**Effect of Initial Reactant Concentration on the Calcium Sulfate Size Distribution**

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| **Abstract**  In ancient Egypt and medieval Europe, gypsum, known as alabaster, was used for wall decorations and reliefs (Jeong et al., 2019). Gypsum, a mineral abundant in nature, consists of calcium sulfate (CaSO4). In parallel with developing technology, traditional practices have also become widespread. The ability to control the size distribution during crystallization in synthesis has enabled its use in various fields. [1,2].  This study investigates the effect of initial concentrations of reactants on the size distribution of CaSO4 crystals that precipitate at low temperatures through the reaction of calcium chloride (CaCl2) and sodium sulfate (Na2SO4) spontaneously. The sizes of the resulting crystals were measured via SEM analysis to determine their size distribution. (This study was prepared from the student's master's thesis.) |
| Keywords: Concentration, CaSO4, Calcium sulfate, Size distribution, Crystallization, Bassanite |

1. **Introduction**

Calcium sulfate is a naturally occurring mineral and is commonly found in gypsum and anhydrite forms. This compound, whose chemical formula is CaSO4, consists of calcium and sulfate ions. It is used in many different areas due to its form that can be shaped with water and its resistance to heat [3]. Plaster was used in wall decorations and reliefs in ancient Egypt. In medieval Europe, plaster emerged as an important material in the construction of buildings and the restoration of works of art.

It is widely used in the construction industry, especially in the production of drywall and plaster [5]. Its hydrated form (CaSO4·2H2O) loses its water when exposed to heat and becomes Plaster of Paris. This form, which hardens after drying, is preferred in many areas such as wall correction, ceiling and wall decoration. Calcium sulfate is used as a soil conditioner in agriculture. It is preferred to meet the calcium and sulfate needs in the soil, to improve the structure of heavy soils and to regulate soil acidity. It is also a source of nutrients for plants [7]. CaSO4, also known as E516, is widely used as an additive in the food industry and is applied as a coagulant in cheese making and as a stabilizer in bread and other bakery products. For this reason, it is found in many processed foods and beverages as an additive [8,9].

CaSO4 is obtained especially through mining activities. These ores contain large amounts of calcium sulfate dihydrate (CaSO4·2H2O). This material is then processed and used in various forms [10]. Apart from this, CaSO4 is sometimes produced synthetically in industrial processes, especially as a byproduct of phosphoric acid production. This creates an opportunity for situations and regions where there is no mineral production [11]. In these processes, formation occurs by crystallization. Crystallization is the process by which ions in a solution combine to form a solid structure. This process varies with factors such as temperature, concentration of the solution and pH. The size and shape of the crystal structure also varies depending on these factors and the speed of the crystallization process [12]. The crystal structure and size of calcium sulfate are also important depending on the area of ​​use. The crystal structure of the plaster used in the construction industry affects the hardness and durability of the material. In the food industry, homogeneity and purity of the crystal structure are important [13]. For this reason, it will be preferred to work with crystals with different structures. Recovery of calcium sulfate from industrial waste is important in waste management and sustainable production practices. Calcium sulfate formed during the production of phosphoric acid also finds a place in various applications [14].

This material finds its place in more areas with developing technology and innovative applications. Research on calcium sulfate-based implants and bone grafts shows that they also have uses in medicine [15]. In addition, the use of filling material CaSO4 in the production of light and durable composite materials may find interest especially in the automotive and aviation industries [2]. In 3D printing technologies, calcium sulfate has been seen as an option for the production of biocompatible materials and objects with complex geometries [16]. Technological progress and applications involving environmentally focused innovations will expand the use of this material [17,18].

In this study, the effect of the initial concentration of the reactant on the size distribution of CASO4 crystals precipitated as a result of the reaction using CaCl2 and Na2SO4 is revealed. The sizes of the obtained crystals in SEM photographs were measured and a statistical study was conducted to obtain information about their sizes.. Changes in crystal size distribution were observed with varying initial reactant concentrations.

1. **Materials and Methods**

A mechanical stirrer (IKA Eurostar 20) and a circulation-cooled water bath (Polyscience) were used in the experiments. CaCl2·2H2O (ACS reagent > 99%) and Na2SO4 (ACS reagent > 99.5%) used in the experiments were obtained from Sigma. In the experiments, the reactants were equimolar and the reactions were carried out spontaneously at 0.04 M, 0.05 M, 0.06 M, 0.07 M, and 0.08 M concentrations. Experiments were carried out in a 1 L capacity jacketed glass reactor. The temperature was set at 30°C and the stirring speed set at 300 rpm also. The precipitate obtained as a result of the reaction was dried in a vacuum oven at 80 °C for approximately 12 hours. XRD and SEM analyzes were performed on the resulting powder. The examination of the powder materials was carried out using X-ray diffraction with a Bruker D8 Discover device. The analyses were performed using a Carl Zeiss Sigma 300 VP field emission scanning electron microscope [19].

In a previous study, XRD analyses showed that the materials produced in all experiments consisted of monoclinic calcium sulfate in the Bassanite form. Table summarizes the Bassanite forms identified in the XRD analyses and their properties. [19].

**Table 1.** Properties of the Sythesized Bassanite Crystals [19]

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Reference Code** | **Chemical Name** | **Chemical Formula** | **Calculated Density (g/cm³)** | **Volume of Cell (106 pm3)** |
| 98-001-1607 | Calcium Sulfate(VI) 0.67-hydrate - Alpha | Ca(SO4) (H2O)0.67 | 2.80 | 1055.96 |
| 98-003-4677 | Calcium Sulfate Hemihydrate | Ca(SO4) (H2O)0.5 | 2.73 | 1058.07 |
| 98-002-8108 | Calcium Sulfate Hydrate (1/1/0.6) | Ca(SO4) (H2O)0.6 | 2.76 | 529.88 |

1. **Results and Discussion**

While preparing the width and length distributions of the crystals, at least 97 measurements were made for each size shown in the SEM photographs. These measurements were then statistically analyzed and represented in graph form. The average length of the material synthesized with a 0.04 M concentration was 23.86 ± 15.85 µm. Under the same conditions, the minimum crystal length was 2.79 µm, and the maximum crystal size was 96.98 µm. Similarly, the average width was 5.70 ±3.96 µm (Figure 1).

 

**Figure 1.** Size distributions of synthesized material with equimolar reactant concentration of 0.04 M

Figure 2 shows the size distributions generated from the size measurements taken from the SEM image of materials produced using a 0.05 M starting concentration. According to these results, the average height was 25.21 ±19.63 µm, and the average width was 5.11 ±3.64 µm.

 

**Figure 2.** Size distributions of synthesized material with equimolar reactant concentration of 0.05 M

Figure 3 shows the size distributions of the material obtained using a 0.06 M starting concentration, determined through size analysis using the same method. The data indicate that the average length of the material was 26.51 ±12.17 µm, and the average width was 5.57 ±4.70 µm.

 

**Figure 3.** Size distributions of synthesized material with equimolar reactant concentration of 0.06 M

The size distributions of the material prepared using a 0.07 M starting concentration are shown in Figure 4. The statistical processing of this material yielded an average length of 26.55 ±13.00 µm and an average width of 4.17 ±2.17 µm.

 

**Figure 4.** Size distributions of synthesized material with equimolar reactant concentration of 0.07 M

Figure 5 presents the size distributions of the material produced with a 0.08 M starting concentration. According to the statistical data based on size measurements, the average length was 32.30 ±14.36 µm, and the average width was 4.12 ±2.58 µm. The maximum measured length of the crystals was 83.84 µm, and the maximum width was 21.46 µm. The same measurements found the minimum length to be 7.84 µm, and the minimum width to be 1.17 µm (Table 2).



**Figure 5.** Size distributions of synthesized material with equimolar reactant concentration of 0.08 M

Table 2 summarizes the data on standard deviation, median, minimum, and maximum values related to the calculated average length and width values, based on the measurements.

**Table 2.** Effect of reactant initial concentration on dimensions

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| --- | --- | --- | --- | --- | --- | --- | --- |
| **Initial Conc., M** | **Dimension** | **N total** | **Mean, m** | **Sum** | **Minimum, m** | **Median, m** | **Maximum, m** |
| 0.04 | Length | 97 | 23.86 ± 15.85 | 2314.54 | 2.79 | 21.18 | 96.98 |
| Width | 110 | 5.57 ± 3.96 | 612.68 | 1.05 | 4.168 | 19.22 |
| 0.05 | Length | 131 | 25.21 ± 19.63 | 3302.92 | 6.60 | 20.00 | 158.99 |
| Width | 105 | 5.12 ± 3.64 | 537.08 | 1.38 | 3.89 | 17.22 |
| 0.06 | Length | 122 | 26.51 ± 12.17 | 3234.58 | 1.02 | 24.33 | 61.21 |
| Width | 128 | 5.57 ± 4.70 | 712.97 | 0.86 | 4.03 | 28.77 |
| 0.07 | Length | 125 | 26.55 ± 13.00 | 3319.31 | 9.39 | 22.91 | 90.81 |
| Width | 124 | 4.17 ± 2.17 | 517.49 | 1.06 | 3.80 | 13.49 |
| 0.08 | Length | 121 | 32.31 ± 14.36 | 3909.15 | 7.84 | 30.04 | 83.84 |
| Width | 115 | 4.12 ± 2.58 | 474.26 | 1.17 | 3.69 | 21.46 |

1. **Conclusion**

In this study, micron-sized calcium sulfate crystals were synthesized through spontaneous reactions using CaCl2 and Na2SO4 solutions, and the synthesized crystals were identified as bassanite via XRD analysis. Measurements taken from SEM photographs were then statistically analyzed to obtain size distributions. It was observed that the average length value increased with the rise in the reactant starting concentration in the experiments. While the increasing starting concentration did not significantly affect the maximum value, a decrease in this value was noted. An increase in the starting concentration value resulted in a rise in the median value.

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