Stability of CaCO₃ in Ca(OH)₂ solution

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Abstract

The effect of calcium hydroxide (Ca(OH)₂) on the stability of calcium carbonate (CaCO₃) particles was investigated with respect to the surface potential and particle size. Both CaCO₃ and Ca(OH)₂ were dissolved in ultrapure water at concentrations up to 100 mM. The solubility limits were about 18 mM for Ca(OH)₂ and about 0.13 mM for CaCO₃ at 23 °C in water. Dissolution of commercial CaCO₃ in 10 mM of Ca(OH)₂ solution and dissolution of Ca(OH)₂ in 10 mM of CaCO₃ slurry were also studied at similar conditions. Conductivity, pH, zeta potential, and average particle sizes were measured for each solution. The morphological characteristics of the particles were analyzed by the SEM images. It was found that the zeta potential of CaCO₃ particles was greater than +30 mV when they were placed in the Ca(OH)₂ solution compared to a zeta potential value of −10 mV in water. It was concluded that the Ca(OH)₂ solution is a stabilizer for the CaCO₃ particles.

1. Introduction

Calcium carbonate (CaCO₃) is one of the most abundant minerals in nature and widely used as filling material in various industries in order to decrease the product costs and to improve some of the mechanical properties of the composite materials. The enhancement in the physical and mechanical properties of the polymeric composite materials is more pronounced when the particles are in nano-sizes (Lin et al., 2008). Nano-calcite can be produced by recrystallization methods utilizing calcium hydroxide (Ca(OH)₂) and carbon dioxide (CO₂) as in the carbonization method, and calcium chloride (CaCl₂) and sodium carbonate (Na₂CO₃) as in the chemical method (Carmona et al., 2003a, 2004; Chen et al., 2000; Ukrainczyk et al., 2007). However, obtaining CaCO₃ particles in nano-sizes with homogeneous size distribution, and different morphologies is difficult due to agglomeration of newly synthesized clusters (Gebauer et al., 2008; Kellermeier et al., 2012; Kılıc and Özdemir, 2015; Pouget et al., 2009), which is related to the surface potential of the colloidal CaCO₃ particles (Agnihotri et al., 1999; Holysz et al., 2003; Moulin and Roques, 2003; Pouchet et al., 2013). CaCO₃ is also one of the principal constituents of hard scale formed in many industrial and heating installations. One of the causes for scale formation is the surface charge which is one of the most important parameters in dissolusion and precipitation of CaCO₃ (Chibowski et al., 2003a, 2003b; Yuan et al., 2008).

Calcium carbonate has three different anhydrous polymorphs known as calcite, aragonite, and vaterite. Calcite is the most stable form of the CaCO₃ at standard conditions. Aragonite and vaterite are not stable, but they can transform into the stable calcite (Stepkowska et al., 2003). CaCO₃ has also other hydrous forms such as calcium carbonate monohydrate, calcium carbonate hexahydrate, and amorphous calcium carbonate (ACC)(García-Carmona et al., 2003; Gunasekaran and Anbalagan, 2008; Jung et al., 2000; Montes-Hernández et al., 2008; Xu et al., 2007).

Classical crystallization mechanisms claim that a nucleation step is required before crystal growth (Xu et al., 2007). However, novel crystallization mechanisms require a prenucleation process in which ions form stable clusters (Gebauer et al., 2008). These clusters are charged particles in equilibrium with their ions and they can grow or collide to produce amorphous CaCO₃ nuclei (Bots et al., 2012). Therefore, certain additives were introduced into the crystal growing medium to alter the surface charge of the growing nuclei and to inhibit the CaCO₃ growth (Liu et al., 2008; Seo et al., 2005; Sheng et al., 2004).

The surface potential of the colloidal system is related to the magnitude of the zeta potential. Zeta potential is also the most effective parameter to calculate interaction energy between particles for the colloidal stability. Particles with zeta potentials more positive than +30 mV or more negative than −30 mV are considered stable (Kes, 2007). However, a neat consensus could not be arrived by the authors on the zeta potential for the CaCO₃ in the literature because sometimes positive, sometimes negative, and sometimes variable zeta potential values have been reported (Moulin and Roques, 2003). The zeta potential for CaCO₃ was reported to be about −10 mV (Chibowski et al., 2003b) indicating that the newly produced CaCO₃ clusters are naturally unstable. It is the reason why newly formed particles in the literature with the chemical or carbonization methods were aggregated and formed micron sized particles (Carmona et al., 2003a, 2003b; Kılıc and Özdemir, 2015; Kitamura et al., 2002; Rodríguez-Blanco et al., 2011;
Tai and Chen, 1998; Yan et al., 2008). It was understood that the surface potential for CaCO₃ is affected by various parameters such as aging (Chibowski et al., 2003b), additives (Yuan et al., 2008), surface modifiers (Agnihotri et al., 1999), and ions (Holysz et al., 2003; Pourchet et al., 2013). For instance, the zeta potential for CaCO₃ was positive when Ca⁺⁺ ions were in excess in the solution, and it was negative when CO₃⁻ ions were in excess in the solution (Chibowski et al., 2003b; Holysz et al., 2003; Pourchet et al., 2013). Therefore, the presence of other ions, called the potential determining ions (PDI) (Moulin and Roques, 2003) such as crystal lattice ions, surface hydrolysis ions, and adsorbing ions in solution, are highly important for the aggregation and growth of CaCO₃ on the surfaces as well as production of stable nano-CaCO₃ particles.

In our previous paper, we have reported the production and aggregation of nano-clusters in CaCO₃ crystallization (Kilic and Ozdemir, 2015). We have shown that monodispersed nano-CaCO₃ particles could be produced if the stability of the clusters could be achieved in the colloidal solution. Here, the stability of CaCO₃ particles in Ca(OH)₂ solution was investigated in an effort to stabilize the newly produced CaCO₃ clusters before their aggregation into the growing crystals.

2. Materials and methods

2.1. Materials

Calcium hydroxide was purchased from Merck with a purity of 96% of which 3% was CaCO₃, and 1% was other impurities (mainly 0.05% of Na, K, Fe, Sr; 0.5% of Mg; 0.01% of SO₄²⁻, and 0.005% of Cl⁻). Calcium carbonate was also purchased from Merck with a purity of 98.5%–100.5%. Ultrapure water was obtained with a MilliQ (Millipore-Elix UV5/Milli-Q) water purification system with a purity of 18.2 μΩ at 25 °C.

2.2. Dissolution of Ca(OH)₂ in ultrapure water

The dissolution of Ca(OH)₂ was performed in a 5-neck jacketed reactor at 23 °C as shown in Fig. 1. Before the experiments, nitrogen gas (N₂) was fed into the reactor to maintain a CO₂-free atmosphere in the reactor. Conductivity and pH values were measured by Thermo Orion 5 star pH meter with pH and conductivity probes. The measured data were monitored and recorded with a Thermo Star Navigator 21 software program. Initially, 250 ml of ultrapure water was filled into the five neck reactor and stirred at 550 rpm on a magnetic stir plate. Both pH and conductivity were monitored for about 15 min. Then, 0.0185 g of Ca(OH)₂ were added in the ultrapure water to obtain a 1 mM of Ca(OH)₂ solution. Both pH and conductivity were monitored during the dissolution process for about 30 min. After 15 min of stirring, about 1 ml of sample was withdrawn from the solution into a UV cuvette and size and size distribution were measured using a particle size analyzer (Malvern nano ZS model). A 1 ml of sample was also withdrawn from the solution into a zeta cell and zeta potential values were measured. Solutions were returned to the reactor after each measurement. Reported size and zeta potential values are the average of at least five measurements conducted on the same sample and reported their average values. In order to increase the Ca(OH)₂ concentration, 0.037 g, 0.0375 g, 0.092 g, 0.093 g, 0.185 g, 0.371 g, and 0.926 g of Ca(OH)₂ powders were added sequentially into the solution to obtain 3 mM, 5 mM, 10 mM, 15 mM, 20 mM, 30 mM, 50 mM, and 100 mM of Ca(OH)₂ solutions, respectively. At the end of each addition, both particle size distribution and zeta potential measurements were conducted.

2.3. Dissolution of CaCO₃ in ultrapure water

The dissolution of CaCO₃ was also performed in the same set-up as shown in Fig. 1. 250 ml of ultrapure water was placed in the five neck reactor and stirred at 550 rpm on a magnetic stir plate. Both pH and conductivity values were monitored online using the Thermo Orion pH-meter software. Then, 0.025 g of CaCO₃ powder was added to the ultrapure water to obtain 1 mM of CaCO₃ solution. After about 15 min of stirring, 1 ml of sample was withdrawn to measure the particle size distribution and another 1 ml of sample was withdrawn from the reactor to conduct the zeta potential measurements. The solutions were returned into the reactor after each measurement. In order to increase the CaCO₃ concentration in the reactor, 0.05 g, 0.05 g, 0.125 g, 0.125 g, 0.250 g, 0.501 g, and 1.151 g of CaCO₃ powder was added.

Fig. 1. A five neck glass reactor for the stability study of CaCO₃ in Ca(OH)₂ solution.

Fig. 2. Change of pH and conductivity in the presence of various Ca(OH)₂ additions.

Fig. 3. Conductivity and pH values with Ca(OH)₂ concentration and a comparison with the literature data.
sequentially into the solution to prepare a 3 mM, 5 mM, 10 mM, 15 mM, 20 mM, 30 mM, 50 mM, and 100 mM CaCO₃ solutions, respectively.

2.4. Dissolution of Ca(OH)₂ in 10 mM of CaCO₃ slurry

The dissolution of Ca(OH)₂ in 10 mM of CaCO₃ solution were performed with the same procedure. Initially, 10 mM of CaCO₃ solution was prepared by adding 0.25 g of CaCO₃ powder into 250 ml of ultrapure water by stirring at 550 rpm on a magnetic stir plate. Both pH and conductivity values were monitored during the dissolution. After equilibration, both particle size distribution and zeta potential values were measured with the Malvern zeta sizer by withdrawing 1 ml samples for each as explained above. Then, 0.0185 g of Ca(OH)₂ powder was added into the solution to obtain 1 mM of Ca(OH)₂ solution in 10 mM CaCO₃ slurry. Both pH and conductivity values were monitored. After about 15 min, both particle size distribution and zeta potential values were measured by withdrawing 1 ml of samples for each. Sequential addition of Ca(OH)₂ powders was done into the slurry in order to prepare 5 mM, 10 mM, and up to 100 mM of Ca(OH)₂ solutions, respectively, in 10 mM of CaCO₃ slurry.

2.5. Dissolution of CaCO₃ in 10 mM of Ca(OH)₂ solution

The dissolution of CaCO₃ in 10 mM of Ca(OH)₂ were also conducted with the same procedure explained above. Initially, 10 mM of Ca(OH)₂ solution was prepared by adding 0.185 g of Ca(OH)₂ powder into a 250 ml of ultrapure water by stirring at 550 rpm on a magnetic stir plate. Both pH and conductivity values were monitored as briefly described before. After equilibration, both particle size distribution and zeta potential values were measured with the Malvern zeta sizer by withdrawing 1 ml sample for each. Then, 0.018 g of CaCO₃ powder was added into the solution to obtain 1 mM of CaCO₃ solution in 10 mM of Ca(OH)₂ solution. Both pH and conductivity measurements were conducted and monitored during dissolution. After about 20 min, both particle size distribution and zeta potential values were measured by withdrawing 1 ml of sample for each. 0.0815 g of CaCO₃ powder was added into the solution in order to prepare 4 mM slurry, and subsequently additional CaCO₃ powders were added to prepare 10 mM, 15 mM, and up to 100 mM of CaCO₃ slurries, respectively, in 10 mM of Ca(OH)₂ solution.

3. Results and discussion

3.1. Dissolution of commercial Ca(OH)₂ in ultrapure water

Commercial Ca(OH)₂ was dissolved in the ultrapure water in a step-wise fashion at concentrations up to 100 mM. Fig. 2 shows the pH and conductivity values by time after each addition of Ca(OH)₂ powders into ultrapure water. The initial concentration for Ca(OH)₂ was 1 mM and it was expected that the whole powder added into the solution dissolved completely according to chemical speciation to an equilibrium as summarized in Eqs. (1) through (3) (Chibowski et al., 2003b).

\[
\text{Ca(OH)}_2(s) \rightleftharpoons \text{Ca(OH)}_2(aq) \quad \text{pK}_a = -2.45 \quad (1)
\]

\[
\text{Ca(OH)}_2(aq) \rightleftharpoons \text{Ca}^{+2} + \text{OH}^- \quad \text{pK}_a = -1.37 \quad (2)
\]

\[
\text{Ca(OH)}^- \rightleftharpoons \text{Ca}^{+2} + \text{OH}^- \quad \text{pK}_a = -1.40 \quad (3)
\]

Wang (Wang et al., 1998) studied the dissolution mechanism of Ca(OH)₂ by the rotating disk method and reported that while the Ca^{+2} ions dissolved into the solution, OH⁻ ions remained on the surface as shown in Eq. (4). Later on, the OH⁻ ions released from the surface were attacked by the free Ca^{+2} ions in the solution as shown in Eq. (5). The dissolution of powder Ca(OH)₂ was also studied by Johannsen and Rademacher (Johannsen and Rademacher, 1999). The authors suggested that the particle size and therefore the surface area were the main factors in Ca(OH)₂ dissolution kinetics.

\[
\text{Ca(OH)}_2 \rightarrow \text{Ca}^{+2} + 2\text{OH}^- \quad \text{(surface)} \quad (4)
\]
Ca\(^{++}\) + 2OH\(^{-}\) (surface) → Ca\(^{++}\) + 2OH\(^{-}\) (bulk solution) \hspace{1cm} (5)

Sequentially added \(\text{Ca(OH)}_2\) powders were allowed to dissolve in a solution composed of previously produced Ca\(^{++}\), OH\(^{-}\), and Ca(OH\(^+\)) ions, as well as the clusters and solid particles in the solution. As can be seen in Fig. 2, the conductivity and pH values increased proportionally by the subsequent additions of \(\text{Ca(OH)}_2\) powders, however, no significant changes were observed above the saturation concentration of \(\text{Ca(OH)}_2\), which is about 18 mM at 23 °C (Lide, 1995).

Conductivity and pH values obtained after each \(\text{Ca(OH)}_2\) addition are shown in Fig. 3. Literature data are also included in the figure for comparison. As shown in the figure, the conductivity values increased linearly with Ca\(^{+}\) ions and possible surface attachments of ions on the undissolved impurities such as impurity CaCO\(_3\) particles. Burns and Jachuck (Burns and Jachuck, 2005) stated that the conductivity values deviated about 24% from the theoretical values. This difference may explain the complex formation between the Ca\(^{+}\) and OH\(^{-}\) ions and possible surface attachments of ions on the undissolved impurities. As shown in Fig. 3, the linear increase in conductivity values could be related to the Ca\(^{+}\) concentration up to the solubility limit since beyond that point, the conductivity values did not change with further addition of Ca\(^{+}\). From the slope in Fig. 3,

\[
\text{Conductivity} = 0.4268 \left[\text{Ca(OH)}_2\right] \quad \text{(6)}
\]

where conductivity is in mS/cm and \(\left[\text{Ca(OH)}_2\right]\) is in mM. The [Ca\(^{+}\)] ion concentration could be related to the linearity of \(\left[\text{Ca(OH)}_2\right]\) concentration up to the solubility limit of \(\text{Ca(OH)}_2\) provided that 1 mol of [Ca\(^{+}\)] ion were produced from 1 mol of Ca\(^{+}\) dissolved. Therefore, the [Ca\(^{+}\)] ion concentration in the Ca\(^{+}\) solution can be estimated from the measured conductivity values by using Eq. (7).

\[
\text{[Ca}^{++}\text{]} = \text{Conductivity} \times \frac{1}{\text{slope}}
\]

(7)

The \([\text{OH}^{-}]\) ion concentration can be calculated from the measured pH values as given in Eq. (8).

\[
[\text{OH}^{-}] = 10^{-14 / (pH)}
\]

(8)

The [Ca\(^{+}\)] and [OH\(^{-}\)] ion concentrations during the addition of Ca\(^{+}\) solution were calculated respectively from Eqs. (7) and (8), and shown in Fig. 4. Theoretically, 15 mM [Ca\(^{+}\)] and 30 mM [OH\(^{-}\)] ion concentrations would be obtained when a stoichiometric 15 mM of Ca\(^{+}\) was dissolved in ultrapure water. Moreover, [OH\(^{-}\)] ion concentration would theoretically be two times bigger than the [Ca\(^{+}\)] ion concentration. However, as shown in the figure, while the [Ca\(^{+}\)] ion concentration was estimated to be about 15 mM, the [OH\(^{-}\)] ion concentration was calculated to be about 22 mM, which was smaller than the theoretical value (Lide, 1995) as described also by Burns and Jachuck (Burns and Jachuck, 2005). The [OH\(^{-}\)] ion concentration was not 2 times higher than [Ca\(^{+}\)] ion concentration, indicating that surface adsorption of ions on the solid particles, new particle formation, and clustering of ions can take place in the solution. As understood from these [Ca\(^{+}\)] and [OH\(^{-}\)] ion concentration data, surface charge and clustering may affect the size distribution and the zeta potential values of particles in aggregation and growth of CaCO\(_3\) as well as nano-CaCO\(_3\) production.

Fig. 5 shows SEM images of as-received commercial Ca\(^{+}\) powder and any residues remained in 10 mM of dissolved Ca\(^{+}\). As shown in the figure, the commercial Ca\(^{+}\) is composed of fine particles aggregated into big flocks. As mentioned before, the Ca\(^{+}\) used in the experiments had an impurity of 3% of CaCO\(_3\) and 1% of the other impurities. The composition of the powders and the resulting dissolution products were not analyzed as a matter of fact they were both commercial Ca\(^{+}\) and CaCO\(_3\). As shown in Fig. 5b, the impurities obtained after centrifugation of 10 mM of Ca\(^{+}\) solution were needle-like aragonite type CaCO\(_3\) and the average particle size was bigger than the measured value of 300 nm. Therefore, the reported nano-particles were most probably the newly synthesized nano-CaCO\(_3\) particles with a zeta potential value of about 20 mV. Upon subsequent addition of Ca\(^{+}\) to the previously Ca\(^{+}\) dissolved solution, the zeta potential value for the Ca\(^{+}\) was seen to increase gradually to about 40 mV while the average particle size remained the same up to the solubility value of about 18 mM. Chibowski et al.
(2003a, 2003b, 2003c) stated that the positive net charge on the CaCO₃ surface depends on the surface Ca⁺⁺ sites (Chibowski et al., 2003c). The authors also stated that zeta potential of precipitated CaCO₃ from equimolar concentration of Ca⁺⁺ and CO₃⁻⁻ was around zero or, slightly higher than zero. It was understood that the zeta potential of CaCO₃ precipitated from excess of CO₃⁻⁻ was negative, and the zeta potential of CaCO₃ precipitated from excess of Ca⁺⁺ was positive. It was presumed that the Ca⁺⁺ ion concentration seemed to be higher in the fully dissolved Ca(OH)₂ solution than the CO₃⁻⁻ ion concentration resulting in a net positive zeta potential value. Upon further addition of the Ca(OH)₂ powder into the solution, the average particle size showed an increase up to 4 μm due to the insoluble Ca(OH)₂ powder, and the zeta potential values decreased from 40 mV to 30 mV and then to 23 mV at the highest concentration of 100 mM. The measured positive zeta potential values higher than +30 mV indicate that the newly produced nano-CaCO₃ particles were abundant and in stable form in the solution, exhibiting no aggregation after they formed.

3.2. Dissolution of CaCO₃ in ultrapure water

Fig. 7 shows the change in pH and conductivity values with time during sequential addition of commercial CaCO₃ into ultrapure water. The solubility of CaCO₃ was reported to be about 0.013 g/kg-water in the literature (Perry et al., 1984), which is very low compared to that for the Ca(OH)₂. As can be seen in the figure, both pH and conductivity values slightly increased at low concentrations up to about 0.13 mM of CaCO₃ solutions. Although the increase in the conductivity was slight, it was not relatively stable due to the formation of additional ions and clusters (Chibowski et al., 2003b). Dissolution of small amount of CaCO₃ at concentrations less than 0.13 mM resulted in Ca⁺⁺ and CO₃⁻⁻ ions to present in the solution according to Eqs. (9) and (10) (Chibowski et al., 2003b; Holysz et al., 2003; Moulin and Roques, 2003).

\[
\text{CaCO}_3(s) \rightleftharpoons \text{CaCO}_3(aq) \quad \text{pK}_a = -5.09 \quad (9)
\]

\[
\text{CaCO}_3(aq) \rightleftharpoons \text{Ca}^{++} + \text{CO}_3^{--} \quad \text{pK}_a = -3.25 \quad (10)
\]

However, the free CO₃⁻⁻ ions in the solution caused a carbonate buffer to form, forming a CO₂ gas and additional HCO₃⁻ and OH⁻ ions. The steady increase in the conductivity was probably due to the formation of other ions in the solution. In the presence of CO₂ gas or when the CaCO₃ solution is open to the atmosphere, the carbonate buffer also affected the CaCO₃ dissolution dynamics as well as the surface potential according to Eqs. (11) to (13) (Chibowski et al., 2003b; Holysz et al., 2003; Moulin and Roques, 2003).

\[
\text{CO}_3^{--} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^{--} + \text{OH}^- \quad \text{pK}_a = -3.67 \quad (11)
\]

\[
\text{HCO}_3^{--} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^- \quad \text{pK}_a = -7.65 \quad (12)
\]

\[
\text{H}_2\text{CO}_3 \rightleftharpoons \text{CO}_2(g) + \text{H}_2\text{O} \quad \text{pK}_a = +1.47 \quad (13)
\]

In the presence of carbonate buffer, additional ions, clusters, and nano-particles could form due to dissolution and recrystallization of...
crystals in the solution according to Eqs. (14) and (15) (Chibowski et al., 2003b; Holysz et al., 2003; Moulin and Roques, 2003).

$$\text{Ca}^{2+} + \text{HCO}_3^- \leftrightarrow \text{CaHCO}_3^+ \quad \text{pK}_a = +0.82 \ (14)$$

$$\text{CaHCO}_3^+ \leftrightarrow \text{CaCO}_3 \text{aq} + \text{H}^+ \quad \text{pK}_a = -7.90 \ (15)$$

Fig. 8 shows the pH and conductivity values at different concentrations of CaCO₃. As shown in the figure, the conductivity values showed a linear increase at concentrations up to almost 0.13 mM of CaCO₃ solution. The changes in conductivity and pH values were insignificant for the subsequent CaCO₃ powder addition up to a 100 mM. Therefore, the CaCO₃ solution became slurry at CaCO₃ concentrations higher than 0.13 mM.

Fig. 9 shows the SEM images of as-received commercial CaCO₃ particles and CaCO₃ particles obtained from the 10 mM of CaCO₃ slurry. As shown in the images, the commercial CaCO₃ particles are in aggregated form with a cubical shape with sizes from about 2 μm to 10 μm each. Neither the size nor their surface morphologies of the CaCO₃ particles were affected when they added into water for dissolution.

Fig. 10 shows the measured zeta potential values and average particle sizes in the CaCO₃ solution at different concentrations. As shown in the figure, the zeta potential was about −3 mV and the average particle size was about 2 μm for the freshly dissolved CaCO₃ particles at concentration of about 1 mM. With the subsequent addition of CaCO₃ powder into the already ionized solution, it is seen that while the zeta potential decreased to about −11 mV, the average particle size remained the same at about 4 μm. We attribute the subsequent increase in zeta potential to Ca⁺⁺ and CO₃⁻⁻ ions formed in the solution upon dissolution of CaCO₃ particles. At high pH, Ca⁺⁺ and OH⁻ ions form complexes leaving CO₃⁻⁻ ions in the solution alone, and therefore, increasing the concentration of the CO₃⁻⁻ ions in the slurry. The remained CO₃⁻⁻ ions then proceed into formation of carbonate buffer and adsorb onto the surface of CaCO₃ particles resulting in a net negative charge for the CaCO₃ particles. The measured zeta potential of −11 mV is in a very good agreement with the literature data (Chibowski et al., 2003b; Moulin and Roques, 2003).

3.3. Dissolution of Ca(OH)₂ in 10 mM of CaCO₃ slurry

The dissolution of Ca(OH)₂ powder in 10 mM of CaCO₃ slurry was studied. Initially, a powder of commercial CaCO₃ was added into ultra-pure water to prepare 10 mM of CaCO₃ slurry. Since the dissolution of CaCO₃ in ultrapure water is very low, about 0.13 mM, only small amount of CaCO₃ ionized in the slurry, resulting in a pH value of about 9.3 and a conductivity value of about close to zero. Fig. 11 shows pH and conductivity values during the addition of Ca(OH)₂ powders into a 10 mM of CaCO₃ slurry. As shown in the figure, pH and conductivity values...
increased with the subsequent addition of Ca(OH)$_2$ powders into the 10 mM of CaCO$_3$ slurry up to its saturation concentration of about 18 mM, similar to the pure Ca(OH)$_2$ dissolution in ultrapure water.

Fig. 12 shows the SEM images of the samples taken from each suspension during the addition of Ca(OH)$_2$ powders in 10 mM of CaCO$_3$ slurry. As seen, the surfaces of the commercial CaCO$_3$ particles are so faultless with sizes varying from 2 μm to more than 10 μm in the suspension. The added Ca(OH)$_2$ powder into the solution was expected to fully dissolve at concentrations lower than its solubility limit of about 18 mM. Although the surfaces of some particles were not affected significantly by the addition of very small amount of Ca(OH)$_2$ of 1 mM and 5 mM, it is clearly seen from the SEM images that some newly synthesized particles exist in the solution and they were in nano-sizes, either in aggregated form in the solution or in precipitated form on the surfaces of the CaCO$_3$ particles. We observed that the surfaces of the CaCO$_3$ particles were highly affected by the further Ca(OH)$_2$ additions. It can be seen from the images that the surfaces of the CaCO$_3$ particles deformed or eroded in the presence of excess Ca(OH)$_2$. We think that the observed deformations on the surface of the CaCO$_3$ particles are the consequence of Ca$^{++}$ and CO$_3^{2-}$ ions dissociating from the particle surface and subsequently converting into newly synthesized nano-CaCO$_3$ particles. A surface deformation of the CaCO$_3$ particles and the coverage of CaCO$_3$ particles with the potential determining Ca$^{++}$, CO$_3^{2-}$, and OH$^-$ ions could influence the zeta potential and stability of the CaCO$_3$ particles in the Ca(OH)$_2$ solution.

Fig. 13 shows the zeta potential and average particle sizes during Ca(OH)$_2$ addition into 10 mM of CaCO$_3$. The zeta potential of 10 mM CaCO$_3$ slurry (with zero Ca(OH)$_2$ addition) was measured to be about −2 mV and the particle size was about 3 μm, which is in very good agreement with the literature (Chibowski et al., 2003b). The zeta potential and the particle size were measured to be +24 mV and about 1 μm, respectively, upon addition of 1 mM of Ca(OH)$_2$ solution. Further addition of Ca(OH)$_2$ powder into 10 mM of CaCO$_3$ slurry caused the measured zeta potential values to increase up to about +40 mV and the particle sizes to decrease down to about 300 nm up to its solubility limit of about 18 mM. The decrease in particle size from 3 μm to 300 nm and increase in the zeta potential from −2 mV to +40 mV with addition of the Ca(OH)$_2$ powder into the CaCO$_3$ slurry clearly indicated that there was an increase in the population of the newly synthesized nano-CaCO$_3$ particles in the solution and these newly formed particles were more stable in the solution. We think that the measured particle size and zeta potential values were belong to the newly synthesized particles, because bigger particles were expected to settle faster than the smaller particles (Molvá, 2011). Above the saturation limit of the Ca(OH)$_2$, the particles exhibited an increase in size up to about 4 μm most probably due to precipitation of nano-particles on the CaCO$_3$ surfaces and aggregation of undissolved Ca(OH)$_2$ particles in the solution as shown in the images in Fig. 12. But from the Fig. 13, it is clearly seen that at around the solubility limit of Ca(OH)$_2$, the zeta potential of CaCO$_3$ particles is not only positive in the Ca(OH)$_2$ solution but also its value is greater than +30 mV producing stable CaCO$_3$ particles in the Ca(OH)$_2$ solution.

3.4. Dissolution of CaCO$_3$ in 10 mM of Ca(OH)$_2$ solution

A 10 mM Ca(OH)$_2$ solution was prepared in ultrapure water and subsequently different amounts of CaCO$_3$ powder was added into the 10 mM of Ca(OH)$_2$ solution. Fig. 14 shows pH and conductivity values during the CaCO$_3$ addition in 10 mM of Ca(OH)$_2$ solution. As shown in the figure, a pH of about 12 and conductivity of about 42 mS/cm were measured for the 10 mM of Ca(OH)$_2$ solution and both values remained unchanged even though different amounts of CaCO$_3$ powders were added subsequently.

The SEM images of particles during addition of commercial CaCO$_3$ powder into the 10 mM of Ca(OH)$_2$ solution are shown in Fig. 15. Inert particles were obtained from the centrifugation of the 10 mM of Ca(OH)$_2$ solution and observed to be mostly needle-like aragonite type CaCO$_3$ particles. Upon addition of commercial CaCO$_3$ particles, newly synthesized nano-particles were observed to form in the solution with different morphologies. The deformations or erosions on the surfaces of the CaCO$_3$ particles can also be discerned in the images. The surface coverage of the particles and the newly formed nano-CaCO$_3$ particles could affect the zeta potential and the measured particle sizes in the solution.

The measured zeta potential and average particle sizes for the CaCO$_3$ particles in 10 mM of Ca(OH)$_2$ solution are illustrated in Fig. 16. As shown in the figure, the zeta potential and average particle size of the 10 mM of Ca(OH)$_2$ solution were measured to be +38 mV and 350 nm, respectively. We surmise that these measured values would belong to the impurity CaCO$_3$ particles and newly synthesized nano-CaCO$_3$ particles suspended in the 10 mM of Ca(OH)$_2$ solution. Upon addition of CaCO$_3$ particles into 10 mM of Ca(OH)$_2$ solution in a stepwise fashion, while the zeta potential values decreased almost linearly down to +31 mV, average particle sizes did not exhibit a significant change. When the added CaCO$_3$ powder concentration was increased to 30 mM and higher, it was observed that the zeta potential values exhibited a sudden increase from +31 mV to about +47 mV and the average particle sizes exhibited a size less than 1 μm. We believe that the net positive charge on the CaCO$_3$ surface is resulting from the Ca$^{++}$ sites (Chibowski et al., 2003c), and thus the excess Ca$^{++}$ ions inhibit agglomeration between particles, leading to formation of nano-CaCO$_3$ particles. As shown in the figure, the zeta potential of the CaCO$_3$ particles in Ca(OH)$_2$ solution is more than +30 mV, suggesting that CaCO$_3$ particles are stable in the Ca(OH)$_2$ solution. This finding on the stability of newly
formed nano-CaCO₃ particles in the Ca(OH)₂ solution is important for the aggregation and growth of CaCO₃ on the surfaces for scale formation as well as the production of stable nano-CaCO₃ particles.

4. Conclusions

Calcium carbonate is one of the principal constituents of hard scale formed in many industrial and heating installations. One of the causes for scale formation is the surface charge which is one of the most important parameters in dissolution and precipitation of CaCO₃. In order to understand the phenomena occurring in CaCO₃ crystallization in Ca(OH)₂ as in the carbonization method, the zeta potential values of CaCO₃ particles in Ca(OH)₂ solution were investigated. The solubility for CaCO₃ was measured to be about 0.13 mM, which was lower compared to the solubility for Ca(OH)₂ measured to be about 18 mM in ultrapure water. The dissolution of both CaCO₃ and Ca(OH)₂ powders produced ions such as Ca⁺⁺, CO₃⁻⁻, OH⁻, and CaOH⁺ as well as newly synthesized nano-CaCO₃ particles in the solution. The zeta potential values for the particles were measured to be always positive in Ca(OH)₂ solution due to an imbalance between Ca⁺⁺ and CO₃⁻⁻ ions in solution so called the potential determining ions (PDI). It was concluded that the zeta potential of CaCO₃ is more than +30 mV in the Ca(OH)₂ solution and therefore they are more stable. Hence, aggregation and growth of CaCO₃ could be managed and nano-CaCO₃ particles produced in Ca(OH)₂ solution.

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References


