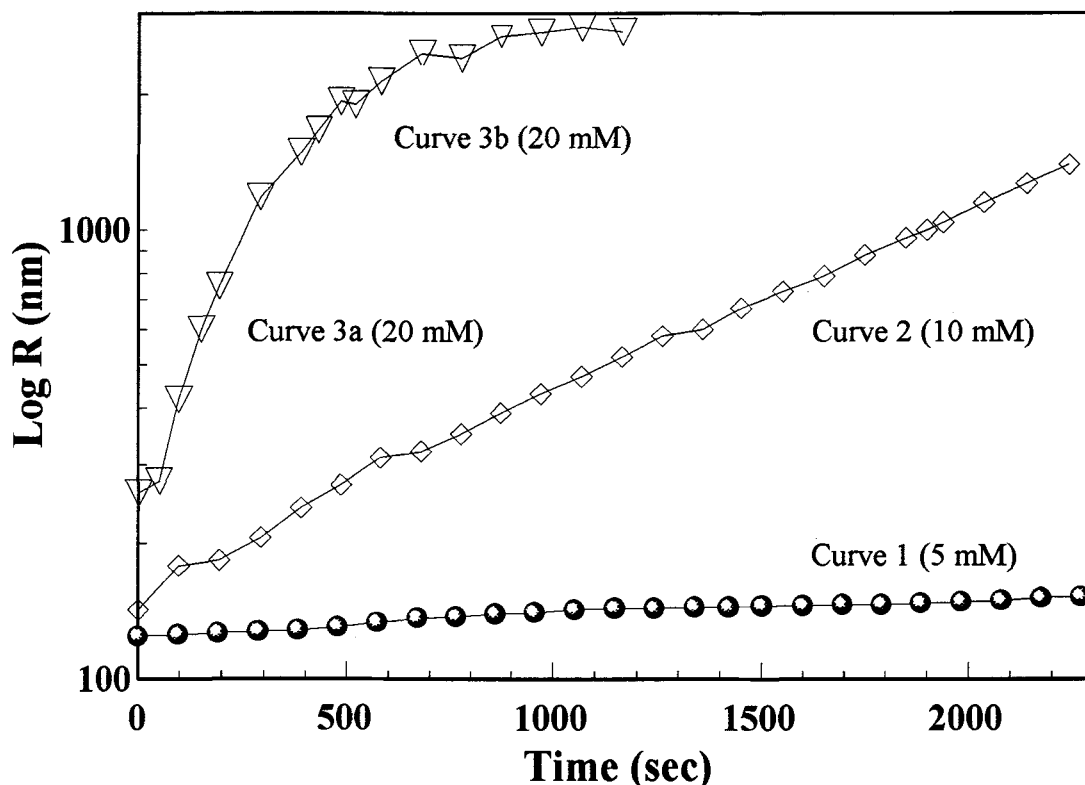
Figure 1. Nano particle cluster size versus time for different salt concentrations.

## Gelation Measurements

The samples for $^2$H NMR gelation studies were prepared by replacing the distilled water in the stock suspension of nano particles with model pond water, using the reverse of the procedure described above. The replacement water contained sodium chloride in concentrations ranging from 5 to 20 mM. Previous experience (Kotlyar et al. 1992b) has shown that this process of water replacement is completely reversible. A series of nano particle suspensions with solids concentrations ranging from 0.4 to 3.1 vol.% (1 to 8 wt.%) were prepared at different salt concentrations; about 7 wt.% of $^2$H$_2$O was added to each of the suspensions.

Deuterium Nuclear Magnetic Resonance spectra were recorded with a Bruker MSL 300 spectrometer in a magnetic field of 7.1 Tesla at a frequency of 46.07 MHz. In typical experiments, 16 transients were acquired in 8K points, with a spectral width of 1000 Hz. In order to obtain consistent results at zero time, each suspension sample was vigorously agitated immediately before loading into the NMR instrument for the first time. This precaution ensured that any gel structure in the sample was destroyed. After the first measurement, the sample tubes were removed and the sol-gel transition was allowed to take place outside the magnetic field. Samples were re-inserted into the instrument at regular time intervals and removed again after completion of each measurement. Spectra for each time interval were compared in order to follow changes in the gelation process.

### RESULTS

#### Flocculation of Dilute Suspensions

The flocculation behavior of nano particles, diluted to 0.06 vol.%, with distilled water or 5 through 20 mM solutions of salt, was monitored by PCS measurement of the mean hydrodynamic radius, $R$, of the growing flocs. In deionized water, the radius of suspended particles remained constant over the test period, suggesting a suspension with high colloidal stability. Resistance to aggregation of approaching particles is generally attributed to the repulsive energy barrier which is greater than the kinetic energy of the particles (Verwey and Overbeek 1948).

Figure 1 shows plots of particle cluster size against time for several concentrations of salt. For suspensions having low 5 mM electrolyte concentration, the repulsive energy barrier between particles is expected to be of the same order of magnitude as their kinetic energy. In these circumstances, aggregation rate is still limited by the need to overcome the repulsion barrier. Nevertheless, a very slow, exponential growth in floc size occurs (Figure 1, curve 1). This regime corresponds
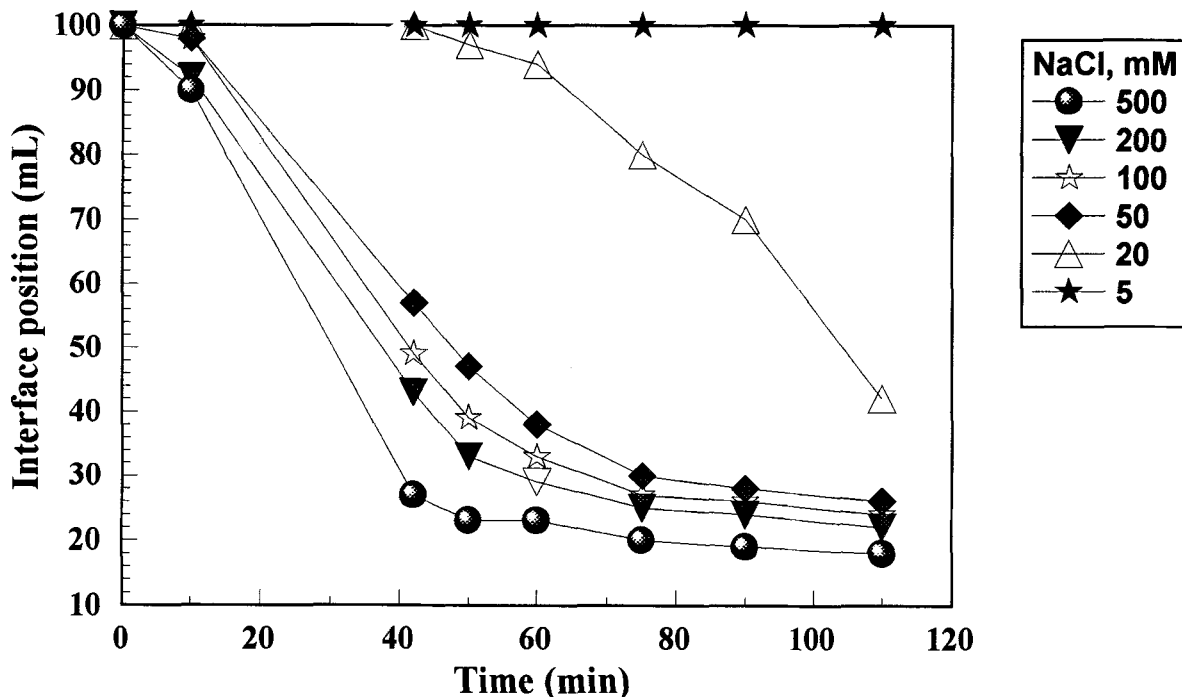
Figure 2.   Time dependence of water release (mL) from dilute suspensions of nano particles in salt solutions of different concentrations.

to reaction limited aggregation and is characterized by a collision sticking probability of less than unity.

An increase in salt concentration to 10 mM results in a further decrease in the repulsive energy barrier. The probability of "sticking" collisions between particles increases and there is a corresponding increase in the aggregation rate (Figure 1, curve 2).

At a salt concentration of 20 mM, two different flocculation regimes are apparent (Figure 1, curves 3a and 3b). Initially, aggregation is reaction limited and exponential growth occurs (Figure 1, curve 3a). Beyond a certain aggregate size, further growth is best described by a power law relationship (Figure 1, curve 3b), corresponding to a diffusion limited regime. In the latter case, the salt concentration is high enough to reduce the repulsive barrier to a level such that the sticking probability for each inter-particle collision is close to unity. These two aggregation regimes are commonly observed for model colloidal systems (Weitz et al. 1991; Cametti et al. 1989; Hoekstra et al. 1992).

It has been reported that, for diffusion limited aggregation (Weitz et al. 1984), the hydrodynamic radius of particle clusters ($R$) may be represented by the following equation:

$$R \sim \left[\frac{4CokT}{3\eta Mo}\right]^{1/d_f} t^{1/d_f} \qquad \text{for } R >> R_0 \qquad [3]$$

where $Co$, $Mo$ are initial particle concentration and mass, while $k$ is Boltzmann's constant, $T$ is temperature, $\eta$ is viscosity, $t$ is time and $d_f$ is fractal dimension of the clusters, or flocs. In this approach, a logarithmic plot of $R$ against $t$ should be a straight line with slope equal to $1/d_f$. A plot of the data from the diffusion limited region (Figure 1, curve 3b) gives a straight line (correlation coefficient is 0.93) with a slope of 0.56, corresponding to a fractal dimension of 1.79. These results indicate that the nano particle component of MFT form fractal clusters.

Settling of Dilute Suspensions

In order to compare the settling behavior of the fractal clusters formed in different aggregation modes, we prepared 0.06 vol.% suspensions of nano particles in both deionized water and salt solutions. In the latter case, a range of 1 to 500 mM included concentrations both lower and higher than that required to induce diffusion limited aggregation. Settling rates, as determined by the position of the interface between sediment and clear water, in terms of mL in the volumetric cylinders, were monitored (Figure 2). Equivalent final volumes, or vol.% of solids in the sediment, were estimated from the volumes of sediment and clear water released.

A photographic record of the suspensions was maintained. Over the study period, suspensions in salt so-
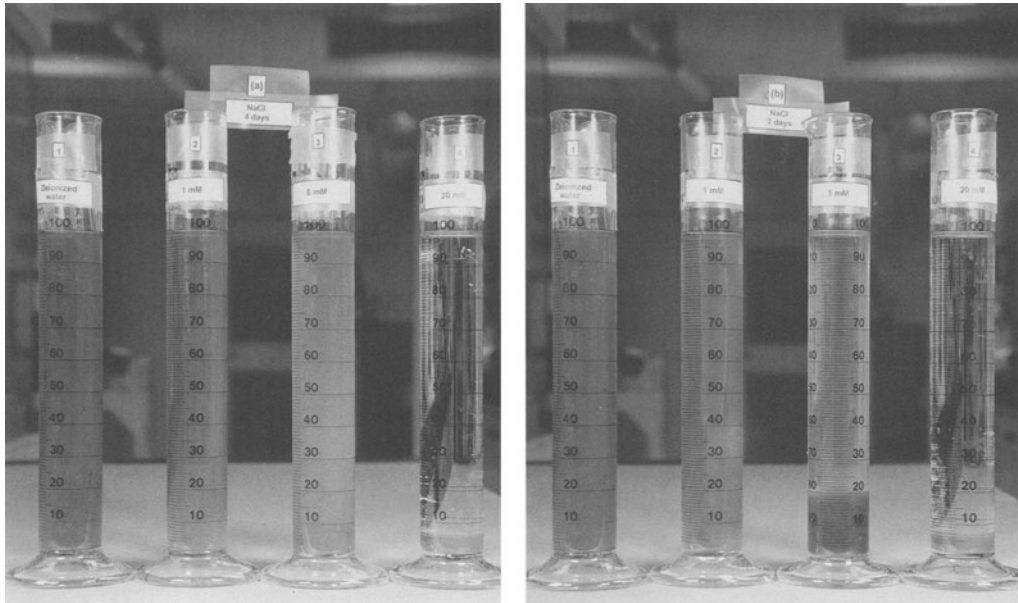
Figure 3.    Effect of salt concentration on the settling behavior of dilute suspensions of nano particles.

lutions of 1 mM or less remained completely stable as shown by cylinders 1 after 4 days and 2 after 7 days (Figure 3a and b). For a salt concentration of 5 mM, flocculation is reaction limited and differential settling behavior is observed. Similar results have been reported by others (Lin et al. 1990). Those particles that have a lower resistance to flocculation, aggregate and settle first. The remaining solids stay in suspension above this faster settling layer (Figure 3, cylinder 3). Variations in particle size, shape, electrical properties and the presence of surface adsorbed organic matter are among the factors responsible for this phenomenon. Differential settling is expected to create conditions favorable for the formation of segregating mixtures. In tailings handling, such a situation is undesirable as it leads to lower overall solids content in the MFT.

At salt concentrations $\geq 20$ mM, diffusion limited aggregation results in a rapid initial aggregation followed by fast settling. The corresponding settling curves are shown in Figure 2. The rate of settling increases with concentration of salt. Rapid aggregation and settling of this type usually results in the formation of non-segregating mixtures where coarser solids are entrapped by the flocs. For tailings disposal, this effect is beneficial as it leads to a sediment with a higher solids' content. Under these conditions the settling interface is typically distinct and the supernatant water completely clear. The suspension in cylinder 4 (Figures 3a and 3b), shows behavior of this type.

These observations of settling behavior also show that changes in interface position, for diffusion ex-

tremely slow after 10 h and reaction limited aggregation modes after 400 h In Figure 4, we plot the final settled solids concentration (vol.%) in the sediments vs salt concentration (mM) in the suspending medium. Initial solids concentration was 0.06 vol.% in all cases. At the lower salt concentrations, reaction limited aggregation produces smaller, more compact clusters compared to the voluminous, fractal clusters formed in the diffusion limited mode at higher salt concentrations (Lin et al. 1990). As a result of this difference in cluster morphology, the concentration of solids in the sediments decreases as salt concentration increases. Consequently, entrapment of the continuous phase is higher under these conditions. This is an undesirable operational result as it leads to higher volumes of MFT for storage and ultimate disposal.

## Flocculation of Concentrated Suspensions

The results discussed so far have shown that the fractal flocs, formed in both aggregation regimes, settle freely until the concentration of nano-sized particles reaches 1 to 1.4 vol.%. At this point, the inter-floc distances are small and the clusters begin to interact. Ultimately, at the critical gel concentration (CGC), a giant cluster, spanning the containment system, is formed (Brinker and Scherer 1990). At this point, the system behaves as a gel and very little compaction occurs. However, solids content may still increase through entrapment of coarser solids settling into the MFT zone.

During the floc growth period steric hindrance substantially reduces the mobility of the clusters and [2]H
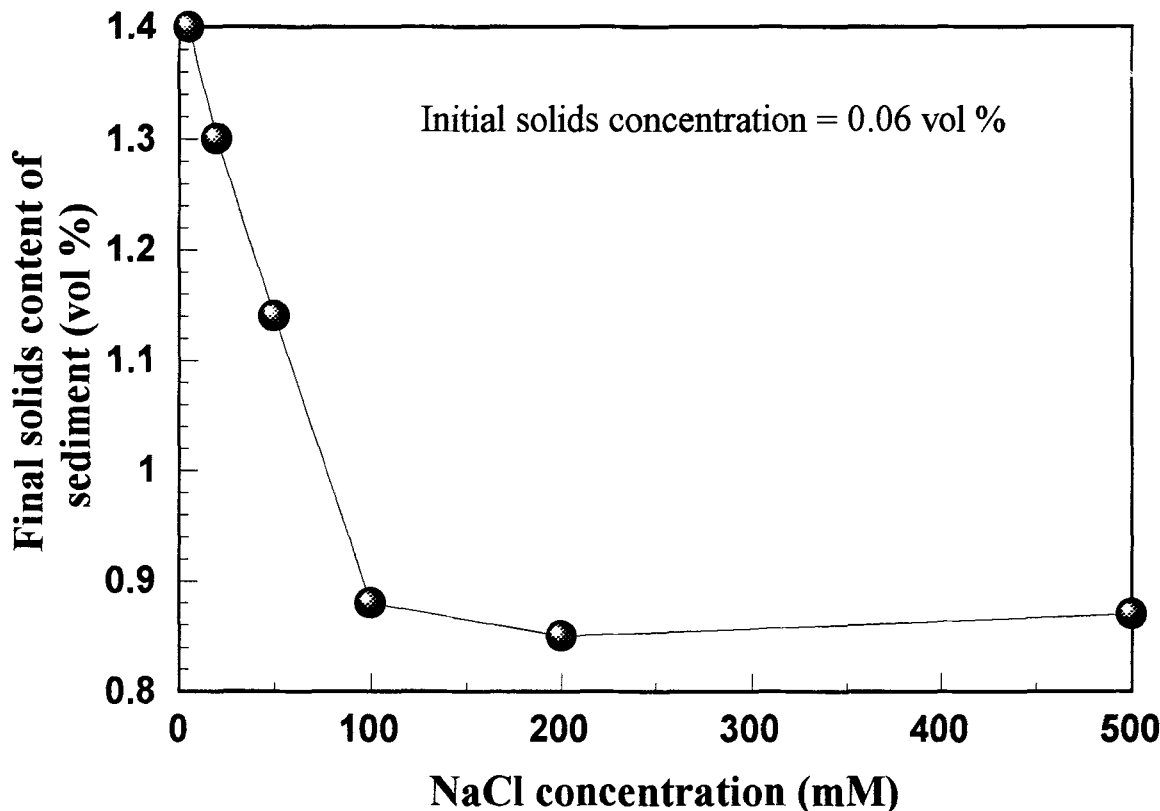
Figure 4.   Effect of salt concentration on solids content of sediments after six months settling.

NMR can be used to monitor the sol-gel transition period, as done by Ripmeester et al. (1993). The method relies on observation of the splitting, $\Delta$, of the deuterium peak as a function of time. This splitting occurs due to the rapid exchange of deuterium molecules between the bulk water and particle surface environments. As a gel structure forms, deuterium exchange is inhibited and the splitting gradually disappears. A gelation index, I, is calculated from the difference between the normalized change in $^2H$ NMR peak splitting at times zero ($\Delta_0$) and t ($\Delta_t$), according to the following equation:

$$I = \{(\Delta_0 - \Delta_t) \times 100\}/\Delta_0 \qquad [4]$$

This index reflects a change in mobility caused by cluster formation, which is itself related to the degree of gelation. Values of I range between 0, (sol or dispersion) to 100 (at the CGC).

In this work, we monitored the growth of gel networks for nano particles dispersed in either distilled water or salt solutions having concentrations ranging from 5 mM through 500 mM. Solids concentrations in the suspensions varied from 0.4 to 3.1 vol.%. The latter concentration is typical for MFT samples from tailings ponds. Observations were continued for up to six days. Figures 5 and 6 are three-dimensional plots exhibiting the dependence of gelation index on time and solids' concentration.

In deionized water, the nano particles remained dispersed, as indicated by a gelation index of zero at all solids concentrations (Figure 5a). The behavior of suspensions in 5 mM solution shows that gelation under these conditions is dependent on both time and solids concentration (Figure 5b). For all samples, gelation index increased rapidly during the first 8 hours. After this initial change, a slower rise in gelation index occurred during the remaining 130 hours of the test. In each case substantial thickening of the suspension occurred, resulting in a mobility loss of 65 to 85 percent. However, none of these samples produced a stiff gel during the observation period.

For 20 mM salt solution, see Figure 6a, gelation was much more pronounced. All suspensions produced a stiff gel after 16 hours. At a salt concentration of 50 mM it took only 8 minutes for a stiff gel to form at all solids concentration, see Figure 6b. Where solids contents were less than the CGC (about 1 vol.%) aggregation and settling of nano particles were very fast. Under these conditions, NMR measurements were not reliable. Suspensions in salt solutions with concentrations ≥100 mM gelled almost instantaneously, but the results are not shown.
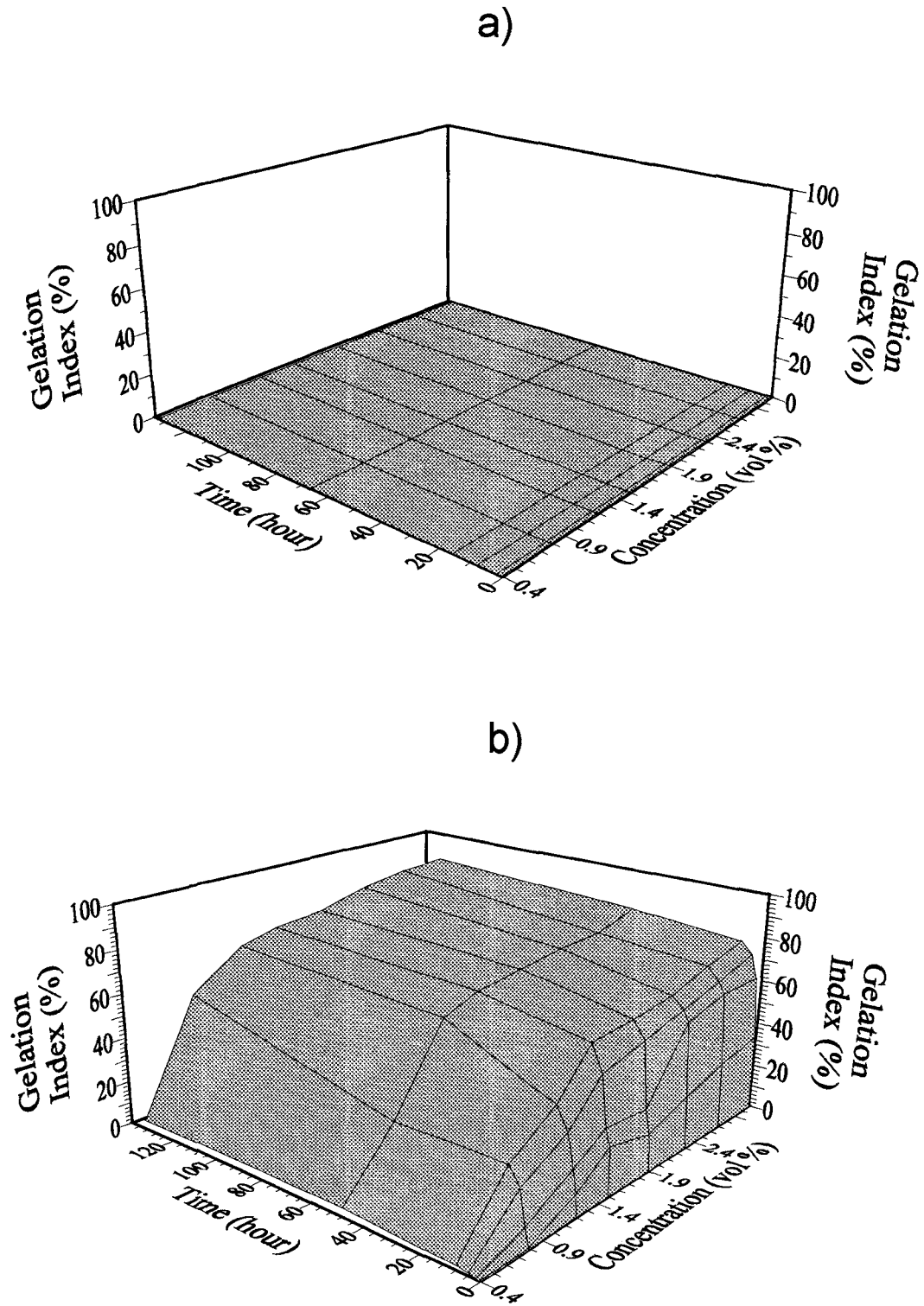
a)



b)



Figure 5. Time and concentration dependence of gelation index for nano particles in a) de-ionized water and b) 5 mM solution of salt.
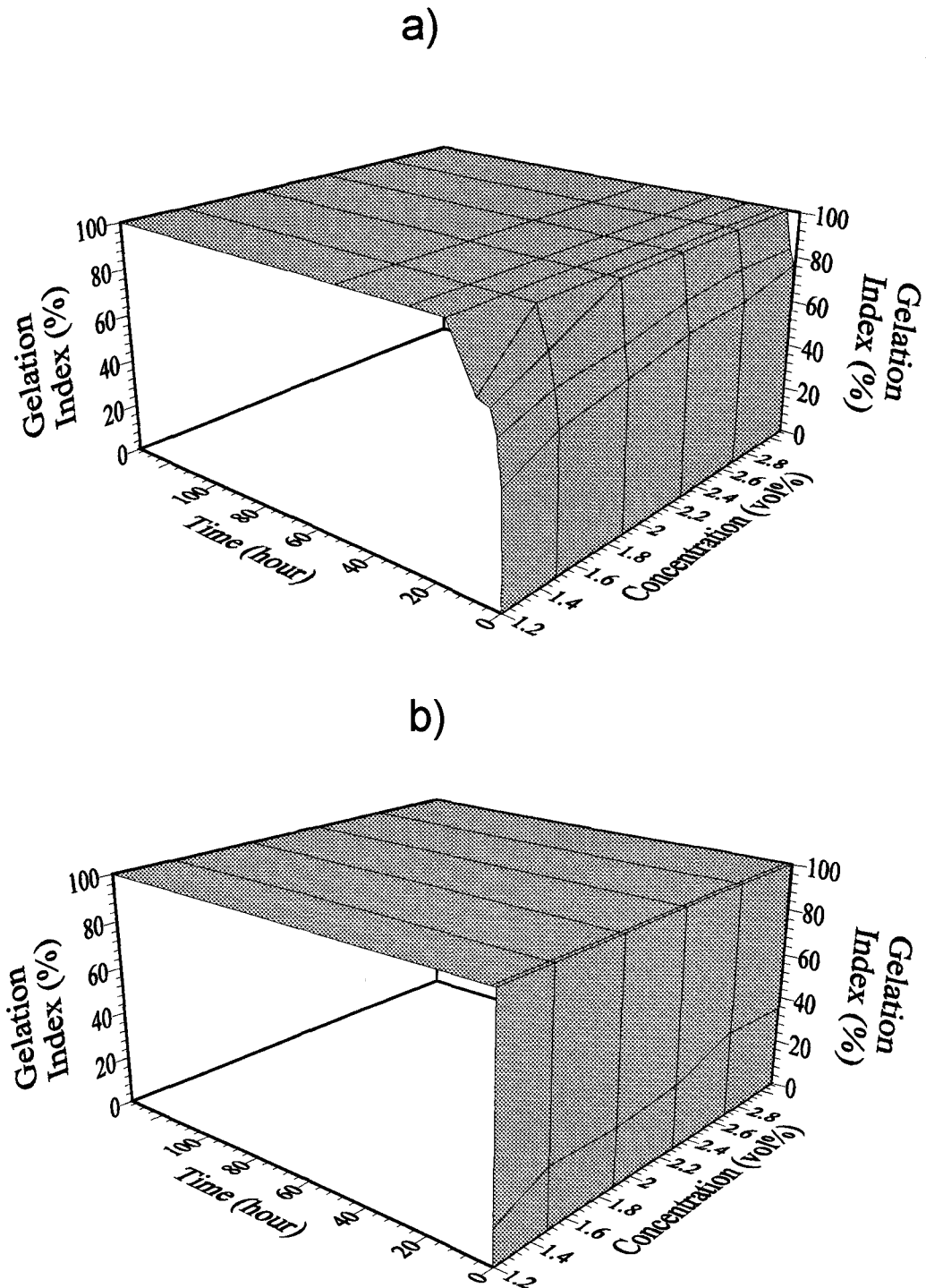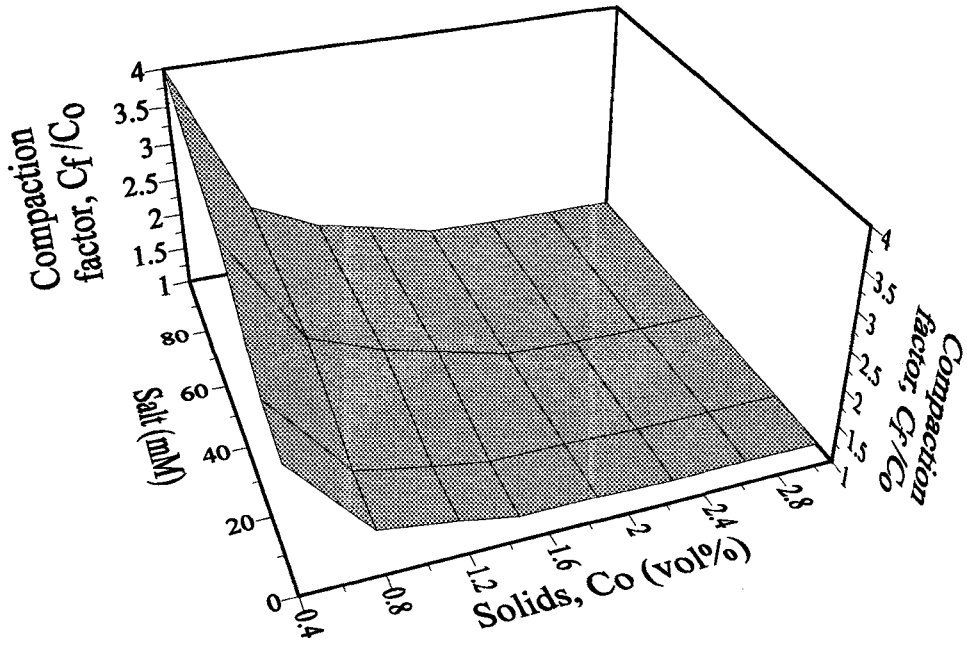
Figure 6.    Time and concentration dependence of gelation index for nano particles in a) 20 mM and b) 50 mM salt solutions.
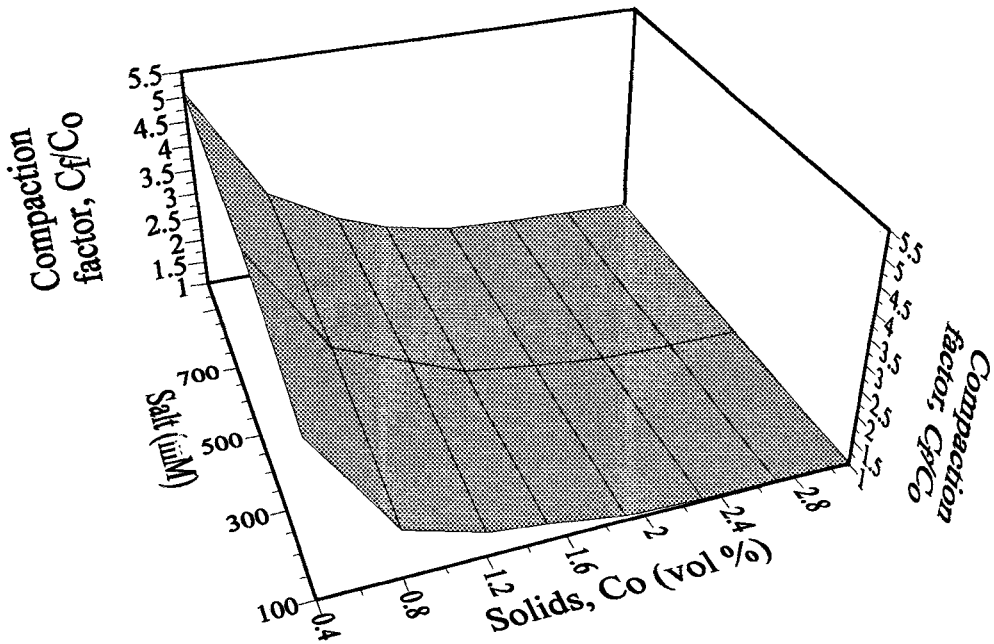
## a)



## b)



Figure 7.   Compaction factors ($C_f/C_0$) as a function of initial solids concentrations for solutions with salt concentrations of a) 5-100 mM and b) 100-1000 mM.

Settling of Concentrated Suspensions

The ultimate objective of this work was to determine the effect of salt concentration on final sediment volumes, or equivalent solids contents. Consequently, clear water release from the settling suspensions was followed for six months or until no further change was detected. It should be mentioned here that suspensions of nano particles in deionized water, at all solids concentrations from 0.4 to 3.1 vol.%, showed no signs of aggregation during this whole period.

Solids concentrations, at time zero ($C_0$) and after six months ($C_f$), were used to calculate compaction factors, $C_f/C_0$, for each suspension. Three dimensional plots, showing $C_f/C_0$ as a function of salt concentration and initial solids concentration, are given in Figures 7a and 7b. At a salt concentration of 5 mM the flocs in the most dilute suspensions settled freely until the CGC (about 1 to 1.4 vol.% solids) was reached, which corresponds to a solids compaction factor of up to 2.4. Where the solids content was initially greater than the CGC the compaction factors remained close to unity, indicating little change in sediment solids' concentration over time. Similarly for 20–100 mM salt solutions, compaction factors for suspensions containing the lowest particle concentrations, decreased from 2.6 to 4.0, for 0.4 vol.% samples, to unity for samples with initial concentrations equal to or greater than the CGC (Figure 7a). Figure 7b shows that for salt solutions with concentrations greater than 100 mM, the general trend for sediment compaction remains the same. However, it should be noted that the most compact flocs are found at the highest salt concentrations used.

### DISCUSSION AND CONCLUSIONS

Nano-sized clay particles are present in oil sands MFT and may be isolated as a separate fraction. In dilute suspensions, the aggregation of these particles were dramatically affected by the amount of electrolyte present in the system. It has been demonstrated that the nano particles form fractal clusters in both reaction and diffusion limited aggregation regimes. From a plant operation standpoint, this is an important feature of these results. Fractal flocs show decreased packing density with increased cluster size (Mandelbrot 1982). In contrast, nonfractal structures are more compact and exhibit a uniform porosity (Brinker and Scherer 1990). The corollary to this observation is that high salt concentrations (>20 mM) will increase rate of water release from the tailings but coincidentally produce a greater final sediment volume through the formation of more open flocs.

The salt concentration in the dispersion medium not only affects particle settling rates, and therefore the rate of water release, but also the type of sediment formed. For example, slow aggregation leads to segregation by particle size, whereas fast aggregation

leads to non-segregating behavior in which coarser particles may become entrapped in the floc network. Both of these parameters are also important characteristics for tailings streams generated by oil sands extraction plants.

The fractal clusters settle freely until steric interference between them produces a weak gel structure. After gelation the reduced mobility of the growing clusters allows use of a $^2$H NMR technique to demonstrate that the gelation process is dependent on time as well as salt and nano particle concentration. A concentration of only 1 to 1.5 vol.% of nano particles is required to produce a space filling, gel network. Solids concentrations, in excess of this amount, produce more flocs that occupy the available spaces, within the limit of the gel network without significantly changing its overall volume.

The individual flocs formed in a tailings pond are voluminous and the resulting gel network is capable of immobilizing large amounts of process water. Salt concentration is the factor that most affects the rate of gelation. However, when the initial concentration of nano particles exceeds the minimum requirement for gelation, the final sediment volumes and the equivalent solids content, are virtually independent of salt and nano particle concentration.

Slower gelation rates produce sediments with the highest compaction factor. However, in a dynamic pond environment, such systems also lead to the undesirable characteristic of size segregation. Fast gelling systems are capable of entrapping coarser solids to produce an MFT with overall higher solids content. Operation of a tailings pond must be optimized to account for these conflicting characteristics.

### REFERENCES

Berne BJ, Pecora R. 1976. Dynamic Light Scattering. New York:Wiley. 376p.

Brinker CJ, Scherer GW. 1990. Sol-gel science: The Physics and Chemistry of Sol-gel Processing. Boston: Academic Press Inc. 908p.

Cametti C, Codestafano P, Tartaglia P. 1989. Aggregation kinetics in model colloidal systems: a light scattering study. J Coll Interf Sci 131:409–422.

Camp FW. 1977. Processing Athabasca tar sand: tailings disposal. Proceedings 26th Can. Chem. Eng. Conference, Symp. on Tar Sands, Toronto. Paper 9a.

Hoekstra LL, Vreeker R, Agterof WGM. 1992. Aggregation of colloidal nickel hydroxycarbonate studied by light scattering. J Coll Interf Sci 151:17–25.

Kotlyar LS, Sparks BD, Schutte R, Capes CE. 1992a. Gel forming attributes of colloidal solids from fine tailings, formed during extraction of bitumen from Athabasca oil sands by the Hot Water process. AOSTRA J Res 8:55–61.

Kotlyar LS, Lynds MM, Sparks BD, Schutte R, Woods JR. 1992b. Colloidal solids from sludge: effect of particle size on gel forming propensity in distilled and pond water. To Oil Sands Fine Tailings Fundamentals Consortium, NRCC Internal Report. EC-1243-92S, Ottawa, Ontario, Canada.

Kotlyar LS, Deslandes Y, Sparks BD, Kodama H, Schutte R.

1993. Characterization of colloidal solids from Athabasca sludge. Clays and Clay Miner 41:341–345.

Kotlyar LS, Sparks BD, Deslandes Y, Schutte R. 1994. The role of biwetted colloidal solids in structure formation in oil sands fine tailings. Fuel Sci Technol 12:923–935.

Lin MY, Lindsay HM, Weitz DA, Ball RC, Klein R, Meakin P. 1990. Universal reaction limited colloid aggregation. Phys Rev 41:2005–2020.

Mandelbrot BB. 1982. The fractal geometry of nature. San Francisco:W.H. Freeman. 460p.

Ripmeester JA, Kotlyar LS, Sparks BD. 1993. $^2$H NMR and the sol-gel transition in suspensions of colloidal clays. Colloids and Surfaces 78:57–63.

Verwey EJW, Overbeek JTG. 1948. Theory of stability of lyophobic colloid. Amsterdam:Elsevier. 205p.

Weitz DA, Huang JS, Lin MY, Sung J. 1984. Dynamics of Diffusion-Limited Kinetic Aggregation. Phys Rev Lett 53: 1657–1660.

Weitz DA, Lin MY, Lindsay HM. 1991. Universality laws in coagulation. Chemomet Intell Lab Syst 10:133–140.