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Masashi Iwata[a]
[a] Department of Chemistry and Biochemistry, Suzuka National College of Technology, Shiroko-cho, Suzuka, Japan

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Solid–Liquid Separation by Use of Particle Immobilization in Calcium Alginate Gel

Masashi Iwata*

Department of Chemistry and Biochemistry, Suzuka National College of Technology, Shiroko-cho, Suzuka, Japan

ABSTRACT

A novel technique utilizing the gelation reaction of alginate has been proposed for the separation of solid from liquid in difficult-to-filter colloidal suspensions. Colloidal suspensions are mixed with a sodium alginate solution, and this mixture is added to a calcium chloride solution, resulting in the entrapment of colloidal particles by the calcium alginate gel. Gel suspensions are then drained gravitationally, followed by mechanical expression of gel particles. This technique is especially effective in the treatment of colloidal muddy water of high solid concentration, which is often produced as wastes of certain construction processes. Fundamental aspects of this process are investigated using sodium bentonite/PMMA as experimental materials. The alginate-bentonite/PMMA mixture is added dropwise to the calcium solution. When an alginate concentration in the droplets is above 1000 ppm, submicron particles are perfectly entrapped in calcium-alginate gels.

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*Correspondence: Masashi Iwata, Department of Chemistry and Biochemistry, Suzuka National College of Technology, Shiroko-cho, Suzuka 510-0294, Japan; E-mail: iwata@chem.suzuka-ct.ac.jp.

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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 bentonite/PMMA gel.

INTRODUCTION

The mud-water-shielding technique for tunnel construction utilizes pressurized muddy water of the high solid concentration in order to prevent water from seeping in and collapsing the tunnel heading. 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

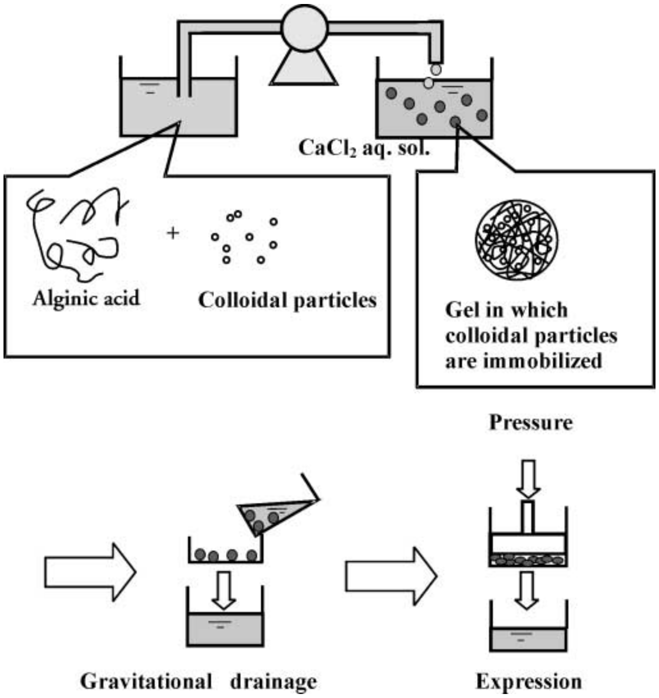

Figure 1. New process for removing colloidal particles.

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 new process utilizing the gelation reaction of alginate in the treatment of muddy wastewater was developed by a Japanese company[1] and 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 immobilized 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. In this paper, the fundamental characteristics of the process will be described.

EXPERIMENTAL

Sodium bentonite (median diameter: *ca.* 2 μm; Hohjun Kogyo, Annaka, Japan), which is typical of the swelling clays used in mud-water-shielding construction techniques, was used as a difficult-to-filter colloidal material. Monodispersed polymethyl methacrylate particles (PMMA: MP1451, MP1000, MP1600; Soken Chemical & Engineering) were also used as colloidal materials. The nominal median diameter of MP1451, MP1000, and MP1600 are 0.15, 0.4, and 0.8 μm, respectively. A bentonite/PMMA 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 3 to 5 mm. The gel suspension was agitated using 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 (27–32 mL) was added dropwise to 80 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 inductively coupled plasma spectrometry (Shimadzu, ICPS 1000-4).

To determine the expression characteristics, the gel particles were preconsolidated 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 1000 kPa. 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[2] of the bed was also conducted.

RESULTS AND DISCUSSION

Alginic acid is an intercellular substance found in brown alga. It comprises 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.

Figure 2 shows the relationship between the form and preparation conditions of particle-free calcium alginate gels.[3] 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, nonspherical, soupy, and

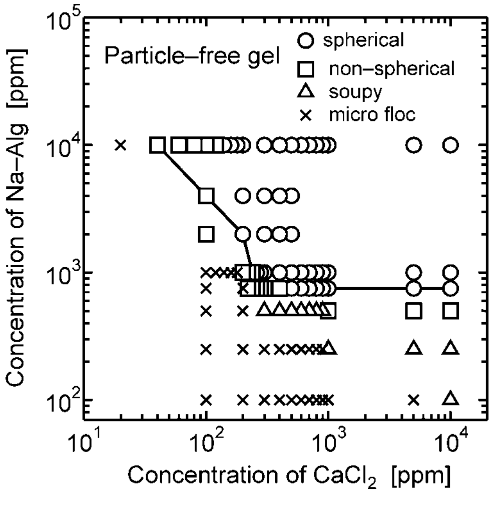

Figure 2. Relation between preparation conditions and forms of alginate gels.

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 1000 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.

When the concentration of sodium alginate in the droplets and that of $CaCl_2$ aqueous solution were both 10000 ppm, bentonite particles in the original solid–liquid mixtures were perfectly entrapped in the calcium-alginate gels.[3] This was also confirmed by using monodispersed PMMA particles with nominal median diameters of 0.15, 0.4, and 0.8 μm as colloidal particles. To explain these results, the compressibility and permeability of particle-free packed gel bed were measured. From the compression-permeability data, the average network aperture of the gel was calculated. Figure 3 shows the relationship between a network aperture D_e and a void ratio of particle-free calcium-alginate gels packed in the consolidation cell. D_e was calculated from the following rearrangement of the Kozeny–Carman

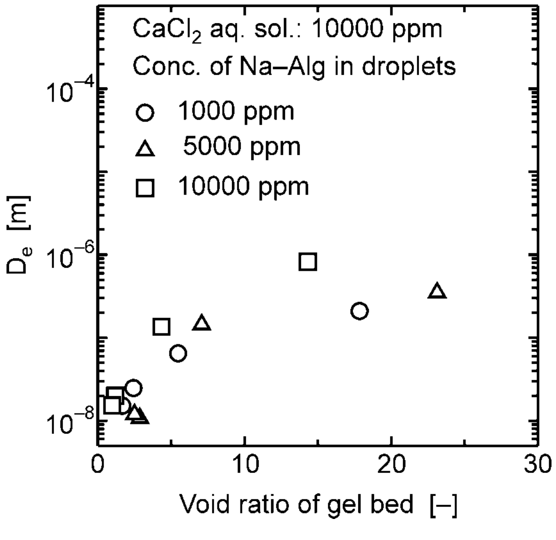

Figure 3. Alginate gel network aperture.

equation[4]:

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

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

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. Although the solid part of gel network is not spherical, we use a value $k = 5$ for the sake of simplicity in calculation. It should be noted that D_e is only a rough estimation of the network aperture because void among gel particles are also included in ε in Eq. (1).The aperture of the gel network was $0.01-1\ \mu$m, and it was sufficiently small to entrap bentonite/PMMA particles. This is the reason for 100% entrapment of colloidal particles. A decrease in alginate concentration in colloid-alginate mixture results in leakage of colloidal particles from a gel network, as shown in Figs. 4 and 5. In the experiment, 100 mL of PMMA-alginate mixture was added dropwise to 500 mL of $CaCl_2$ aqueous solution;

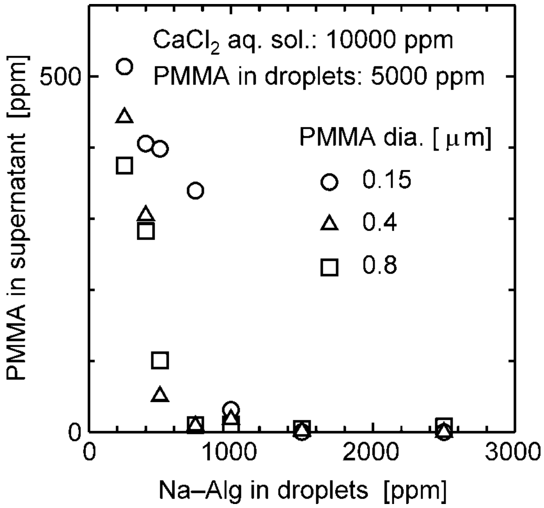

Figure 4. Solid content in supernatant.

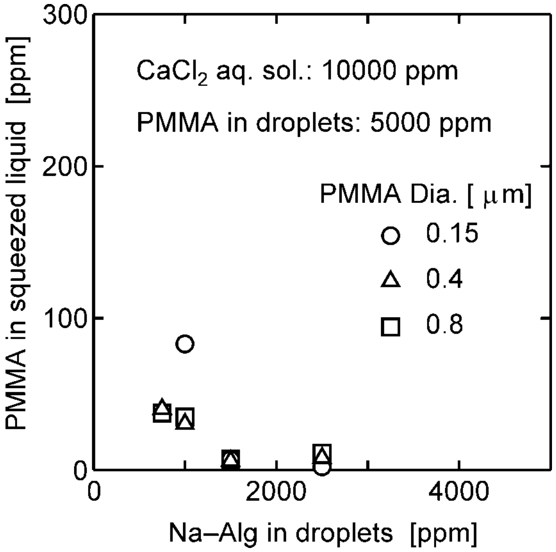

Figure 5. Solid content in squeezed liquid.

the particle concentrations in the supernatant of a gel suspension and in the squeezed liquid of the gel particles were measured. It can be seen from the figures that a concentration of alginate in the mixture must be kept above 1000 ppm for the perfect entrapment of PMMA particles in the gels.

Figure 6 shows the progress of gelation reaction. In the figure, M_θ and M_∞ denote the total amount of Ca^{2+} uptake into droplets of bentonite-alginate mixture at the time θ and ∞, respectively; 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 were obtained at 150 r.p.m. The time course of Ca^{2+} uptake into a sphere from a well-stirred solution of limited volume can be represented by the following equation:

$$\frac{M_\theta}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp(-Dq_n^2\theta/a^2)}{9+9\alpha+q_n^2\alpha^2} \tag{3}$$

where D is the diffusion coefficient of Ca^{2+} in the droplets; the q_ns,

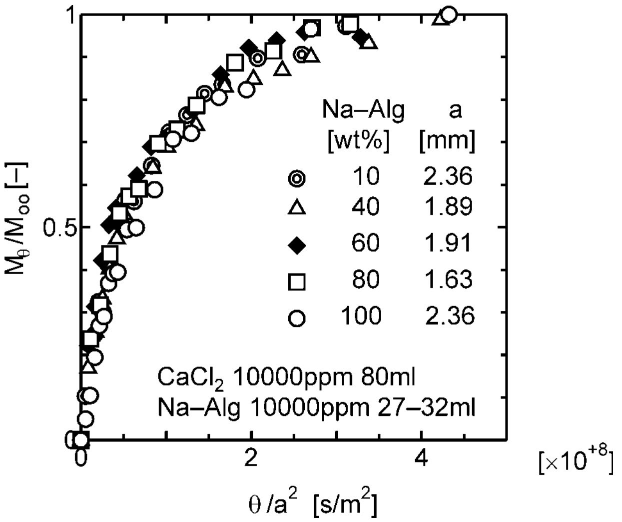

Figure 6. Ca^{2+} uptake by droplets of bentonite-alginate mixture.

the nonzero roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \tag{4}$$

and $\alpha = 3V/(4\pi a^3)$, the ratio of the volumes of the solution and the droplets.[5] According to Eq. (3), 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. Figure 7 represents the diffusion coefficients obtained by fitting Eq. (3) to the experimental data. The diffusion coefficients of Ca^{2+} in alginate gels are *ca.* one-half that of Ca^{2+} at infinite dilution.

Figure 8 compares the expression rate of packed bentonite-alginate gel beds of various compositions. In the figure, U_c is the average consolidation ratio defined by

$$U_c = \frac{L_1 - L}{L_1 - L_\infty} \tag{5}$$

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 semisolid material is

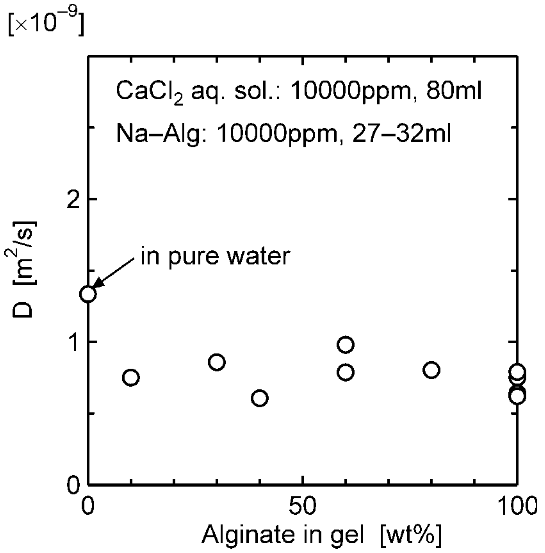

Figure 7. Diffusion coefficient of Ca^{2+} in droplets of bentonite-alginate mixture.

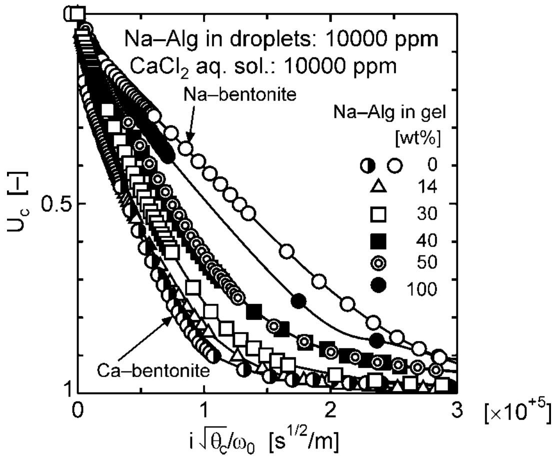

Figure 8. Time course of average consolidation ratio U_c of bentonite-alginate gel.

represented theoretically in the following equation:

$$U_c = 1 - \sum_{n=1}^{\infty} \frac{8}{(2n-1)^2\pi^2} \exp\left\{ -\frac{(2n-1)^2\pi^2}{4} \frac{i^2 C_e \theta_c}{\omega_0^2} \right\} \tag{6}$$

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.[6] 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. (6) is a measure of expression rate and 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. 9. In accord with Fig. 8, 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. The square symbol in the figure indicates C_e of bentonite-alginate

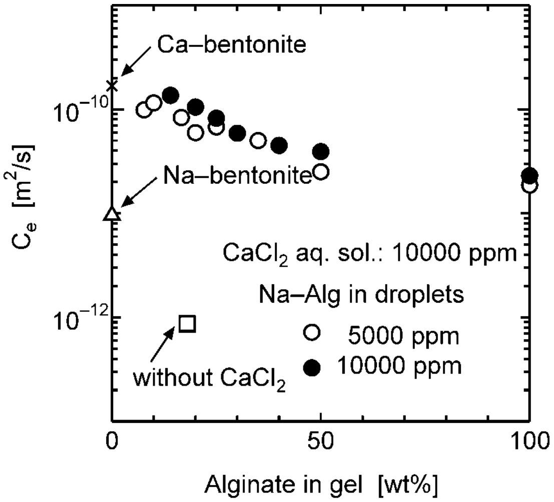

Figure 9. Effect of gel composition on C_e of bentonite-alginate gel.

mixture without gelation reaction; the calcium-free bentonite-alginate mixture is extremely difficult to dewater.

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. It was shown in the previous paper that when the concentration of calcium ions in supernatant is above 1000 ppm, 100% of the sodium bentonite in the droplets is altered to calcium bentonite.[3] The bentonite-alginate gels we prepared were always above this criterion. 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. The expression rates of PMMA-alginate gels are shown in Fig. 10. Since a PMMA particulate bed is

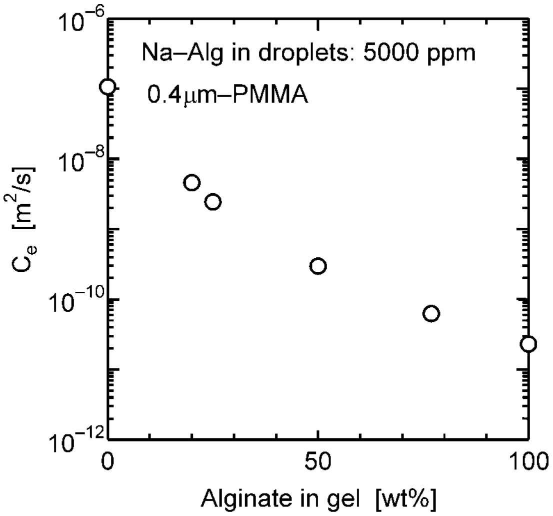

Figure 10. Effect of gel composition on C_e of PMMA-alginate gel.

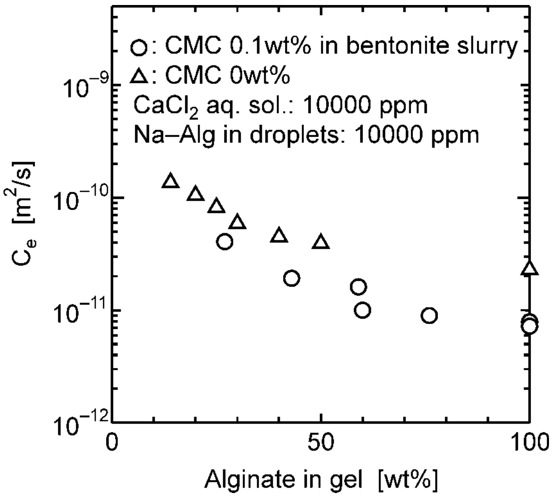

Figure 11. Effect of CMC on C_e of bentonite-alginate gel.

essentially incompressible, C_e decreases with increasing alginate content in the gel. Thus, C_e of alginate gel entrapping colloidal particles is between those of pure colloidal particles and colloid-free alginate gel.

Incidentally, in the mud-water-shielding technique, an aqueous solution of carboxy methyl cellulose (CMC) is often added to stabilize mud water. Figure 11 represents the effect of CMC (Wako Pure Chemical Industries) on the expression rate of stabilized-bentonite-alginate gel. The addition of CMC to bentonite-mud-water results in a decrease in expression rate of bentonite-alginate gel.

Based on Figs. 8–11, for the purpose of rapid removing of colloidal particles from difficult-to-filter colloidal suspension, 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. Figures 4 and 5 suggest the existence of an optimum value for the alginate content in the gel.

CONCLUSIONS

The basic characteristics of a new process for solid–liquid separation by use of particle immobilization in calcium alginate gel have been investigated.

1. When an alginate concentration in colloid-alginate mixture is above 1000 ppm, submicron particles are perfectly entrapped in calcium-alginate gels.
2. 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.
3. The lower the alginate content, the larger the expression rate of the bentonite/PMMA gel. The alginate content of gels should be kept to a minimum to effect rapid removal of colloidal particles from difficult-to-filter colloidal suspensions.

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]
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 packed gel bed [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]

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