

Coagulation of Oil in Water Using Sawdust and Bentonite and the Formation of a Floating Coagulated Material

Tianlei Sun¹ and D. D. L. Chung²

Abstract: The coagulation of oil in water is potentially cost-effective for removing oil from water. A coagulant consisting of sawdust (79.6% by volume), bentonite (15.8% by volume), and calcium hydroxide (4.7% by volume) gives coagulation efficiency of $\geq 94\%$ and coagulation time of ≤ 45 s. The resulting coagulated material (a semisolid) floats on water. Its oil (liquid) content, which decreases with a decreasing amount of oil originally present in the water, ranges from 69–81% by volume. This paper provides the first identification of multiple forms of oil in a coagulated material that is made from a single form of oil. The oil consists of strongly bonded oil (16% by volume, with relative dielectric constant 32) and weakly bonded oil (84% by volume, with the same relative dielectric constant of 2.0 as the original oil). The maximum and minimum volumes of oil per unit area that can be coagulated by $0.022 \text{ cm}^3/\text{cm}^2$ of coagulant volume per unit area are 0.116 and $0.052 \text{ cm}^3/\text{cm}^2$, respectively. Below the minimum amount of oil, the coagulated material sinks in water, thus hindering oil removal. DOI: 10.1061/(ASCE)EE.1943-7870.0000725. © 2013 American Society of Civil Engineers.

CE Database subject headings: Coagulation; Oil spills; Water pollution; Bentonite.

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Introduction

The removal of oil from water is relevant to oil-spill cleanups, water treatment, and water resource management. The coagulation of oil in water is an effective method for removing oil from water (Alther 1999; Badawy and Ali 2006; Canizares et al. 2008; Elost and Shtewi 2011; Qiu et al. 1995; Tansel and Vilar 2005; Xu et al. 2001). In particular, bentonite is an attractive coagulant, due to its low cost and environmental friendliness (Alther 1999; Badawy and Ali 2006; Elost and Shtewi 2011; Qiu et al. 1995; Tansel and Vilar 2005; Xu et al. 2001). However, bentonite suffers from its high density, which causes it to sink. It is desirable for the coagulated material to float on water so that it can be removed from above the water by methods such as scooping. Moreover, the sinking of the coagulated material is environmentally unfriendly; for example, in the case that the water source is an ocean, it may affect the ecology of the ocean floor.

By the combined use of bentonite and sawdust, with sawdust being the vast majority, the coagulated material floats in the form of a semisolid sheet (Fu 2011; Fu and Chung 2011). The sheet has a continuous matrix involving oil, bentonite, and sawdust, and there is apparently no upper limit to the sheet size. Without sawdust, the aggregates (which take the place of the sheet) sink in water and the coagulation efficiency is low. The sawdust functions as a

fibrous framework for the attachment of the coagulating oil and bentonite, thus facilitating the formation of a floating sheet, which may be conveniently removed.

A number of questions need to be answered regarding the previously mentioned process of coagulation through using the combination of bentonite and sawdust:

1. The main component of the coagulated material is oil, which is also the component with a density less than that of water. What is the minimum amount of available oil required for the coagulated material to float?
2. What is the upper limit for the amount of oil that can be contained in the coagulated material?
3. What is the relationship between the amount of available oil and the structure of the coagulated material?
4. How fast does the coagulation occur?
5. What is the difference, if any, between the nature of the as received oil and that of the oil in the coagulated material?
6. Is all of the oil in the coagulated material the same in nature? If not, how do the different forms of oil differ?

Prior papers used the method of microscopy to follow the process of coagulation, particularly in relation to the associated process of coalescence of the oil droplets (Tansel and Dimitric-Clark 2002). However, because of the wetness of the coagulated material and the fact that the coagulated material consists mainly of oil, with the solid component being a minority, it is difficult to observe the structure of the coagulated material by microscopy. Indeed, the microscopic structure of the coagulated material is quite different after drying (Fu and Chung 2011). In contrast, this paper uses dielectric constant measurement to characterize the coagulated material. This method is suitable because

- The dielectric constant differs between oil and the coagulant.
- The dielectric constant depends not only on the proportions of the components but also on the continuity of the medium in which ionic or partially ionic species can move.
- The dielectric constant of a given phase increases when the polarizability of the phase increases and the polarizability relates to the structure of the phase.

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In addition, this paper uses oil desorption measurement to characterize the oil in the coagulated material, thereby providing the first identification of multiple forms of oil in a coagulated material that is made from a single form of oil.

The objectives of this paper relate to (1) the investigation of the process of coagulation of oil in water using sawdust and bentonite as the main components of the coagulant and (2) the characterization of the structure of the coagulated material. In particular, this paper addresses the amount of available oil that is suitable for the oil coagulation, such that the coagulated material floats on water. In addition, the authors address the rate of the coagulation process and the possible presence of different oil forms in a coagulated material that is made from a single form of oil.

Experimental Methods

Materials

The oil is Hy-Gard Hydraulic/Transmission Oil from John Deere Construction and Forestry Division, Moline, IL. Its density is 0.88 g/cm^3 ; its pour point is -40°C ; its flash point is 227°C . The bentonite is sodium bentonite powder (M325) from Asbury Graphite Mills, Inc., Asbury, NJ. Its density is 2.0 g/cm^3 . It is a tan powder with negligible solubility in water. The calcium hydroxide is from J. T. Baker, Phillipsburg, NJ. Its density is 2.24 g/cm^3 . It contains 97.0% by weight Ca(OH)_2 ; 2.3% by weight CaCO_3 ; 0.02% by weight chloride (Cl); 0.03% by weight iron (Fe); and 0.9% by weight magnesium and alkali salts (SO_4). A local carpenter shop provided the sawdust. Its density is 1.05 g/cm^3 . The particle size of the sawdust is rendered small by sieving, using a metal sieve with pores of area 1.0 mm^2 . The water is tap water.

The coagulant is a mixture of 0.375 g bentonite, 1.000 g sawdust, and 0.125 g calcium hydroxide, totaling 1.500 g, unless stated otherwise. In cases in which the calcium hydroxide mass varies, the masses of bentonite and sawdust do not change. The coagulant (all solid) is to be distinguished from the coagulated material, which is the oil-containing semisolid material obtained after coagulation.

Coagulant Amount per Unit Area and Oil Amount per Unit Area

This section relates the amount of coagulant with the amount of coagulant per unit area of the water surface, which is defined by the inner diameter of the beaker containing the water. In addition, this section relates the amount of oil with the amount of oil per unit area of the water surface. The inner diameter of the beaker is 83 mm, so the area (S) of the liquid surface is 54.1 cm^2 .

The mass of the coagulant, m_t , is fixed at 1.500 g. The mass of the added oil (i.e., the oil added to the water), M_o , ranges from 1.000–7.000 g.

For 1.500 g of the coagulant, the mass of the coagulant per unit area is given by

$$m_t/S = (1.500 \text{ g})/(54.1 \text{ cm}^2) = 0.028 \text{ g/cm}^2 \quad (1)$$

and the volume of the coagulant per unit area is given by

$$\begin{aligned} \text{mass per unit area/density} &= (0.028 \text{ g/cm}^2)/(1.26 \text{ g/cm}^3) \\ &= 0.022 \text{ cm}^3/\text{cm}^2 \end{aligned} \quad (2)$$

The quantities per unit area are useful for application of the coagulation technology to reservoirs of different sizes.

Coagulation Procedure

The authors used the following coagulation procedure, unless stated otherwise. The authors put tap water in the amount of 250 mL in a 500-mL glass beaker with a 83-mm diameter. They added oil in the amount of $M_o = 5.000 \text{ g}$ to the water. They stirred the mixture of liquid with a magnetic stirrer at 70 rpm for 30 min. After stirring, the oil droplets were allowed to move naturally toward the top surface of the water due to floatation over a period of 1 min. The authors manually mixed bentonite, calcium hydroxide, and sawdust according to the ratio mentioned in the section titled “Materials” to form the coagulant in the amount of 1.500 g. Then, they manually sprinkled the coagulant little by little on the surface of the liquid by using a plastic spoon so that the coagulant spread on the liquid surface uniformly. After the application of the coagulant, oil coagulation was allowed to take place over a period of 75 min, although the coagulation process actually took less than 1 min to complete. The coagulated material floated on the water and was removed from the liquid by scooping it with the plastic spoon. The authors then placed the scooped-material on a sheet of filter paper that had already been folded and placed in a glass funnel for the purpose of separating the coagulated material from most of the water that was included in the scooped-material. This filtration occurred for 45 min.

Coagulation Efficiency Determination Method

The coagulation efficiency (E) refers to the fraction of oil that is coagulated divided by the oil available for coagulation. This section describes the method for determining E . Immediately after the completion of the procedure described in the section titled “Coagulation Procedure,” the authors poured the remaining water out of the beaker and used another sheet of filter paper to collect the oil adhered to the inside surface of the beaker and the surfaces of the spoon by rubbing these surfaces with the filter paper. They rubbed the inside surface of the beaker until it appeared dry. After this, they placed both sheets of filter paper (the first sheet mentioned in the section titled “Coagulation Procedure and Holding the Coagulated Material”) in a vacuum (i.e., rough vacuum) oven at 110°C for 30 min to remove the remaining water in the sheets. After this baking, they allowed the coagulated material and filter paper to cool in air at room temperature and to absorb room moisture for 24 h.

It is assumed that heating at 110°C for 30 min removes water and does not remove oil. This assumption is supported by the effect of heating for up to 48 h at this temperature, as described in the section titled “Oil Desorption Characteristics of the Coagulated Material,” which shows by weight loss measurement that oil desorption during the first 30 min of the heating is negligible compared to that afterward. This is reasonable, because the boiling point of water is 100°C and the flash point of the oil is 227°C . The boiling point of oil is above the flash point. In the section titled “Oil Desorption Characteristics of the Coagulated Material,” it has been confirmed that in the absence of water or oil, the coagulant does not change in weight when heated.

The authors separately weighed the first sheet of filter paper with the coagulated material on it and the second sheet of filter paper with the adhered oil. It is assumed that the weight of the filter paper itself is not affected by the 30-min 110°C drying process. The authors obtained the amount of oil that was not involved in coagulation by subtracting the weight of the filter paper (unused) from the weight of the filter paper with the adhered oil. Hence, they obtained the oil available for coagulation by subtracting the weight of the adhered oil from the original weight of the oil, which is 5.000 g (unless noted otherwise).

The authors calculated the coagulation efficiency (E) from the following equation:

$$E = (m_{cf} - m_b - m_h - m_s - m_f) / [M_o - (m_{af} - m_f)] \quad (3)$$

where m_{cf} = the mass of the coagulated material together with the filter paper holding it, m_b = the mass of the bentonite, m_h = the mass of the calcium hydroxide, m_s = the mass of the sawdust, m_f = the mass of a sheet of unused filter paper, M_o = the mass of added oil (5.000 g unless stated otherwise), and m_{af} = the mass of oil adhered to the inside surface of the beaker and the surfaces of the spoon together with the sheet of filter paper used to rub these surfaces. For each value of M_o , the authors experimentally determined the coagulation efficiency E three times.

Microscopic Observation of the Coagulation Process

The authors observed the coagulation process by using optical microscopy. They obtained a micrograph once every 10 s to follow the process. They obtained the first micrograph at 5 s after the application of the coagulant to the oil-containing water.

Relative Dielectric Constant Measurement Method

Taking the measurement of the relative dielectric constant involved measuring the capacitance at three different thicknesses of the specimen, which was sandwiched by two electrodes in a parallel-plate capacitor configuration (Chung 2010). The electrodes served as electrical contacts for imposing an alternating-current (AC) electric field in the direction perpendicular to the plane of the parallel-plate capacitor. Measurement at three thicknesses allowed for decoupling of the capacitance of the specimen from that of the interface between the specimen and each of the two electrodes. The relative dielectric constant κ of the specimen relates to the reciprocal of the slope of the plot of the reciprocal of the measured capacitance versus the specimen thickness.

The authors measured the capacitance by using a precision RLC meter from QuadTech 7600, QuadTech, Inc., Marlborough, MA at 1.000 kHz. The two electrodes were two square copper plates of thickness 6.42 mm (top plate) and 6.38 mm (bottom plate), as illustrated in Fig. 1. Each plate had a square area of 100×100 mm. The pressure provided by a copper plate and the steel weight on top of it on the specimen during relative dielectric constant measurement was 2.32 kPa. The authors used glass fiber fabric-reinforced Teflon film (from the CS Hyde Company, Lake Villa, IL) of thickness 0.07 mm, square area 100×100 mm, and relative dielectric constant 2.08 (measured at 1.000 kHz) as an electrically

insulating film between the specimen and each of the two copper electrodes.

The authors cut a polyester (polyethylene terephthalate) film, an electrically insulating film of thickness 0.14 mm and relative dielectric constant 2.34 measured at 1.000 kHz, to form a frame for holding the specimen. The square frame is like a picture frame, with outer dimensions 100×100 mm and a 60×60 mm square through-hole in the middle. The specimen is contained in the hole, referred to as the cavity. The authors consecutively stacked one, two, or three pieces of this film to hold specimens of three different thicknesses, abbreviated as l and equal to 0.14, 0.28, and 0.42 mm.

The amplitude of the AC voltage is 1.000 V. This corresponds to an AC electric field of 3.6, 2.4, and 1.8 kV/m for the specimen thicknesses of 0.14, 0.28, and 0.42 mm, respectively.

To make sure that the specimen held by the square frame is neither too little (thus, involving air pockets) nor too great (thus, making the thickness of the specimen inaccurate), the amount of specimen that should be placed in the dielectric constant measurement cavity needs to be calculated prior to the placement of the specimen. The calculation is based on the density of the coagulated material and the volume of the cavity that involves one polyester film.

With the specimen of mass, m_p , present in the cavity that involved one polyester film, the authors measured the capacitance C_1 . Similarly, they measured C_2 by using two films stacked up and twice the amount of coagulated material. Similarly, with three films stacked up, they obtained C_3 .

The capacitance C is for the composite consisting of the specimen and the frame (in parallel electrically), with inclusion of the effect of each of the two interfaces between this composite and the two Teflon-lined electrodes. The two interfaces and this composite are in series electrically. Hence

$$1/C = (2/C_i) + [l/(\epsilon_0 \kappa A)] \quad (4)$$

where C_i = the capacitance of one of the two composite-electrode interfaces; ϵ_0 = the permittivity of free space, i.e., 8.85×10^{-12} F/m; κ = the relative dielectric constant of the composite; A = the area of the electrode, which is the same as the area of the composite, i.e., 0.0100 m²; and l is the thickness of the frame. According to Eq. (4), $1/C$ is plotted against l , as illustrated schematically in Fig. 2. The value of C_i is obtained from the intercept (equal to $2/C_i$, with the factor of 2 being attributable to the presence of two interfaces) at the $1/C$ axis at $l = 0$, and the value of κ is obtained from the slope, which is equal to $1/(\epsilon_0 \kappa A)$.

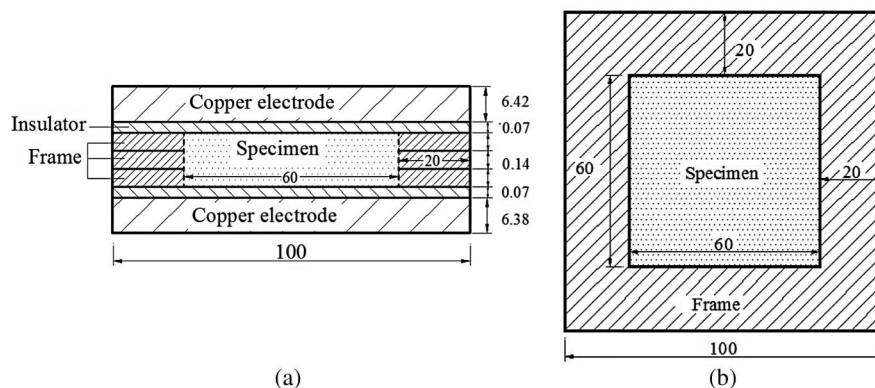


Fig. 1. Configuration for measuring the relative dielectric constant; all dimensions are in mm: (a) side view, with the horizontal and vertical scales being different; (b) top view

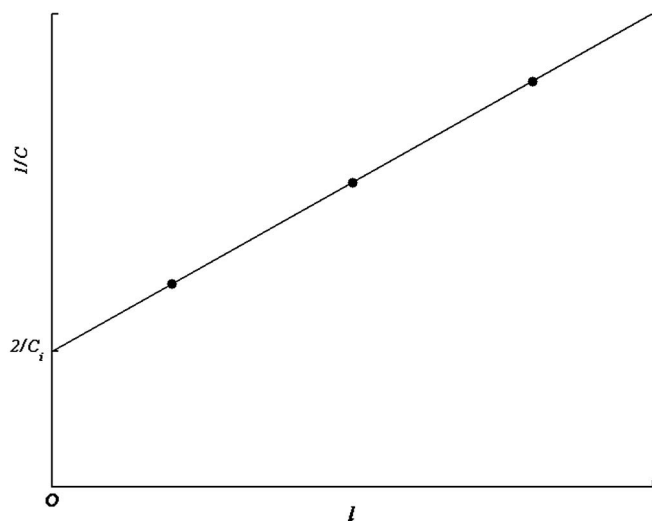


Fig. 2. Schematic plot of $1/C$ versus l for the determination of C_i and κ

The relative dielectric constant (κ) of this composite (specimen plus frame) is related to that of the specimen κ_c and that of the frame κ_p by the Rule of Mixtures

$$\kappa = \kappa_c v_c + \kappa_p v_p \quad (5)$$

where v_c = the area fraction of the specimen and v_p = the area fraction of the frame.

Determination of the Relationship between the Relative Dielectric Constant and the Amount of Water Coexisting with the Coagulated Material after Towel-Drying

Water tends to coexist with the coagulated material after scooping the coagulated material from the water. Because the relative dielectric constant of water is higher than those of oil and the coagulant, the coexistence of water with the coagulated material is expected to increase the relative dielectric constant.

The authors measured the relative dielectric constant of the coagulated material for four conditions, using the method described in the section titled "Relative Dielectric Constant Measurement Method." The first condition corresponds to the situation in which the coagulated material has been scooped and filtered, immediately followed by drying using a paper towel; it corresponds to the state in which the coagulated material coexists with water. The second condition corresponds to the situation in which the towel-dried material has been further dried in the air at room temperature for 24 h; it corresponds to the state in which the coagulated material has most, if not all, of the water with which it coexists removed by evaporation. The third condition corresponds to the situation in which the room temperature-dried material has been further dried in a vacuum (rough vacuum) oven at 110°C for 30 min; it corresponds to the state in which the coagulated material does not have any water coexisting with it. The fourth condition corresponds to the situation in which the room temperature-dried coagulated material has been further dried in a vacuum oven at 110°C for 48 h; it corresponds to the state in which the coagulated material does not have any water coexisting with it, in addition to having its weakly bonded oil removed. The distinction between weakly bonded oil and strongly bonded oil is described in the section titled "Oil Desorption Characteristic of the Coagulated Material."

The difference in mass between the first and third conditions provides a measure of the mass of water present with the coagulated material under the first condition. The authors weighed the coagulated material, in the presence of considerable water in case of the first condition, for each of the four conditions immediately before taking the measurement of the relative dielectric constant. A comparison of the results for the first, second, and third conditions allows for a study of the effect of water content on the relative dielectric constant.

The mass of coagulated material (second condition), m_p , that should be placed in the dielectric constant measurement cavity formed by the frame that involves one polyester film is obtained by consideration of the specimen density and the cavity volume. The mass of the coagulated material is essentially not affected by heating at 110°C for 30 min, so the amount of material that should be placed in the cavity can be the same for the second and third conditions. However, a separate determination needs to be carried out for the first condition.

The authors performed an experiment involving weighing the coagulated material (possibly in the presence of water) in the first, second, and third conditions previously mentioned to determine the volume fraction of water for the first condition. The mass of this material was fixed at 1.500 g. The mass of the material under the second condition (after drying at room temperature for 24 h) was 1.18 ± 0.32 g. The mass of the material under the third condition (after drying at 110°C for 30 min) was 1.15 ± 0.12 g. The mass decreased substantially from the first condition to the second condition, but it essentially did not change from the second condition to the third condition. This means that the extent of desorption during the drying at 110°C for 30 min is negligibly small, as essentially all of the water is desorbed by evaporation during drying at room temperature for 24 h. The authors obtained the amount of the towel-dried coagulated material (the first condition) that should be placed in the cavity formed by the frame that involves one polyester film from the density of this material and the volume of the cavity.

Oil Desorption Characteristic of the Coagulated Material

After 24 h of room temperature drying of the coagulated material for removal of the water in the material (i.e., the second condition), the authors measured the weight loss during desorption at 110°C for 48 h to monitor the process of oil desorption. Completion of 48 h of 110°C drying gives the fourth condition.

The backbone of the coagulated material is defined as the solid part of the coagulated material. The liquid part is oil. The term backbone reflects the interconnected nature of the solid (Fu and Chung 2011). There are two forms of oil in the coagulated material: one form is strongly bonded oil, which is bonded to the backbone strongly and is difficult to be removed from the coagulated material by heating; the other form is weakly bonded oil, which is easily removed from the coagulated material by heating.

The authors placed the coagulated material on a sheet of filter paper in a vacuum oven at 110°C for 48 h to remove the oil by evaporation and by absorption by the filter paper. They completely removed the coagulated material from the filter paper by scraping using a stainless steel spatula before each weighing of the coagulated material. They conducted the weighing every hour in the first 6 h and every 2 h in the subsequent period. Every 12 h, they replaced the filter paper by a new one to maintain adequate absorption ability. The mass of the coagulated material thus obtained at a given time of heating, with the mass of the coagulant deducted, gives the mass of oil in the coagulated material at this time.

The coagulant itself showed no weight loss during heating (see the section titled “Oil Desorption Characteristics of the Coagulated Material” in “Results and Discussion”). The authors plotted the mass of oil versus the time of drying. Due to the leveling off of this curve as time progresses, this curve allowed for the distinction between weakly bonded oil, which desorbs during the drying, and strongly bonded oil, which does not desorb.

Determination of the Relative Dielectric Constant of the Coagulated Material and Its Components

The authors measured the values of the relative dielectric constant of the coagulated material corresponding to the second and fourth conditions by using the method described in the section titled “Relative Dielectric Constant Measurement Method.” The amount of the coagulant (1.000 g of sawdust; 0.375 g of bentonite; 0.125 g of calcium hydroxide, totaling 1.500 g; mass per unit area 0.28 g/cm²; volume per unit area 0.022 cm³/cm², as described in the sections titled “Materials” and “Coagulant Amount per Unit Area and Oil Amount per Unit Area”) was fixed. The amount M_o of added oil was varied systematically.

The authors obtained the weakly bonded oil in the absence of the solid component of the coagulated material by squeezing the coagulated material (after room temperature drying, i.e., the second condition) by using a plastic syringe, and they measured the relative dielectric constant of this oil by using the method described in the section titled “Relative Dielectric Constant Measurement Method.” To obtain the relative dielectric constant of the backbone and that of the strongly bonded oil from the measured values of the coagulated material by using the Rule of Mixtures, they needed the volume fractions of the strongly bonded oil and the weakly bonded oil. They used the parallel electrical configuration for the backbone and the oil in the calculation, even though the two components were randomly mixed.

Results and Discussion

Effects of Initial Oil Concentration and the Amount of Calcium Hydroxide on the Coagulation Efficiency

Table 1 shows the coagulation efficiency E , as obtained by using Eq. (3), for the case in which $M_o = 5.000$ g. The results are consistent with those of prior papers (Fu and Chung 2011). Table 2 shows the coagulation efficiency for different values of M_o ranging from 2.500–5.000 g. When M_o is less than 2.500 g, the coagulated material sinks while the coagulant that has not participated in the coagulation process floats on the water; as a result, the mass of the coagulant that participates in the coagulation cannot be determined. When M_o exceeds 5.000 g, some oil that has not been coagulated coexists with the coagulated material, such that the combination floats on the water; as a result, the mass of the oil that has been coagulated cannot be determined. Consequently, the

Table 1. Coagulation Results for $M_o = 5.000$ g and $E = 0.9459 \pm 0.0093$

(g)	Test 1	Test 2	Test 3
m_{cf}	7.422	7.236	7.293
m_b	0.375	0.375	0.375
m_h	0.125	0.125	0.125
m_f	1.146	1.160	1.159
m_s	1.000	1.000	1.000
m_{af}	1.261	1.312	1.222
E	0.9552	0.9439	0.9386

Table 2. Coagulation Efficiency E for Various Combinations of M_o and Calcium Hydroxide Mass in Coagulant

Mass of $\text{Ca}(\text{OH})_2$ (g)	Mass of oil M_o (g)	Coagulation efficiency E
0.250	5.000	0.949 ± 0.008
0.125	2.500	0.949 ± 0.010
	3.500	0.944 ± 0.009
	5.000	0.946 ± 0.009
0.060	5.000	0.931 ± 0.010

coagulation efficiency can be determined only for M_o ranging from 2.500–5.000 g. Table 2 shows that there is essentially no effect of M_o on the coagulation efficiency.

The authors needed the volume fraction of the oil in the coagulated material for the purpose of calculating the relative dielectric constant of the solid part (the backbone) of the coagulated material. For obtaining the volume fraction of oil in the coagulated material, they needed the coagulation efficiency.

To investigate the possible effect of the amount of calcium hydroxide in the coagulant on the coagulation efficiency, the authors used different amounts of calcium hydroxide (0.060, 0.125, and 0.250 g, with the intermediate value of 0.125 g being the typical value used in this paper), such that the amount of oil was fixed at 5.000 g and the amounts of sawdust and bentonite in the coagulant were fixed at 1.000 and 0.375 g, respectively. The coagulation efficiency with different amounts of calcium hydroxide in the coagulant, as shown in Table 2, essentially does not vary with the amount of calcium hydroxide in the range studied.

Microscopic Monitoring of the Coagulation Process

The authors examined the coagulation process by optical microscopy. Fig. 3 shows the optical micrographs taken in real time during coagulation.

Coagulation starts to occur immediately (within 5 s) upon application of the coagulant to the oil-containing water. Because of the high density of the coagulated material (whether the coagulation is complete or not) compared to the oil, the coagulated material (whether the coagulation is complete or not) sinks within the layer of oil located on the water's surface. However, the coagulated material remains above the water, because of its low density compared to that of water. This sinking causes oil that has not been coagulated to be present on top of the coagulated material, to the extent that the coagulated material cannot be observed from the top. Thus, the coagulated material is observed as bright finger-like patches (shown at the left part of the micrograph) at 5 and 15 s, vaguely at 25 and 35 s, and not at 45 s and beyond. The dark regions in the micrographs are oil, with the very bright curves being reflections from the oil, as caused by the uneven oil surface topography resulting from the sinking of the coagulated material. In Fig. 3, the solid arrow points to a piece of the coagulated material (bright, finger-like patch) and the open arrow points to a part of the oil (dark background). The micrographs essentially do not change after 45 s, because both the sinking process and the coagulation process have been completed. This means that the coagulation process mostly occurs in the first 25 s, such that it continues in an incremental fashion from 25 to 35 s and is essentially complete in the first 45 s.

Oil Desorption Characteristics of the Coagulated Material

The authors separately tested the coagulant (mixture of sawdust, bentonite, and calcium hydroxide) and the coagulated material

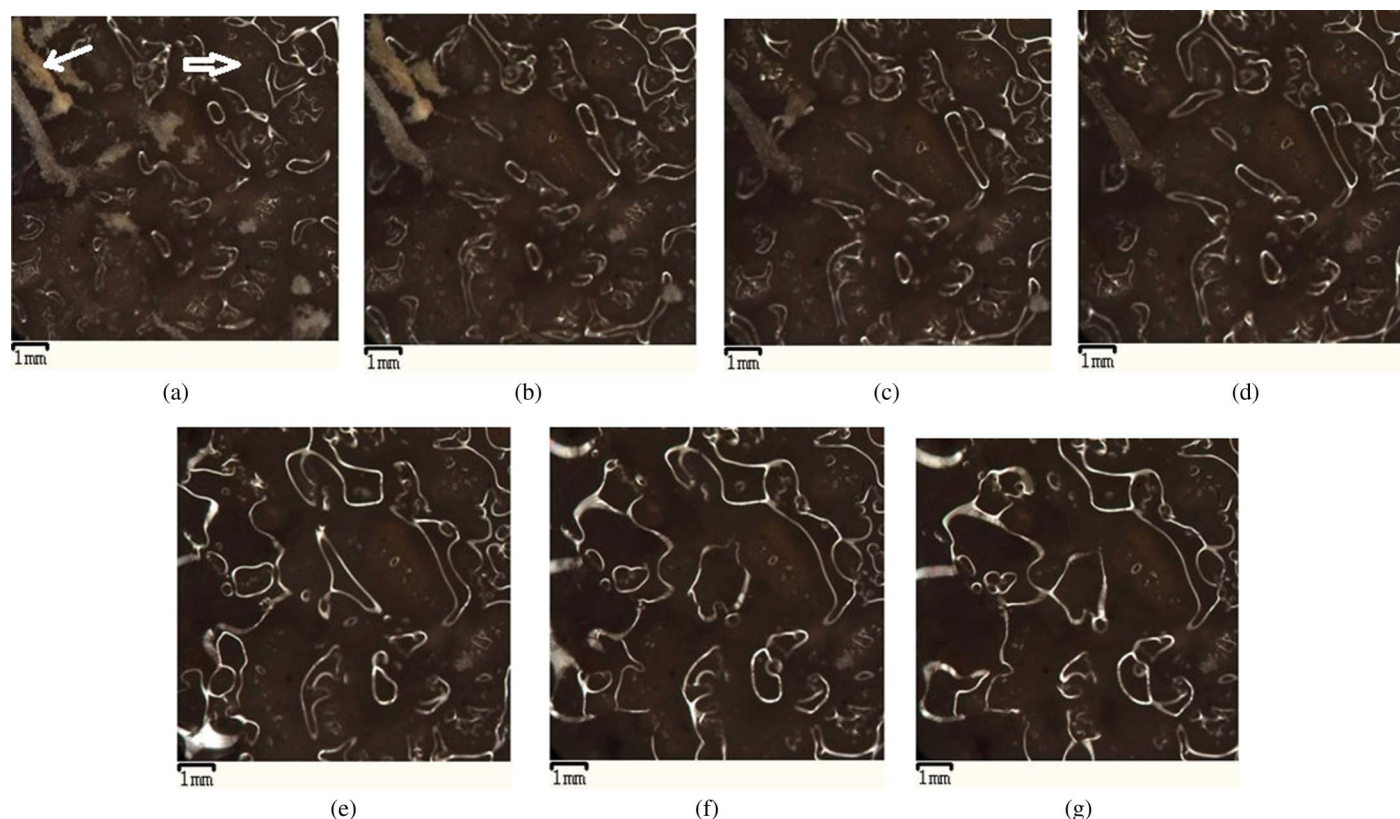


Fig. 3. Optical micrographs obtained at different times after coagulant application

in terms of their weight loss, if any, during heating in a vacuum oven at 110°C for 48 h. They removed the specimen from the furnace for each weighing, which was conducted in air at room temperature. The coagulant showed no weight loss, whereas the coagulated material showed significant weight loss, because of oil desorption.

After drying the coagulated material at room temperature for 24 h for the purpose of removing the water, the authors dried the coagulated material at 110°C in a vacuum oven for up to 48 h. Fig. 4 shows photographs of the coagulated material before (i.e., the second condition) and after the 110°C drying (i.e., the fourth condition). Before drying, the coagulated material was connected and appeared as a sheet-like material, whereas after drying it

was loose and disconnected (Fu and Chung 2011). In other words, the coagulated material was less continuous after drying.

As shown by the curve of the mass of the oil remaining in the coagulated material versus the 110°C drying time for different values of M_o , the oil desorption was essentially complete in 24 h, such that most of the oil desorption occurred in the first 5 h, for any of the values of M_o . The extent of desorption during the first 30 min was relatively minor. After 24 h of desorption, the curve leveled off and the remaining oil was strongly held. In contrast, the oil that was desorbed was weakly bonded. Table 3 shows the masses of strongly bonded oil (not desorbed) and weakly bonded oil (desorbed). The fraction of oil that was strongly bonded was essentially independent of M_o and was around 0.16. The strongly bonded oil

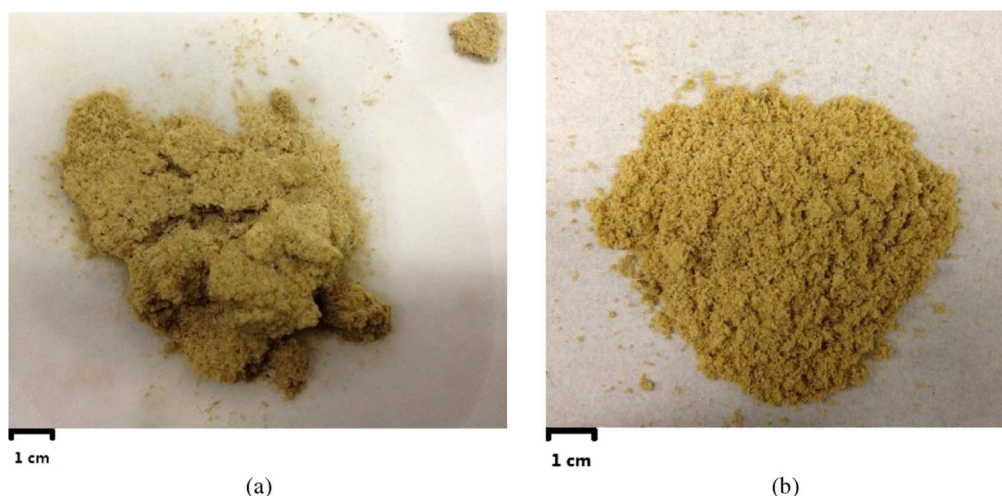


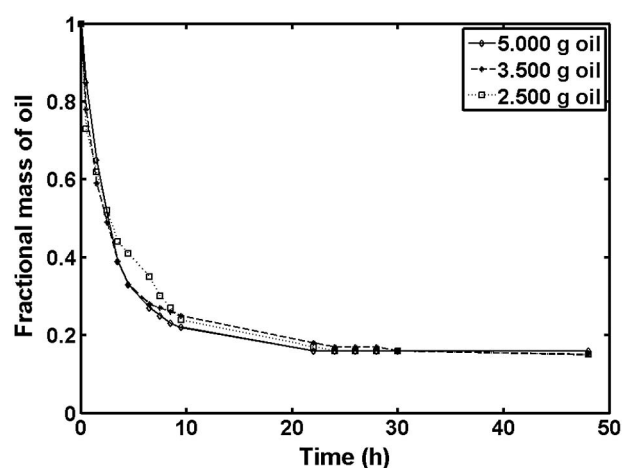
Fig. 4. Coagulated material: (a) second condition; (b) fourth condition

Table 3. Mass of Strongly Bonded Oil, and Mass of Weakly Bonded Oil in Coagulated Material for Various Values of M_o

M_o (g)	Mass of strongly bonded oil (g)	Mass of weakly bonded oil (g)	Fraction of oil that is strongly bonded
5.000	0.75	3.87	0.16
3.500	0.55	2.70	0.17
2.500	0.37	1.86	0.17

apparently interacted significantly with the backbone, probably because of the partially ionic character of the backbone (the bentonite part of the backbone) and the polarizability of the oil (attributable to bond movement). In contrast, the weakly bonded oil probably just clung to the strongly bonded oil by van der Waals force. This means that the oil that participated in the coagulation included both strongly bonded oil (minority) and weakly bonded oil (majority). This paper provides the first observation of multiple forms of oil in a coagulated material that is made from a single form of oil. Fig. 5 shows the curve of the fractional mass of oil remaining in the coagulated material versus the 110°C drying time for each of the three values of $M_o = 5.000$ g, 3.500 g, and 2.500 g of available oil. The oil removal rate is independent of M_o .

The authors obtained the volume fractions of the backbone, strongly bonded oil and weakly bonded oil in the coagulated material under the second condition, as shown in Table 4. That the total oil amounts to 81% by volume of the coagulated material for the case of $M_o = 5.000$ g is consistent with prior papers (Fu and Chung 2011). As M_o decreased, the volume fractions of total oil, strongly bonded oil, and weakly bonded oil all decreased. For M_o in the range from 2.500–5.000 g, the total oil content ranges

**Fig. 5.** Fractional mass of the oil (relative to the value before drying at 110°C but after drying at room temperature for 24 h) in the coagulated material during drying at 110°C for 48 h**Table 5.** Volume Fractions of Backbone and Strongly Bonded Oil in Coagulated Material under Fourth Condition

Mass of oil M_o (g)	Volume fractions of solid components				Volume fraction of strongly bonded oil
	Sawdust (%)	Bentonite (%)	Ca(OH) ₂ (%)	Backbone ^a v'_e (%)	v'_g (%)
5.000	47	9	3	59	41
3.500	53	11	3	67	33
2.500	60	11	4	75	25

^aTotality of the solid components.

from 69–81% by volume and the solid content ranges from 31–19% by volume. The decrease in M_o caused mainly the volume fraction of the weakly bonded oil to decrease, while that of the strongly bonded oil decreased only slightly. Decrease in M_o also caused the volume fraction of the backbone to increase. The sawdust dominated the backbone volume.

Table 5 shows the volume fractions of the backbone and strongly bonded oil in the coagulated material under the fourth condition. In contrast to the oil-dominated coagulated material under the second condition (Table 4), the backbone volumetrically dominated the coagulated material under the fourth condition (Table 5). As M_o decreased, the volume fraction of strongly bonded oil decreased while that of the backbone increased (Table 5), as expected.

To investigate the possible effect of the amount of calcium hydroxide in the coagulant on the proportion of strongly bonded oil in the coagulated material, the authors used different amounts of calcium hydroxide (0.060, 0.125, and 0.250 g, with the intermediate value of 0.125 g being the typical value used in this paper), such that the amount of oil was fixed at 5.000 g and the amounts of sawdust and bentonite in the coagulant were fixed at 1.000 and 0.375 g, respectively. They placed the coagulated material obtained for each amount of calcium hydroxide in a vacuum oven at 110°C for 48 h for the purpose of determining the proportion of strongly bonded oil. As shown in Fig. 6, the amount of calcium hydroxide Ca(OH)₂ in the range studied did not affect the proportion of strongly bonded oil. The pH was not measured, but a change in the calcium hydroxide amount was expected to cause a change in the pH. Thus, the pH is not an influential parameter.

Relative Dielectric Constant Measurement Results

First, this section will discuss the coagulated material in the presence of different amounts of water. Fig. 7 shows representative curves of $1/C$ versus thickness l . The curves are all straight lines, as expected based on Fig. 2. The relative dielectric constant κ_c is 25.91 ± 2.63 for the material under the first condition (after drying with paper towel); 7.50 ± 0.53 for the material under the second condition (after drying at room temperature for 24 h); and 7.05 ± 0.38 for the material under the third condition (after drying at 110°C for 30 min).

Table 4. Volume Fractions of Solid Components, Strongly Bonded Oil, and Weakly Bonded Oil in Coagulated Material under Second Condition

Mass of oil M_o (g)	Volume fractions of solid components				Volume fractions of oil		
	Sawdust (%)	Bentonite (%)	Calcium hydroxide (%)	Backbone ^a v_e (%)	Strongly bonded oil v_g (%)	Weakly bonded oil v_k (%)	Total oil (%)
5.000	15	3	1	19	13	68	81
3.500	20	4	1	25	12	63	75
2.500	24	5	2	31	11	58	69

^aTotality of the solid components.

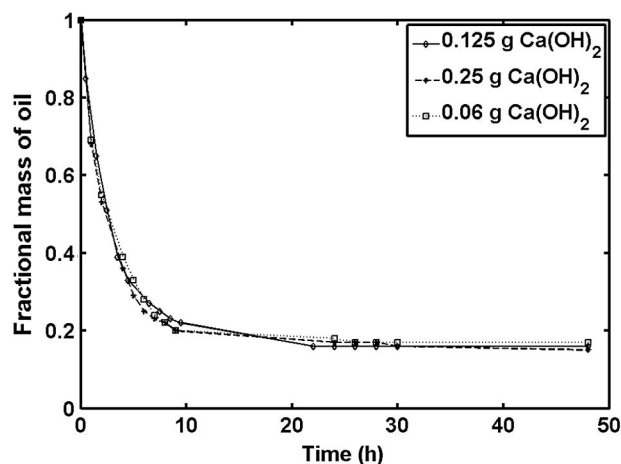


Fig. 6. The fractional mass of oil in the coagulated material during drying at 110°C for 48 h for different amounts (0.060, 0.125, and 0.250 g) of calcium hydroxide Ca(OH)_2 in the coagulant

Both the mass (see the section titled “Determination of the Relationship between the Relative Dielectric Constant and the Amount of Water Coexisting with the Coagulated Material after Towel-Drying”) and the relative dielectric constant κ_c decreased substantially from the first condition to the second condition, but they essentially did not change from the second condition to

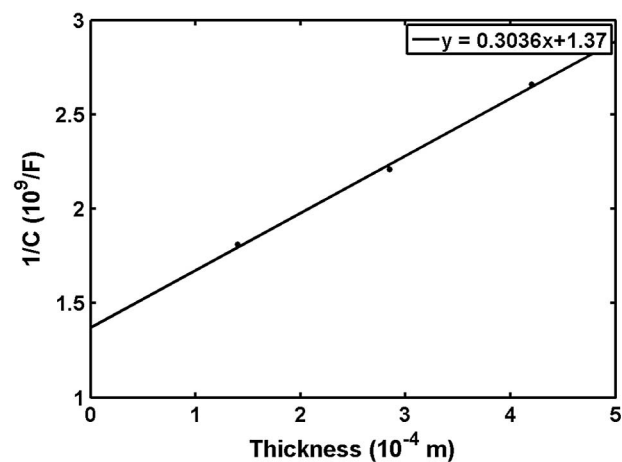


Fig. 8. Representative curve of $1/C$ versus thickness l for the coagulated material (second condition, plus the frame) for $M_o = 6.000$ g

the third condition. This trend is consistent with the high value of the relative dielectric constant of water and the small amount of desorption during drying at 110°C for 30 min (see the section titled “Determination of the Relationship between the Relative Dielectric Constant and the Amount of Water Coexisting with the Coagulated Material after Towel-Drying”).

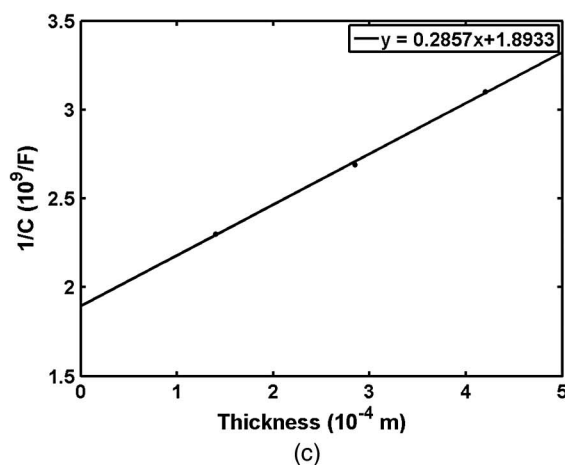
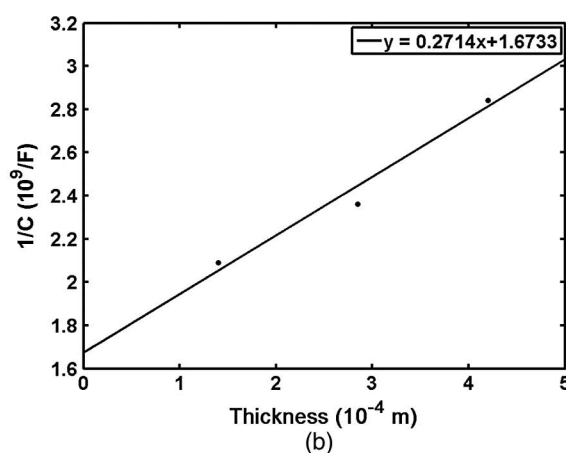
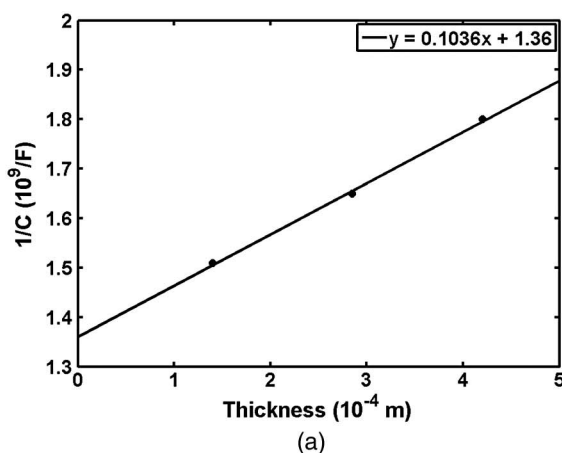


Fig. 7. Representative curves of $1/C$ versus thickness l for the coagulated material (plus the frame) for $M_o = 5.000$ g: (a) first condition; (b) second condition; (c) third condition

Table 6. Relative Dielectric Constant κ_c of Coagulated Material for Second Condition and Relative Dielectric Constant κ'_c of Coagulated Material under Fourth Condition for Different Values of M_o

Mass of oil M_o (g)	Relative dielectric constant κ_c	Relative dielectric constant κ'_c
5.000	7.11 ± 0.75	13.42 ± 0.53
3.500	7.09 ± 0.30	11.09 ± 0.48
2.500	7.05 ± 0.38	8.92 ± 0.63

Table 7. Maximum/Minimum Volume of Coagulant and Maximum/Minimum Volume of Coagulant per Unit Area for Different Amounts of Available Oil

Volume of oil (km ³)	Volume of coagulant (km ³)		Volume of coagulant per unit area (cm ³ /cm ²)	
	Maximum	Minimum	Maximum	Minimum
5.00	2.10	0.953	0.00131	0.000595
10.0	4.19	1.91	0.00262	0.00119
50.0	20.1	9.53	0.0131	0.00595
100	41.9	19.1	0.0262	0.0119
150	62.9	28.6	0.0393	0.0179

Next, this section will discuss the coagulated material for different amounts of added oil. This section pertains to studying the effect of M_o on the coagulated material. The curves of $1/C$ versus thickness in Figs. 7(b) and 8, both for the second condition but for two different values of M_o , are straight lines. Such linearity is obtained for all types of specimens in this paper.

The authors used the volume fractions of the backbone in the coagulated material under the second condition (v_e) and fourth condition (v'_e); the volume fractions of the strongly bonded oil under the second condition (v_g) and fourth condition (v'_g); and the volume fractions of the weakly bonded oil (present under the second condition, but not under the fourth condition) for calculating the relative dielectric constant of the backbone under the second condition (κ_e) and fourth condition (κ'_e) and that of the strongly bonded oil under the second condition (κ_g) and fourth condition (κ'_g), using the Rule of Mixtures.

The relative dielectric constant of the coagulated material under the second condition, as shown in Table 6, was essentially independent of M_o . Because the coagulation efficiency was essentially independent of M_o (Table 2), the amount of oil in the coagulated material increased with M_o . In spite of this, the relative dielectric constant of the coagulated material was essentially independent of M_o . This unexpected result was because

- The oil in the coagulated material consisted of strongly bonded oil (minority) and weakly bonded oil (majority) (see the section titled "Oil Desorption Characteristics of the Coagulated Material").
- The decrease in oil content mainly impacted the weakly bonded oil (see the section titled "Oil Desorption Characteristics of the Coagulated Material").
- The relative dielectric constant of the strongly bonded oil was much higher than that of the weakly bonded oil (as shown below).

The relative dielectric constant of the weakly bonded oil was 1.98 ± 0.03 , which was essentially equal to that of the as-received oil (1.95 ± 0.02). This was expected, because the weakly bonded oil clung to the strongly bonded oil with essentially no interaction with the coagulant.

According to the Rule of Mixtures, the relative dielectric constant κ of the coagulated material under the second condition is given by

$$\kappa = \kappa_e v_e + \kappa_g v_g + \kappa_k v_k \quad (6)$$

where κ_e = the relative dielectric constant of the backbone in the coagulated material under the second condition, κ_g = the relative dielectric constant of the strongly bonded oil in this coagulated material, and κ_k = the relative dielectric constant of the weakly bonded oil in this coagulated material.

For the case of $M_o = 5.000$ g, Eq. (6) becomes

$$7.05 = \kappa_e 0.19 + \kappa_g 0.13 + 1.98 \times 0.68 \quad (7)$$

Rearrangement of Eq. (7) gives

$$\kappa_e = -0.68\kappa_g + 30.02 \quad (8)$$

For the case of $M_o = 3.500$ g, Eq. (6) becomes

$$7.09 = \kappa_e 0.25 + \kappa_g 0.12 + 1.98 \times 0.63 \quad (9)$$

Rearrangement of Eq. (9) gives

$$\kappa_e = -0.48\kappa_g + 23.37 \quad (10)$$

For the case of $M_o = 2.500$ g, Eq. (6) becomes

$$7.11 = \kappa_e 0.31 + \kappa_g 0.11 + 1.98 \times 0.58 \quad (11)$$

Rearrangement of Eq. (11) gives

$$\kappa_e = -0.35\kappa_g + 19.23 \quad (12)$$

Fig. 9(a) shows the plots of Eqs. (8), (10), and (12). The three lines obtained meet at a point, which gives the solution to these three equations. Hence, $\kappa_e = 7.6$, and $\kappa_g = 32$.

The relative dielectric constant κ' of the coagulated material under the fourth condition (after drying at 110°C for 48 h) is similarly measured and shown in Table 6. According to the Rule of Mixtures, κ'_c is given by

$$\kappa'_c = \kappa'_e v'_e + \kappa'_g v'_g \quad (13)$$

where κ'_e = the relative dielectric constant of the backbone under the fourth condition and κ'_g = the relative dielectric constant of the strong bonded oil under the fourth condition.

For the case of $M_o = 5.000$ g, Eq. (13) becomes

$$13.42 = \kappa'_e 0.59 + \kappa'_g 0.41 \quad (14)$$

Rearrangement of Eq. (14) gives

$$\kappa'_e = -0.69\kappa'_g + 22.75 \quad (15)$$

For the case of $M_o = 3.500$ g, Eq. (13) becomes

$$11.09 = \kappa'_e 0.67 + \kappa'_g 0.33 \quad (16)$$

Rearrangement of Eq. (16) gives

$$\kappa'_e = -0.49\kappa'_g + 16.55 \quad (17)$$

For the case of $M_o = 2.500$ g, Eq. (13) becomes

$$8.92 = \kappa'_e 0.75 + \kappa'_g 0.25 \quad (18)$$

Rearrangement of Eq. (18) gives

$$\kappa'_e = -0.33\kappa'_g + 11.89 \quad (19)$$

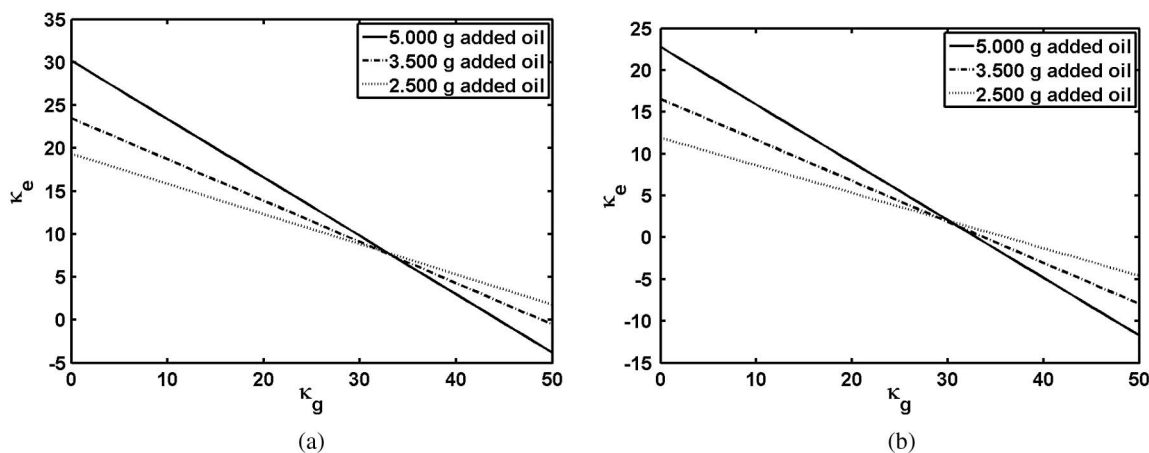


Fig. 9. Plots of the relative dielectric constant of the backbone versus that of the strongly bonded oil in the cases of 5.000, 3.500, and 2.500 g of available oil: (a) second condition; (b) fourth condition

Fig. 9(b) shows the plots of Eqs. (15), (17), and (19). The three lines obtained meet at a point, which gives the solution to the three equations. Hence, $\kappa'_e = 1.6$, and $\kappa'_g = 31$.

The values of the relative dielectric constant of the strong bonded oil under the second condition (κ_g) and fourth condition (κ'_g) are essentially equal. This is consistent with the notion that the drying removes the weakly bonded oil only. Conversely, the values of the relative dielectric constant of the backbone under the second condition (κ_e) and fourth condition (κ'_e) are quite different, suggesting that the drying results in less continuity of the medium in which ionic (or partially ionic) species can move under the influence of an applied electric field. The decreased continuity after drying is supported by the photographs in Fig. 4.

Criteria behind the Floating and Sinking of the Coagulated Material

Fig. 10 shows that when $M_o = 2.000$ g, the coagulated material sinks while the coagulant that has not participated in the coagulation floats. Fig. 11 shows that the coagulated material floats when $M_o = 2.500$ g. In other words, the coagulated material floats

when $M_o = 2.500$ g or greater but sinks when $M_o = 2.000$ g or less. The sinking phenomenon is because of the high density of the coagulant (1.26 g/cm^3) compared with the density of water (1.00 g/cm^3). Although oil has a low density of 0.88 g/cm^3 , the density of the coagulated material is higher than that of water when the amount of oil in the coagulated material is not sufficiently high.

Fig. 12 shows that the amount of oil that has not been coagulated and that floats on top of the coagulated material because of its low density (the oil appearing as shiny regions because of light reflection and as a relatively dark oil pool in the central region of the circular area) increases as M_o increases from 5.000 to 6.000 g and then to 7.000 g. In contrast, the coagulant that had not been coagulated because of the low value of M_o appeared as white powder, which was clearly observed when $M_o = 5.000$ g [Fig. 12(a)]. The amount of the coagulant (white powder) decreased abruptly as M_o increased beyond 5.000 g. Fig. 13 shows that the coagulated material appeared as a floating sheet. As shown from the view from the bottom of the sheet [Fig. 13(b)], the sheet was continuous, though the thickness had undulations within the sheet.

For 1.500 g (mass per unit area 0.028 g/cm^2 , volume per unit area $0.022 \text{ cm}^3/\text{cm}^2$) of the coagulant, the amount of oil below

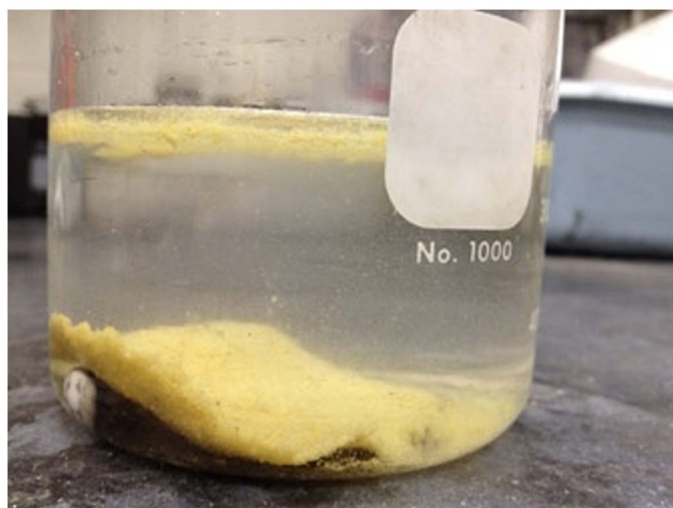


Fig. 10. Side view of the beaker containing the coagulated material for the case of $M_o = 2.000$ g; the inner diameter of the beaker is 83 mm

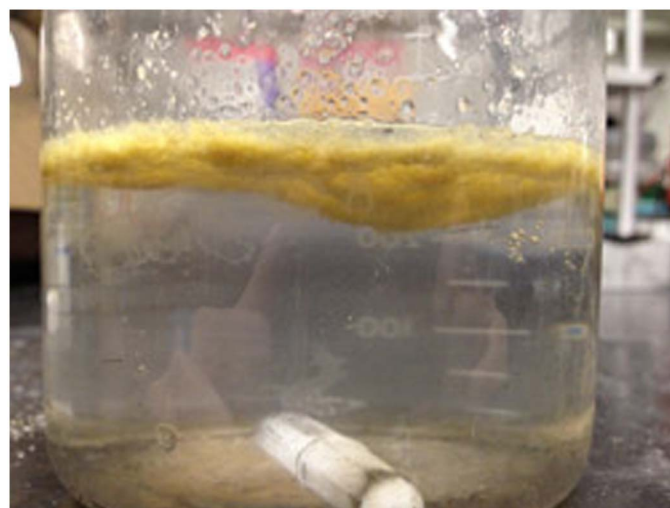


Fig. 11. Side view of the beaker containing the coagulated material for the case of $M_o = 2.500$ g; the inner diameter of the beaker is 83 mm

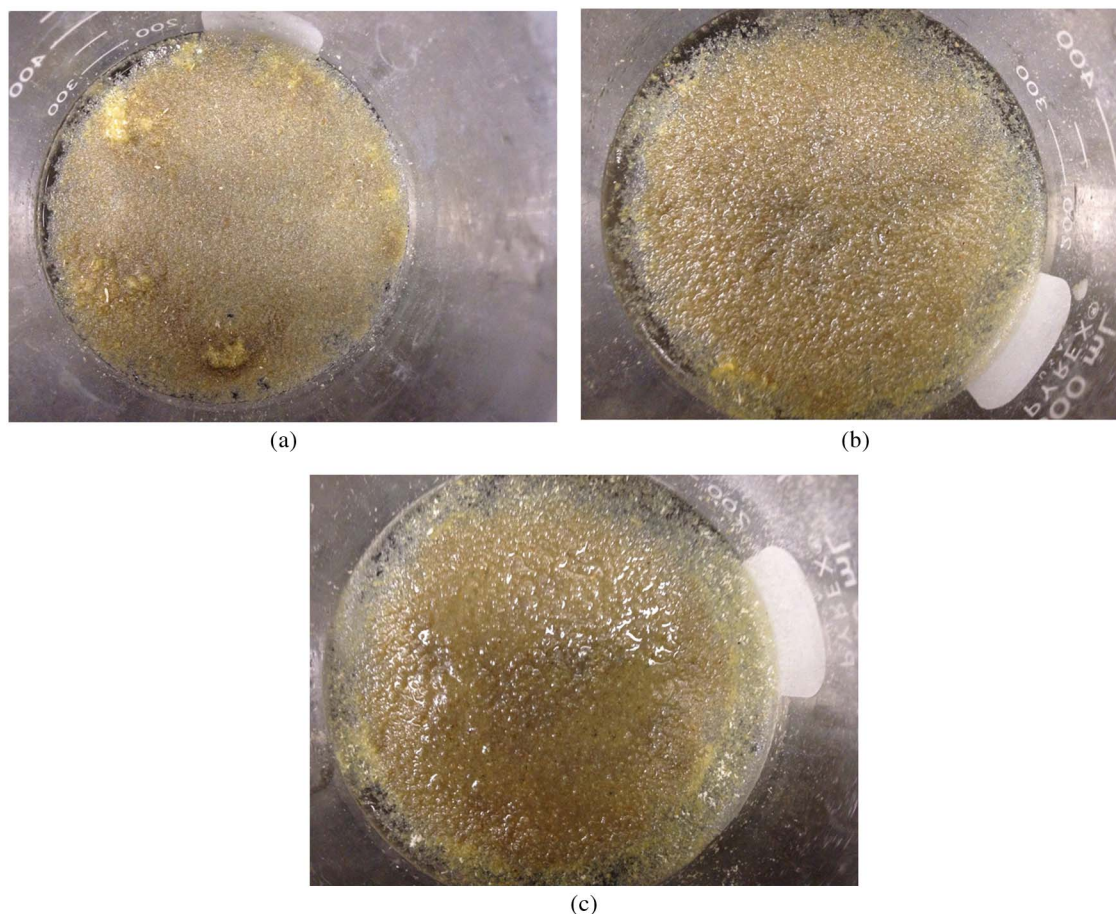


Fig. 12. Top view of the complete circular mouth of the beaker containing the coagulated material for the case of (a) $M_o = 5.000$ g; (b) $M_o = 6.000$ g; (c) $M_o = 7.000$ g; the inner diameter of the beaker is 83 mm

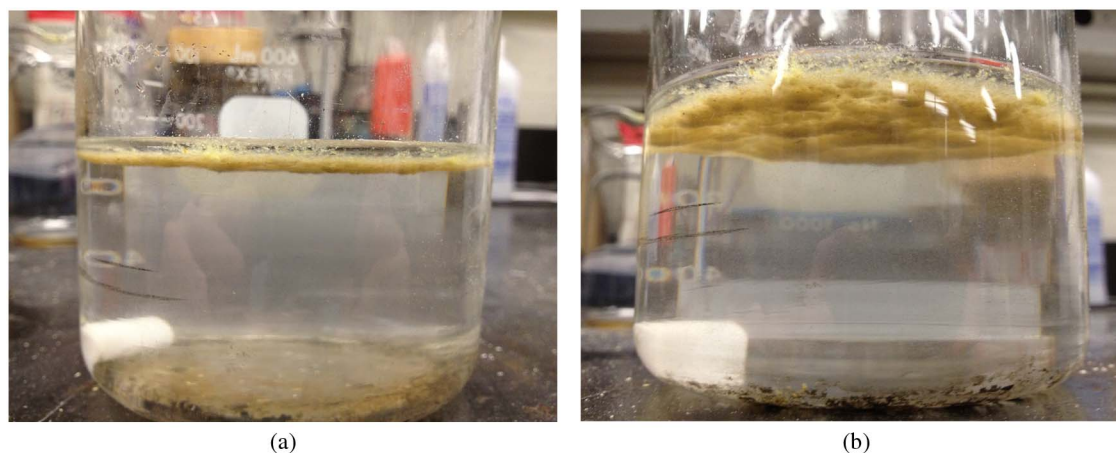


Fig. 13. The coagulated material for the case of $M_o = 7.000$ g: (a) side view of the beaker; (b) side-bottom view of the beaker; the inner diameter of the beaker is 83 mm

which sinking occurs for the coagulated material is $M_o = 2.500$ g (mass per unit area 0.046 g/cm^2 , volume per unit area $0.052 \text{ cm}^3/\text{cm}^2$). As the sinking is not desirable for oil removal, this value of M_o can be considered the minimum amount of oil for effective oil removal. Hence, the ratio of the minimum added oil volume per unit area to the coagulant volume per unit area is $0.052/0.022 = 2.4$, and the ratio of the minimum added oil mass per unit area to the coagulant mass per unit area is

$0.046/0.028 = 1.6$. In other words, the maximum coagulant volume per unit area for unit available oil volume per unit area is 0.42, and the maximum coagulant mass per unit area for unit available oil mass per unit area is 0.63.

For 1.500 g (mass per unit area 0.028 g/cm^2 , volume per unit area $0.022 \text{ cm}^3/\text{cm}^2$) of the coagulant, the amount of added oil above which a part of the oil did not get coagulated corresponded to a value between $M_o = 5.000$ g (mass per unit area 0.092 g/cm^2 ,

volume per unit area $0.105 \text{ cm}^3/\text{cm}^2$) and $M_o = 6.000 \text{ g}$ (mass per unit area $0.111 \text{ g}/\text{cm}^2$, volume per unit area $0.126 \text{ cm}^3/\text{cm}^2$). For convenience, the authors took $M_o = 5.5 \text{ g}$ (mass per unit area $0.102 \text{ g}/\text{cm}^2$, volume per unit area $0.116 \text{ cm}^3/\text{cm}^2$) as the maximum amount of added oil for complete oil coagulation. Hence, the ratio of the maximum added oil volume per unit area to the coagulant volume per unit area was $0.116/0.022 = 5.3$, and the ratio of the maximum added oil mass per unit area to the coagulant mass per unit area was $0.102/0.028 = 3.6$. In other words, the minimum coagulant volume per unit area for unit volume per unit area of added oil was $0.022/0.116 = 0.19$, and the minimum coagulant mass per unit area for unit mass per unit area of oil was $0.028/0.102 = 0.27$.

Table 7 shows the maximum and minimum volumes of coagulant and the maximum and minimum volumes of coagulant per unit area for different amounts of available oil. The volume of coagulant increases with the volume of oil, as expected.

Conclusion

The mixture of sawdust (79.6% by volume), bentonite (15.8% by volume), and calcium hydroxide (4.7% by volume) as the coagulant gives high efficiency of oil coagulation in water. The efficiency reaches 94% or above, in agreement with prior papers (Fu and Chung 2011). The oil content in the coagulated material decreases with a decreasing amount of added oil. It ranges from 69–81% by volume, and the solid content ranges from 19–31%.

This paper provides the first identification of multiple forms of oil in a coagulated material that is made from a single form of oil. The oil in the coagulated material consisted of strongly bonded oil and weakly bonded oil. The strongly bonded oil (remaining after drying at 110°C for 48 h) amounts to 16% by volume of the oil and exhibited relative dielectric constant 32, because of interaction with the coagulant. The weakly bonded oil amounts to 84% by volume of the oil and its relative dielectric constant remains at 2.0 (the value for the as-received oil). In spite of the presumed interaction of calcium hydroxide with bentonite in the coagulant, variation of the calcium hydroxide amount in the range from 0.060–0.250 g in the coagulant has essentially no effect on the coagulation efficiency or the proportion of strongly bonded oil in the resulting coagulated material.

The solid part of the coagulated material forms the backbone of the coagulated material. It exhibits relative dielectric constant 7.6 before drying at 110°C for 48 h and 1.6 after drying. The decrease upon drying is because of the decrease in the extent of physical continuity.

Coagulation starts as soon as (within 5 s) the coagulant touches the oil. The coagulation process mainly occurs in the first 25 s, continues in an incremental fashion between 25 and 35 s, and is essentially complete at 45 s.

When the amount of added oil is too small (i.e., when the proportion of coagulant is too high), the coagulated material sinks in water, because of the substantial proportion of coagulant that does not participate in the coagulation process. For a given amount of

added oil, the minimum amount of coagulant is taken as the amount below which the coagulated material sinks. There is also a limit to the amount of oil that can be coagulated by a given amount of coagulant. With the use of a beaker of diameter 83 mm for holding the oil-containing water, for 1.500 g coagulant (1.000 g sawdust; 0.375 g bentonite; 0.125 g calcium hydroxide; mass per unit area $0.028 \text{ g}/\text{cm}^2$; volume per unit area $0.022 \text{ cm}^3/\text{cm}^2$), the minimum amount of added oil required for the coagulated material to float is 2.500 g (mass per unit area $0.046 \text{ g}/\text{cm}^2$, or volume per unit area $0.052 \text{ cm}^3/\text{cm}^2$), and the maximum amount of added oil that this amount of coagulant can coagulate is 5.5 g (mass per unit area $0.102 \text{ g}/\text{cm}^2$, or volume per unit area $0.116 \text{ cm}^3/\text{cm}^2$). In other words, the maximum mass of oil that can be coagulated by the unit mass of the coagulant is 3.67 g; the minimum mass of oil that can be coagulated by the unit mass of the coagulant without sinking is 1.67 g; the maximum mass of the coagulant above which sinking occurs for the unit mass of oil is 0.60 g; the minimum mass of the coagulant for coagulating the unit mass of oil is 0.27 g.

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