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Microwave Assisted Demulsification of Iraqi Crude Oil Emulsions Using Tri-octyl Methyl Ammonium Chloride (TOMAC) Ionic Liquid

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Abstract

In the present work, the efficiency of Tri-octyl Methyl Ammonium Chloride (TOMAC) ionic liquid was investigated as new and green demulsifier for three types of Iraqi crude oil emulsions (Nafut Khana (NK), Kirkuk and Basrah). The separation efficiency was studied at room temperature and by using microwave heating technique. Several batch experiments were done to specify the suitable conditions for the emulsification and demulsification which were specified as 45 minutes and 3000 rpm for crude oil emulsification while the ionic liquid doses were (500,300,150,50) ppm and the conditions of microwave heating were 1000 watt and 50 second as irradiation time. The results were very encouraging especially for NK and Kirkuk crude oil emulsions where the separation efficiency was between (100%-95%) in both cases (by microwave heating and at room temperature demulsification). The separation percentages of Basrah crude emulsion varied but as a general result, the efficiency was acceptable for high doses at the same time, while for low doses, the water removal ratio was not good as the previous one.

Keywords: demulsification, crude oil, w/o emulsion, microwave, TOMAC

Introduction

Crude oil is seldom produced alone because it is generally commingled with water. The water creates several problems and usually increases the unit cost of oil production. Furthermore, sellable crude oil must comply with certain product specifications, including the amount of basic sediment and water (BS and W) and salt, which means that the produced water must be separated from the oil to meet crude specifications [1]. Emulsions of crude oil and water can be encountered at many stages during drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities, transportation systems and refineries. In each case, the presence and nature of emulsion can determine both the economic and technical success of industrial process concerned. A good knowledge of petroleum emulsions is necessary for controlling and improving processes at all stages. Many studies have been carried out in the last 40 years and have led to a better understanding of these complex systems [2]. The formation of stable water-in-crude oil emulsions is frequently encountered during oil production, mainly due to high shear rates and zones of turbulence that prevail at the wellhead in the choke valve. These complex and generally viscous systems significantly increase the technical problems related to oil-water separation in production surface facilities [3]. These emulsions can be very stable due to the presence of polar compounds such as asphaltenes and resins that play the role of “natural emulsifiers” and to the presence of low molecular weight fatty acids, naphthenic acids in addition to many types of fine solids (crystallized waxes, clays, scales, etc.).These materials help in the formation of resistant films at the crude oil/water interface [4]. Because of the technical problems of water in oil emulsions, the emulsion breaking process which is known demulsification becomes very crucial and important in order to get oil with high quality and with minimum cost in all production and refinery stages. The water content must be less than 1% and typically 0.3% - 0.5% because increasing water content in oil leads to increasing transportation costs [5, 6]. The complex nature of typical water-in-crude oil emulsions is one of the main difficulties for the development of adequate separation techniques in the petroleum industry. Despite the huge efforts that have been made in the last 30 years for the development of reliable and efficient demulsification techniques, most water-in-crude oil emulsions cannot be broken in short times [7]. Many separation techniques were used during past decades like mechanical, heating, electrical and chemical demulsification. Every method has merits and defects. Until now there is no method that could reach complete destabilization without a combination with another one. However, the chemical demulsification is an important method for W/O emulsion treating [8, 9]. Due to more and more severe environmental constraints, there is now a strong need in the oil production to restrict the use of chemicals and to utilize safer formulations, less toxic but at least as efficient as classical demulsifiers [10]. Many efforts have been performed to develop new strategies for achieving an efficient breaking of W/O emulsions in crude oil and, consequently, to remove water, salt and solids [11]. The efforts were focused on greener techniques to reach effective demulsification with minimum pollution and cost because creating a "green" brands demulsifiers is justified not only environmental, but also economic as a biodegradable agent does not require, or at least reduces the cost of cleanup and disposal of waste containing it. One of green technologies that has been focused on by recent studies and has provided interesting results for the treatment of crude oil emulsions is based on the application of microwave radiation. This kind of energy is effective, clean and economic especially it began to substitute the conventional ones in many scientific fields [12]. The principle of microwave-assisted demulsification processes is the change in the composition of the system through the use of specific compounds that have high dielectric properties, thus enhancing the absorption of radiation by the sample. Moreover, these additives can be chosen to act in not only the heating system but also the mechanisms involved in the process. In this direction, ionic liquids (ILs) have been widely used as additives in processes involving microwave heating [13]. Ionic liquids (ILs) have attracted many researchers in the areas including physics and chemistry because of their characteristics that are different from conventional molecular liquids and, today; ILs have been one of interesting subjects of scientific study. They are defined as specific class of molten salts with high dielectric properties, consisting of organic cations combined with anions of organic or inorganic nature. The chemical structure of ILs allows many combinations of anions and cations, enabling one to obtain compounds with properties quite varied, which means that tailor-made ILs can be produced for a given application. Their boiling point is always less than 100 °C [14, 15]. In the present work, efforts were focused to test the efficiency of ionic liquids as new green demulsifiers with the combination of microwave heating technology .The research aims to assess the performance of these different materials as emulsion breaker for Iraqi crude oil types for the first time.

Experimental Work

Materials

1. Crude oils: Three types of Iraqi crude oils were used. The physical properties of these oils are listed in Table 1:

Table 1: Physical properties of different Iraqi crude oils

Property	NK	Kirkuk	Basrah
Sp.Gr.	0.8095	0.8509	0.8681
API	40	31	26
Asph.(%wt)	0.08	1.29	2.1
Kin.Viscosity (Cst) at 15° C	5.89	11.6	21.7
Sulfur content % wt	0.58	2.33	3.33
IBP °C	37	46	43

2. Sodium chloride was obtained from local markets
3. TOMAC ionic liquid of purity of 98% ,404.16 g/gmol M.wt, 550 cP viscosity , -20 °C melting point ,100°C melting point was supplied by JandK CHIMICA, China

Emulsion Preparation

The emulsion was prepared by adding different initial water ratios (30%, 15%, 8%) with (3% wt. NaCl) to the different types of crude oil at room temperature. The emulsification was carried out by using a mixer at a speed of 3000 rpm for 45 minutes to get a stable W/O emulsion. The emulsions prepared in this way were stable for months without apparent phase separation [16].

Demulsification

Several batch experiments were done to detect effects of some variables on emulsion breaking process and to assess the separation efficiency of TOMAC ionic liquid for the three types of Iraqi crude oil emulsions in both cases with microwave heating and at room temperature. The prepared emulsion was heated by using microwave irradiation for 50 seconds and 1000 Watts power. After heating, it was left at room temperature for 180 minutes and the total water removal percentage (W %) was calculated according to Eq. 1 :

$$W\% = \frac{separated\ water\ volume}{intial\ water\ volume} \times 100 \quad \ldots(1)$$

Where W %:= separation efficiency

Results and Discussion

1. Stability of Prepared Emulsion

The stability of prepared emulsions was measured by two methods. The first test was aging test and the second test was droplets size distribution (DSD) measurement of droplets by using microscope (model N117M with fitted 5Mp Digital Camera, Beijing NOVEL Optics Co., Ltd/China). The two tests proved that prepared emulsions could be classified as tight emulsions where the emulsions did not show any clear separation over a period more than 6 months. Table 2 shows DSD of emulsions.

Table 2: Drop size distribution of emulsions

Crude oil type	30% emulsion droplet size (micron)	15% emulsion droplet size (micron)	8% emulsion droplet size (micron)
NK	13-16	7-10	5.5-7
Kirkuk	6.5 -9	5-7.45	5-6.45
Basrah	6.-8	4.5 -6	3.5-5.5

2. Water Content Effect

The effect of initial volume fraction of internal phase (water) was studied for the three crude oil types containing different water content ratios using TOMAC. Fig. 1 shows this effect.

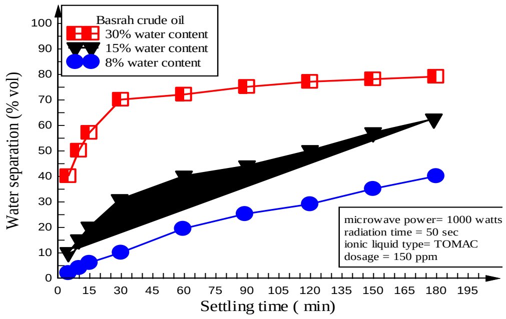

Fig. 1: Effect of water content on separation efficiency

According to the figure above, the maximum emulsion resolution was obtained for emulsion with greater initial water content (30% vol.). It is important to mention here that because dielectric properties are influenced by medium composition, it is necessary to understand the relationship between these properties and the emulsion WC. This is especially important in demulsification processes, where WC variations are expected to occur. Besides, emulsion WC can also influence the coalescence efficiency during the demulsification process, leading to a reduced distance between droplets in the sample. This distance can be severely narrowed with the increase of the volume of the aqueous phase in the emulsion, raising the probability of collision between the droplets.

3. Asphatene Content Effect

The asphaltene content effect on emulsion breaking process for three types of crude oil emulsions is shown in Fig. 2

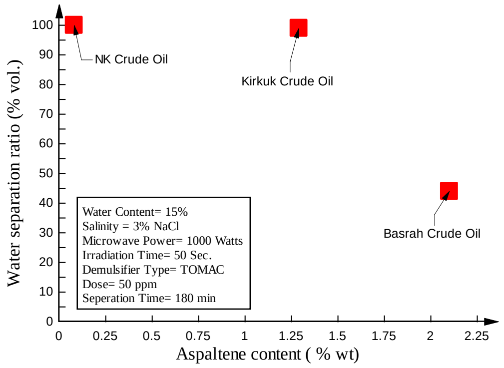

Fig. 2: Effect of asphaltene content on separation efficiency

Fig. 2 showed the separation efficiency is (99 % vol.) for Kirkuk emulsion with 1.29%wt. asphaltene content, and it is about 44 %vol. for Basrah emulsion which has 2.1% wt. asphaltene when the dose is 50 ppm and 180 minutes settling time while the separation percentage was 100% for NK emulsion with less than 50 ppm and 10 minutes. Asphaltene content may play a role over the interfacial properties of the emulsion and over stability. The asphaltene molecules aggregate with each other or with wax molecules and migrate to water /oil interface and form a layer surrounding the water droplet. This elastic layer prevents and inhibits the coalescence process. When the asphaltene content increases, the thickness of this layer will increase because of the increase in the aggregate rate of its molecules and its precipitation at w/o interface.

4. Dose Effect

Fig. 3 shows the effect of demulsifier dose on the separation efficiency for Basrah crude oil emulsion.

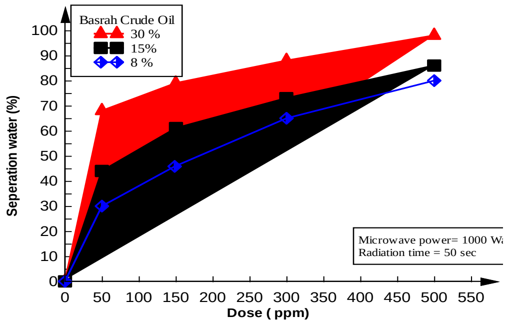

Fig. 3: Dose effect on separation efficiency for Basrah crude oil emulsion

As it is seen in Fig. 3, the maximum separation ratio was obtained at the maximum dose of TOMAC and this behavior is the same for the three initial water contents. Demulsification efficiency increases as the concentration of the demulsifier increases up to a certain value. At this concentration, the demulsifier molecules perform a complete coverage of the water/oil interface, dragging the asphaltenes away from the interface. As a result, the protecting film present around the dispersed water droplets thins and then it ruptures and coalescence eventuates.

5. Salt Content Effect

Different salt contents were examined to study its effect on the water separation efficiency. The maximum chosen concentration was 30000 ppm because it is the concentration of most oilfield emulsions. Fig. 4 shows the effect of salt concentration on demulsification efficiency.

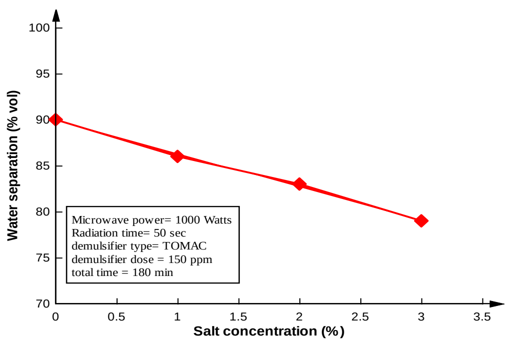

Fig. 4: Salt Content Effect on separation efficiency

It is noticed that the demulsification efficiency decreased when salt content increased. For 0 % salt content, water separation percentage reached to 90% but this percentage decreased with increasing salt concentration to reach 79% at 3% salt content. This reduction of the separation efficiency with the increase of the salt content (or ultimately of the ionic strength) could be explained by the reduction of the power applied by the microwave device. In this way, the microwave interaction with the polar species in the interfacial film is expected to be poorer, resulting in weaker perturbations of this interface and then in reduced coalescence rates

TOMAC Separation Assessment

A. Ionic Liquid Efficiency Combined with Microwave Irradiation

The performance of ammonium based ionic liquid is examined as crude oil demulsifier. TOMAC ionic liquid was tested as demulsifier for the three crude oil types as following:

NK crude oil emulsion showed no need for heating because it was completely separated at room temperature. TOMAC performance with Kirkuk crude oil emulsion was also very great. For the three water contents (8%, 15 %, and 30%), the separation percentage is between 99% to 100%. Figs. 5, 6 and 7 clarify the TOMAC efficiency to demulsify this emulsion.

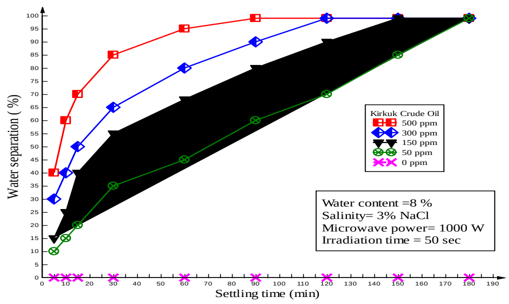

Fig. 5: TOMAC efficiency with 8% water content Kirkuk crude oil emulsion

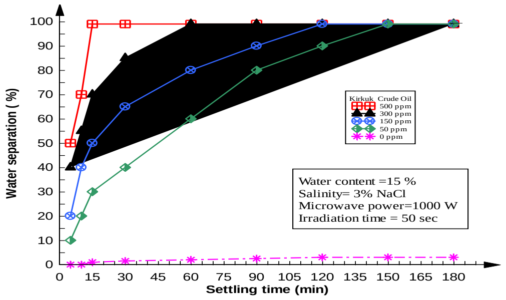

Fig. 6: TOMAC efficiency with 15% water content Kirkuk crude oil emulsion

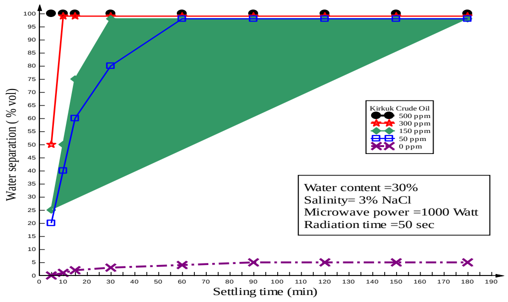

Fig. 7: TOMAC efficiency with 30% water content Kirkuk crude oil emulsion

Figures 5, 6 and 7 show that the emulsion breaking process was effective for all doses. But the differences were in settling time where it varied from less than 5 minutes to 180 minutes as maximum for three types of Kirkuk emulsions.

Basrah, emulsions with different water initial water contents were examined by using microwave and TOMAC ionic liquid. The water separation efficiency was very good for high doses. The results of the three water contents were acceptable as shown in Figs. 8, 9 and 10.

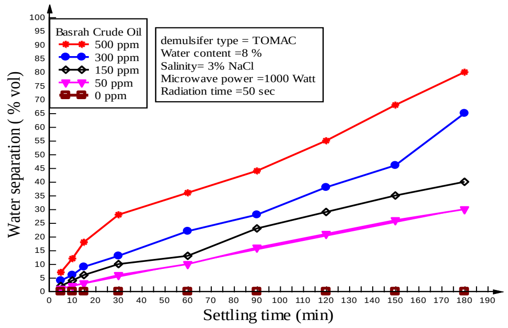

Fig. 8: TOMAC performance for 8 % Basrah crude oil emulsion

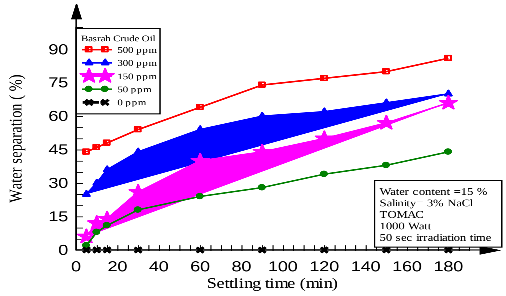

Fig. 9: TOMAC performance for 15 % Basrah crude oil emulsion

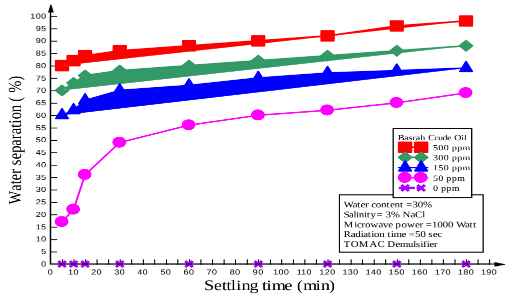

Fig. 10: TOMAC performance for 30 % Basrah crude oil emulsion

The results in the figures clarify the performance of TOMAC for Basrah emulsions where the results are acceptable. The percentages for high doses are very good and they reached 98% water separation for 500 ppm while separation percentages began to decrease with low dose.

In Fig. 10, the maximum water removal percentage was (98%) for 500 ppm whereas the ratio was (69%) for 50 ppm after 180 minutes settling time. From Fig. 9, the results of emulsion breaking were between (86%) for 500 ppm and (44%) for 50 ppm. In Fig. 8, the same behavior was detected. At 500 ppm demulsifier dose, the separation percentage was (80%) while with 50 ppm, the percentage did not exceed (30%).

The effectiveness and the high activity of TOMAC can be attributed to Chloride anion which exists in TOMAC ionic liquid which has a main and important role in demulsification process. This anion has effective ability to dissolve asphaltene - resin network aggregates by interaction with molecules of this network. This interaction makes the coalescence process of droplets faster.

B. TOMAC Efficiency at Room Temperature

One of the important characteristics for successful demulsifier is its ability to work at wide temperate range. In the previous sections, the range of temperature was about (50 -70) °C when the microwave heating was used. In this part, the performance of ionic liquids was investigated at room temperature which was about (28-33) °C.

For NK crude oil emulsion, a complete separation (100%) was achieved for the three water content ratios, but the time at which this separation was reached was different where it was 5, 15, and 30 minutes for (8%,15% and 30%), respectively. The used TOMAC dose was 50 ppm.

Fig. 11 shows that the efficiency is excellent for 30% Kirkuk crude oil emulsion for all TOMAC doses ranging between 99% - 95 %. The same behavior was observed for 15% and 8% water content emulsions as shown in Figures 12 and 13, but in general the separation percentages were lower than the previous ratio.

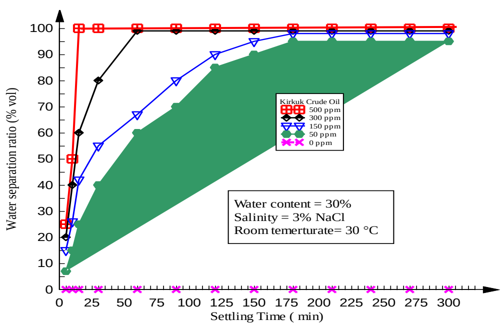

Fig. 11: TOMAC performance for 30%Kirkuk crude oil emulsion at room temperature

Whereas, the behavior was different for Basrah crude oil emulsions when they were tested at room temperature. The performance varied according to the initial water content and TOMAC doses. In general, the demulsification process at high water content and high doses was very good as shown in Fig. 14, but the separation percentages at low water contents and small doses were not high enough to be considered as it is shown in Figures 15 and 16.

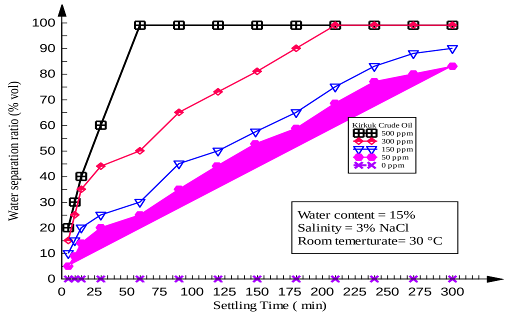

Fig. 12: TOMAC performance for 15%Kirkuk crude oil emulsion at room temperature

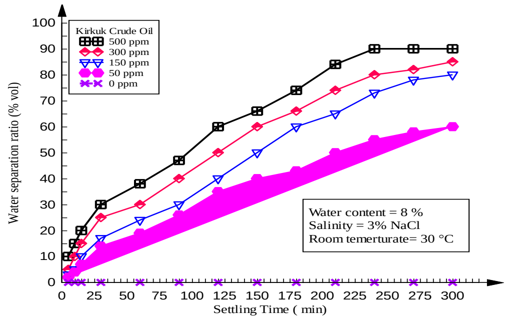

Fig. 13: TOMAC performance for 8 %Kirkuk crude oil emulsion at room temperature

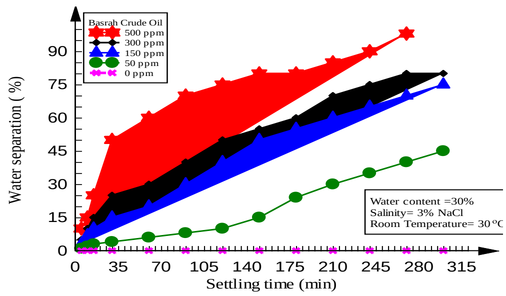

Fig. 14: TOMAC performance for 30% Basrah crude oil emulsion at room temperature

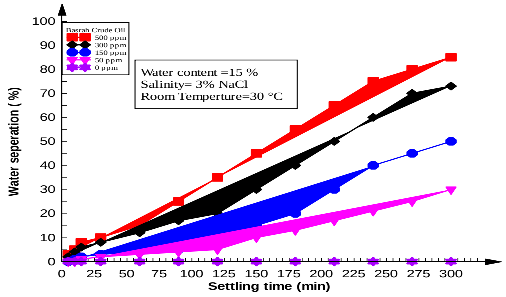

Fig. 15: TOMAC performance for 15% Basrah crude oil emulsion at room temperature

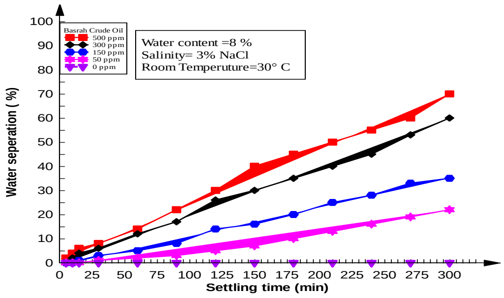

Fig. 16: TOMAC performance for 8 % Basrah crude oil emulsion at room temperature

From Figures 14, 15 and 16, it is also noticed that the separation required more than 180 minutes. The separation process at room temperature needs about 300 minutes to reach 98% for 500 ppm dose and 30 % initial water content emulsion. At the same time, the behavior is alike for 15% and 8 % initial water content emulsions with lower separation ratios. This might be attributed to the difference in crude oil composition like asphaltenes and wax content and also to the higher viscosity and density for Basrah crude oil which is very clear from TOMAC behavior with this type of emulsion. The time required to achieve the same separation efficiency is twice that needed for Kirkuk crude oil emulsion which has density, viscosity and asphaltene content less than the former emulsion.

Conclusions

1. Ionic liquids (TOMAC) showed high efficiency as green demulsifier for different grades of Iraqi crude oil emulsions.
2. For NK emulsion, the experiments showed complete separation at room temperature with dose less than 50 ppm and there is no need to use heating.
3. For Kirkuk crude oil emulsions, the water separation percentages were about (100%-99%) for all doses when the microwave heating was used.
4. At room temperature , the separation ratios for Kirkuk emulsions were between (100% - 95%) for all doses with different settling times but the maximum settling time was recorded for lower dose 50 ppm.
5. For Basrah emulsions, the maximum separation was recorded for 30% initial water content and 500 ppm dose with using MW.
6. At room temperature, the separation ratios varied for different doses and initial water ratios but the maximum separation was recorded for 30% initial water content. The settling time was longer than that obtained with MW heating.

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