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Thaumasite formation in stabilized coal combustion by-products

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Abstract

The by-products of the desulfurization process in a spray drier usually contain a mixture of hannebachite ($CaSO_3 \cdot 1/2H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and the finer fraction of the fly ash. This material was mixed with an additional fly ash and stabilized by adding about 3 wt% lime kiln dust (LKD). The stabilized product was used either as a structural fill or was left in the storage yard for several years. Samples extracted from these sites were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The analytical results show the formation of thaumasite ($Ca_3Si(OH)_6(CO_3)(SO_4) \cdot 12H_2O$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), and an intermediate phase with varying chemical composition of calcium, aluminum, silicon, and sulfur. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Spray dryer ash; Ettringite; Thaumasite; Gypsum; Hannebachite; FGD

1. Introduction

In the last three decades, there has been a continuous effort by electric utility companies to reduce sulfur dioxide emissions from coal burning power plants. To achieve the desired concentration of sulfur dioxide in the exhaust gases, they are processed in desulfurization plant. The most widely used method of removal of sulfur dioxide is the treatment of the flue gas with calcium oxide. In this process, calcium reacts with sulfur dioxide to produce hannebachite and/or gypsum. The by-products from the desulfurization process also contain the finer fractions of fly ash. These materials are then typically disposed of in a controlled landfill. Recently, there have been some attempts made to use them as structural fill or some other value-added applications. There has been a significant amount of data generated on the physical properties of flue gas desulfurization (FGD) products [1–4]. Samples of compacted FGD tested at various time intervals clearly show that the behavior of the material in an engineered structure changes with time. Much of this change has been attributed to the formation of minerals comprised of varying proportions of the FGD constituents. Some of the physico-mechanical properties such as strength and stiffness are equal to or greater than those found in most naturally occurring soils. There have been attempts made to replace soil with FGD products for engineering applications [1–3].

Satisfying the physico-mechanical characteristics should not be the only criteria used to justify the use of these materials in engineering applications. One needs to thoroughly understand the chemical and mineralogical changes of these materials in the field. In previous studies, it has been shown that these materials undergo mineralogical transformation when exposed to moisture [4–7].

In this study we have characterized the stabilized fill materials from the storage yard as well as materials used as structural fill in Virginia, USA.

2. Experimental

The collected samples were dried. Each sample was examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2.1. XRD

Representative portions of each of the three samples were taken at over a period of six months. The samples were first dried at 60 °C for 18 h. The material was then ground to a fine powder in a ball mill for several minutes.

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Approximately 2 g of the powdered material was weighed on a Denver microbalance and was mixed with approximately 15% by weight fluorite (CaF_2). Fluorite is used as an internal standard because of its consistent diffraction intensities and few interfering peaks. The samples were then reground in methanol by hand using a corundum mortar and pestle. The samples were left to air dry and then back-loaded into a standard aluminum holder. The samples were run from 4.0° to 64.0° 2θ on a Philips 3100 X-ray generator using 45 KV and 35 mA monochromatic copper radiation at 1.0° $2\theta/$ min with a step size of 0.05° 2θ. Quantitative analysis was performed on each sample using the internal standard method. Standard reference materials mixed with fluorite were used to derive calibration coefficients for each mineral detected in the samples. The weight percentage of the glass component was determined from the intensity of the amorphous "hump" between 20° and 30° 2θ due to anomalous scattering of the glass. Some samples were analyzed without an internal standard.

2.2. SEM

Representative portions of each sample were mounted into 10 ml plastic beakers and impregnated with epoxy. Upon hardening, the surface of each sample was finely polished. The samples were carbon coated and analyzed using a SEM in the backscattered electron mode (BSE) with an accelerating voltage of 20 KeV. The backscattered intensity was set to the same parameters for each sample. The chemical composition of the particulates and the homogenous groundmass is determined from the collection of the energy dispersive spectra (EDS) of the X-rays that are generated from the particle by the electron beam.

3. Results and discussion

The mineralogy of the stabilized FGD samples consists of a series of minerals. There are several crystalline phases as determined by XRD: quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), calcite ($CaCO_3$) hannebachite ($CaSO_3 \cdot 0.5\ H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) and thaumasite ($Ca_3Si(OH)_6(CO_3)(SO_4) \cdot 12H_2O$). Fig. 1 shows the XRD spectrum of one of the samples. The (1 0 0) peak of pure ettringite should have a *d*-spacing of 9.72 Å while the *d*-spacing of the (1 0 0) of pure thaumasite should be 9.59 Å. The phase present in the samples has a *d*-spacing of 9.61 Å which indicates that while not pure, its structure is more like thaumasite than ettringite. The XRD results are not conclusive about this phase. One can only conclude the presence of ettringite like phases in the system.

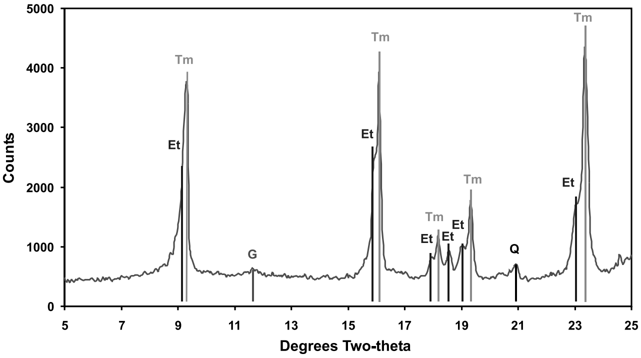

Fig. 1. XRD pattern of stabilized CCB (thaumasite (Tm), ettringite (Et), gypsum (G), and quartz (Q)).

A detailed SEM study was carried out to establish the microstructure of the stabilized FGD ash. The presence of quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), and a Ca-silicate/Al-silicate glass indicates these minerals formed during the high temperature combustion of bituminous coal in a boiler. The coal ash in this study was derived from a stoker boiler. The shapes of most of the ash particles are irregular (Fig. 2). There are also a small percentage of spherical ash particles similar to those from a regular boiler.

Hannebachite and gypsum formed in the system during the FGD process. In the FGD process, lime is injected into the scrubber in a low temperature, low oxygen environment. Sulfur, derived from the coal burning process is unable to oxidize to sulfate (SO_4) due to the limited amount of oxygen available. The sulfur instead oxidizes to sulfite (SO_3) and reacts with the lime to form the mineral hannebachite. Hannebachite is distributed throughout the matrix as small discrete particles (Fig. 3). Gypsum on the other hand is most deposited as massive crystals (Fig. 4). These two minerals were difficult to distinguish from the backscattered intensity. Fig. 5 shows the microstructure of a calcite particle, also present in the system.

Ettringite and thaumasite are not present in the fly ash, bottom ash, or the desulfurization by-products. These compounds are secondary minerals formed from the reaction of the scrubber residue with water. Fig. 6 shows the mode of thaumasite deposition in the system. These occur as fine crystals growing adjacent to massive deposits of gypsum (the bright materials on the left image). It is worth noting that the EDS spectrum shows that the crystals contain some small amount of aluminum. Apparently, this deposit is not pure thaumasite. Fig. 7 shows another growth type of the crystals, the chemical composition is neither consistent with ettringite nor thaumasite. These are either a mixture of ettringite and thaumasite or a solid solution between thaumasite and ettringite [8]. Collectively, these phases are known as SAS (calcium sulfo–alumino silicate hy-

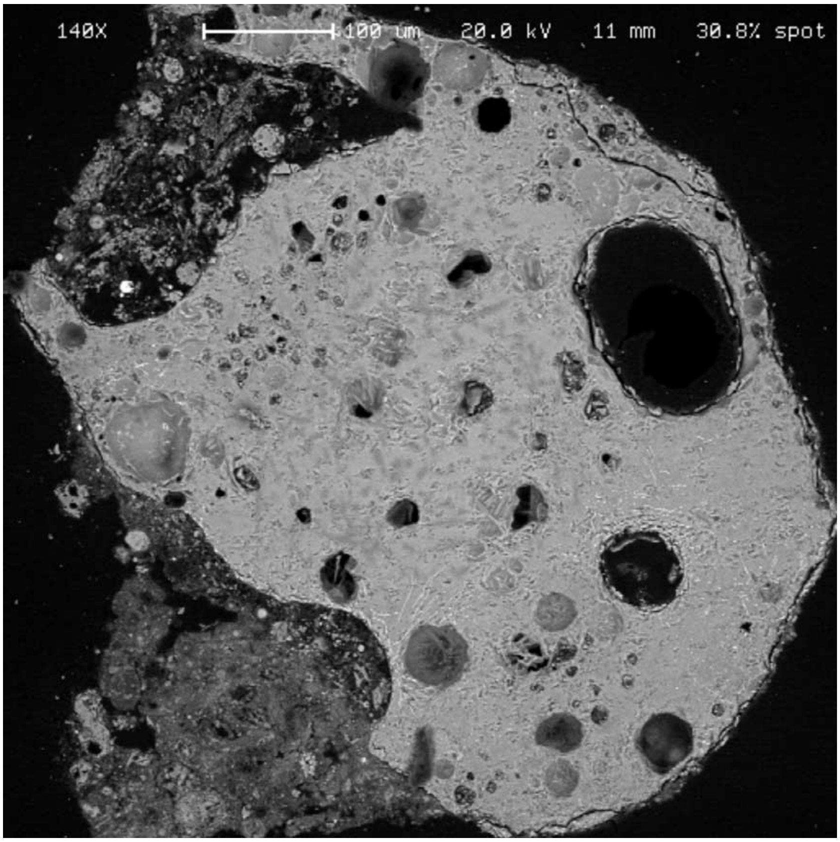

Fig. 2. Morphology of a typical stoker boiler ash particle.

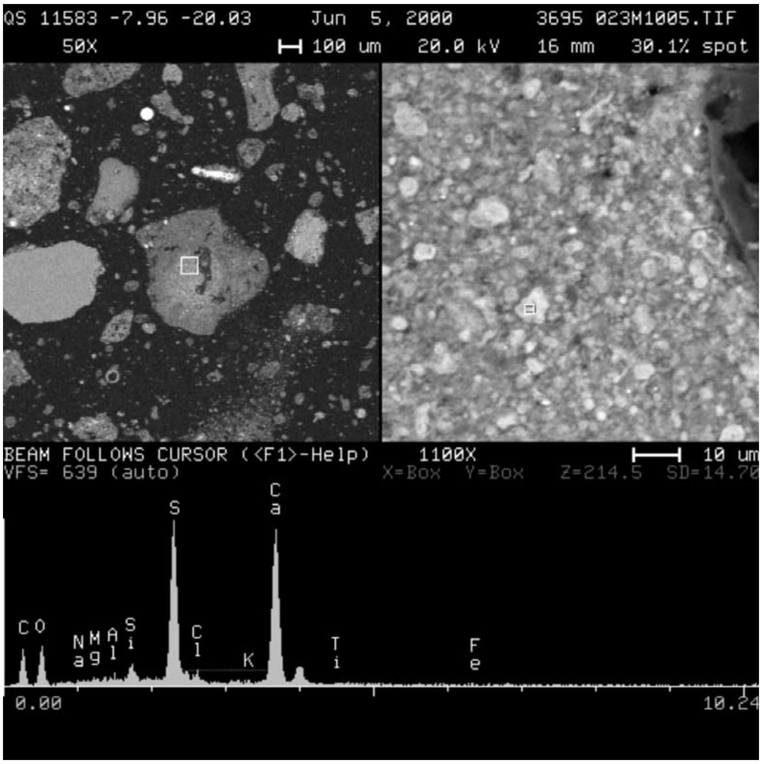

Fig. 3. BSE image showing the morphology and composition of hannebachite.

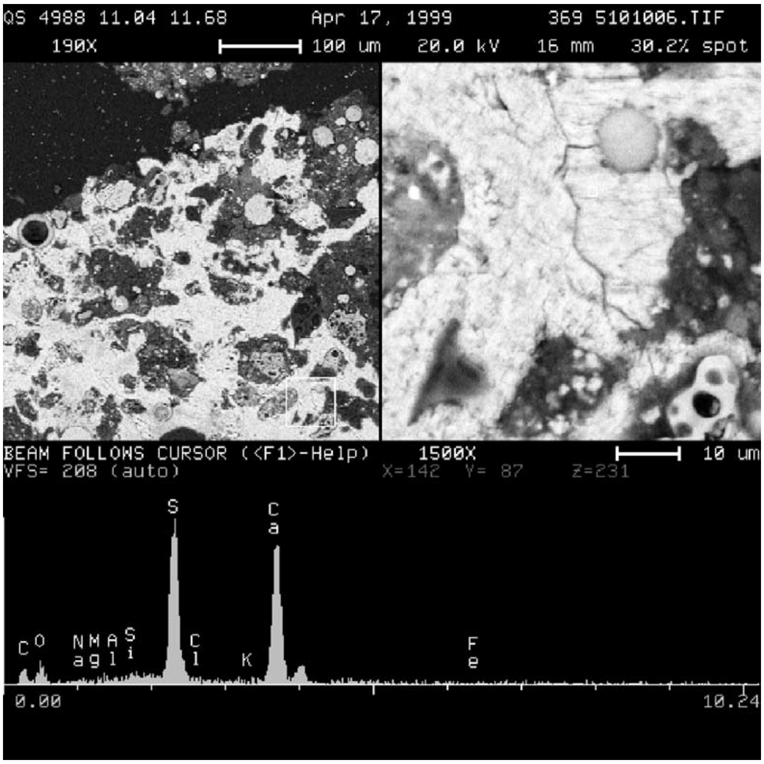

Fig. 4. BSE image showing the morphology of gypsum.

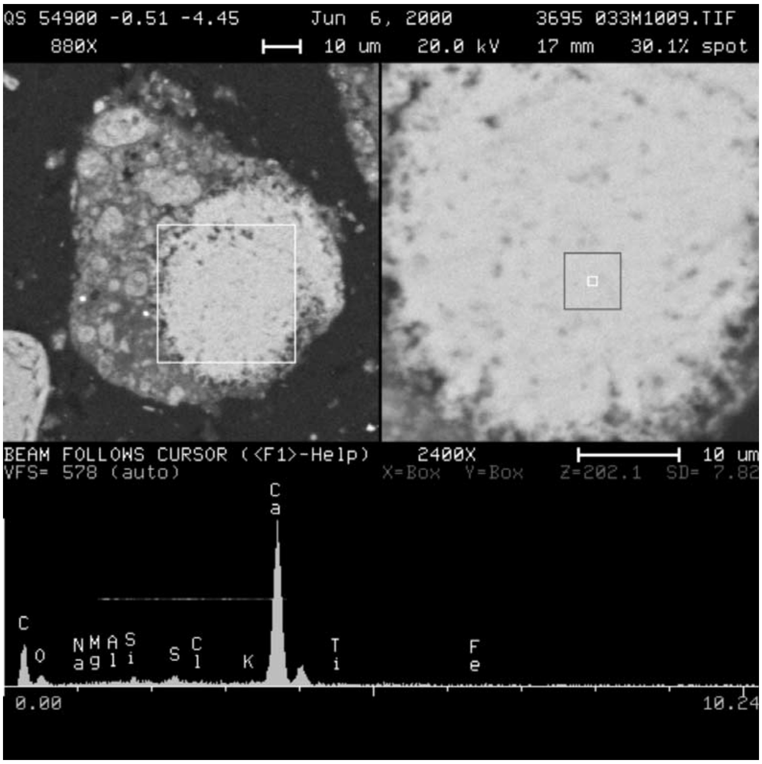

Fig. 5. BSE image showing the microstructure of $CaCO_3$.

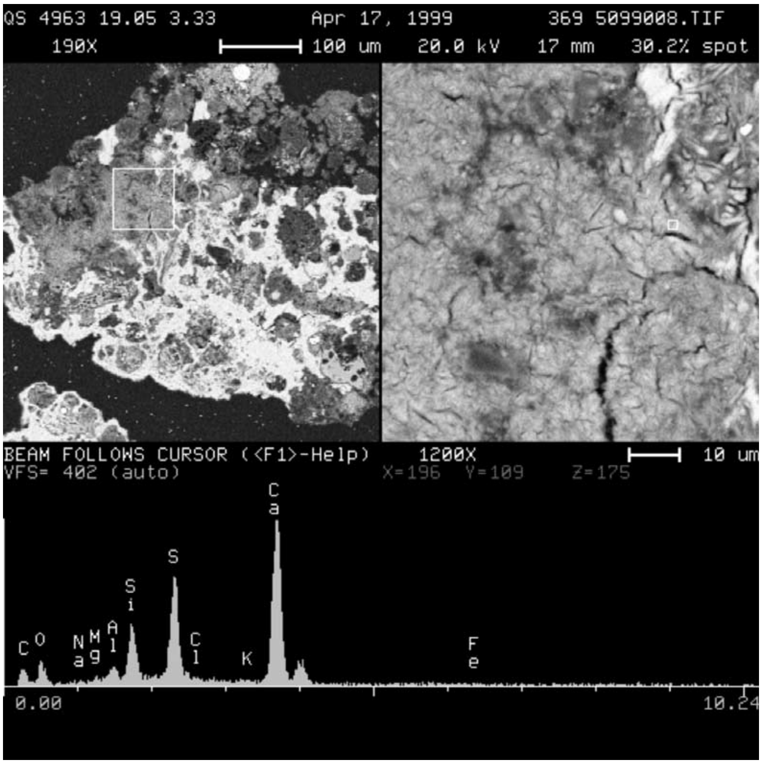

Fig. 6. BSE image showing the mode of deposition and morphology of thaumasite.

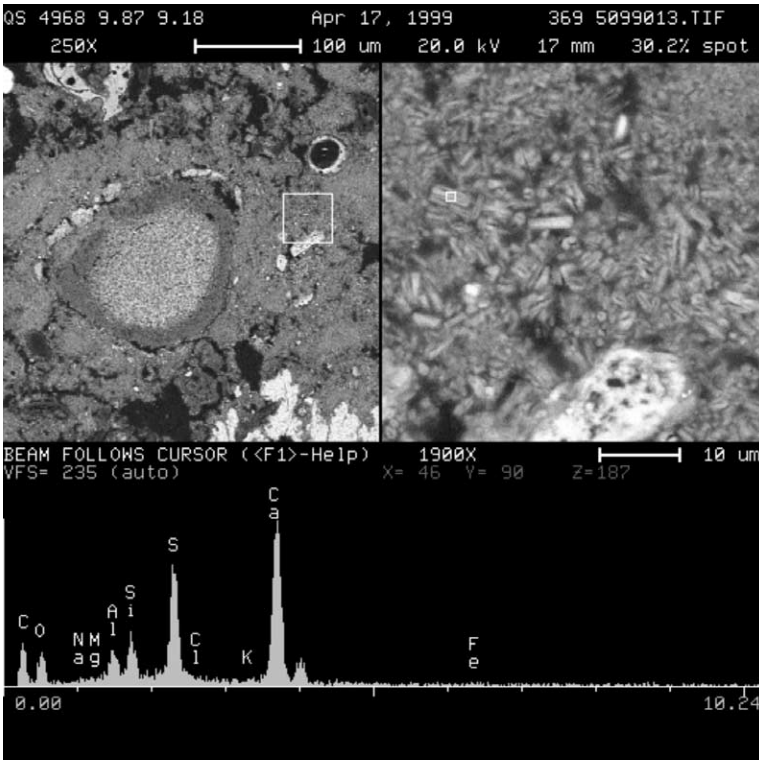

Fig. 7. BSE image showing the deposition of intermediate phase between thaumasite and ettringite (SAS).

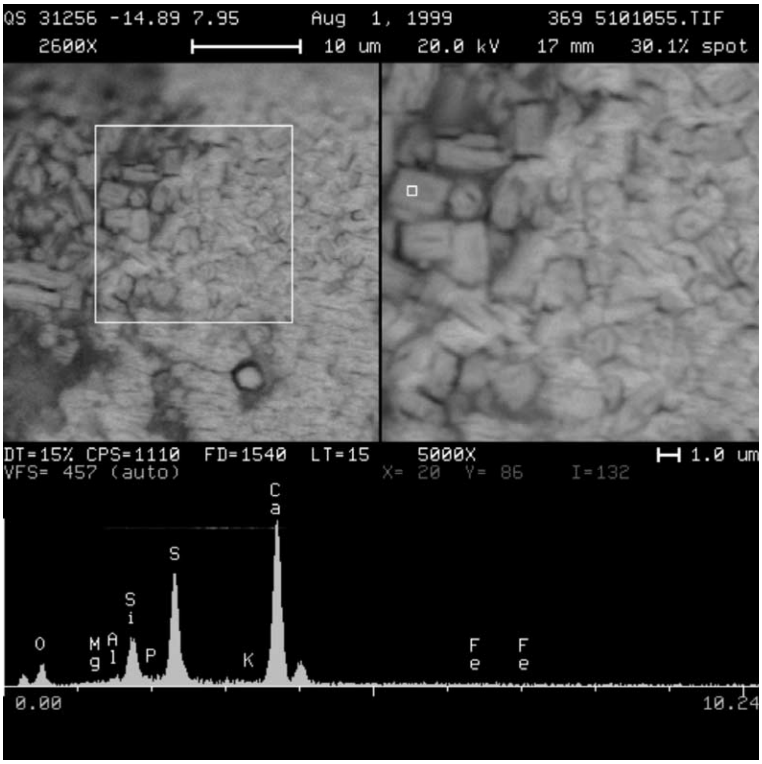

Fig. 8. BSE image showing the morphology of thaumasite in the matrix of CCB.

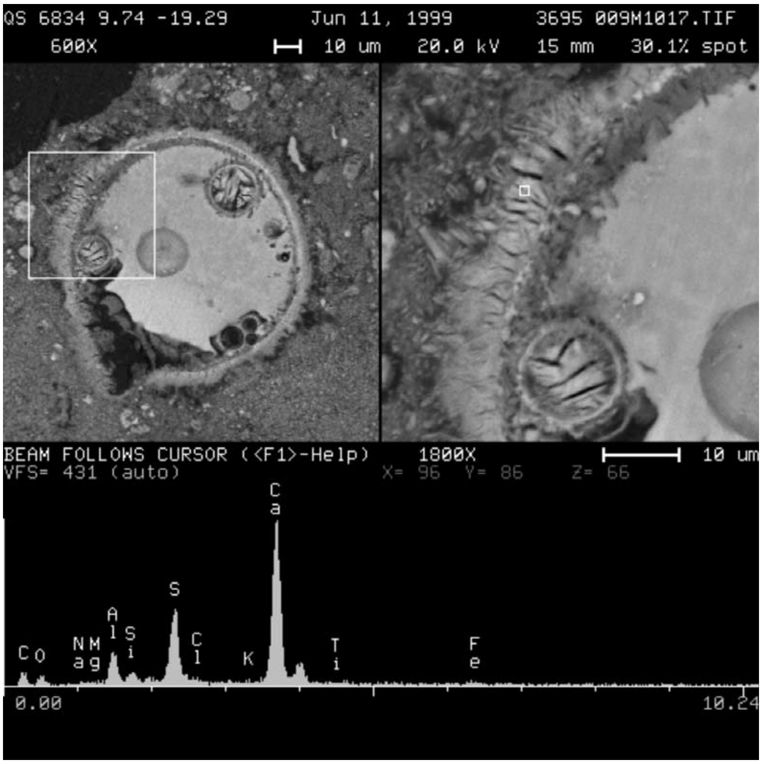

Fig. 9. BSE image showing growth of ettringite on a fly ash particle.

drates) [9]. Fig. 8 shows stubby crystals of thaumasite growing within a matrix of gypsum. The occurrence of pure ettringite is also observed in these samples. The deposits are found only in isolated locations. This is most likely due to the availability of a saturated lime environment in order to maintain a pH of greater than 12, critical in the formation of ettringite. Fig. 9 is a typical example of ettringite growth on the surface of a spherical fly ash particle. Ettringite is also seen growing inside the void spaces of the fly ash.

Considering the in-homogenous nature of this material in microscale, the minerals formed in the system are not uniform all through the matrix. There are plenty of sulfate and aluminum ions available in the system to form ettringite. The availability of calcium ions in solution is far more critical in determining whether or not ettringite will form. For the formation of thaumasite, carbonate ions must also be available in the system. The SEM micrographs clearly show that gypsum crystals act as nucleating sites for the formation of thaumasite.

4. Conclusions

FGD derived coal combustion by-products have not found many useful applications. Most of these by-products end up in landfills. There are other alternatives for high volume use of these materials in such applications as structural fills, embankments, and road sub-bases. It is of paramount importance to thoroughly understand the possible changes in mineralogy and stability of the CCBs when used in these new applied environments.

The present investigation shows that the phases present in original CCB materials undergo changes to form thaumasite and ettringite in the system. Most of the thaumasite formed in the system is growing directly from the gypsum matrix. Thaumasite is also growing in the void space. Thaumasite grown in the system occur as short stubby crystals. Ettringite crystals, on the other hand, grow in isolated pockets when the conditions of a saturated lime environment are available.

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