

Centrifugal consolidation of MgO-suspensions – The Influence of Superplastisizers on Particle Packing

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ABSTRACT

The effect of superplasticizers on the centrifugal consolidation behaviour of magnesia suspensions has been studied. The superplasticizers adsorb onto the MgO surface and infer a steric repulsion that reduces the degree of flocculation. The density profiles of the particulate cakes have been measured and the maximum volume fraction of the consolidated particle network is related to the inter-particle force. The implications of this simple compression rheological method for evaluating the stabilizing mechanism of superplasticizers are discussed.

INTRODUCTION

The durability of concrete is promoted by a low porosity of the binder, which is related to the packing of the particles and the following hydration reactions. However, the placement of concrete is facilitated by a high water content that improves the flowability. The maximum volume fraction of solids, Φ_m , is strongly dependent on the particle size distribution and the particle size. A broad particle size distribution usually results in a higher value of Φ_m because the small particles can fit into the voids between the large particles. However, while the geometric packing rules are useful when dealing with coarse particles in concrete, like stones, the situation becomes more difficult when dealing with the smallest fraction of cement and sand and fine particle additions like silica fume. The

inter-particle forces and thus the colloidal stability of the suspension have a profound influence on the packing of fine particles. If the particles in suspension are flocculated they will stick upon first contact and thus not be able to rearrange during consolidation. Colloidally stable suspensions, characterised by a repulsive inter-particle force of sufficient range and magnitude to keep the particle dispersed, usually facilitate a homogeneous mixing of powders. Due to this, the particle packing is usually not as efficient in an originally flocculated suspension as in an originally dispersed suspension (see Fig. 1). However, it can be easier to obtain a uniform mass distribution throughout the consolidated cake of a flocculated suspension, whereas a stable suspension, with its net repulsive force, will have a tendency to segregate during consolidation because the denser particles will settle first¹.

This study deals with the effect of superplasticizers on the consolidation behaviour of MgO suspensions. Polycarboxylate polymers with a similar backbone but different lengths of the grafted ethylene oxide side chains have been adsorbed onto the MgO particles and the density of the particle network was

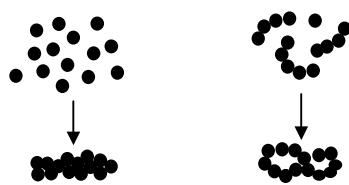


Figure 1: Consolidation behavior of dispersed and flocculated suspensions.

determined after centrifugation. The inter-particle forces of this relatively non-reactive model system for cement were estimated by applying realistic theoretical models and using prior knowledge on the thickness of the adsorbed polymers. It was found that strongly attractive interactions result in a compressible particle network that resists consolidation while a more weakly flocculated particle network only displays a small density gradient.

THEORY

Inter-particle forces

The dominating inter-particle forces in cement and concrete are the van der Waals, double-layer (electrostatic), and steric (polymer induced) forces. The *van der Waals* force, which is always attractive between like materials, arises from the interaction of atomic and molecular electric dipoles whose orientations are correlated so they attract each other. The van der Waals force between two particles of equal radius a and material (1) acting across a medium (2) can be approximated by^(2, 3):

$$F_{vdW} \approx -A_{12} \cdot f_{retardation} \cdot \frac{dH}{dh} \quad (1)$$

where A_{12} is the so-called Hamaker constant, $f_{retardation}$ is a retardation factor that incorporates the retardation of the dipole interaction over large distances, H is a geometrical factor dependant on the shape of the interacting particles and h is the separation distance. The Hamaker constant is given by⁽⁴⁾:

$$A_{12} = \frac{3}{2} k_B T \sum_{m=1}^{\infty} \sum_{s=1}^{\infty} \frac{1}{s^3} \left[\frac{\varepsilon_2(i\xi_m) - \varepsilon_1(i\xi_m)}{\varepsilon_2(i\xi_m) + \varepsilon_1(i\xi_m)} \right]^{2s} \quad (2)$$

where $\varepsilon(i\xi)$ is the dielectric response function of the material and medium, respectively. The determination of the dielectric response function for different

materials and water has been described by Flatt² and Bergström et al⁴ and will not be discussed further here. $f_{retardation}$ is given by:

$$f_{retardation} = \left(1 + \left[\frac{n_2 \sqrt{n_1^2 + n_2^2}}{4\sqrt{2}} \cdot \frac{h\pi\omega_{UV}}{c} \right]^2 \right)^{-\frac{3}{2}} \quad (3)$$

where n represents the refractive indices of material and medium, c is the speed of light in vacuum and ω_{UV} is a characteristic frequency in the ultraviolet range.

For two spheres, dH/dh is given by⁽⁵⁾:

$$\frac{dH}{dh} = \frac{4a^2 D}{6} \left[\frac{1}{(D^2 - 4a^2)^2} + \frac{1}{D^4} - \frac{2}{(D^2 - 4a^2)D^2} \right] \quad (4)$$

Where $D=2a+h$ is the distance between the particle centres.

Immersing an inorganic particle in an aqueous solution usually results in the build-up of a charge at the solid-liquid interface. Ions of opposite charge (counterions) are attracted to the charged interface and form a diffuse ion “cloud” adjacent to the charged particle surface. The *double layer force* between two charged particles is related to the osmotic pressure created by an increase in the ion-concentration of the overlapping ion “clouds”. The double layer force can be described by⁽²⁾:

$$F_{Electrostatic} = -2\varepsilon_0 \varepsilon_r a \pi \psi_0^2 \frac{\kappa e^{-\kappa h}}{1 + e^{-\kappa h}} \quad (5)$$

where ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of the medium, ψ_0 is the surface potential of the particle and κ is the inverse of the so-called Debye-length. The Debye-length is a measure of the thickness of the double-layer, which determines the range of the double layer interaction and is given by⁽⁶⁾:

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{2e^2 N_A I}} \quad (6)$$

where e is the charge of an electron, N_A is Avogadros constant and I is the ionic strength of the electrolyte. The range of the double layer interaction is controlled by the valency and concentration of ions in solution while the magnitude is controlled by the charge density of the particle.

It is also possible that a repulsive interaction can develop between two particles at close proximity due to an orientation of the molecules in the polar liquid, usually water. This effect is called the *solvation force*. For oxidized surfaces, the dominating interaction between the water molecules and the surface groups will probably be hydrogen bonding. The range of the solvation force has been reported to vary from 3 Å (one water molecule layer) up to 50 Å depending on the material, ionic strength and pH⁽⁷⁻⁹⁾. There is a lack of theoretical models that go beyond a phenomenalistc description and the solvation force will therefore not be included in the calculations.

The adsorption of surfactants and polymers onto the particle surface can induce a polymer-induced interaction that can be both attractive and repulsive. The interpenetration of the polymer layers upon the close approach of two particles covered with adsorbed polymers gives rise to a repulsive interaction, the so-called steric repulsion. The net interaction of a colloidal system will either be repulsive (fully stabilized) or weakly attractive (partly stabilized) depending on the range of the steric repulsion and the van der Waals attraction. The interaction between two spheres having adsorbed polymers on the surface can be described by this simplified expression^(2, 5):

$$F_{Steric} = 2\pi a \frac{\phi_2^2}{V_3} k_B T \left(\frac{1}{2} - \chi \right) (h - 2\delta) \quad (7)$$

where ϕ_2 is the volume fraction of chains in the adsorbed layer, V_3 is the partial molecular volume of the medium, χ is the polymer segment-solvent interaction parameter and δ is the thickness of the steric layer.

The total interaction force can then be determined by summing up all the contributions:

$$F_{total} = F_{vdW} + F_{Electrostatic} + F_{Steric} \quad (8)$$

EXPERIMENTAL

Materials

The reactivity of cement particles makes it difficult to perform experimental studies that can provide a fundamental understanding of the stabilisation mechanisms and the rheological properties of the fresh paste. It is not only the surface properties of the cement particles that change continuously with time. The hydration reactions that occur when cement is mixed with water create a supersaturated solution at a very high ionic strength of mainly Ca²⁺, SO₄²⁻, K⁺, and Na⁺ at a high pH ≈ 12-13. Previous work by Flatt et al.¹⁰ has shown that MgO is a relatively unreactive material that mimics the surface properties of cement, e.g. an isoelectric point (iep) at pH 12.4. Recent work has shown⁽¹⁰⁾, that MgO displays an inert period for about 3.5 hours following an initial 30 minutes reaction.

The MgO used in this project has a particle size distribution (PSD) as shown in Fig. 2. For comparison, the PSD of a mix of ordinary Portland cement and 5 mass-% silica fume is also shown.

Ordinary Portland cement has a relatively broad PSD ranging from 1μm-100μm while the commonly added pozzolanic filler material silica fume, has a PSD ranging from around 0.06 μm to around 1μm. Hence, the MgO used in this

study displays a significantly more narrow PSD than the cement-silica fume mix. This is motivated by the need to have a relatively well-defined average particle size for the calculations of the inter-particle forces.

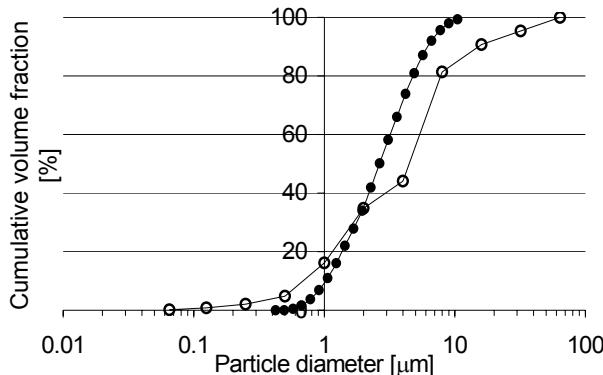


Figure 2: The particle size distributions of MgO (●) and a mix of 95 weight-% Ordinary Portland cement and 5 weight-% silica fume (○).

As the electrolyte, a concentrated salt solution with an ionic strength of 0.415 M has been used (Table 1).

Table 1: Composition of the electrolyte solution.

Salt	CaSO ₄ ·2H ₂ O	Na ₂ SO ₄	NaOH
[g/L]	2.0658	12.4960	2.9167

Four different modified anionic acrylic ester type polymers have been used in this study (PCP1, PCP2, PCP3, and PCP4). These novel types of superplasticizers mainly differ with respect to the length of the grafted ethylene oxide chains. The adsorption isotherms of these polymers and the thickness of the adsorbed layer has been determined previously⁽¹¹⁾ (see Table 2).

Table 2: Steric layer thickness as measured by Atomic Force Microscopy (AFM)¹¹.

	PCP1	PCP2	PCP3	PCP4
KCl	2	3	3-4	4-5
CaSO ₄	1	4-5	3-4	4-5

Methods

The suspensions were centrifuged in a Mistral 2000 Small Capacity Bench

centrifuge using polyallomer centrifuge tubes with the dimension ø25mm and length 89 mm. The tubes are round-bottomed and have been filled with an epoxy/lead ball mix to obtain a flat bottom, to create an even radial stress on the suspension and the resulting cake. To determine the time of equilibrium (when no further consolidation occurs) the height of the resultant cake was monitored during centrifugation.

Particle size distributions were determined by means of a Malvern Mastersizer 2000, Model APA2000 using a refractive index for MgO of 1.735 and zero light absorption.

Experimental procedure

Suspensions with a solids concentration of 20 volume% were made in 60 mL batches in 150mL beakers. After mixing the MgO powder with the salt solution (see Table 1), the suspension was ultrasonicated in an ultrasonic bath for 5 minutes and then left with magnetic stirring for 30 minutes. The polymers were added and the suspension was again ultrasonicated for 5 minutes and then equilibrated for 30 minutes under magnetic stirring. Approximately 2 × 30 g of each suspension were transferred from the beaker into two weighed and marked tubes and centrifuged at 400 rpm for approximately 3 hours. The centrifugation was terminated when the consolidation process had reached steady state, determined by following the consolidation cake height. The tubes were removed from the centrifuge and the round end of the centrifuge tube was cut off and the cake was pushed out using a custom-made piston. The cake was cut into slices of a thickness of 2-3 mm following a modification of the procedure described by Meeten¹². The water content, and thus the packing fraction of the slices, was determined by measuring the weight loss after drying at 105°C.

RESULTS

The addition of superplasticizers to the MgO suspensions results in significant changes in the consolidation behaviour. Fig. 3 shows the density of the centrifuged cakes at steady state. The transient consolidation process was followed, by measuring the cake height as a function of centrifugation time and it was found that a centrifugation time of 3 hours at 400 rpm was sufficient to reach steady state for this relatively coarse powder. Calculation of the area under each curve yielding the mass of the suspension shows similar masses for all suspensions indicating a good reliability of the measurements.

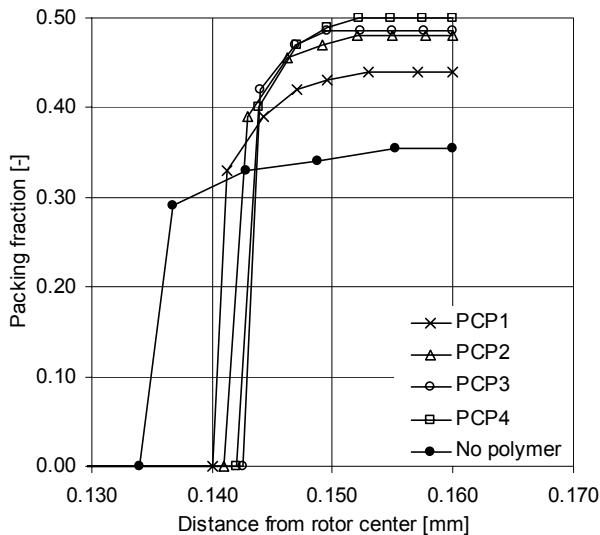


Figure 3: The packing fraction profiles of centrifuged MgO suspensions where •)no polymer, ×)PCP1, Δ)PCP2, o)PCP3, and □)PCP4 has been added.

The density of all the centrifuged cakes increases towards the bottom of the centrifuge tube. This can be related to the stress gradient that develops in a particle network subjected to a centrifugal force field. In concentrated flocculated suspensions, a continuous particle network forms, which can support some stress up to a critical value. Once this critical stress, also called the compressive yield stress, P_y , is exceeded, the network consolidates to a higher volume fraction with a higher critical stress. The density profile of the centrifuged cakes thus gives information on the

compressibility of the particle networks as the stress on the particle network increases towards the bottom of the cake. The compressible nature of all the particle networks suggests that all the suspensions are flocculated; a stable suspension is expected to display an essentially incompressible consolidation behavior^(5, 13).

The maximum packing fraction, Φ_m , varies with the addition of superplasticizer. The suspension where no polymer was added displays a relatively low maximum packing fraction, $\Phi \approx 0.36$. Adsorbing super-plasticizers onto the MgO powder results in a significant increase in the maximum packing fraction, $\Phi_m \approx 0.44\text{-}0.50$. The increase of the maximum packing fraction shows that adsorption of superplasticizers results in a significant reduction in the compressive yield stress of the particle network.

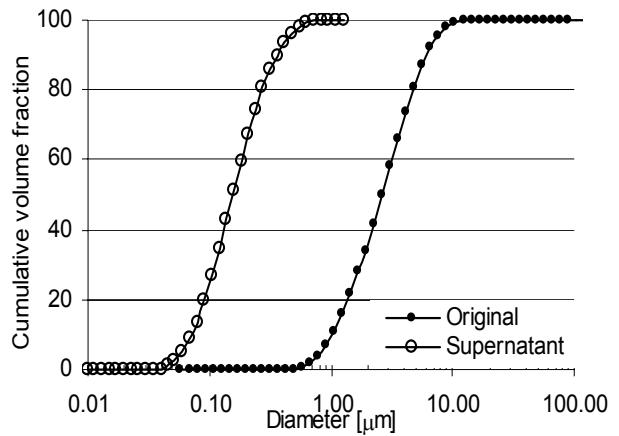


Figure 4: The particle size distribution of the original MgO powder (●) and the fine fraction in the supernatant (○).

It was also found that the addition of superplasticizers yields a “milky” supernatant that contains a small concentration of very fine particles. The MgO suspension without any addition of polymer results in the formation of a clear supernatant after centrifugal consolidation, which is typical for a strongly flocculated suspension. This suggests that at least a fraction of the MgO particles are stabilized by the addition of the superplasticizers. The

particle size distribution was determined. It was found that it is a very fine submicron fraction that remains in the supernatants of the polymer-containing suspensions (Fig. 4). Hence, addition of superplasticizers results in a segregation of the polydisperse MgO powder where the finest fraction is stabilized and not incorporated in the particle network.

DISCUSSION

The consolidation behaviour of the flocculated MgO suspensions has been analysed as a function of the inter-particle forces. The inter-particle forces in the different systems have been estimated using Eqs. 1-8 and the input values given in Table 3. Considering that the artificial electrolyte solution contains neither Cl⁻ or K⁺-ions the AFM data for the adsorbed polymer layer obtained in the CaSO₄-solution are used¹¹. PCP2 is not included in this discussion as the effect of the sulphate ions on the conformations of the adsorbed molecules and possible desorption is unclear. The double layer force was assumed to commence outside the steric polymer layer instead of directly at the particle surface. In the calculations, a mean particle radius of 1325 nm has been used.

Table 3: Input values for the force calculations

n ₁ [-]	n ₂ [-]	ω _{UV} [rad/s]	ε ₀ [C ² /Nm ²]	ε _r [-]
1.735	1.325	1.71·10 ¹⁶	8.854·10 ⁻¹²	80
ϕ ₂ [-]	V ₃ [m ³]	χ [-]	I [mol/m ³]	
0.7	2.6·10 ⁻²⁸	0.35	412	
Mix no.	1	3	4	5
ψ ₀ [10 ⁻³ V]	-0.5	-0.2	0.5	0.2
δ [nm]	1	3-4	4-5	-

The calculated force curves are shown in Fig. 5. A positive value of the interaction force represents attraction. The figure shows how the inter-particle attraction increases as the separation distance decreases. Adsorption of the superplasticizers is assumed to infer a steep repulsive barrier that prevents the particles from coming into

close contact. Hence, a polymer that yields a thick adsorbed layer, like PCP4, is expected to reduce the inter-particle bond strength more than a polymer that only results in a thin adsorbed layer, like PCP1. The values that are inserted in Fig. 5 represents the maximum bond strength at a separation distance that is twice the adsorbed layer thickness; hence, the point where the adsorbed polymer layers prevent the particles from coming into closer contact.

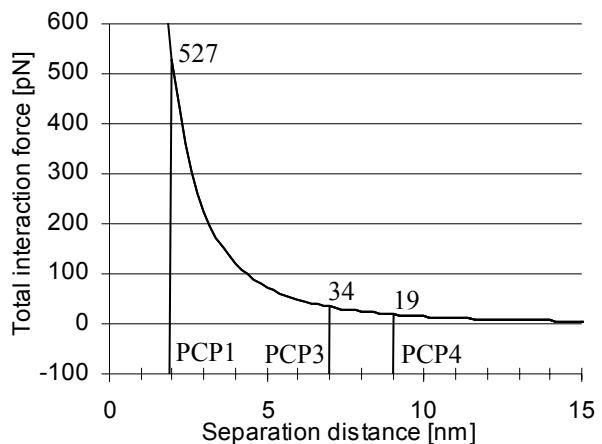


Figure 5: The calculated inter-particle force for MgO particles with PCP1, -3 and -4 adsorbed.

It is found that there is a good correlation between the estimated inter-particle bond strength (Fig. 5) and the experimentally obtained maximum packing fraction (Fig. 3). The results suggest that a thicker adsorbed polymer layer results in a particle network that is more easily consolidated to high packing fractions.

The addition of polymers to the MgO suspensions did not only facilitate consolidation of the particle network to a higher packing fraction, but it also stabilized a part of the particles. A suspension can be stabilized by the addition of polymers when the steric layer screens the van der Waals attraction to such a level that the particles do not stick when in contact. As a rule of thumb, a colloidally stable dispersion is obtained when the maximum inter-particle attraction is less than 2kT (where k is the

Boltzmann constant and T is the temperature). While the range of the van der Waals attraction decreases with decreasing particle size (see Eqs. 1 and 4), the range of the steric repulsion should be independent of particle size if the thickness of the adsorbed polymer layer is not affected by the surface curvature. Hence, a small particle may be stabilized by a specific polymer while a larger particle still will flocculate, see Fig. 6.

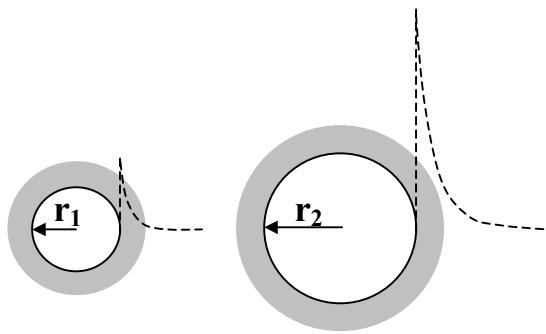


Figure 6: Schematic illustration of the increasing screening of the van der Waals attraction as a function of decreasing particle size ($r_1 < r_2$). The gray area is the steric layer and the dotted line represents the van der Waals attraction.

This effect can explain why a fine fraction of the MgO powder is stabilized by addition of the polymers (Fig. 4). The particles that remained in the supernatant have a mean particle size radius of 70 nm. Estimates of the maximum attractive inter-particle energies for MgO particles of this size were performed using the procedure described previously. It was found that the estimated attractive energies are in the range of 1-2 kT for the PCP3 and PCP4 superplasticizers, while adsorption of PCP1 is estimated to result in a significantly higher attraction energy.

It is also necessary to consider the effect that the removal of the fine fraction can have on the packing of the consolidated system. Considering only geometrical circumstances, the omission of the smallest part of the particles would decrease the maximum obtainable degree of packing. However, the fine fraction has a profound

influence on the compressibility and consolidation resistance of aggregated particle networks. The compressive yield strength is expected to increase with a decrease in particle size, thus making it more difficult to attain a high packing fraction under relatively low compressive stresses. The fact that it was the same particle size fraction that stayed in suspension in all the polymer-modified experiments means that it is possible to compare the different systems.

CONCLUSION

MgO particles have been used as a model material for cement. The consolidation behaviour of the particle networks has been investigated with different polymeric additions yielding different steric layer thickness. It has been experimentally shown that the higher the maximum attractive inter-particle force is, the lower the consolidated packing fraction will be.

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REFERENCES

- Chang, J.C., Velamakanni, B.V., Lange, F.F., Pearson, D.S. (1991). “Centrifugal Consolidation of Al_2O_3 and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ Composite Slurries vs Interparticle Potentials: Particle Packing and Mass Segregation”. *J. Am. Ceram. Soc.* **74** [9], 2201-2204

2. Flatt, R. (1999) "Interparticle Forces and Superplastisizers in Cement Suspensions". *PhD-thesis, EPFL*.
3. Pedersen, H. (1998). "Particle Interactions: An AFM Study of Colloidal Systems". *PhD-thesis. Technical University of Denmark*.
4. Bergström, L. (1997). "Hamaker Constant in Inorganic Materials". *Advances in Colloid and Interface Science* **70**: 125-169.
5. Bergström, L., Schilling, C.H., Aksay, I.A. (1992) "Consolidation Behavior of Flocculated Alumina Suspensions". *J. Am. Ceram. Soc.* **75** [12], 3305-3314.
6. Hunter, R. (1993). "Introduction to modern Colloid Science". *Oxford University Press*.
7. Butt, H.-J. (1991) "Measuring electrostatic, van der Waals, and hydration forces in electrolyte solutions with an atomic force microscopy". *Biophys. J.*, **60**, December, 1438-1444.
8. Raviv, U., Klein, J. "Fluidity of Bound Hydration Layers". (2002) *Science*, **297**, August, 1540-1543.
9. Vigil, G., Xu, Z., Steinberg, S., Israelachvili, J. (1994) "Interactions of Silica Surfaces". *J. Colloid and Interface Science*, **165**, 167-185.
10. Flatt R.J., Bowen P., Siebold A., Houst Y.F., "Cement model powders for superplasticizer properties studies", Proc. 11th ICCC, Durban, May 2003, Tech Book International, New Delhi, India, Vol. **2**, 676-685.
11. Superplast. Ongoing EU-funded project. Confidential.
12. Meeten, G.H. (1993) "A dissection method for analyzing filtercakes". *Chem. Eng. Science*. **48** [13], 2391-2398
13. Bergström, L. (2001). "Colloidal Processing of ceramics". *Handbook of Applied Surface and Colloidal Chemistry*. John Wiley & Sons, Ltd.