The Integrity of Synthetic Magnesium Silicate in Charged Compounds

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Abstract

Magnesium silicate is an inorganic compound which can be used as an ingredient in product formulations for many different purposes. Since its compatibility with other ingredients is critical for product quality and stability, it is essential to characterize the integrity of magnesium silicate in different solutions used for various product formulations. In this paper, we have determined the magnitude of dissociation of synthetic magnesium silicate in positive, neutral, and negative charged compounds using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and verified the results using Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS). Negatively charged compounds were found to significantly impact magnesium silicate dissociation, resulting in physio-chemical separation between magnesium and silicate ions while the positively charged compound had a minor effect on dissociation due to ion competition, and the neutral compound did not have such an impact on magnesium silicate dissociation. Further, when the magnesium ions are dissociated from the synthetic magnesium silicate, the morphology is changed accordingly, and the structural integrity of the synthetic magnesium silicate is damaged. The results provide a scientific confidence and guidance for product development using the synthetic magnesium silicate.

Introduction

Magnesium silicate is widely used in pharmaceuticals, food, and cosmetics, among other fields in industry. In the food industry, it is used as a fragrance or flavor carrier, an anticaking agent in animal feed, an anticaking agent or pigment for confectionary, and a bleaching agent in vegetable oil production^{1,2}. In pharmaceuticals, magnesium silicate is used in oral formulations as an anticaking agent³, as an antacid, as an antifungal, in cosmetics, and as an acne treatment^{4,5}. Additional industrial uses include as a pigment for paint¹, a filler for paint, paper, polymers, or rubber/silicone products^{1,6-8}, as an insecticide⁴, as an adsorbent for chromatography^{4,9}, in low carbon cements⁴, as well as a purifying or filtering agent for frying oil regeneration, biodiesel, and polyol production^{2,4-10}. With such broad applications, a method of characterizing the integrity of synthetic magnesium silicate at different conditions for formulation is vital.

Compared with the polycrystalline structure of natural magnesium silicate minerals, synthetic magnesium silicate commercially available is amorphous and porous, which could result in greater dissociation in a liquid dispersion system. For example, when synthetic magnesium silicate meets a chelating agent or a solution with pH less than 7, Mg ions are leached out, i.e., dissociate from the silicate ion pairs. This can result in the generation of magnesium complexes and will alter product integrity and physical properties upon storage. Consequently, there is a need to determine the amount of dissociation of synthetic magnesium silicate in various solutions and to monitor possible morphology changes.

Previous studies in the literature have used Energy Dispersive X-ray Spectroscopy (EDS) to investigate magnesium silicates. For example, hydroxy-magnesium silicate in lubricant has been investigated for self-repairing technology of metals where EDS is used to determine the extent of hydroxy-magnesium

silicate filling of wear cracks in metal components¹¹. Further, EDS has been used to aid in the determination of silicate scales formed under different pH conditions during high pH Alkaline Compound Polymer flooding during oil production¹². This work found that lower pH conditions resulted in less magnesium silicate and more amorphous silicon dioxide, indicating greater magnesium silicate dissociation.

Here, we have used Scanning Electron Microscopy (SEM) and EDS to determine the dissociation of synthetic magnesium silicate as a function of pH in positive, neutral, and negative charged compounds. Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS) was used to verify and confirm the observation mechanism of the disassociation of Mg ions from magnesium silicate. The results provide a scientific confidence and guidance for product development using synthetic magnesium silicate. This study facilitates the use of SEM/EDS for characterization of magnesium silicate integrity and provides useful information for ingredient selection when formulating new consumer products.

Results

SEM and EDS. To better understand the difference between the effect of positive, neutral, and negative charged compounds on magnesium silicate dissociation, SEM and EDS analysis were conducted. Representative 1000x magnification SEM images of the raw synthetic magnesium silicate particles and the particles collected from each compound solution at each pH are shown in Fig. 1 and Fig. 2, respectively. Images at additional magnifications can be found in the supplementary material in **Figures S1-3**. All samples collected from positively charged cetylpyridinium chloride (CPC) and neutral lauryl glutamate consist of porous spheres and the morphology of the raw material was not obviously changed after pH adjustment. However, samples collected from negatively charged sodium cocoyl glutamate solutions have clearly been degraded as the images show many small particles. EDS spectra and mapping images were obtained to determine the elemental composition of the collected solid.

Point EDS spectra were measured for at least six particles for each of the nine samples. Only silicon (Si), magnesium (Mg), and oxygen (O) were included as elements of interest and a ratio of the resultant percent Si over the percent Mg was calculated. A plot of the average ratios is shown in Fig. 3 representative spectra and a table of the calculated ratios can be found in **Figures S4-12** and **Table S1** in the supplementary material. The ratio of Si/Mg increases when there is greater magnesium silicate dissociation and both pH and charge of compounds affect Mg ion dissociation.

To verify point EDS spectra were a true measurement of the solid particles, simulations of Monte Carlo electron-sample interactions were performed¹³. CASINO software was used to simulate 200,000 electrons targeting MgSiO (ratio determined from typical ratio of Mg, Si, and O from EDS point spectra of the neutral compound) at 10 KeV and a beam radius of 125 nm. The software was used to generate characteristic X-rays for each element. The $\Phi(\rho z)$ curves and radial distributions are shown in Fig. 4. The $\Phi(\rho z)$ curves give information on the X-ray generation depth of each element in the sample while the radial distributions give lateral information. For each element we can determine that the X-rays are only

measured at a depth no more than 700 nm into the sample and no more than 1500 nm radially from the center of the beam. Since the typical particle size used for EDS point spectra was 6–10 μm we can be positive that the results are obtained from the particle with no interference from the filter paper or substrate.

From the EDS mapping results in Figs. 5–7, it is apparent that the amount of Mg decreases as the pH decreases while the amount of Si remains unchanged. This is seen in the color of the background around the particles. In the Si EDS mapping images there are distinct particles seen for all compound solutions at each pH. However, the Mg EDS mapping results show increasingly diffuse color in the background as pH decreases. This is especially apparent for the negative sodium cocoyl glutamate solution at acidic pH. This indicates a decreasing Mg concentration in these samples. Overlap of Mg and Si in the other samples indicates that the elements are still combined in the magnesium silicate particle. We can conclude from these mapping images that both the structural and chemical integrity of the original magnesium silicate are dissociated under low pH.

LC-HRMS. To further understand the interaction from dissociated Mg ions with charged compounds, simple solutions were prepared of magnesium chloride with two negatively charged compounds, sodium cocoyl glycinate and sodium cocoyl glutamate, as well as neutral lauryl glucoside separately. For both negatively charged compound solutions, a significant amount of precipitate was formed. No precipitate was formed in the lauryl glucoside solution. The differences are related to the charges. Lauryl glucoside is neutral and does not react with the positive Mg ions. Therefore, no precipitate can be formed. In contrast, sodium cocoyl glycinate and sodium cocoyl glutamate are negatively charged compounds and the interaction between the negative heads on the compounds and positive Mg ions is the root cause for the precipitate formation. To confirm this hypothesis, the precipitates formed were analyzed by LC-HRMS.

The precipitate was collected by filtration, dried, and redissolved into methanol. The methanol solution was analyzed by LC-HRMS. Figure 8 demonstrates the LC-HRMS results for the precipitate formed from magnesium chloride with sodium cocoyl glycinate. The precipitate formed can be explained by one mole of the positive Mg ion chelated with two moles of negative ions from glycinate or glutamate functional groups at the compound head. The chemical complex structures formed for each negative compound are shown in Fig. 9. The mixtures of magnesium chloride with lauryl glucoside and of magnesium chloride with CPC were also analyzed by LC-HRMS. No Mg-compound complexes were found.

Discussion

The SEM/EDS data illustrates that pH has the greatest effect on magnesium silicate dissociation. Since the ratio of Si/Mg increases as pH decreases for all compounds, the dissociation of synthetic magnesium silicate is shown to be greater at low pH. Using HCl to adjust the pH caused dissociation of magnesium silicate to form magnesium chloride (MgCl_2), silicon dioxide (SiO_2), and water as shown in equation 1 below.

Once reacted in the low pH solutions, the highly water soluble MgCl_2 is removed in the washing steps while insoluble SiO_2 remains, resulting in lower elemental concentration of Mg in the EDS spectra of the particles.

Further, the negatively charged compound, sodium cocoyl glutamate, resulted in even greater dissociation, especially at acidic pH, compared to the neutral lauryl glucoside. The positively charged compound, CPC, also resulted in increased dissociation compared to the neutral compound due to competition between ions. We can conclude from these EDS point spectra that Mg ions were leached from the original raw material as an effect of decreasing pH and with greater leaching facilitated by ionic compounds, particularly negatively charged compounds.

The LC-HRMS results indicate the negatively charged compounds, which favor dissociation, will bond with the Mg ions dissociated from synthetic magnesium silicate, which supports the structural change shown in the SEM and EDS results. Because the negatively charged compound facilitates the dissociation of the Mg ions, compared with positively charged and neutral compounds, the Si/Mg ratio of the collected particles of the negatively charged compound with magnesium silicate is higher, which indicate more Mg ions are leached out from the magnesium silicate particles. Further, because Mg ions are leached out, the structural integrity is destroyed, and the large spherical particles of the raw material deteriorate into small particles.

The structural changes may significantly affect the properties of synthetic magnesium silicate or negate the original purpose for using it in the formulation of the final product. For example, if the porosity of synthetic magnesium silicate is the major targeted property, the structural change or the loss of structural integrity will significantly reduce its porosity. As a result, the absorption property of magnesium silicate in the product will be significantly reduced and/or the viscosity of the final product will be significantly reduced. Further, the Mg ions leached from synthetic magnesium silicate will bond with the negatively charged compounds in the formulation or the final products, and insoluble particles or clusters can be formed. The insoluble particles may appear as big lumps in the final products, and the product quality may be challenged.

Thus, from the results obtained in this paper, during formulation or product development, attention should be paid to the pH level of the products, as well as the selection of charged compounds, when using synthetic magnesium silicate. A higher pH level will better preserve synthetic magnesium silicate.

Further, positively charged and/or neutral compounds will not speed up the dissociation of synthetic magnesium silicate in the low pH condition. Thus, in a low pH formulation or product, the positively charged or neutral compounds are preferred.

Conclusions

SEM, EDS, and LC-MS have been used to investigate the chemical and structural integrity of synthetic magnesium silicate as a function of pH and in solution with charged compounds. The results show that Mg ions leach out from synthetic magnesium silicate at low pH conditions. Negatively charged compounds, such as sodium cocoyl glycinate or sodium cocoyl glutamate, significantly impact magnesium dissociation. These charged compounds react with Mg ions leached from synthetic magnesium silicate, resulting in physio-chemical separation between the Mg and silicate ions. Further, the reaction between Mg ions and charged compounds increases the dissociation and the structural integrity of the spherical shaped particles is destroyed. As a result, the large spherical shaped particles are turned into small particles.

Therefore, for applications of synthetic magnesium silicate which rely on its morphology and porosity, the pH level should be considered during the formulation process to avoid destroying the structural integrity of the spherical shaped particles. Further, since Mg ions are leached out from the particles at low pH level, and they will bond with negatively charged compounds, it is important to consider the possible phase separations of Mg ions and the other compounds to avoid inhomogeneity in the final formulation and product. To obtain a more stable magnesium silicate which would be compatible with negatively charged compounds if a low pH level has to be used in the formulation, further processing of the material is needed, such as thermal annealing, which can transform magnesium silicate from amorphous to crystalline states [4]. Further, if possible, neutrally charged compounds should be selected to reduce the dissociation of Mg ions and to enhance the structural integrity of synthetic magnesium silicate; in other words, to better utilize the desired properties of magnesium silicate.

The results from this research show that it is critical to consider the pH value and the charge properties of the compounds used during the formulation of products using synthetic magnesium silicate to avoid possible issues caused by dissociation of Mg ions. Further, SEM/EDS is an easy and straightforward method to provide key information about the stability of different ingredients for products during the formulation process.

Materials And Methods

To prepare solutions for pH tests, three solutions of cetylpyridinium chloride (CPC, a positive compound, Sigma Aldrich, St. Louis, MO), lauryl glucoside (a neutral compound, BASF, Ludwigshafen, Germany), and sodium cocoyl glutamate (a negative compound, BASF, Ludwigshafen, Germany) were prepared by dissolving 1 mole of each compound in 30 mL of deionized water. After the synthetic magnesium silicate (The Dallas Group of America, Inc, Whitehouse, NJ) was filtered (Whatman Grade 2 filter paper) and dried in a vacuum oven at 100°C, 1 mole (based on anhydrous molar mass) was dispersed in each of the solutions. Solid samples were collected from these solutions after centrifugation and washing with deionized water five times. Magnesium silicate dissociation as a function of pH was investigated by collecting solid at the natural pH of each solution (approximately 10), then adjusting the pH of each solution with hydrochloric acid (Sigma Aldrich, St. Louis, MO, 36%) to approximately 7 and 5, repeating the centrifugation and washing steps at each pH to obtain a total of nine solid samples which were

collected, dispersed in 2-propanol, deposited and dried on a membrane filter used as a support substrate for imaging, and analyzed using SEM/EDS as described.

Further, to determine the formation of magnesium complexes a simple magnesium salt, magnesium chloride, was combined in solution with the charged compounds. First, 10% magnesium chloride (Sigma Aldrich, St. Louis, MO) and 10% lauryl glucoside were prepared individually in deionized water. The two solutions were randomly mixed with variable ratios and no precipitation was observed. The pH ranged from 6 to 10. For the control experiment, 10% sodium cocoyl glycinate (a negative compound, BASF, Ludwigshafen, Germany) solution and 10% sodium cocoyl glutamate were prepared in deionized water. When magnesium chloride solution was mixed with sodium cocoyl glycinate solution and sodium cocoyl glutamate solution separately, precipitation was observed. The precipitate was collected and re-dissolved in methanol solution and analyzed using LC-HRMS. The molecular structures of the charged and neutral compounds used are shown in Fig. 10.

SEM/EDS. A workstation (Crossbeam XB 540 FIB/SEM, Zeiss) was used to analyze the solid samples obtained at each pH. SEM imaging was optimized at an accelerating voltage of 2 kilovolts and a beam current of 200 picoamperes. EDS point spectra and mapping images were obtained at an accelerating voltage of 10 kilovolts and a beam current of 2 nanoamperes. SEM samples were prepared by dispersing each sample in 1.5 mL of 2-propanol and allowing 10 μ L of the dispersion to dry on a membrane filter used as a support substrate for imaging purposes. The resultant solid samples on membrane filters were mounted and coated with gold/palladium through a sputtering process to reduce charging during SEM/EDS analysis.

LC-HRMS. The precipitate made from magnesium chloride or synthetic magnesium silicate with negatively charged compounds was filtered and washed with water. The precipitate was dried and redissolved into methanol for LC-HRMS analysis with a direct injection technology. The liquid chromatography–mass spectrometry analysis was carried out with a Q-Exactive™ Orbitrap™ mass spectrometer (Thermo Scientific, San Jose, USA) equipped with a heated electrospray ionization source (HESI-II). Samples were analyzed in full scan MS mode under positive polarity conditions using electrospray ionization. The compound and source parameters were optimized for both modes for all four solutions. The samples were introduced by direct injection and delivered by a HPLC mobile phase of 50% methanol-water. The optimized parameter settings common for both the modes were: sheath and auxiliary gas flow rate at 30 and 10 respectively, spray voltage 3.2 kV, capillary temperature 320 C, S-lens RF level 50, auxiliary gas heater temperature 400 C. Software used for operating the LC-HRMS was Xcalibur™ (version 4.1).

Declarations

Competing interests. The authors declare none.

Supplementary material. SEM images of each solid collected at each pH for each charged compound at additional magnifications can be found in the supplementary material. Representative EDS point spectra

for each compound at each pH as well as a table of all the Si/Mg ratio measured can also be found in the supplementary material.

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Figures

10 μm

Figure 1

SEM image of original raw material of synthetic magnesium silicate dispersed in 2-propanol, deposited, and dried on a membrane filter used as a support substrate for imaging purposes

Figure 2

SEM images of synthetic magnesium silicate dispersed in CPC, lauryl glucoside, and sodium cocoyl glutamate solutions and collected at basic, neutral, and acidic pH. After pH adjustment in solution, solid sample was collected, dispersed in 2-propanol, deposited, and dried on a membrane filter used as a support substrate for imaging purposes

Figure 3

Ratio of percent Si over percent Mg in multiple point EDS spectra of synthetic magnesium silicate in basic, neutral, and acidic solutions of CPC, lauryl glucoside, and sodium cocoyl glutamate

Figure 4

Generation of characteristic X-rays for 200,000 electrons targeting MgSiO at 10 KeV with a beam radius of 125 nm. a-c) $\Phi(\rho z)$ curves for each element of a MgSiO sample. d-f) X-ray intensities for each element as a function of radial distance (nm) from electron beam center

Figure 5

SEM images (top) cetylpyridinium chloride , Si EDS mapping images (middle), and Mg EDS mapping images (bottom) of synthetic magnesium silicate from basic, neutral, and acidic CPC solutions. After pH adjustment in solution, solid sample was collected, dispersed in 2-propanol, deposited, and dried on a membrane filter used as a support substrate for imaging purposes

Figure 6

SEM images (top), Si EDS mapping images (middle), and Mg EDS mapping images (bottom) of synthetic magnesium silicate from basic, neutral, and acidic lauryl glucoside solutions. After pH adjustment in solution, solid sample was collected, dispersed in 2-propanol, deposited, and dried on a membrane filter used as a support substrate for imaging purposes

Figure 7

SEM images (top) Si EDS mapping images (middle), and Mg EDS mapping images (bottom) of synthetic magnesium silicate from basic, neutral, and acidic sodium cocoyl glutamate solutions. After pH adjustment in solution, solid sample was collected, dispersed in 2-propanol, deposited, and dried on a membrane filter used as a support substrate for imaging purposes

Figure 8

LC-HRMS results for the complex of magnesium-bis-cocoyl glycinate in methanol formed from magnesium chloride with sodium cocoyl glycinate: a) experimental results, b-d) theoretical results for complexes with varying chain lengths.

Figure 9

The chemical structure of a) magnesium-bis-cocoyl glycinate and b) magnesium-mono-cocoyl glutamate in $[\text{M}+\text{H}]^+$ LCMS detection mode

Figure 10

Molecular structure of the compounds: a) cetylpyridinium chloride (CPC), b) lauryl glucoside, c) sodium cocoyl glutamate, and d) sodium cocoyl glycinate

Supplementary Files

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