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Removal of Colloidal Particles Utilizing Gelation Reaction of Sodium Alginate

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Abstract−A novel technique utilizing the gelation reaction of natural polymers has been proposed for the separation of solid from liquid in difficult-to-filter colloidal suspensions. This technique is especially effective in the treatment of colloidal muddy water of high solid concentration, which is often produced as a byproduct of certain construction processes. Colloidal suspensions are mixed with a sodium alginate solution, and this mixture is added to a calcium chloride solution, resulting in the entrapping of colloidal particles by the calcium alginate gel. Gel suspensions are then drained gravitationally, followed by mechanical expression of gel particles. Fundamental aspects of this process are investigated by using sodium bentonite as an experimental material. The alginate-bentonite mixture is added dropwise to the calcium solution. Decreasing the droplet size of the mixture expedites gelation since the diffusion of calcium ions into droplets determines the rate of gelation reactions. Reducing the alginate content expedites expression of the gel since alginate content is inversely proportional to the rate of expression.

Key words: Expression, Drainage, Colloidal Suspension, Gelation, Alginate

INTRODUCTION

The mud water shielding technique for tunnel construction utilizes pressurized muddy water of the high solid concentration in order to prevent leakage of ground water. Earth drilling techniques for pile driving involve filling pile-holes with high-density muddy water, which braces the holes against collapse while still permitting the extraction of excavated material. Thus, construction projects utilizing these types of construction techniques must also include a method for disposing of large quantities of muddy wastewater. Unfortunately, however, inorganic flocculants are ineffective in the treatment of muddy wastewater with a high solid-to-liquid ratio. On the other hand, the treatment of muddy water by using polymer flocculants results in sticky aggregates that are difficult to dewater.

Recently, a Japanese company [Asahi and Yukawa, 1994] developed a new process utilizing the gelation reaction of alginate in the treatment of muddy wastewater that has been used to good effect at many construction sites. This process consists of the following procedures (see Fig. 1). A sodium alginate aqueous solution is mixed with a colloidal suspension. This mixture is added to a calcium chloride aqueous solution, resulting in calcium alginate gel. Colloidal particles are entrapped in calcium alginate gel. The gel suspension is dehydrated gravitationally, followed by mechanical expression of gel particles. During the expression, the colloidal particles remain in the gel. The expressed cake is then discarded. This process was developed empirically, and a theoretical model has yet to be fully elucidated, but there are four points that are known to be crucial to the effectiveness of the process.

1. Gelation reaction must occur with great rapidity.

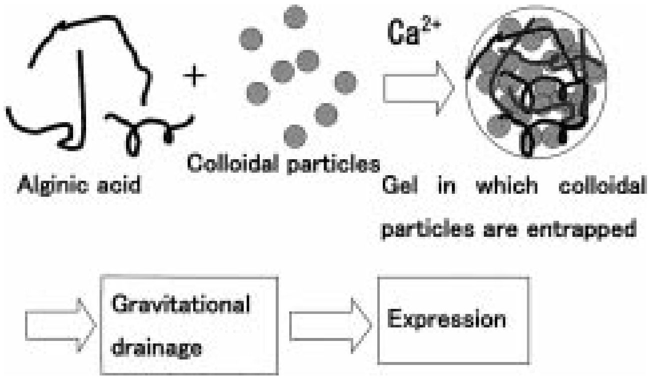

Fig. 1. New process for removing colloidal particles.

2. Gravitational and mechanical dewatering must occur with great rapidity.
3. Removed liquid must be clear.
4. Content of sodium alginate must be kept to a minimum.

In this paper, the fundamental characteristics of the process will be described.

EXPERIMENTAL

Sodium bentonite (Hohjun Kogyo, Annaka, Japan), which is typical of the swelling clays used in mud water shielding construction techniques, is used as a difficult-to-filter colloidal material. A bentonite suspension was mixed with a sodium alginate (Nacalai Tesque, 1000 cps grade) aqueous solution, and the mixture was added dropwise to a calcium chloride aqueous solution by using a peristaltic pump, resulting in calcium alginate gel particles. Nozzles with a variety of apertures were used to produce droplets with a diameter of approximately 2 to 4 mm. The gel suspension was agi-

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tated with propeller blades, 5 cm in diameter, for 24 h.

The time course of calcium ion uptake by the droplets was measured to elucidate the gelation process. An alginate aqueous solution (10-20 ml) was added dropwise to 150 ml of calcium chloride aqueous solution for 30 s, followed by the sampling of supernatant at the specified time intervals. The concentration of calcium ion in the supernatant was determined by titration with the reagent disodium ethylene-diamine-tetraacetate.

To determine the expression characteristics, the gel particles were pre-consolidated under a pressure of 100 kPa in a consolidation cell with an inner diameter of 60 mm to produce a packed gel bed. This bed was then expressed under the greater pressure of 1,000 kPa (Fig. 2). The change in thickness L of the bed with time θ_c was measured by a dial gauge fitted on the cell. A compression-permeability test [Grace, 1953] of the bed was also conducted.

RESULTS AND DISCUSSION

Alginic acid is an intercellular substance found in brown alga. It consists of a mannuronic acid block, a glucuronic acid block, and the block in which mannuronic acid and glucuronic acid are alternately connected. Alginic acid molecules are cross-linked by a divalent metal ion such as Ca^{2+}, and gels form.

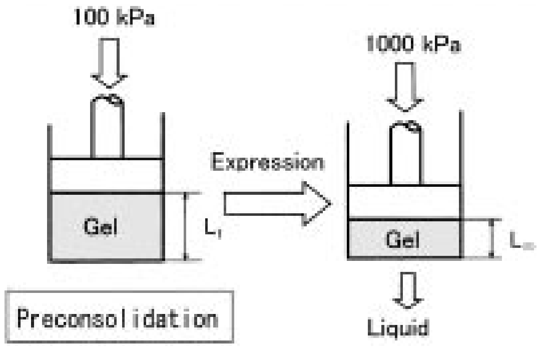

Fig. 2. Constant pressure expression test.

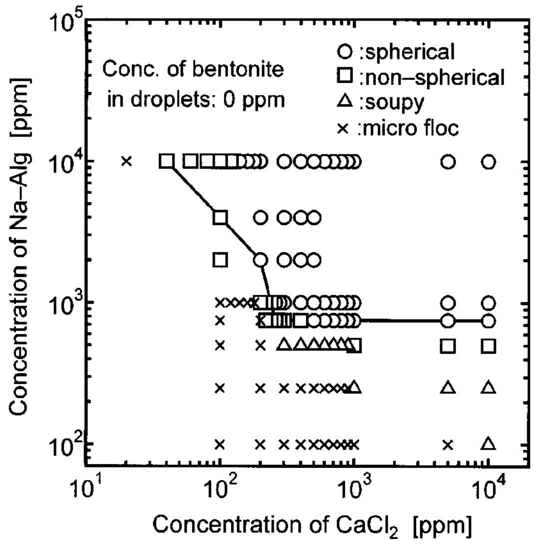

Fig. 3. Relation between preparation conditions and forms of alginate gels.

Fig. 3 shows the relationship between the form and preparation conditions of calcium alginate gels. In this experiment, the diameter of the droplet of an alginate solution is *ca.* 2 mm; the distance between the tip of tube and the surface of calcium chloride solution is *ca.* 5 mm. Gels are classified into four groups: spherical, non-spherical, soupy, and micro-flocs. In the region above the solid lines in the figure, gel particles had sufficient mechanical strength that after the gravitational drainage by means of a sieve with an aperture of 0.84 mm, all gel particles remained on the sieve. In other words, using a sodium alginate solution and calcium chloride solution both above 1,000 ppm, one can get spherical calcium alginate gel with sufficient strength for gravitational drainage. This region will shift upward, if colloidal particles are entrapped in alginate gels.

Fig. 4 shows the percent recovery of bentonite particles in the gel compared to their total amount in the original solid-liquid mixtures. Here, the concentration of Na-Alg in the figure implies that of sodium alginate in the droplets. Bentonite particles in the origi-

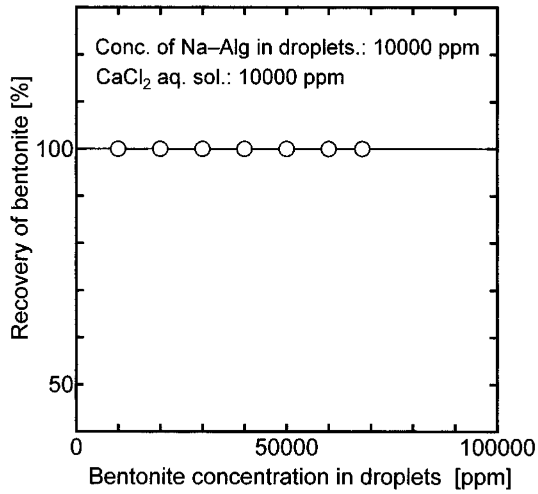

Fig. 4. Percent recovery of bentonite from original mixture into alginate gel.

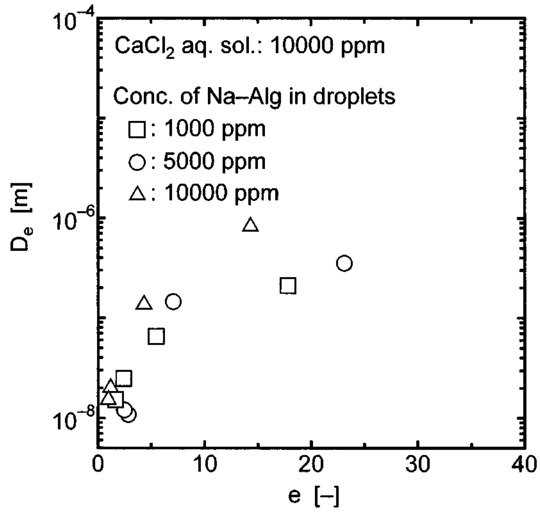

Fig. 5. Alginate gel network aperture.

nal mixture were perfectly entrapped in the gels. To explain this result, the compressibility and permeability of packed gel bed was measured. From the compression-permeability data, the network aperture of the gel was calculated. Fig. 5 shows the relationship between a network aperture D_e and a void ratio e of bentonite-free gels packed in the consolidation cell. D_e was calculated from the following rearrangement of the Kozeny-Carman equation [Carman, 1937].

$$D_e = \frac{4\varepsilon}{S_0(1-\varepsilon)} \tag{1}$$

$$S_0 = \sqrt{\frac{\alpha\rho_s\varepsilon^3}{k(1-\varepsilon)}} \tag{2}$$

where ε is the porosity of the packed gel bed; S_0, the specific surface area of gel network; α, the specific hydraulic resistance of the bed; ρ_s, the true density of dry alginate gel; and k, the Kozeny constant (k=5 in this study). Median diameter of bentonite particles used in this study was about 2 μm. The aperture of the gel network was 1 μm or less and it was sufficiently small to entrap bentonite particles. This is the reason for 100% entrapment of bentonite particles.

Fig. 6 shows the progress of gelation reaction. In the figure, M_θ and M_∞ denote the total amount of Ca^{2+} uptake to droplets of alginate solution at the time θ and ∞, respectively; D, the diffusion coefficient of calcium ions in the droplets; and a, the radius of the droplets. In the experiment, the aqueous solution of calcium chloride was thoroughly stirred by the propeller blades. Increasing the rotational speed of the blades to more than 100 r.p.m did not affect the time course of Ca^{2+} uptake. That is, the mass transfer resistance outside the droplet is negligible above this speed. The data in the figure was obtained at 150 r.p.m. The solid line in the figure represents the value from the following equation

$$\frac{M_\theta}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{Dn^2\pi^2\theta}{a^2}\right) \tag{3}$$

which represents the time course of calcium ion uptake by a sphere when the concentration of calcium ions at the surface of the sphere is constant [Crank, 1975]. The theory explains well the empirical results within experimental errors. According to theory, gelation time is proportional to the square of the radius of gel particle. Thus, it is essential to minimize the size of the droplets of the alginate solution to effect rapid gelation.

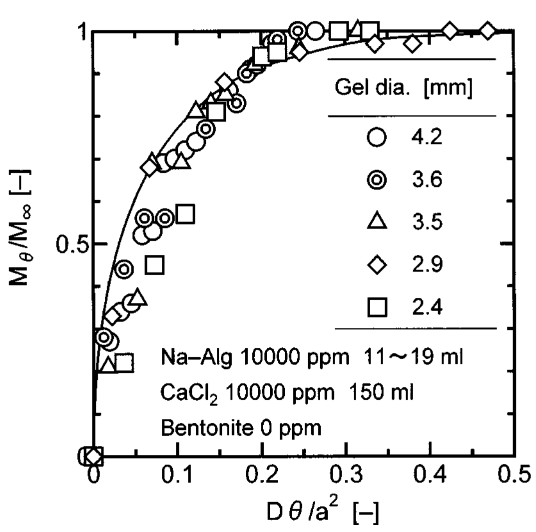

Fig. 6. Ca^{2+} uptake by droplets of alginate solution.

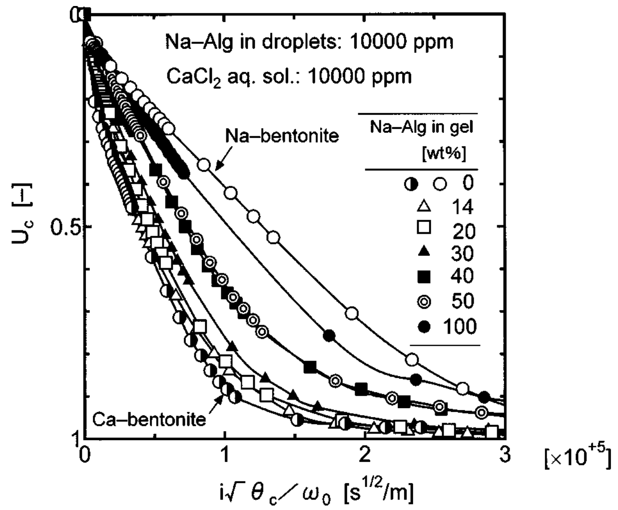

Fig. 7. Time course of average consolidation ratio U_c.

Fig. 7 compares the expression rate of packed gel beds of various compositions. In the figure, U_c is the average consolidation ratio defined by

$$U_c = \frac{L_1 - L}{L_1 - L_\infty} \tag{4}$$

where L_1 and L_∞ are the equilibrium thickness of the gel bed under preconsolidation pressure and expression pressure, respectively; and L, the thickness at time θ_c. U_c of a homogeneous semi-solid material is represented theoretically in the following equation [Shirato et al., 1967],

$$U_c = 1 - \sum_{n=1}^{\infty}\frac{8}{(2n-1)^2\pi^2}\exp\left\{-\frac{(2n-1)^2\pi^2}{4}\frac{i^2C_e\theta_c}{\omega_0^2}\right\} \tag{5}$$

where ω_0 is the total solid volume per unit cross-sectional area; i, the number of drainage surfaces of a compression cell; and C_e, the modified consolidation coefficient. In the figure, the results of expression of pure sodium bentonite and calcium bentonite are also shown. It can be seen from the figure that the expression rate of calcium bentonite is the largest and that of sodium bentonite is the smallest; the lower the alginate content in the gel, the larger the expression rate. C_e in Eq. (5) is a measure of expression rate that can be determined by the fitting method. A larger C_e implies a larger expression rate. The relationship between C_e and composition of the gel is shown in Fig. 8. In accord with Fig. 7, C_e increases as the alginate content of the gel lessens. C_e of gels seem to be distributed between those of pure calcium bentonite and bentonite-free alginate gel, although we used sodium bentonite as an experimental material. Incidentally, the square symbol in the figure indicates C_e of bentonite-alginate mixture without gelation reaction. The calcium-free bentonite-alginate mixture is extremely difficult to dewater. Fig. 9 represents relation between equilibrium void ratio and

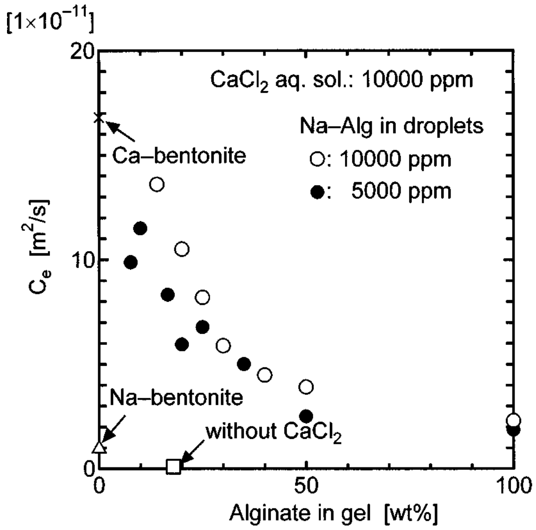

Fig. 8. Effects of gel composition on C_e.

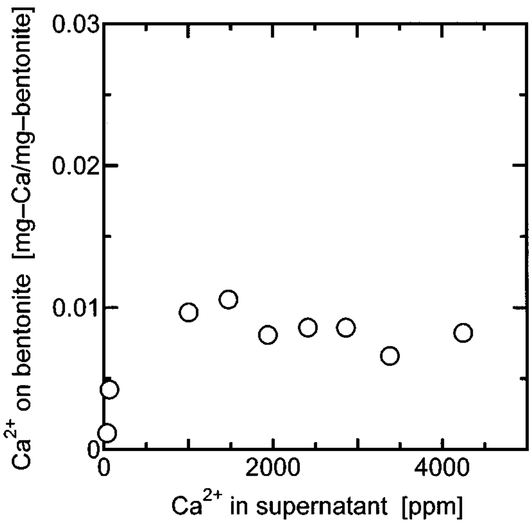

Fig. 10. Adsorption isotherm of bentonite with respect to Ca^{2+}.

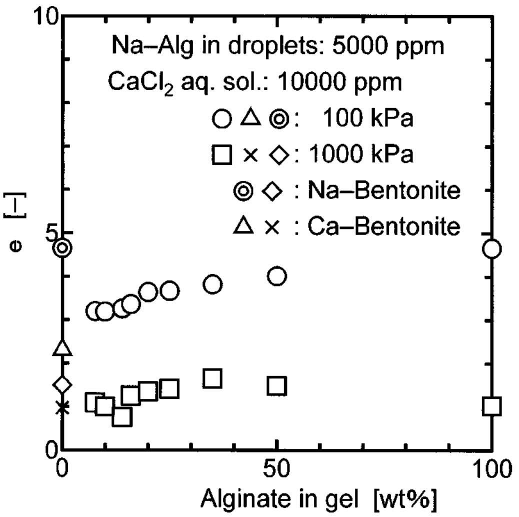

Fig. 9. Equilibrium compression data.

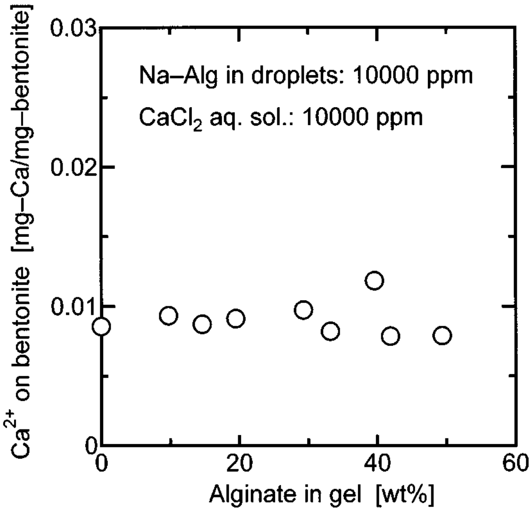

Fig. 11. Ion exchange capacity of bentonite in gel.

gel composition. Again, void ratios of gels seem to distribute between those of pure calcium bentonite and bentonite-free alginate gel.

Bentonite minerals are composed of hydrous aluminum silicate in the form of extremely small particles. They take up water between their layers, causing swelling, and change the interlayer spacing according to the mineral variety. Sodium bentonite has sodium ions as intercalation ions, while calcium bentonite is intercalated calcium ions. In our experiments, sodium bentonite particles are contacted with a calcium chloride aqueous solution when the bentonite-alginate mixture is added dropwise to the calcium solution; this will result in ion exchange between sodium and calcium ions. Fig. 10 represents the adsorption isotherm of sodium bentonite with respect to calcium ions. In the experiment, sodium bentonite was mixed with a calcium chloride aqueous solution of various concentrations, followed by continuous stirring for 24 h. Analyzing the decrease in calcium ion concentration in the supernatant, we calculated the quantity of ion exchange between Na^+ and Ca^{2+}. It can be seen from the figure that ion exchange capacity of bentonite is *ca.* 0.01 mg-Ca/mg-bentonite. That is, when the concentration of calcium ions in supernatant is above 1,000 ppm, 100% of the sodium bentonite is altered to calcium bentonite. The bentonite-alginate gels we prepared were always above this criterion. Fig. 11 shows the amount of calcium ions bounded by bentonite particles in bentonite-alginate gel. The amount of ion exchange of the bentonite particles in the gel is almost 0.01 mg-Ca/mg-bentonite. That is, bentonite particles are perfectly converted from sodium type to calcium type, even if the bentonite particles are entrapped in gel. In other words, gel particles, in which bentonite particles are entrapped, are the mixtures of calcium bentonite and calcium alginate gel. The expression rates of the gels entrapping bentonite particles are consequently between those of calcium bentonite and a bentonite-free alginate gel. Based on Fig. 8, for the purpose of rapid removal of bentonite particles from wasted muddy water in the tunnel construction using the mud water shielding technique, the alginate content in gels should be reduced as much as possible. On the other hand, gels are not formed, if the alginate content is too small. Therefore, an optimum value for the alginate content in the gel seems to exist.

CONCLUSIONS

The basic characteristics of a new process for solid-liquid separation using the gelation reaction of alginate have been investigated.

1. For rapid gelation, the droplet size of the alginate solution should be kept to a minimum since the diffusion rate of calcium ions into the droplets is dependent upon droplet size.

2. The lower the alginate content, the larger the expression rate of the gel. The alginate content of gels should be kept to a minimum to effect rapid removal of colloidal particles from difficult-to-filter bentonite suspensions.

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NOMENCLATURE

a : radius of gel particle [m]
C_e : modified consolidation coefficient [m^2/s]
D : diffusion coefficient of Ca ion [m^2/s]
D_e : alginate gel network aperture [m]
e : void ratio of packed gel bed, defined by $\varepsilon/(1-\varepsilon)$ [-]
i : number of drainage surfaces of compression cell [-]
k : the Kozeny constant [-]
L : thickness of expressed material [m]
L_1 : initial thickness of material [m]
L_∞ : final thickness of material [m]
M_θ : total amount of Ca ions in gels at θ [mol]
M_∞ : total amount of Ca ions in gels at $\theta=\infty$ [mol]
S_0 : volumetric specific surface of gel network [m^2/m^3]
U_c : average consolidation ratio [-]
α : hydraulic specific resistance of packed gel bed [m/kg]
ε : porosity of packed gel bed [-]
θ : gelation time [s]
θ_c : expression time [s]
ρ_s : true density of gel network [kg/m^3]
ω_0 : total solid volume per unit cross-sectional area [m^3/m^2]

REFERENCES

Asahi, K. and Yukawa, Y., The Published Unexamined Patent Application of Japan, H6-182349 (1994).

Carman, P. C., "Fluid Flow through Granular Beds," *Trans. Inst. Chem. Eng. (London)*, **15**, 150 (1937).

Crank, J., In "The Mathematics of Diffusion," 2*nd* ed., Clarendon Press, Oxford (1975).

Grace, H. P., "Resistance and Compressibility of Filter Cakes," *Chem. Eng. Prog.*, **49**, 303 (1953).

Shirato, M., Murase, T., Kato, H. and Fukaya, S., "Studies on Expression of Slurries under Constant Pressure," *Kagaku Kogaku*, **31**, 1125 (1967).