EFFECT OF CALCINATED MAGNESITE ON RHEOLOGY OF BENTONITE SUSPENSIONS. MAGNESIA-BENTONITE INTERACTION

Kenan CINKU[*], Fırat KARAKAS[**], Feridun BOYLU[**]

[*] University of Istanbul, Engineering Faculty, Mining Engineering Department, Avcilar, Istanbul, Turkey
[**] Istanbul Technical University, Faculty of Mines, Mineral Processing Engineering Department, 34469, Maslak, Istanbul, Turkey, boylu@itu.edu.tr

Abstract: In this study, the effect of calcination temperature and time on the structure of calcinated magnesite was investigated. In addition, the effect of calcinated magnesite on rheology when added into bentonite suspension was also examined. Electrokinetic, rheological and stabilization studies including coagulation and gelation tests were performed to explain the mechanism of viscosity increase in bentonite suspension upon addition of the calcinated products. FTIR, SEM, BET analyses and rheological data were used to determine the transition degree of $MgCO_3$ to MgO, and evaluate the structure of MgO and bentonite suspensions. The results from this study showed that specific surface area (SSA) and mean pore radius (MPR) values for the calcinated products were directly affected by the calcination temperature and time. According to the ignition loss and transition ratio from $MgCO_3$ to MgO of the calcinated samples, it was found that the calcination was completed above 800 $^{\circ}$C. In order to obtain a bentonite suspension with higher viscosity, interaction of the sufficient amount of MgO particles with bentonite particles were necessary. Based on these results, the formation of gelation and heterocoagulation between MgO and bentonite particles were found to be responsible for these effects.

Keywords: MgCO₃, MgO, activation, bentonite, interaction, viscosity

Introduction

Typical production process of MgO is thermal treatment of naturally occurring minerals such as magnesium hydroxide and carbonate that occurs abundantly in nature (Aramend et al., 2003). Hydromagnesite and magnesite are distributed locally in Russia (22%), North Korea (24%) and China (27%). Dolomite ($CaMg(CO_3)_2$) is more widely distributed in the world and provides cost benefits (Sasaki et al., 2013). Magnesium oxide is manufactured in various kinds of kilns by one of the following reactions as shown in Eq.1. and Eq. 2. using calcination process where $MgCO_3$

thermally decomposes to produce MgO and CO_2, when it is heated from 700 to 1000 °C

$$MgCO_3 + \text{heat} \rightarrow CO_2 + MgO, \qquad (1)$$

$$CaCO_3 \cdot MgCO_3 + \text{heat} \rightarrow 2CO_2 + CaO \cdot MgO \text{ (dolomitic magnesia)}. \qquad (2)$$

The calcination process directly affects the reactivity of the magnesium oxide, therefore it is the most important step to determine how the final product will be used (Aphane et al., 2007).

MgO can be obtained in various reactivity grades based on the temperature and duration at which it is heat treated. Medium reactive magnesia, called as light burnt or caustic magnesia, is produced by calcinations of magnesium carbonate in the temperature range between 700–1000 °C while hard burnt magnesia with an average surface area of 0.1-1.0 m^2/g is produced in the temperature range between 1100–1650 °C. Due to its narrow range of reactivity, this grade is typically used in applications where slow degradation or chemical reactivity is required such as with animal feeds and fertilizers. Dead burnt magnesia or refractory grade magnesia is produced by calcination between 1450–2200 °C and its average surface area is <0.1 m^2/g.

Among magnesia forms, caustic ones have the largest specific surface areas ranged from 1.0 m^2/g to 250 m^2/g. Fused magnesia is normally produced by melting caustic magnesia.

Due to the material's wide reactivity range, industrial applications are quite varied and include plastics, rubber, paper and pulp processing, steel boiler additives, adhesives, and acid neutralization. In bentonite industry, it is also an interesting additive for producing gel like materials (Aphane et al., 2007)

Gel like materials like clays can be used in a number of applications such as paints, adhesives, and drilling muds etc. Some inorganic materials can be used to improve the gelation property of clay. For example, Na-bentonite (Wyoming) and MgO mixture was evaluated as an additive in water-borne paints (Karakas et al., 2011). According to this study, flowability and stability of Na-bentonite was improved by the addition of MgO, and the optimum MgO dosage was found as 1.5 wt.% of Na-bentonite (Karakas et al., 2011). Karaguzel et al. (2010) also reported the thickened bentonite suspension with MgO for preparing of drilling mud. However, it is worth to mention that the addition of MgO into the suspension significantly increases the viscosity of bentonite suspensions, whereas in the case of calcium and mixed bentonite activation with MgO, initial soda activation is required as shown in our previous study (Karaguzel et al., 2010). In addition, it was reported that among magnesium based additives only MgO with the very low dissolution rates regulates the viscosity behaviors of clay suspensions (Alther, 1986) and others such as $MgCO_3$, $Mg(OH)_2$, $MgCl_2$ do not work well (Abut and Girgin, 2005; Cinku, 2008). This is an interesting point that the positive effect of Mg ions in bentonite suspensions was announced in literature, however, without emphasizing the effect of MgO particles in suspensions. Since MgO

does not dissolve well in bentonite suspensions, the effect of dissolved Mg ions on suspension viscosity can be eliminated. Therefore, the positive effect of MgO addition on increased suspension viscosity appears by the other factors which were aimed to be clarified in this study.

In this study, the interaction mechanism of the bentonite suspension with magnesium was investigated in detail. The electrokinetics, rheology, coagulation, and gelation experiments were also performed to understand the interaction mechanism between MgO and bentonite particles.

Material and methods

Centrifugally concentrated Na-bentonite sample was used in this study. The detailed method to prepare this sample was explained elsewhere (Boylu et al., 2010; Boylu et al., 2012). The raw Na-bentonite sample (ROM) used in this study was obtained from Tokat-Resadiye (Turkey) with the sample which is mainly dacitic tuffs (Akbulut, 1996), and having CEC value of 78 meq/100 g, swelling index of 21 $cm^3/2$ g and FANN viscosity values of 20 and 35 mPa·s (at 300 and 600 rpm) at 6% solids. Following the pretreatment, the purification resulted in the production of concentrated Na-bentonite with CEC of approximately 103 meq/100 g, swelling index of 45 and FANN viscosity values of 32 and 56 mPa·s (at 300 and 600 rpm) at 6% solids. Further experiments were performed with the concentrated Na-bentonite sample. The increase on CEC value of pretreated bentonites points out its high purity. The raw magnesite sample (ROM) was hand collected from Kutahya Region (Turkey) with quartz content less than 1.5%, which can be attributed to a quite pure $MgCO_3$. Prior to the final use in the experiments, the ROM magnesite was purified through high intensity dry magnetic separation to remove the colorful impurities such as magnetite, hematite etc. Further calcination tests were also performed to produce MgO at different calcination degrees.

The zeta potential measurements for the bentonite suspensions were conducted using Zeta-Meter System 3.0 at 0.1% wt following the previous reports (Sabah et al., 2007). The rheological measurements were carried out with the hydrocyclone products of 4.75% (w/w). The bentonite slurries were blended at 1200 rpm for 5 min using an Arcelik brand blender and kept in stretched film covered beakers to prevent vaporization of the water during 24 h. Following a day period, the suspensions were re-agitated at low mixing rates (1200 rpm) for 5 min before the viscosity measurements. A Brookfield RVD [++] viscometer and small sample adapter with the spindles of SC 21 and 28 # were utilized for data acquisition. Viscosities of the suspensions were measured with the spindle speeds ranging from 0.5 to 100 rpm at 100 rpm (93 s^{-1} shear rate) where the viscosities versus spindle rate remain constant were considered.

The gelling index of the hydrocyclone products were determined by using graduated cylinders containing 10 cm^3 water with various amounts of solids ranging from 0.5 to 1.3 g. Following shaking of the cylinders, the samples were left for a day

to allow gel development. After a day, the cylinders were bent in 45° to allow the suspensions flow out. The amount of samples in the suspensions, which allow the flow to last for more than a minute was determined and the ratio of 10 (cm^3)/sample amount (g), was defined as the gelling index.

All measurements were reproducible. Zeta potential measurements of bentonite particles in the absence and presence of calcinated $MgCO_3$ were performed on at least 20 individual particles and the final results were recorded based on the average values. Only repeated viscosity measurements exhibiting small changes in the range of 5–10% were used and this is a well-known and tolerated behaviour.

It is known that one of the production methods of MgO is calcination of $MgCO_3$. In this process CO_2 is separated from the structure and pure MgO is produced by the influence of heat above 1400 °C. Stoichiometrically, 52.3% of weight loss occurs upon the exact transition from $MgCO_3$ to MgO. Transition ratios of $MgCO_3$/MgO were calculated based on dividing 52.3% by the weight losses found in experiments conducted with different calcination temperatures.

Results and discussion

Characterization of Calcinated Products

Figure 1 shows transition ratio changes depending on the calcination temperature and time. As seen from Fig. 1, calcination starts at 600 °C for 30 min and for the same calcination time a 90% of transition was achieved at 800 °C while calcination was completed at 1000 °C. The increase on calcination time resulted in a complete calcination at relatively lower temperatures. Viscosity tests were performed with MgO products in different calcination degree (calcination time was selected as 30 min).

The FTIR analyses for the calcinated samples at different temperatures are shown in Fig. 2. As can be seen from Fig. 2 that carbonate peaks at 1420 °C and HCO_3^- peaks (also indicates the dehydration) at 850 °C for the calcinated samples disappeared, hence the calcination process completed above 800 °C.

The changes in the specific surface areas (SSA) and mean pore radius (MPR) of the calcination products are shown in Fig 3. Interestingly, the sample calcinated at 800 °C has the biggest SSA with 76m^2/g, whereas the sample calcinated at 600 °C has the biggest MPR with 26.0 nm. These results were also in agreement with the literature (Liu et al., 2007).

It is apparent from the results that the increasing trend in SSA and MPR at relatively lower calcination temperatures changed with the increasing calcination temperature because of sintering process which caused melting of surfaces by covering the porous structure at above 1200°C.

In another study, the optimum calcination temperature was found to be at around 600 °C. This is possible because of the changes in the heating rate and particle size
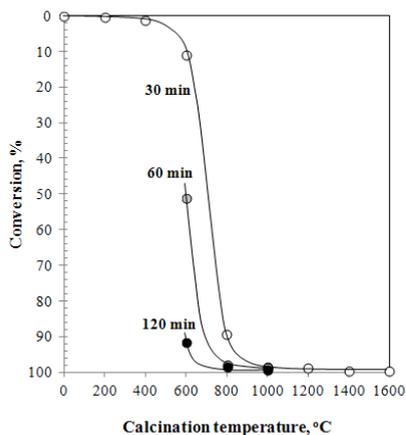
Fig. 1. Conversion degrees of MgCO$_3$/MgO at different calcination temperatures and durations
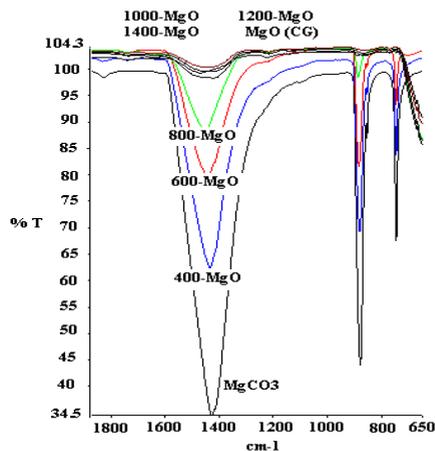
Fig. 2. FTIR patterns of the ROM and calcinated MgCO$_3$ at different calcination temperatures for 30 min calcination time
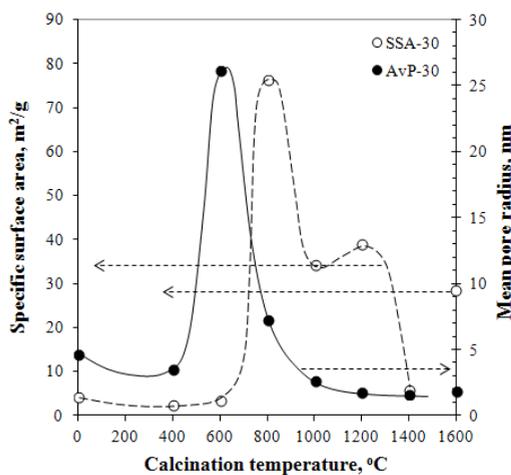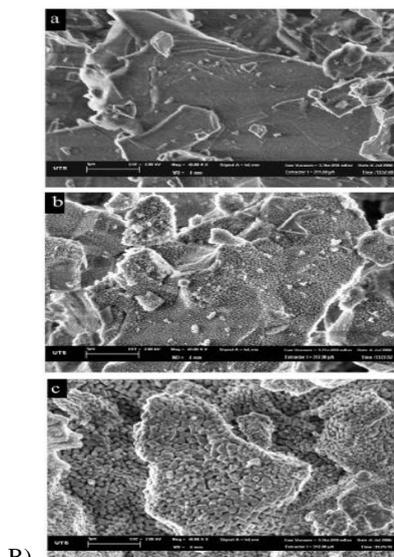
A)   B)

Fig. 3. A) SSA, MPR values of calcinated MgCO$_3$ as a function of calcination temperature, B) SEM analyses (40000 x of MgCO$_3$ (a), calcinated MgCO$_3$ at 600 °C (b) and 1000 °C (c) (from Liu et al., 2007 with the permission of the publisher)

which affect the calcination degree. The SEM pictures of MgCO$_3$ (a) and samples calcinated at 600 °C (b) as well as at 1000 °C (c) in Fig. 3b from the study of Liu et al. (2007) showed porous structure, supporting the changes in SSA and MPR values as

explained in the previous section (Liu et al., 2007). In agreement with Liu's study, the calcination tests in this study revealed that the largest SSA (76 m^2/g) was obtained at around the optimum calcination temperature of 800 °C. When the SSA of calcinated samples compared to ones from Liu's study, a porous system as in Fig 3b (b) can be expected with our calcinated product at temperature of 800°C. SSA and MPR values of samples obtained at 1000°C, which is the completion temperature of calcination process, are 35–40 m^2/g and 2.5–3.0 nm, respectively.

When the SSA and MPR values of the samples obtained at different calcination temperatures are compared to those of the chemical grade MgO, it will be seen that the samples calcinated at 1000-1200 °C have similar properties with the chemical grade MgO.

Rheology of the bentonite-Calcinated Magnesite suspensions

The rheological measurements were carried out for the bentonite suspensions (4.75 % solid by weight) with the addition of $MgCO_3$/MgO obtained at various calcination temperatures. The results are shown in Figs 4-6. The amount of $MgCO_3$/MgO added into the bentonite suspensions was kept constant (2% wt.).
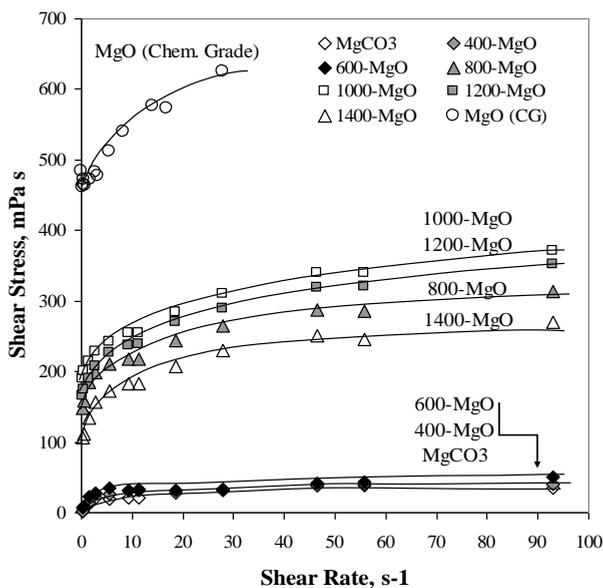
Fig. 4. Rheology of bentonite suspensions with calcinated $MgCO_3$ (2%) depending on the calcination temperature

It was found that all the suspensions have pseudoplastic flow and their rheological behaviors are compatible with the Hersell Bulkley model $\tau = \tau_c + \kappa\gamma^n$, where τ_c is the yield stress (Pa), κ consistency index, and n is the flow index, as shown in Fig. 4. The

rheological behavior of the bentonite suspension prepared with the chemical grade of MgO is also presented. In Figs 4–6, the chemical grade of MgO yields the thickest suspensions characterized by its highest viscosity and yield stress values because of its purity. For the evaluation of calcinated products, the bentonite suspensions, including MgO obtained by calcination at 1000–1200 °C, gave the highest viscosity. The calcination process conducted above 1200 °C deteriorated the positive effect of MgO addition on the viscosity of the bentonite suspensions.

When the SSA and MPR of calcinated samples are evaluated in terms of calcination temperature, it is seen that SSA increases up to 800 °C and it decreases above this temperature, while the MPR value is maximum at 600 °C and it again decreases above this temperature. Using of MgO with SSA of 35–40 m^2/g and MPR of 2.0–2.5 nm have definitely an advantage considering viscosity increase of bentonite suspensions. Therefore, there is no considerable effect of SSA and MPR values difference on viscosity increase of bentonite suspensions.
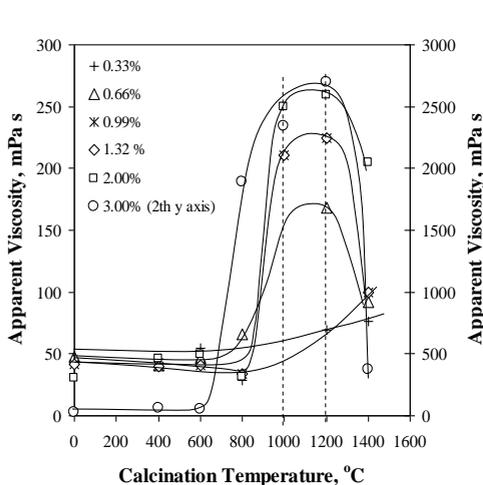
Fig. 5. Apparent viscosities of bentonite suspensions (solid ratio is 4.75 %) with calcinated MgO_3 depending on the MgO addition (at legend) and calcination temperature at shear rate of 93 s^{-1}
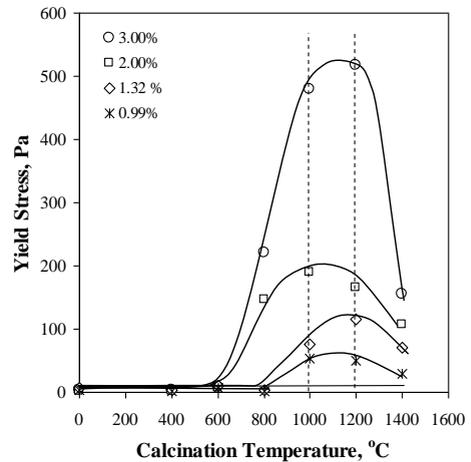
Fig. 6. Yield stress of bentonite suspensions with calcinated $MgCO_3$ depending on the MgO addition (at legend) and calcination temperature at shear rate of 93 s^{-1}

The similar trend in shear stress/shear rate was also observed for apparent viscosity and yield stress as presented in Figs 5 and 6. When the shear stress/shear rate lines are examined in detail, it is realized that the apparent viscosity changes (Fig. 5) are due to yield stress changes shown in Fig. 6. When the formula proposed by the Hersell Bulkley model is used, it can be seen that one of the biggest parameters which causes the viscosity increase of a system is yield stress designated as τ_o, in the equation. An increase in τ_o value indicates an increase in apparent viscosity of a system. Even if shear stress τ, flow index n, and consistency k do not change, an increase in τ_o value directly makes an increase in the viscosity. Therefore, the increase in the apparent

viscosity of bentonite suspensions can be directly related to the properties of $MgCO_3/MgO$ which change the yield stress. Changing of the yield stresses is a result of medium pH and particle-particle interaction. For this reason, electrokinetics, coagulation and gelation properties of different calcinated samples resulted in the increase in viscosity and yield stresses of the bentonite suspensions. Lagaly and Ziesmer (2003) stated that coagulation conditions can also be indicated by viscosity and starting point of a dramatic increase in viscosity and can be defined as critical coagulation point.

Dissolution properties of calcinated $MgCO_3$ products and resultant pH of the system

It is well known from literature that MgO has the lowest solubility in comparison to other magnesium compounds (6 mg/100 cm^3 of water). However, when it is added to bentonite suspension at pH 10, which is the natural pH of the bentonite suspension, some $Mg(OH)_2$ are formed through hydrolysis. $Mg(OH)_2$ is a very strong hydrogel, and hinders the penetration of water molecules into the MgO particles, making a film on the surface.

The concentration of total dissolved ions (TDS) versus accompanying pH for the calcinated samples at different temperatures is shown in Fig 7. Similar properties were also observed for both pure $MgCO_3$ and $MgCO_3$ calcinated at 400 °C with the medium pH values varying from 7.8 to 10.2, and TDS values from 25 ppm/50 cm^3 water to 30 ppm/50 cm^3 water. The samples calcinated at 600 °C changed the pH and TDS values from 9.8 to 11 and from 45 to 50 ppm/50 cm^3 water, respectively.
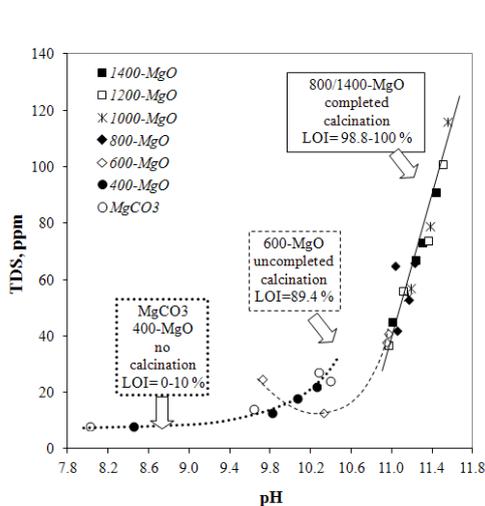
Fig. 7. Total dissolved solids concentrations and pHs of $MgCO_3$ calcinated at various temperatures
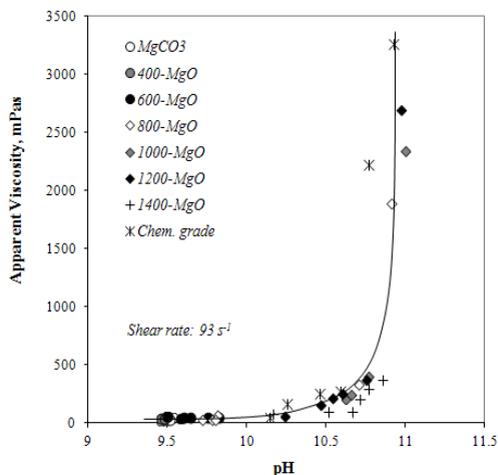
Fig. 8. Apparent viscosities of bentonite suspensions with the addition of 3 % $MgCO_3$ calcinated at various temperatures

Both pH and TDS values for the calcinated $MgCO_3$ suspensions produced at starting and completion temperature of calcination and even at the temperature necessary for forming sinter magnesite were dramatically increased and their TDS values were measured as 120 ppm/50 cm^3 water. Interestingly, a greater transition from $MgCO_3$ to MgO resulted in more soluble calcinated products. This can be attributed to transition of magnesite with relatively higher solubility to $Mg(OH)_2$, which has very low solubility due to hydrolysis of magnesite in water

$$MgCO_3 + H_2O \leftrightarrows Mg(OH)_2 + CO_2. \tag{3}$$

On the other hand, these products increased the pH of distilled water to 11.8. According to Fig. 8, which shows the relationship between the apparent viscosity and pH, the viscosity of bentonite suspensions increased with the increase of pH of these suspensions. It is known that apparent viscosity of bentonite suspensions increased at higher pHs from neutral pH value (van Olphen, 1963; van Olphen, 1977; Tombacz and Szekeres, 2004). At this point, beside the particle-particle interaction, which was the proposed mechanism by us for viscosity increase of bentonite suspensions, dissolved Mg ions and increased pH of media might be responsible for increase of the viscosity.

The additional rheological tests were performed to investigate whether the increase in pH and dissolved Mg ions caused an increase on viscosity of bentonite suspensions or not. For the tests of the MgO samples obtained by calcinations at 1000 and 1400 °C were dissolved in distilled water for a day with the amount equal to 3% of bentonite addition. After a day, sample was centrifuged and supernatant were added into the bentonite suspensions. With this supernatant addition, the same dissolved ion concentration and medium pH were achieved with the solid MgO addition into bentonite suspensions for comparison. Next, the rheological measurements were conducted with bentonite suspensions including the supernatants. The relative rheological behavior and apparent viscosity values of bentonite suspensions with and without solid MgO particles were presented in Figs 9 and 10. As shown in Fig 9, the bentonite suspension with supernatant of MgO suspension shows similar properties to the original bentonite suspensions. It can be concluded from this that there is a need to add solid MgO particles to the bentonite suspensions in order to obtain highly viscous bentonite suspensions. The reason for this is particle-particle interaction and heterocoagulation. It is thought that pH of the aqueous solution and dissolved Mg ions show no significant effect on the viscosity.

The electrokinetic studies, including zeta potential and iep determination, of bentonite and MgO samples obtained by calcination of $MgCO_3$ at different temperatures were performed to evaluate the particle-particle interaction and show its effect on viscosity in detail. The zeta potential measurements were carried out at different pH values in distilled water and neutral pH of supernatant obtained from the bentonite suspension. The results from the measurements are given in Fig 11. It was found that the iep values for pure $MgCO_3$ and $MgCO_3$ calcinated at 400 °C are close to

7 while the iep values for MgCO$_3$ samples calcinated at 600 °C or higher are at around 11–12.
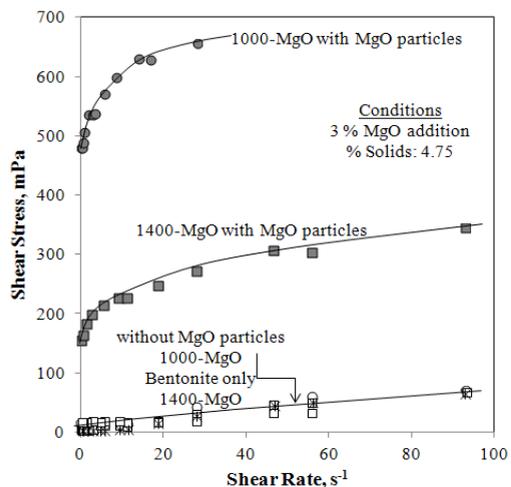
Fig. 9. Rheological behavior of bentonite suspensions in the presence of MgCO$_3$ calcinated at various temperatures
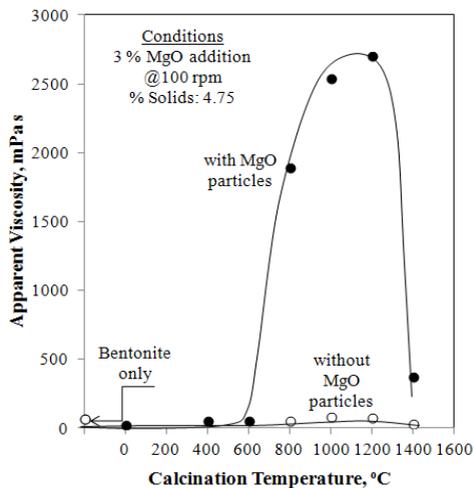
Fig. 10. Apparent viscosities of bentonite suspensions in the presence of MgCO$_3$ calcinated at various temperatures
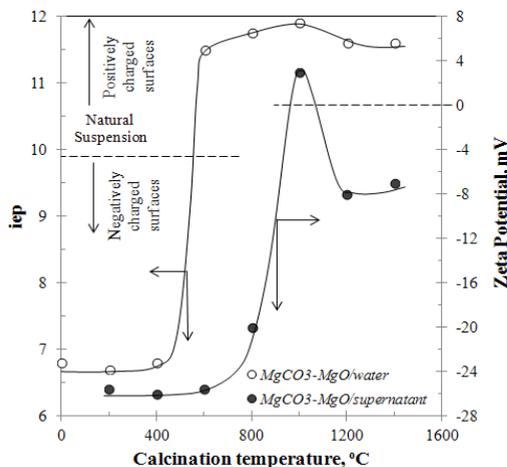
Fig. 11. Electrokinetics of MgCO$_3$ particles in water and supernatant
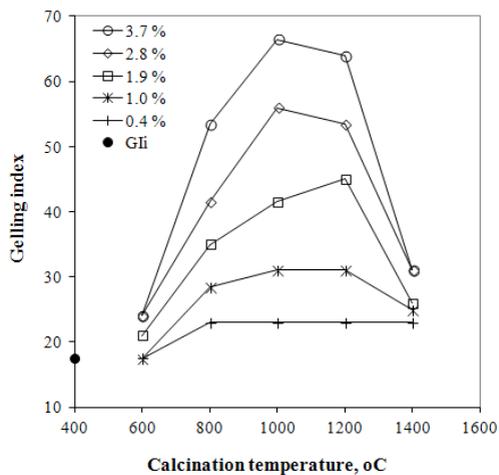
Fig. 12. Gelation characteristics of bentonite suspensions with MgCO$_3$ calcinated at various temperatures

These results agree with literature data because Gence et al. (2006) found the iep value of MgCO$_3$ as 6.8. Moreover, Rynkowski and Dobrosz-Gomez (2009) and Tari et al. (1997) declared the iep value of calcinated MgO as 12.0 and 10.8 (not confirmed

by our study), respectively, while it is around 11–12.4 for sinter magnesite found by Flatt et al. (1997) (Rynkowski and Dobrosz-Gomez, 2009; Tari et al., 1997; Flat et al., 1997). The probable reason for small differences between our and their results is purity of the $MgCO_3$ samples used in the studies.

Bentonite surface at natural pH 9 has a negative charge in a broad range of pH. Meanwhile, while pure $MgCO_3$ particle is negatively charged, the calcinated and sinter magnesite particles are positively charged. Therefore, it is clear that the calcinated and sinter magnesite particles have an attraction interaction with bentonite particles due to electrostatic forces while pure magnesite has repulsion. It was found by zeta potential measurements conducted on supernatant obtained from bentonite suspensions that the surface potential is positive only for $MgCO_3$ particles calcinated at 1000 °C while it is negative for $MgCO_3$ particles calcinated at 600, 800, 1200 and 1400 °C.

The surface charge and structure of $MgCO_3$ particles change when calcination is performed above 1200 °C. Material calcinated above 1200 °C loses its porosity, hydrogel form and surface charge avoiding the particle-particle interactions (heterocoagulation) and gelling ability. These findings support obtaining the highest viscosity of the bentonite suspensions with $MgCO_3$ calcinated at 1000 °C. A similar heterocoagulation behavior for MgO with alumina was reported in literature (Tari et al., 1997; Rao, 1987; Rao, 1988a; Rao, 1988b).

Since original bentonite and the calcinated magnesite particles have different surface charges, it is expected that heterocoagulation can occur between bentonite and magnesite particles. For this reason, the coagulation tests were performed to explain the mechanism between these particles. The results indicated that there is no coagulation process occurring up to a month of waiting period despite the addition of 30% MgO.

The gelation tests were also performed as a next step, because gelation is the other form of particle–particle interaction and MgO is in a hydrogel form. The tests were carried out with original bentonite suspensions and bentonite suspension including different concentrations of $MgCO_3$ calcinated at different temperatures. The results are shown in Fig 12. The calcinated magnesite produced at 1000 and 1200 °C showed the highest gelation index. Moreover, gelation index values increased with increasing the amount of $MgCO_3$/MgO addition for all the calcinated samples and the gelation index of bentonite suspensions increased from 17.8 to 68 with the addition of $MgCO_3$ calcinated at 1000–1200 °C.

In the previous studies, one of the main effects to obtain a bentonite suspension with a high viscosity was a sufficient amount of Na ions increasing delamination in the suspension (Abend and Lagaly, 2000). It was also indicated that some Mg ions are also useful and the highest viscosity will be obtained with Na:Ca:Mg ratio of 60:20:20, respectively (Abend and Lagaly, 2000; Erdogan and Demirci, 1996). However, the results of this study showed that MgO is superior among the magnesium compounds in order to increase the viscosity of bentonite suspensions. MgO has the lowest solubility among the rest of the magnesium compounds. Although past studies

indicated the importance of Mg ions, in this study the effect of MgO particles, not Mg ions was emphasized. The effect of MgO addition was explained by particle-particle interaction, heterocoagulation mechanisms and gelation effect of the remaining, non-dissolved, MgO particles.

Conclusions

In this study, the interaction mechanism of MgO with bentonite suspensions was studied in detail, and several possible mechanisms of the process were evaluated. When the specific surface area (SSA) and mean pore radius (MPR) values of the sample are considered, it was observed that the $MgCO_3$ calcinated at 800 °C gave the largest SSA of 76 m^2/g, even though more viscous bentonite suspensions were obtained with $MgCO_3$ calcinated at 1000 °C which had the SSA of 35–36 m^2/g. This result is similar to that with chemical grade MgO, which gave the most viscous bentonite suspensions. It was also found that the optimal MPR values should be around 30–40 nm.

The degree of the calcination also affected the concentration of total dissolved solids (TDS) of the suspension due to hydration of the calcinated products to $Mg(OH)_2$, and this increased the pH of the magnesia solutions. The increase in pH also improved the rheology of the bentonite suspension. Additionally, the high degree calcination products increased the pH of the solution and apparent viscosity of the suspensions as well. However, further experiments showed that a sufficient amount of MgO particles and interaction of these particles with bentonite particles are necessary to get the bentonite suspension having greater viscosity even if pH and the total amount of dissolved ions of the suspension slightly change.

In contrast to the solubility and pH of the suspension, there was no relationship between the SSA and MPR values and apparent viscosity of the suspension. It is believed that coagulation is mostly dominated by the particle-particle interaction mechanism. Hence it causes an increase in the viscosity of the suspension.

The electrokinetic studies showed that the zeta potential of the calcination products changed from negative to positive values with increasing degree of calcination. Moreover, the iep values of $MgCO_3$, calcinated magnesite, and sintered magnesite were obtained as 6.8, 12.0, and 11.0, respectively. While the zeta potential of $MgCO_3$ particles in the presence of the bentonite suspensions at neutral pH (~9) was negative, the zeta potential of calcinated and sintered magnesite was positive, or very close to neutral. Therefore, an electrostatic interaction takes place between negatively charged bentonite and either calcinated or sintered magnesite. However, the coagulation tests showed that no coagulation occurred even with the addition of MgO in the amount of 30% of bentonite.

Finally, the gelation tests showed that the gelation capabilities of the magnesite calcinated products increase with the calcination degree. Consequently, the gelation

was caused by the increase of the viscosity of the bentonite suspension upon the addition of MgO.

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