TITLE: *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, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 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 $\sim 250^\circ\text{C}$. 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 $\sim 700^\circ\text{C}$.

KEYWORDS:

Gypsum, anhydrite, differential thermal analysis/thermogravimetric analysis, x-ray diffraction

1.0 INTRODUCTION:

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

1) the calcination reaction – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{heat} \rightarrow \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 3/2 \text{H}_2\text{O} (\text{g})$, and

2) the rehydration reaction – $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{excess water} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{excess water} (\text{g})$.

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 $\sim 105^\circ\text{C}$ where the adsorbed water is driven off, 2) a second endotherm ending $\sim 175^\circ\text{C}$ where 75% of the crystalline water is driven off to achieve the metastable phase, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (commonly known as plaster of Paris or hemihydrate), 3) a third endotherm ending $\sim 220^\circ\text{C}$ 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 $\sim 400^\circ\text{C}$ 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, 3, 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 of its use is its limited effectiveness as a heat sink that results from the evaporation of crystalline water from gypsum molecule, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (dihydrate).

In a typical house, about 200 ft² (~18.6 m²) 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 minutes where the surface temperature of the panel does not exceed ~200°F (~100°C) during which the crystalline water evaporates. [1, 5, 6, 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 (SiO₂). Gypsum from flue gas desulfurization often contains unreacted limestone (CaCO₃), dolomite (CaMgCO₃), unburnt coal particles, and heavy metals. [8]

It is hypothesized that impurities¹ 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

¹ Compound, impurity and additive are used interchangeably to address any chemical that is not a CaSO₄ 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 CaSO₄ 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 CaSO₄ phase is an impurity.

the definition of a type X gypsum board changes from being based on a 100 ft² (9 m²) 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]. Figure 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 Figure 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

Figure 1: Time:Temperature plot of a thermocouple placed in the exposed cavity of an ASTM E119 test vs the thermal insulation test (TI). The designated points indicate the temperatures where major thermal events occur during the heating of a gypsum panel or cast.

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.

2.0 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 SO₂ 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

Table 1: Gypsum Sources in the United States; FGD – flue gas desulfurization gypsum ore, LP – landplaster or raw gypsum ore, HM – hemihydrate or plaster of Paris, RG – reagent grade, RH – rehydrated.

State	Gypsum Source Reported	LP Specimen ID	Hemihydrate Specimen ID
Southeast	100% FGD Gypsum	LPdce-05	
West	100% Gypsum Ore	LPdce-08	HMdce-08
West	Unknown	LPdce-12	
Southeast	75% FGD Gypsum 25% Gypsum Ore	LPdce-01	
Southeast	FGD Gypsum	LPdce-SJR	
Southeast	FGD Gypsum	LPdce-PE2	
Midwest	65% FGD Gypsum 35% Gypsum Ore	LPdce-14	
Midwest	100% FGD Gypsum	LPdce-13	
Mid Atlantic	100% FGD Gypsum	LPdce-04	
Southwest	Unknown	LPdce-10	
Mid Atlantic	100% FGD Gypsum	LPdce-02	
Mid Atlantic	100% FGD Gypsum	LPdce-03	HMdce-03
Mid Atlantic Commercial	100% FGD Gypsum Reagent grade	LPdce-06 RHdce-RG	HMdce-RG

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 1L stainless steel container) by mixing on low speed for 23 seconds.

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 seconds. 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.

2.2 X-Ray Diffraction (XRD): The Panalytical X'pert Pro X-ray diffractometer with accompanying HighScore Plus powder analysis software at the New Mexico Bureau of Geology and Mineral Resources, Socorro, NM, was used for the peak and pattern analysis and semi-quantitative compositional analysis. The XRD machine parameters were Cu K α , 2 θ range 5-70°, step time 10.16 s, step size 0.017°, 40 mA at 45kV. The diffraction patterns were compared to the ICDD database² and the associated planes are identified in hkl notation. The as received or rehydrated specimens were crushed with an agate mortar

² International Centre for Diffraction Data®, Newtown Square, PA 19073-3273 U.S.A., <http://www.icdd.com/>

and pestle to powder. Mortar and pestle is preferred over grinding, which generates heat and causes calcination of the gypsum which could result in erroneous results.

3.0 RESULTS AND DISCUSSION:

3.1 DTA/TGA General Comments:

This study presents only the heating cycle because the laboratory evaluation of the gypsum wallboard only considers the heating cycle and the panel is rendered useless for its intended purpose after a fire. The data presented represents one result per specimen. This study is a survey of selected available sources; thus, no replicates were made unless there was a test malfunction such as a loss of power, computer glitch, loss of purging gas flow, etc.

All of the specimens exhibited the thermal and gravimetric profiles typical of calcium sulfate dihydrate decomposition and crystal reordering at $<500^{\circ}\text{C}$ and diverse (individually different) profiles when the temperature was $>500^{\circ}\text{C}$. At temperatures where the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is dehydrating ($<250^{\circ}\text{C}$), any other compounds showing thermal or gravimetric activity in the same temperature range are masked by the large endotherm and mass loss occurring from the evaporation of the crystalline water in the dihydrate. Likewise, similar activity where the anhydrite crystal reordering occurs could be masked by the exotherm from the large mass of CaSO_4 present. Alternatively, compounds present or synthesized *in situ* could also enhance or suppress the endo- or exotherm present, which could be revealed or hidden in the data. Some of the potential factors confounding these results were:

1. Some changes in DTA or TGA may not be evident because they are too small to identify,
2. New compounds formed during rehydration where other salts are formed during recrystallization,
3. New compounds formed by thermal reactions with air atmosphere (oxide formation) and subsequent decomposition at higher temperatures,
4. Other thermal or decomposition activity masked by the large presence of CaSO_4 ,

5. Interactions occurring at the same temperature resulting in an increase or decrease in enthalpy, *e.g.*, the oxidation of coal dust in FGD, decarbonation of carbonate salts, and the dehydroxylation of clays or other compounds containing crystalline water,
6. Phase changes could occur at crystal boundaries in salts that are formed during the aqueous rehydration of the hemihydrate.

Figure 2: Overlay of Heating Profile, DTA trace and TGA trace (δ Mass). Vertical lines at ~14 minutes, ~26 minutes, ~45 minutes, and ~66 minutes (85°C, 150°C, 250°C, and 365°C, respectively) are defined to be the points at which A) the free water is evaporated (~85°C), B) the hemihydrate phase is formed (~150°C), C) all of the water in the dihydrate phase is evaporated (250°C), and D) the monoclinic crystal habit is modified to orthorhombic (~365°C).

The specimens tested exhibited the thermal and gravimetric profiles typical of calcium sulfate dihydrate decomposition into the temperature range of ambient to 250°C. From an overlay of the DTA, TGA, and heating traces, the following reaction temperatures and mass loss values are extracted at markers indicated in the zoomed inset of Figure 2:

1. Adsorbed or free water (A – Figure 2): Extract temperature and mass loss at onset of the dehydration of the crystalline water; $\sim 85^{\circ}\text{C}$, $mass\ loss_{fw}$;
2. Hemihydrate formation (B – Figure 2): Extract temperature and mass loss at end of the first endothermic period; $\sim 150^{\circ}\text{C}$;
3. Anhydrite formation (C – Figure 2): Extract temperature and mass loss at end of second endothermic period; $\sim 250^{\circ}\text{C}$, $mass_{250}$.
4. Anhydrite Crystal Reordering (D – Figure 2): Exotherm indicative of crystal reordering from monoclinic to orthorhombic.

The theoretical purity of the phase can be estimated by multiplying the “component measured” by the appropriate gravimetric factor (Table 2) by searching the thermal data to locate the time or temperature of the thermal event and obtaining the corresponding mass loss from the gravimetric data. For a thermogravimetric analysis of a gypsum sample, the absolute value of the mass loss is a) divided by the original sample weight, b) multiplied by 100 to convert it to percentage, and c) multiplied by the gravimetric factor, 4.7677, to obtain the % purity of gypsum in the original sample. Values in excess of 100% are assumed to be from a contaminant that also contains crystalline water which evaporates in the same temperature range as the gypsum. Thus, any deviations from these thermal and gravimetric patterns are presumed to be evidence for the presence of some other chemical or mineral other than a CaSO_4 phase.

Table 2: Gravimetric Factors to determine Purity of Gypsum specimens

Mineral – Chemical Sought	Molecular Weight	Component Measured	Molecular weight	Calculation	Factor
Gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	172.172	H_2O	18.056	$172.172/(2*18.056)$	4.7677
Bassanite – $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	145.088	H_2O	18.056	$145.088/(0.5*18.056)$	16.0709
CaCO_3	100.09	CO_2	44.01	$100.09/44.01$	2.2743
MgCO_3	84.32	CO_2	44.01	$84.32/44.01$	1.9159
$\text{CaMg}(\text{CO}_3)_2$	184.41	CO_2	44.01	$184.41/(2*44.01)$	2.0951

3.1.1 DTA Normalization: An equation (Equation 1 A and B) was determined using regression analysis of the DTA zero curve (a trace of empty alumina crucibles run through the same heating program contemporaneously with the original sample run) to estimate the offset from the baseline of the DTA experimental data. The data used in this study were conducted in two separate time periods, thus a regression equation of the zero curve was established for each data set. These data for the LP test cycle were best described by a 3rd order polynomial regression equation and a power equation for the rehydrated specimen test cycle (Figure 3); where DTA_i = value of DTA signal at the i^{th} point in μV ; X_i = temperature ($^{\circ}\text{C}$) at the i^{th} point; and original specimen mass in mg. It is important with this technique that all of inherent instrument error is determined and used to set the baseline of the DTA data. Many data acquisition and analysis packages provided with the DTA instrument include techniques to determine the baseline of the data. The next step used these adjusted DTA traces to normalize the data with respect to a specific sample by dividing the DTA value (μV) by the mass (mg), which resulted in a normalized reading in microvolts per milligram ($\mu\text{V}/\text{mg}$).

Equation 2: Calculation and Normalization of TGA Values

$$\begin{aligned}
 \text{Dry_wgt}(mg) &= \text{Original_mass} - |\text{mass_loss}_{fw}| \\
 \text{corrected_mass_loss}_i &= |\text{mass_loss}_i| - |\text{mass_loss}_{fw}| \\
 \text{corrected_mass_loss}_{250} &= |\text{mass_loss}_{250}| - |\text{mass_loss}_{fw}| \\
 \text{Normal_Mass_Loss}_i &= \frac{\text{corrected_mass_loss}_i}{\text{corrected_mass_loss}_{250}}
 \end{aligned}$$

3.1.2 TGA normalization: The TGA zero curve was also used to adjust the mass data curve to the baseline.

It was assumed that all of the mass loss between point A and 250°C (Fig. 2) is the result of the dehydration of the crystalline water in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The mass loss due to the gypsum is normalized to unity (one) using the series of equations shown in Equation 2; where i = mass loss at the i^{th} temperature ($T, ^\circ\text{C}$); mass_loss_{250} is the mass loss at $T = 250^\circ$.

Therefore, any additional mass change results in a deviation from unity; an increase in mass loss means that there is contaminate volatility and a decrease in mass loss means that there was a reaction with the

Equation 1: A - Normalization of the DTA signal from LP test series; B – Normalization of the DTA signal from the Rehydrated Hemihydrate test series.

A – Landplaster Test Series $\text{Normal DTA}_i =$

$$\frac{(DTA_i - 6.997421831 + 0.2822448061X_i - 0.0001979375671X_i^2 - 6.569174976 \times 10^{-8}X_i^3)}{\text{Original Specimen Mass}}$$

B – Rehydrated Hemihydrate Test Series

$$\text{Normal DTA}_i = \frac{DTA_i - 0.01607926381 \times X_i^{0.8419653538}}{\text{Original Specimen Mass}}$$

purging gas that formed a new chemical, which, in this study, is expected to be an oxide. If there is a reaction among the compounds present in the specimen, an exotherm or endotherm could occur signifying the formation of the new compound from the ions present; however, that formation is not observed in the gravimetric traces because this change is likely a density, or volumetric change.

3.1.3 DTA/TGA analysis: The change in the trace profile before and after the crystalline water is evaporated at ~250°C can be observed in Figure 2 (point C). This change allows the traces to be separated thermally into two segments — below 250°C and above 250°C. Using this natural division, the gravimetric data separate into the mass change caused by the water bound in the gypsum crystal from other sources. Analysis addresses only those reactions above 250°C because the changes below 250°C are confounded by

Figure 3: Correlation equations used to base line the DTA data.

the overwhelming activity from the thermal decomposition of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

3.1.3.1 Temperature <250° C: The traces (Figures 4A and 4B) exhibit the usual two endotherm pattern of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ being transformed into CaSO_4 , that is, a strong endotherm culminating at about 150°C, which is indicative of the formation of the metastable hemihydrate phase ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) followed by a second endotherm culminating at about 175°C indicative of the formation of the unstable anhydrite III phase as the temperature of the test specimen returns to the chamber temperature. The anhydrite is stable at ~225°C.

3.1.3.2 Temperature >250° C: If the specimens are pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the only expected thermal change is an exotherm at ~ 400°C, which indicates the reordering of the monoclinic crystal habit of the dihydrate, hemihydrate, and anhydrite III phases into the orthorhombic crystal habit of anhydrites I and II. Any other thermal activity is the result of impurities present in the raw ore.

3.1.3.3 Combination of Normalized DTA and TGA: There was a commonality previously discussed that allows the interpretations shown in Figures 5A-B for the ore data and in Figures 6A-C for rehydrated

Figure 4: A – DTA traces of the submitted specimens. The dashed line at 250°C indicates the point at which all of the crystalline water in the dihydrate is assumed to have evaporated. B – Comparison of DTA traces of Hemihydrate made from a source of natural, FGD, and reagent grade. All of the specimens were rehydrated with distilled water. The rehydrated natural and FGD hemihydrates are compared to their ores.

specimens. Evidence to support the hypothesis that other reactions are occurring is depicted in these two figures, which are discussed below. In particular, there are specific thermal changes noted that can be linked to the source of the gypsum ore and changes and effects that related to the rehydration reaction of the calcined hemihydrate.

If the trace falls below a value of 1, the specimen has gained mass, which in the technique used for this DTA/TGA analysis is likely an oxidation reaction of a thermally reactive compound or element found in ore. Pure dihydrate specimens should stay near 1. If the specimen contains other compounds that that decompose above 250°C, then the normalized TGA should be greater than 1 and depending at what temperature the increase in mass loss occurs, should be an indicator of the compound that is thermally active.

In Figure 5, the portion of the DTA/TGA study after the dehydration stage is enhanced. The gravimetric change, the upper section of each graph for each specimen, is normalized to highlight deviations from the gypsum or FGD mass loss. The lower section of the graph is the DTA trace. The two

Figure 5: Ore DTA/TGA composite graph showing differences in traces after dehydroxylation of gypsum; A - no wgt loss; B - wgt loss.

graphs in Figure 5, represent those specimens that do not continue to lose mass (A) and those that continue to lose weight (B). The specimens showing anomalies are identified and discussed below.

Two traces that show evidence for the exothermic crystal reordering in LPdce-06 retest and LPdce-01 are highlighted in Figure 5A. The inset in Fig. 5A shows a small decrease in mass which is regained almost immediately. This isolated change, which is coincident with the exotherm associated with the crystal reordering in an FGD Gypsum, is hypothesized to be an oxidation reaction with a trace material found in the coal that was carried over in the gas stream from which the calcium sulfate dihydrate ore was synthesized. The other traces exhibit a similar exotherm at the crystal reordering temperature, although not as strongly, but without the associated mass loss seen in the LPdce-06 retest. Furthermore, a slight increase in the mass loss at about 700°C is indicative of the decomposition of carbonate containing compounds into the oxide and CO₂ (decarbonation). [12]

The specimens (Figure 5B) that continue to have mass losses at temperatures >250°C exhibit numerous changes in the traces. LPdce-03 has an unusual profile in that there is a reaction occurring between ~375° and 500° where there is a strong exotherm coincident with an increase in the mass of the specimen. This change is hypothesized to be an oxidation reaction with a metal found in the coal that was carried into the ore. At ~500°C the mass is lost suggesting that the oxide was calcined and the mass returned to its previous value. Traces LPdce-02, LPdce-05, and LPdce-10 exhibit the characteristic exotherm from the crystal reordering to anhydrite. A strong endotherm in LPdce-14 accompanied by a large mass loss ~800°C is hypothesized to be a dehydration reaction from a clay mineral; the natural ore source in this specimen is from a site known to have clay contamination.

If the rehydration reaction merely reproduces the original dihydrate state before calcination, then the expectation is that the DTA and TGA ore curves should be replicated by the rehydration curves. Figures 6A, 6B, and 6C highlight the differences in the original dihydrate and rehydrated hemihydrate in three

different temperature ranges; A – 200°C to 450°C spans the end of the dehydration stage through the anhydrite crystal reordering stage, B – 550°C to 800°C spans the decarbonation stage of any carbonate minerals that may be present, and C – 900° to 1050°C spans the dehydroxylation stage of any clay minerals that may be present. The FGD specimen (LPdce-03) exhibits the largest difference in that the after rehydration, it does not lose mass and resembles the pattern of the other specimens. Additionally, the rehydrated specimens exhibit the anhydrite crystal reordering more pronouncedly than the ore specimens (Fig. 6A), especially in the LPdce-08 and reagent grade specimens. The decarbonation reaction in Fig. 6B at ~700°C is confirmed by a mass loss in the rehydrated specimens from LPdce-03 (solid diamond) and LPdce-03 (x); a mass loss is not shown in the rehydrated reagent sample (solid circle). In Fig. 6C, there is no additional mass loss in any of the rehydrated specimens.

3.2 XRD analysis: To identify the differences indicated by the DTA/TGA data, the XRD data are similarly separated based on whether or not there is weight loss after the 250°C calcination temperature. A compositional analysis (Table 3) of the specimens based on the XRD data indicates the presence of carbonate compounds and contamination of the specimens with anhydrite and bassanite. Bassanite,

Figure 6: Evolution of DTA and TGA changes with respect to temperature. Plot A covers the temperature range from 200°C to 450°C; B covers the temperature range from 550°C to 800°C; C covers the temperature range from 900°C to 1050°C.

Figure 7: XRD traces of specimens showing no weight loss above 250°C. The legend on the right identifies the source of each trace; major peaks identified by source and plane (A (hkl))

$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, is not normally found in ore specimens; however, its presence could be explained by contamination of the source by off-quality hemihydrate being disposed of and mixed with the raw ore used as the process feed. Calcite and dolomite, carbonate compounds, are normally found in natural gypsum deposits and as unreacted material in an FGD process. Specimens LPdce-03, LPdce-10, LPdce-PE2 and LPdce-SJR are FGD sources which are expected to be high purity gypsum. LPdce-08 is a high purity natural source.

The XRD traces of the ores that did not lose weight above 250°C exhibit a few differences (Figure 7). It is noted that in LPdce-01 that there are peaks at $\sim 14^\circ$ and $\sim 27^\circ$ 2θ that are not present in the others. Additionally, there are numerous peaks between $\sim 28^\circ$ and $\sim 38^\circ$ 2θ that are of varying intensity and width. In this range there are many other minerals that are present in gypsum ores that are hidden within the peak widths.

In the data group of specimens that continued to lose weight (Figure 8), there are two, LPdce-02 and LPdce-06, which exhibit differences at $\sim 17^\circ$ 2θ which is indicative of anhydrite or bassanite.

Figure 8: XRD traces of specimens showing weight loss above 250°C. The legend of the right identifies the source of each trace; major peaks identified by source and plane (A (hkl)).

These discrepancies merit further investigation by removing the CaSO₄, which is masking lower concentrated impurities.

Because the hemihydrate samples are rehydrated, a comparison of the ore and its hemihydrate is made to evaluate the validity of use of the hemihydrate as a surrogate for the ore. Figure 9 depicts the natural and FGD Gypsums, their rehydrated hemihydrate samples and the rehydrated reagent grade hemihydrate. The traces are grouped by source; the bottom two traces are the natural ore and its rehydrated hemihydrate, respectively; the center two are the FGD and its hemihydrate, respectively; the top trace is the rehydrated reagent grade hemihydrate.

An obvious demonstration of the continuity can be seen in the third and fourth traces (FGD, LPdce-03 and Rehydrated HMDce-03). There is a small peak at ~18° 2θ in the FGD Gypsum trace (third trace) that is replicated in the rehydrated FGD (fourth trace). One difference noted is that the intensity of some of the peaks, especially at approximately 20°, 24°, and 45° 2θ, are stronger after the recrystallization of the

Figure 9: Selected rehydrated hemihydrate from ore and reagent grade specimens. The legend on the right identifies the origin of each trace;major peaks identified by source and plane (A (hkl))

hemihydrate to dihydrate. This analysis provides evidence that the use of the hemihydrate as a surrogate for the original ore, provided that hemihydrate is rehydrated with distilled water, provides a suitable estimation of the original ore composition. However, this assumption cannot be extended to manufactured gypsum board core because it contains other additives which increase the compositional complexity.

3.3 Comparison Compositional Analysis from DTA/TGA and XRD Analysis

The compositional reconstructions based on the mass loss determined in the DTA/TGA study relies on the evolution of gasses from the thermal decomposition of the impurities found in the gypsum ore and an estimation of the quantity based on the assumption that the suspected impurities are decomposing at a specific temperature. In contrast, a compositional reconstruction based on and XRD semi-quantitative analysis provides an estimation of the compounds present in the sample; however, compounds present at <5% may not be detected.

3.3.1 Compositional Reconstruction of Specimens based on DTA/TGA: Assuming, 1) that the mass loss between 100°C and 250°C is due solely to the crystalline water from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and 2) any mass loss beyond that temperature is due to other compounds, such as clays, or other hydrates, and carbonate compounds (~750°C), specimens LPdce-05 and LPdce-08 contain another compound that also loses mass in the same temperature range as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ because these two show a negative amount of “% Unknown” compounds. [7, 8, 12] A possible compositional reconstruction of the specimens is shown in Table 3 based on the gravimetric factors shown in Table 2 in the columns headed “DTA/TGA”.

3.3.2 Compositional Reconstruction of Specimens based on XRD: The compositional analysis is an estimation of the mineralogical composition as determined by the HighScore Plus powder analysis software. The information is shown in Table 3 in the columns headed “XRD”.

3.3.3 Comparison of Composition determination by DTA/TGA and XRD: The discrepancy between the two test methods could be due to the component labeled as “Unknown” in the DTA/TGA composition, which may be the result of other hydrates, such as clay, at levels below the detection limits of the XRD method.

These hydrates are detected by the TGA because of their mass loss at higher temperatures. Due to the nature of the hydrated compounds in this study an XRD with a heated sample mount would be beneficial. The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ contents as determined by either method demonstrate a reasonable level of agreement with the exception of specimens LPdce-03 and LPdce-10.

The differences in results of LPdce-03 may be due to two different $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ standard files being identified with the XRD traces because there are minor variations in the FGD recrystallization processes. The reported data were determined by summing the reported semi-quant values as total $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The difference between DTA/TGA and XRD for LPdce-10 could be attributed to the presence of NaCl (sodium chloride or halite) which is known to affect the calcination behavior of the dihydrate.

If the assumption is made that the XRD semi-quantitative analysis is accurate, then the effect of halite can be ascertained by comparing LPdce-08 and LPdce-10 (Figure 10). The calcination of gypsum is completed at $\sim 150^\circ\text{C}$. The temperature of the hemihydrate transition for LPdce-08 is 151.7°C at a DTA value of $-37.567 \mu\text{V}$ with a heat change of about $-179.2 \mu\text{V}/\text{mg}$ and the temperature of the hemihydrate transition for LPdce-10 is 148.8°C at a DTA value of $-37.544 \mu\text{V}$ with a heat change of about $-133.3 \mu\text{V}/\text{mg}$. Although there is insufficient data to make a categorical statement that halite reduces the calcination temperature of gypsum, the data confirm anecdotal information regarding the effect of NaCl on the heating of gypsum.

The portion of hemihydrate cannot be estimated by DTA/TGA because the mass loss is included in the second endotherm. Anhydrite, quartz and halite, which were identified by the XRD analysis, are not thermally reactive in the temperature range studied. DTA/TGA results are more sensitive to smaller quantities of carbonates, calcite and dolomite than XRD because the temperature at which CO_2 evolves is relatively free from interferences from the other impurities in gypsum ores.

4.0 CONCLUSIONS:

This study of gypsum ores provided evidence to support a hypothesis that the impurities found in natural, FGD, and blends thereof exhibited thermal activity in a temperature realm greater than 250°C, which confirms anecdotal information regarding the variation in thermal performance from different sources. Variations in the DTA/TGA traces, in conjunction with XRD, were used to estimate the chemical composition and effect of that impurity on the high temperature performance of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ores. Representative hemihydrate phases from natural and FGD sources and reagent grade calcium sulfate were rehydrated with distilled water and compared by DTA/TGA and XRD. A graphical review of the data shows analogous patterns separated by the conversion to anhydrite (~250°C). Discrepancies were identified in compositional reconstructions that were based on the DTA/TGA data or the XRD data, especially with respect to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and CaSO_4 as well as the presence of carbonate compounds. The DTA/TGA analysis demonstrated the presence of unidentified compounds that undergo thermal changes above the temperature (~400°C) where the crystal reorders to anhydrite.

Compositional reconstructions yield comparable results for dihydrate, whether estimated from the DTA/TGA or XRD data. Anhydrite, silica and halite were reported by XRD; silica and halite cannot be confirmed by DTA/TGA because they are not thermally active in the temperature range (ambient to 1050°C) evaluated. The presence of carbonate compounds (*e.g.*, calcite and dolomite) were indicated by XRD and estimated from the thermal decomposition reaction ~700°C. These minerals are normally present in natural, FGD, and blends thereof.

The rehydration of the hemihydrates showed an increase in the intensity of the XRD peaks. Also observed are that the DTA traces are different than the corresponding ore specimens, which when reconstituted causes the soluble ingredients to be recrystallized. Furthermore, differences in impurities (Fig 10), specifically halite, between two sources, LPdce-08 and LPdce-10, exhibit a reduction in the temperature of conversion to hemihydrate on these two natural ores.

A method to concentrate the impurities to facilitate identification by extracting the CaSO_4 phases is important for the identification of impurities and compositional changes in future work. This separation is necessary because of the high concentration of CaSO_4 phases conceal the impurities present at levels <2%, especially when the thermal events or XRD peaks are in close proximity to the CaSO_4 phase. Additional future work is required to clarify the high temperature performance of gypsum castings containing common additives and extraction of those additives/impurities from the gypsum castings.

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Table 3: Comparison of Composition based on TGA mass loss and XRD Data. Columns Headed DTA/TGA based on mass loss data and columns headed XRD based on se composition from XRD evaluation.

Specimen ID	Adsorbed Water	Gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		Bassanite – $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	Anhydrite – CaSO_4	Quartz – SiO_2	Carbonate Salts	Calcite – CaCO_3	Dolomite – $\text{CaMg}(\text{CO}_3)_2$	Halite NaCl
Estimation based on	DTA/TGA	DTA/TGA	XRD	XRD	XRD	XRD	DTA/TGA	XRD	XRD	XRD
LPdce-01 ^{A+}	0.3	88.2	83	8	—	5	1.3	—	—	—
LPdce-02	0.1	87.2	87	9	4	—	6	—	—	—
LPdce-03	0.3	89.3	98	2	—	—	0.8	—	—	—
LPdce-04 ⁺	0.2	89.4	87	—	—	—	—	13	—	—
LPdce-05	0.5	98.5	97	—	—	—	4.8	—	3	—
LPdce-06 ⁺	0.2	50	42	58	—	—	1.2	—	—	—
LPdce-08	0.6	98.5	100	—	—	—	4.4	—	—	—
LPdce-10	0.3	92.8	99	—	—	—	1.4	—	—	1
LPdce-12 ^{B+}	0.0	86.5	—	—	—	—	0.4	—	—	—
LPdce-13	0.1	92.3	94	—	—	—	4.3	6	—	—
LPdce-14	0.1	72.9	72	4	22	2	9.5	—	—	—
LPdce-PE2 ⁺	11.5	97.2	94	—	—	6	—	—	—	—
LPdce-SJR ⁺	5.4	98.3	100	—	—	—	—	—	—	—
LPdce-06 - retest ⁺	0.5	46.5	—	—	—	—	53.5	—	—	—
LPdce-13 - retest	0.1	92.2	—	—	—	—	6.9	—	—	—

A: XRD semi-quant reported that it also might contain Lithium Aluminum Silicate Chloride ($\text{Li}_8(\text{AlSiO}_4)_6\text{Cl}_2$) at a level of 4%. The presence of this material is not a routinely encountered impurity in gypsum sources.

B: XRD semi-quant reported that the sample contained gypsum, bassanite, quartz, and brushite ($\text{CaPO}_3(\text{OH}) \cdot 2\text{H}_2\text{O}$); semi—quantitative values were not reported.

+: These specimens did not lose additional mass when heated above 250°C.

Specimens LPdce-06 and LPdce-13 were retested to confirm the observed the mass losses in the original test.

Figure 10: DTA Comparison of Two Natural Sources; LPdce-08 (no NaCl) and LPdce-10 (contains NaCl).

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