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Thermal analysis of calcium sulfate dihydrate sources used to manufacture gypsum wallboard

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ABSTRACT

Gypsum wallboard has been used for over 100 years as a barrier to the spread of fire in residential and commercial structures. The gypsum molecule, $CaSO_4{\cdot}2H_2O$, provides two crystalline waters that are released upon heating providing an endothermic effect. Manufacturers have recognized that the source of the gypsum ore is a factor that affects all aspects of its performance; thus, it is hypothesized that the impurities present in the gypsum ore are the causes of the performance differences. Differential Thermal Analysis/Thermogravimetric Analysis (DTA/TGA) and X-ray Diffraction (XRD) were used to compare and characterize samples of gypsum ore representing sources of natural, synthetic from a Flue Gas Desulfurization process (FGD) and blends thereof. The hemihydrate phase of representative natural, FGD, and reagent grade calcium sulfate were rehydrated with distilled water and evaluated by DTA/TGA. Analysis of the data shows distinct areas of similarity separated by the conversion to anhydrite ~250 °C. Compositional reconstructions based on DTA/TGA and XRD data were compared and although, the results were comparable, the DTA/TGA suggests thermally active compounds that were not detected by XRD. Anhydrite, silica and halite were reported by XRD but were not thermally reactive in the temperature range evaluated by DTA/TGA (ambient to 1050 °C). The presence of carbonate compounds (*e.g.*, calcite and dolomite) were indicated by XRD and estimated from the thermal decomposition reaction ~700 °C.

1. Introduction

Gypsum products are created from two simple reactions [1]:

$$\text{the calcination reaction}-CaSO_4{\cdot}2H_2O + \text{heat} \rightarrow CaSO_4{\cdot}½H_2O + 3/2H_2O(g), \text{ and} \quad (1)$$

$$\text{the rehydration reaction}-CaSO_4{\cdot}½H_2O + \text{excesswater} \rightarrow CaSO_4{\cdot}2H_2O + \text{excesswater}(g). \quad (2)$$

An ore of 100% calcium sulfate dihydrate should exhibit four distinct thermal reactions evident in the DTA and TGA evaluations; 1) the first is an endotherm ending ~105 °C where the adsorbed water is driven off, 2) a second endotherm ending ~175 °C where 75% of the crystalline water is driven off to achieve the metastable phase, $CaSO_4{\cdot}½H_2O$ (commonly known as plaster of Paris or hemihydrate), 3) a third endotherm ending ~220 °C where the remaining 25% of the crystalline water is driven off to unstable phase known as anhydrite III; also known as “soluble anhydrite”. The dehydration is complete and stable at about 250 °C. The fourth thermal change is an exotherm at ~400 °C where the monoclinic crystal habit, present in the first three thermal changes, undergoes reordering to the orthorhombic structure present in the anhydrite I and anhydrite II phases. Once this final thermal change is reached, there should be no other reactions occurring up to the study’s maximum temperature of 1050 °C [2–4].

What is not understood or appreciated are the effects that impurities have on the high temperature performance, *i.e.*, when the temperature exceeds 250 °C and more specifically, the temperature between 500 °C and 1000 °C. This paper is a study of the thermal differences in gypsum ore when heated in air by examining the effects that compositional differences have on gypsum ores heated to this temperature range.

Gypsum based panels are widely used as an interior partition surfacing material; among the properties that make it suitable are easy decoration, rapid installation, and a monolithic appearance when the joints are properly finished. An important benefit

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of its use is its limited effectiveness as a heat sink that results from the evaporation of crystalline water from gypsum molecule, $CaSO_4 \cdot 2H_2O$ (dihydrate).

In a typical house, about 200 ft^2 (~18.6 m^2) of gypsum based panels are needed to enclose potential fire sources like garages, around water heaters and furnaces. This area has about 425 lbs (~205 kg) of gypsum, which consists of about 85 lbs (~41 kg) of chemically combined water. When heated from 70 °F to 212 °F (21°–100 °C), this mass of gypsum board absorbs ~ 12,070 BTUs (~12,730 kJ). In practical terms, this means that there is a period of about 20 min where the surface temperature of the panel does not exceed ~200 °F (~100 °C) during which the crystalline water evaporates [1,5–7].

When the crystalline water in the gypsum has evaporated (~250 °C ≤ temperature), the minor impurities found in gypsum sources, whether naturally occurring or the result of an acid neutralization process, assume greater significance. In natural deposits the impurities are usually chloride and other sulfate salts, phyllosilicate clays typically from the kaolinite and smectite groups, carbonates, such as limestone, and silica (SiO_2). Gypsum from flue gas desulfurization often contains unreacted limestone ($CaCO_3$), dolomite ($CaMgCO_3$), unburnt coal particles, and heavy metals [8].

It is hypothesized that impurities[1] in the gypsum source could act like a dopant, form mixtures, or new compounds that affect the dimensional stability of the cast at elevated temperatures. This study is designed to characterize the impurities present in a commercial gypsum source and categorize their effect on high temperature performance of gypsum casting. Characterization of these effects are important because it is essential to understand how these different impurities affect the performance of gypsum castings exposed to elevated temperatures, i.e., >400 °C. This information becomes more important when the definition of a type X gypsum board changes from being based on a 100 ft^2 (9 m^2) wall system test specified in ASTM C1369 [9] to a small scale product performance test. Many patents contain specific recommendations on additives to enhance high temperature performance without specifically disclosing how the additive affects the thermal performance. Thus to engineer thermal properties into the gypsum casting, those specific effects have to be understood; especially as new performance specifications are developed.

An effort to replace the definition of a type X gypsum board in ASTM C1396 [9] resulted in the development of three small scale tests to evaluate the high temperature performance of gypsum board. These test methods characterize the performance with respect to High Temperature Core Cohesion (HTC), High Temperature Thermal Insulation (TI) and High Temperature Shrinkage (SH). The cohesion test rates the ability of board to stay intact when the panel is heated by high temperature gas burners. The other two tests, TI and SH, characterize the board at specific temperatures, 500 °C and 850 °C respectively [10].

The thermal commonality between the TI test and the type X test prescribed by ASTM C1396 [9] is demonstrated when the temperature data from the TI test are plotted with the data from a thermocouple placed between the gypsum board and the stud in the ASTM E119 test [11]. Fig. 1 depicts this comparison which also exhibits the significant effect that the crystalline water has on the temperature modification in a fire.

The lower temperature depicted in Fig. 1 by the "Thermocouple on [the] Unexposed Side [of the] Panel" (dash—dash line) is presumed to be the result of moisture in the cavity or wood studs used to the test wall. Following the constant rate period, the temperature increases faster because the condition in the furnace to which each specimen is exposed is different; the ASTM E119 standard test method is ramped from ~600 °C–800 °C and the TI test is preheated to 500 °C. This usual depiction of thermal performance is not sufficiently detailed to exhibit the changes that result in shrinkage and cracking, which are manifested between 250 °C and 1000 °C at a macro and micro level within the casting, especially across the thermal gradient through the panel.

2. Experimental

Samples of ground gypsum ore (LP – landplaster) ready for introduction to the board production process used by several US manufacturers of gypsum wallboard were provided for evaluation. The source of the ore is known and classified as Gypsum Ore (naturally occurring), FGD Gypsum (flue gas desulfurization, which is a byproduct from an SO_2 capture and neutralization process in coal-fired power plants), or a blend of these two primary ore sources (Table 1). A third source, reagent grade calcium sulfate hemihydrate was rehydrated with distilled water as an exemplar of "pure" gypsum (designated RHdce-RG). Reagent grade dihydrate is available; however, the hemihydrate phase was used because the pure dihydrate could not be calcined. If commercially available reagent grades calcium sulfate dihydrate and calcium sulfate hemihydrate are used, there is no assurance that the chemicals were from the same source or synthesized by the same technique. Thus, the reagent grade hemihydrate form was selected and rehydrated with distilled water to create the dihydrate phase.

When the primary ore samples were obtained, corresponding commercially calcined specimens made from the same landplaster were obtained. Based on the results from the DTA/TGA studies, specimens were grouped according to the similarity of their traces and representative specimens of the natural and FGD sources were selected. The sample that was representative of naturally occurring dihydrate ore was designated HMdce-08; the representative sample of the FGD Gypsum was designated as HMdce-03, and the reagent grade hemihydrate (Acros Organics, code: 385350025, lot: A0317491, CAS: 10034-76-1) was designated HMdce-RG. All of the hemihydrate specimens were received as a powder and rehydrated with distilled water; a slurry consisting of 1 part powder and 1.5 parts distilled water by weight was prepared in a Waring Blender (Model 7010HS with a 1 L stainless steel container) by mixing on low speed for 23 s.

2.1. Differential thermal analysis/thermogravimetric analysis (DTA/TGA)

The DTA/TGA was obtained using a Linseis Thermowaage L 81, programmed to operate in two stages in a compressed air atmosphere flowing at 15 mL/min. The first stage was ramped at 5 °C per minute from ambient to 1050 °C and the second stage was ramped down to ambient at 20 °C per minute. The maximum temperature was set at 1050 °C because the maximum temperature specified in an ASTM E119 test is 1800 °F (1032 °C). The temperature and mass were acquired every 5 s. Samples of LP were tested as received or crushed with a Pyrex® mortar and pestle to pass through a US Standard 100 mesh (150 μm) screen. The specimen was placed in an open 0.3 mL alumina crucible; the reference crucible was empty. The rehydrated specimen was cast as a rod 10 mm x 5 mm (length x diameter) to facilitate specimen loading into the crucible.

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[1] Compound, impurity and additive are used interchangeably to address any chemical that is not a $CaSO_4$ phase; compound is used as a generic term to include any chemical present in the cast, which may be an impurity, an additive, or a new chemical created in the manufacturing process; impurity refers to a chemical other than $CaSO_4$ phases present in the ore sample; additive refers to a chemical added at the time of manufacture. However, irrespective of the source anything that is not a $CaSO_4$ phase is an impurity.