Production of Mayenite Nanoparticles from the Toxic Cement Dust

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Abstract: To overcome the key challenges associated with cement dust, such as inhalable size, toxic ions, and the existence of large quantities of useless materials, researchers investigated an innovative and unusual conversion of toxic cement dust into Mayenite nanoparticles. Mayenite is a natural structure that can be used as a filler in a variety of industrial applications. The formation of Mayenite nanoparticles was achieved through a thermal reaction at 1000°C for 2 h between cement dust and aluminum oxide. Different techniques were used to characterize the synthesized Mayenite nanoparticles, revealing the formation of the target phase as well as the reduction of toxic ions present in cement dust. According to Scherrer’s equation, the crystallite size of bypass and synthesized Mayenite nanoparticles is 45 and 30 nm, respectively. Also, with the aid of TEM analysis, the particle size distribution of the produced Mayenite nanoparticles was found to be 27±7 nm. The toxic ions, especially chlorides and sulphates, were reduced by 86% and 50%, respectively, according to X-ray fluorescence results. These findings are important for the future use of Mayenite, 12CaO.7Al2O3 (C12A7), nanoparticles formed from toxic cement dust recycling.

Key words: cement dust, Mayenite, nanoparticles, structural properties, toxic ions reduction

1 Introduction

The cement manufacturing process well-achieved by mixing a preheated mixture of limestone, clay, and sand as sources of calcium, aluminum, iron, and silica. These raw materials at very high temperatures converted to clinker which grinded with other additives to finally for the cement\textsuperscript{1}. During the last few decades, the widespread cement industry has been reported all over the world, which has resulted in a significant, but temporary, increase in CO\textsubscript{2} emissions and cement dust or by-pass which has resulted in a significant, but temporary, increase in the cement industry and this percentage reaches 30\% in the vicinity of the factories\textsuperscript{8}. The main environmental issue with the cement industry its emissions or more specific cement dust which is known as BY-PASS. The latter is mainly composed of oxides of calcium, silicon, aluminum, ferric, magnesium, and other impurities\textsuperscript{9}. These impurities according to XRF analysis obtained from different cement factories are mainly chlorides, sulphates, carbon dioxide, and NO\textsubscript{x}. All of them, especially chlorides and sulphates, have made this dust an environmental problem that poses a threat to the health of everyone who works in the cement industry\textsuperscript{10}. Early literature showed that the gradual specific risks due to cement plant emissions are very low concerning each of the health effects, Toxicological and cancer dangers produced by cement kiln-emitting contaminants\textsuperscript{11}, however, these conclusions have been challenged. Likewise, earlier studies concluded that Long-term cement dust exposure doesn’t contribute to increased morbidity of serious respiratory diseases if compared with several types of blue-collar work\textsuperscript{12,13}.

On the other hand, there are clear and noticeable rela-
tions between exposure to cement dust, persistent deficiency of lung functions, and human respiratory symptoms. Not only skin and mucous membranes of the eyes and respiratory system are irritated by exposure to cement dust, but also its adsorption in the respiratory tract increases the pH value that irritates the exposed mucous membrane\textsuperscript{14, 15}. Various efforts have been devoted to controlling these emissions to minimize their hazards. Different systems are used separately or in combination to control cement dust discharges including mechanical and dust collectors, electrostatic precipitators, and fabric filters\textsuperscript{30}. Zimmwara\textit{et al.} reported that different air pollution control technologies are used for example wet-scrubbers, electrostatic precipitators, and pulse filters. A gas stream is used by wet scrubbers to absorb contaminants until they are sprayed with a liquid to collect cement dust\textsuperscript{17}.

The Mayenite nanoparticles are also known as a calcium-aluminate system that is commonly shown as a portion of the CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} ternary system and comprises five stable CaO/Al\textsubscript{2}O\textsubscript{3} phases. Using cement notation the phases are denoted C\textsubscript{3}A, C\textsubscript{2}A\textsubscript{3}C, CA, CA\textsubscript{2}, and CA\textsubscript{6} from the lime-rich end towards alumina\textsuperscript{18–20}. Different preparation techniques could be applied for the preparation of calcium-aluminate phases. The widely used techniques are high-temperature solid-state preparation, sol-gel preparation from bauxite or/and lime, and combustion with specific raw materials\textsuperscript{21–25}. Both the desired end-product and its application control the choice of preparation technique. The CACs are primarily used as construction cement and concrete. The mixing of varying phases of calcium-aluminate1 and calcium-aluminate-ferrite11 are the main components of these kinds of cement. The manufacturing method of CACs requires high temperatures, whereas the raw materials, bauxites, and limestones are inserted into the top of a rotary kiln to react during the melting. The final products are then tapped into the bottom of the kiln and cooled\textsuperscript{26}.

The phase formation of Calcium aluminates gathered attention in several studies. Williamson and Glasser reported that no specific phases are favorably produced when equi-weight ratios from CaCO\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} mixtures are fired up to 120 h at 1045–1405°C\textsuperscript{27}. An additional study was completed by Mohamed and Sharp at 1150–1400°C using CaO/Al\textsubscript{2}O\textsubscript{3} mixtures to confirm the conclusions of Williamson and Glasser\textsuperscript{28}. S. Iftekhar\textit{et al.} performed experiments including a holding step at 900°C to allow the decomposition of CaCO\textsubscript{3} and ejection of its carbon dioxide. The variance in holding times at 900°C did not affect the compositions of the obtained phase. I.e., only a meta-stable orthorhombic/hexagonal phase CA is formed at 900°C\textsuperscript{27}.

This paper focuses on the reduction of toxic species present in cement dust, as well as the probability of Mayenite nanoparticle formation from cement dust at 1000°C, which is lower than the majority of previously recorded reaction temperatures\textsuperscript{27, 28}. The structural and morphological properties are studied using different techniques. Besides, the particle size distribution, crystallite size, and dislocation density are calculated.

2 Materials and Methods

2.1 Materials

Cement dust was used as received from cement factories and Al\textsubscript{2}O\textsubscript{3} was bought from Sigma Aldrich and applied as received without additional purifications.

2.2 Apparatus

A closed electrical furnace (Thermolyne Benchtop Muffle Furnace; model: F47910; 1200°C) was used for both phase formation and cement dust purification. The samples were handled and heated in a specially made porcelain vessel, which was used as a reactor for the reaction and purification in an environmentally benign technique.

2.3 Measurements

Elemental analyses were observed using the X-ray Fluorescence (XRF) technique (THERMO-WDXRF SPECTROMETER 39 KV 80 Ma). According to the chemical analysis obtained from XRF of cement dust samples, a stoichiometric reaction was set up between cement dust and Al\textsubscript{2}O\textsubscript{3} and heated in the previously mentioned reactor at elevated temperatures of nearly 1000°C and hold at this temperature for nearly 2 h.

X-ray diffraction (XRD) analysis was accomplished by the PANalytical X-ray diffractometer (Empyrean) using Cu K\textalpha radiation (wavelength = 0.154045 nm) at 40 kV accelerating voltage, 35 mA current, and 20°–70° scan range with 0.02° step scan. The average size of the crystallites, D\textsubscript{c}, of the produced nanoparticles was calculated by the Scherer equation\textsuperscript{29}.

\[ D_c = \frac{0.94\lambda}{\beta\cos\theta} \]  

Where \( \beta \) is the corrected full width at half maximum (FWHM), \( \lambda \) and \( \theta \) are the X-ray wavelength and diffraction angle. Scanning electron micrographs (SEM) were captured using Quanta FEG 250 (Switzerland). Transmission Electron Microscopy (TEM) images were captured by the JEOL JEM 1010 TEM, which operates at 100 kV. SEM and TEM samples were prepared by dispersing targeted powder in alcohol and dropping them onto a carbon film supported on a copper grid.

3 Results and Discussion

3.1 Structural properties

The phase determination and the purity of all prepared...
samples were analyzed by the p-XRD technique. Figures 1A-1C illustrates the X-ray diffraction patterns of cement dust (Bypass) and Mayenite (\(12\text{CaO}\cdot7\text{Al}_2\text{O}_3\)) \(\text{(hereinafter C12A7)}\) phase. Figure 1B showed Rietveld refinement of the XRD data to indicate the phase purity of the samples. In the case of the as-received cement dust, it is seen well-defined peaks that matched with mixed oxides of these known as Maynite, Portlandite, and others card no \((00-009-0413)\)\(^{30}\). In the case of the newly formed phase of Mayenite, it is seen a single phase of calcium aluminate with definite peaks, and these peaks matched with the card no \((00-009-0413)\). All the peaks of the produced calcium aluminate are assigned to the body-centered cubic phase \(31\). It was noticed that new peaks appeared which confirm the reaction between the aluminum oxide and the dust. The crystallite sizes of the received Bypass and produced Mayenite nanoparticles were determined using two ways; Scherrer’s equation and the Willamson-Hall equation \(^{32,33}\). The value of crystallite size based on Scherrer’s equation was found to be \(\sim 45\) and \(\sim 30\) nm for bypass and produced Mayenite nanoparticles, respectively. i.e., the average crystallite size of the as-received cement dust was 45 nm while the addition of aluminum oxide to the dust under the action of heat decreases the average crystallite size to 30 nm. Hence, the introduced aluminum oxide under the action of high temperature has a significant effect on the grain size. Under the reaction conditions and during the growth of the new cubic calcium aluminate phase \(^{34,35}\). The concentrations of chlorine and sulfur ions began to decrease with the increase in the reaction temperature, which promotes the crystal growth in calcium aluminate through the dissolution/precipitation process. Figure 1C explores the effect of reaction temperature, \(1000^\circ\text{C} \pm 2\) h, on crystal structure and phase purity of the bypass. The strength of the Mayenite, \(\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}\), peaks at 18.07, 33.28, and 41.24 increased, as seen in this figure, along with the emergence of new peaks at 20.86, 23.69, 27.95, 34.96, 36.66, and 44.04. The majority of the calcium aluminum oxide peaks have also increased, indicating that the sample’s phase purity and crystallinity have improved. Also, the minimum dislocation density was calculated by \(\delta_{\text{min}} = 1/D_c^2\). The value of \(\delta_{\text{min}}\) is increased from \(4.94 \times 10^{-3}\) to \(11.11 \times 10^{-4}\) dislocation/nm\(^2\) by the conversion of cement dust to Mayenite nanoparticles. Williamson Hall method was used to identify the effects of strain on the XRD peaks broadening and determine the size of the crystallite by excluding the strain factor. The effect of crystal-induced expansion in size can be distinguished from strain-induced expansion on the full width at high maximum (FWHM), by Williamson–Hall method according to Eq. 2\(^{36}\).

\[
\beta\cos\theta = \frac{m\lambda}{D_c} + 4\varepsilon\sin\theta
\]  

(2)

Where \(D_c\) is the average crystallite size in nm, \(\varepsilon\) is the strain and \(m\) is a correction factor \((m = 1)\). Figure 2 shows the plot of \(\beta\cos\theta\) versus \(\sin\theta\) for (a) Bypass and (b) produced Mayenite nanoparticles. The crystallite size and strain could be determined from the intercept with the \(y\)-axis and the slope, respectively, of the linear fitting of Fig. 2. The obtained values of \(D_c\) are 89 and 70 nm for
bypass and produced Mayenite nanoparticles, respectively. Almost, the obtained values are based on the Scherrer method half the values obtained based on the Williamson-Hall method. The obtained values based on the Williamson-Hall method could be more accurate for average crystallite size than the Scherrer equation at individual $\beta \cos \theta$ points. Positive strain values, $0.215^\circ$ and $0.554^\circ$ were obtained for bypass and produced Mayenite nanoparticles, respectively. This means the Mayenite nanoparticles strain is increased relative to the cement dust strain. The induced strain is likely to be responsible for the growth of Mayenite nanoparticles of smaller size with broad XRD peaks.

### 3.2 Surface characterization

TEM images were measured to study the sizes and shapes of the bypass and synthesized Mayenite nanoparticles. The samples were agitated ultrasonically in distilled water for 15 minutes to avoid aggregation of the particles. TEM images for cement dust (Bypass) and Mayenite (12CaO.7Al2O3) (hereinafter C12A7) are shown in Figs. 3a and 3b. The cement dust nanoparticles do not have a definite shape. Agglomerated clusters are observed in Fig. 2a. While Mayenite (12CaO.7Al2O3) (hereinafter C12A7) nanoparticles synthesized at 1000°C for 2 h are almost spherical nanoparticles combined with closely packed polygonal particles without agglomeration (Fig. 3b). Figure 3c shows the particle size distribution of Mayenite nanoparticles. The particle size is varied from 14 to 42 nm with an average value of 27 nm. Such a result demonstrates the development of a definite shape with characteristic features that allow these Mayenite nanoparticles to be applied over the fine cement dust for which high environmental and human health hazard effects are well known.

SEM images were also used to study the surface morphologies of the investigated samples. Figures 4a and 4b show SEM images of cement dust (Bypass) and Mayenite (C12A7). Highly condensed and agglomerated nanoparticles were observed for cement dust (Bypass) as observed in Fig. 4a. While the SEM image of Mayenite (C12A7), Fig. 4b, showed a high distribution of small dense nanoparticles. As shown in the inset image in Fig. 4b, the Mayenite nanoparticles self-aggregate together to form a nanoporous structure.

### 3.3 X-ray Fluorescence (XRF) analysis

The XRF analysis is carried out and the obtained data
are presented in Table 1. Also, the values of Loss on Ignition (LOI) were obtained during the measurement of XRF and provided in Table 1. In XRF analyses we obtained the LOI by measuring the crucible weight. The samples are heated at 105°C to remove adsorbed water and then at 1000°C for 1 h to remove both organic matter and carbonate. XRF results revealed a reduction in toxic ions especially chlorides and sulphates by 86% and 50%, respectively. Also, XRF data of our produced Mayenite nanoparticles are matched well with the XRF of cement calcium aluminate phase that is used in Europe especially in Spain which enables the latter to be directly used in construction. It is well-known that the calcium aluminate phase has property over the Portland cement phase in its high hardness and is five times much expensive.

### 4 Conclusion

In conclusion, nano-sized Mayenite, 12CaO.7Al2O3 (C12A7), nanoparticles were successfully fabricated at a temperature of 1000°C. The structural and morphological properties were studied by different techniques. The applied technique worked well in forming the calcium aluminate phase and reducing toxic ions in cement dust, such as chlorides and sulphates, by 86% and 50%, respectively. The Mayenite nanoparticles’ size is varied from 14 to 42 nm with an average value of 27 nm. XRF data is well-matched with the cement calcium aluminate phase, which is widely used in Europe, especially in Spain. Mayenite (C12A7) is a typical phase present in cement and used in concrete science, quite early introduced as a high-oxide conductor and catalyst for the biodiesel production process.

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### Conflicts of Interest

The authors declare no potential conflicts of interest.

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