In 1983, Posey proposed using the visible color change that was noted in the cross section of gypsum wall board as a relative measure of the heat exposure of the wall board during a fire. The color change was thought to be due to the change in the hydration state (calcination) of the gypsum in the wall board sample. Posey proposed the calcined gypsum will appear as a layer of a different color. The theory was that heat from fire exposure drives off bound water within the gypsum molecule, producing incremental layers of discolored gypsum. Posey postulated the hotter the fire, the sharper the line of calcination, and the longer the fire, the deeper this line of demarcation.

Schroeder has further explained the dehydration process and proposed that the change in hydration state can be correlated to both a color change and a change in the texture of the wall board. Techniques for comparing the depth of calcination using field measurements during fire investigation were provided by Kennedy. DeHaan briefly describes the process and suggests the color change within the wall board cross section is due to dehydration of the gypsum and/or presence of combustion products. NFPA 921 includes a section describing the theory of calcination and the probe method for measuring relative depths of fire-affected wall board. Lager has performed extensive crystallographic studies of the low temperature dehydration products of gypsum and presents a thorough explanation of the dehydration mechanism.

There is little in the fire investigation literature regarding the correlation of the hydration state of gypsum as a function of depth below the fire affected surface and an objective comparison of this chemistry with observable or measurable characteristics. This paper presents an alternative method to correlate heat exposure to the chemical dehydration of gypsum, further studies the published field-probing techniques and finally, provides data which leads to caveats and warnings regarding the use of the field techniques.

**Background**

The primary component of common wall board is gypsum which is calcium sulfate dihydrate. (Dihydrate indicates there are two water molecules for each molecule of calcium sulfate.) This water is chemically bound and is an integral part of the crystal lattice and not absorbed water, as is water in a sponge. When heated, this water dissociates and departs the crystal lattice, first forming the calcium sulfate hemihydrate (also known as plaster of paris). The hemihydrate contains approximately a half a water molecule per calcium sulfate molecule. At higher temperatures, the remaining water dissociates and the anhydrous calcium sulfate is formed. This is a gradual dehydration process, sometimes referred to as calcination.

The heat energy delivered to the gypsum to cause the dehydration tends to go into driving off the water rather than increasing the temperature of the mineral. The mineral temperature rises slowly until the water is gone, then increases more rapidly. The endothermic property of this reaction confers the fire resistance to residential structures. In a fire, the materials behind the wall board will remain relatively cool as water is lost from the gypsum, reducing damage to the framing and eventual structural collapse.

Fourier transform infrared spectrometry (FTIR) was found to be an excellent analytical technique for distinguishing the different hydrated forms of calcium sulfate. The change in the crystal lattice due to the loss of the bound water results in a change in the infrared spectrum. Additionally, extremely small sample quantities (as little as 1-2 micrograms) of sample are sufficient when using a beam condenser and a micro diamond cell. This is advantageous when assessing the chemistry of the gypsum across the cross sectional thickness of a wall board specimen.
Dehydration Study

The dehydration/calcination process of gypsum was studied using reagent grade standards of calcium sulfate dihydrate, hemihydrate, and anhydrous, as well as three different manufactured gypsum wallboard products. The standards and wallboard samples were ground to pass a 60 mesh (250 µm/0.0096") sieve, conditioned for three days at 22°C (72°F), and then progressively heated from 38°C (100°F) to 204°C (400°F) in 14°C (25°F) increments. The sample was equilibrated at each temperature plateau for 30 minutes prior to sub-sampling. Finally, a separate sample of each standard and wallboard sample was exposed to 537°C (1000°F) for 30 minutes to approximate real fire conditions. FTIR analysis was used to track the level of dehydration following the heated exposures.

The literature generally lists an initial dehydration temperature of 80°C (176°F) for calcium sulfate dihydrate to form calcium sulfate hemihydrate. Mention of some conversion at temperatures as low as 50°C (122°F) is also present. Complete formation of the hemihydrate occurs at temperatures above 130°C (266°F). None of these temperatures can be considered absolute as the dehydration process is gradual and is dependent on ambient humidity conditions. Calcium sulfate hemihydrate and anhydrous both exist in two crystal forms, designated as the α- and β- forms. Both α- forms transform to the generally more stable β- forms at higher temperatures. The α-hemihydrate begins to convert to the β-hemihydrate above 110°C (230°F) and the α-anhydrous converts to the β-anhydrous beginning at 200°C (392°F). The complete conversion looks something like this:

- Calcium sulfate dihydrate \( \text{CaSO}_4 \cdot 2 \text{H}_2\text{O} \) (gypsum)
- 80°C (176°F)
- Calcium sulfate α-hemihydrate \( \text{CaSO}_4 \cdot 0.5-0.8 \text{H}_2\text{O} \)
- 110°C (230°F)
- Calcium sulfate β-hemihydrate
- 13°C (266°F)
- Calcium sulfate α-anhydrous \( \text{CaSO}_4 \cdot 0.05-0.001 \text{H}_2\text{O} \)
- 200°C (392°F)
- Completely dry calcium sulfate β-anhydrous

Sum beginning to form the hemihydrate occurring at 52°C (125°F) and full conversion to the anhydrous form at temperatures above 191°C (375°F). Differences in the FTIR spectra demonstrated a conversion of the molecular structure at temperatures between 107-121°C (225-250°F). It was not determined if the FTIR results reflect the conversion of the α-hemihydrate to the β-hemihydrate or they are the result of a mixture of the hemihydrate(s) and anhydrous.

The FTIR spectra for the four hydration states of calcium sulfate (including the α- and potential β-hemihydrate forms) are shown in Figures 1-4. No differences in the FTIR were documented between the α- and β-anhydrous forms of calcium sulfate.

Figure 1: Standard calcium sulfate dihydrate (gypsum)

Figure 2: Standard calcium sulfate α-hemihydrate (plaster of paris)

Figure 3: Calcium sulfate β-hemihydrate formed from the standard α-hemihydrate at 225-250°F (107-121°C). (This may also be a combination of hemihydrate and anhydrous.)
Re-hydration Study

The dehydrated reagent grade calcium sulfate standards and gypsum wallboard samples were split; one sample was subjected to 50% relative humidity and 22°C (72°F) for three days, the other was immersed in water for one hour then dried overnight at room conditions. FTIR analysis was again used to measure the potential re-adsorption of water into the various crystal forms.

All the dehydrated/calcined standards and gypsum wallboard samples exposed to 50% relative humidity were stable; no re-adsorption of water was documented in any of the samples. Calcium sulfate dihydrate that formed the hemihydrates and anhydrous species when heated remained as the specific hemihydrate or anhydrous after the humidity exposure.

Both α- and β-hemihydrates formed from the dihydrate during the heating sequence converted back to the dihydrate form when immersed in water and air dried. Anhydrous calcium sulfate was found to be stable; it did not take up any water and remained as the anhydrous species irrespective of the exposure to water.

FTIR analysis following the re-hydration in water of the various forms of the hemihydrates (Figures 2 and 3) show the presence of pure dihydrate (Figure 1); there is no evidence of the presence of trace anhydrous in these results. The lack of detectable anhydrous in the re-hydrated sample indicates none was present prior to the re-hydration step and supports the hypothesis that FTIR analysis can distinguish the α- and β-hemihydrates. In other words, if Figure 3 represented a mix of a hemihydrate and anhydrous, the anhydrous should be visible in the FTIR of the re-hydrated sample.

Figure 4: Standard anhydrous calcium sulfate.

Cone Calorimetry Exposure Study

A Fire Testing Technology Cone Calorimeter (Cone) was used for two purposes: to study the ignition temperature and heat release of the paper surface on the wall board as well as to prepare samples for laboratory analysis after exposure to known heat flux and time exposures. Post exposure specimens were evaluated visually and analyzed by FTIR.

In most cases, the minimum heat flux required to achieve piloted flaming ignition of the unpainted paper on wall board was approximately 42 kW/m². At a heat flux of 50 kW/m² unpainted wall board has an ignition time of 27 seconds, a peak heat release of approximately 100 kW/m², and a flaming duration of less than 30 seconds. This indicates that paper faced wall board is combustible and can contribute to the growth of a fire. In general, tests performed on wall board with a paint coating increased the total heat output and flaming duration. Tests performed on wall board with fabric backed vinyl (wall paper) had notably lower ignition times than painted or unpainted wall board. The minimum heat flux to produce smoldering of the wall board paper was 14 kW/m². The facing paper degraded and delaminated from the surface of the wall board under continued exposure.

Development of the Measuring Probe and Techniques

The depth of dehydration was assessed using several styles of probes. The optimal size and shape was determined to be a blunt blunt with no tapering shoulders. It was found that an Ascot tire gage with the shoulders ground off and having a tip surface with area of 0.95 mm x 3.29 mm (3.12 mm²) was practical and worked well (Figure 5). A Chatillon RS 202 force gauge was used to control the force of the probe penetration (Figure 6). The force gauge has an accuracy of ±0.1 kg (0.02 lb). Through experimentation it was determined that 2.7 kg force (6 pounds) was sufficient to overcome the resistance of the paper surface and to fully penetrate the anhydrous and hemihydrate layers without penetrating the dihydrate material in most cases. (Note this force translates to a pressure of approximately 0.9 kg/mm² (1230 PSI). Table 1 lists experimental probe depths results for the exposed wall board samples using a modified Ascot tire gage compared to FTIR analysis.
Table 1: Experimental probe depths of exposed wall board samples.

<table>
<thead>
<tr>
<th>Specimen Mode and Time</th>
<th>Probe Pressure (kg/mm²)</th>
<th>Probe Force (lbs)</th>
<th>Probe Penetration Depth (mm)</th>
<th>Dihydrate/Hemihydrate Interface Depth (mm) from FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>unexposed</td>
<td>3.52</td>
<td>24.5</td>
<td>full penetration</td>
<td></td>
</tr>
<tr>
<td>43kW for 4 min</td>
<td>0.36</td>
<td>2.5</td>
<td>penetrate surface</td>
<td></td>
</tr>
<tr>
<td>43kW for 4 min</td>
<td>0.46/0.58/0.72/0.87</td>
<td>3/4/5/6</td>
<td>3.2/4.7/5.5/6.3</td>
<td>7</td>
</tr>
<tr>
<td>50kW for 100 sec</td>
<td>0.87</td>
<td>6</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>50kW for 200 sec</td>
<td>0.87</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>50kW for 300 sec</td>
<td>0.87</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Propane for 5 min</td>
<td>0.36/0.58/0.72/0.87/1.03</td>
<td>2/4/6/8/10</td>
<td>4/5/6/6/6</td>
<td>6</td>
</tr>
<tr>
<td>Propane for 10 min</td>
<td>0.36/0.58/0.72/0.87/1.03</td>
<td>2/4/6/8/10</td>
<td>4/7/8/9/9</td>
<td>8</td>
</tr>
<tr>
<td>Propane for 15 min</td>
<td>0.36/0.58/0.72/0.87/1.03</td>
<td>2/4/6/8/10</td>
<td>5/8/9/10/13</td>
<td>10</td>
</tr>
<tr>
<td>Field sample (S wall)</td>
<td>0.67</td>
<td>6</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Field sample (N wall)</td>
<td>0.67</td>
<td>6</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

Manual insertion of a probe may be possible; however, consistent pressure on each application must be utilized for comparable results. The probing technique is sensitive to many variables and reproducible results are not always easily obtained. Some other observations include:

- Voids in the gypsum core are not visible and if sampled by the probe may result in increased depth values.
- Insertion force is critical to comparing probe depth values. A force of 6 lbs on the Ascot tire gauge is ideal for penetration to the hemihydrate/dihydrate interface.
- For moderately dehydrated wall board, probe forces of 6-10 pounds yield similar results.
- A probe force of more than 6 pounds can penetrate the back side paper in samples that have been dehydrated near full thickness.
- In every case where the paper on wall board has been burned, there is associated dehydration (verified by FTIR) of the underlying gypsum.
- Cross sections of samples collected in the field were best prepared for laboratory evaluation by drying at 37°C (100°F), cutting to expose the cross section and polishing. Note that once samples are removed from the fire scene, some information regarding the orientation relative to the scene is easily lost.

Figure 5 (Left photo): Ascot tire gauge with probe gauge with probe shoulders removed.

Figure 6 (Right photo): Probing apparatus using Chatillon force gauge (gauge indicator is upside down). Wall board specimen is resting on spacers to allow potential through-thickness penetration of probe.

Laboratory Analysis of Cone Calorimeter Exposed Samples

Samples prepared in the Cone were tested using the modified Ascot tire gauge and Chatillon force gauge to ensure a consistent force of 0.87 kg (6 pounds). The sample was then cut and ground to expose the cross section at the probe point. FTIR analysis was used to evaluate the degree of dehydration across the cross section of the exposed 1/2" thick wall board samples adjacent to the probe point. Using the diamond anvil cell accessory, samples were assessed at 1 mm intervals; this allowed up to 11 individual measurements across the thickness of the exposed wall board.

Figure 7 depicts the cross section of a painted wall board specimen exposed in the Cone to 50 kW/m² for 206 seconds. A dark band/discoloration is apparent to a depth of approximately 2-3 mm from the exposed surface. The probe penetrated 6 mm into the wall board. FTIR analysis identified the first 2 mm as anhydrous, depths 3-6 mm as the hemihydrate and the depth greater than 7 mm as the dihydrate. In this exposure, it appears the discoloration correlates to the anhydrous/hemihydrate interface and the probe to the hemihydrate/dihydrate interface.
A series of Cone samples were produced using 43 kW/m² exposures for 2, 4 and 8 minute intervals. A visible discolored/dark band was present in the surface layer which penetrated to the hemihydrate layer. Probe results tracked the depth of complete calcination very well. Table 2 presents a summary of the analysis from these samples.

<table>
<thead>
<tr>
<th>Exposure Time (minutes)</th>
<th>2</th>
<th>4</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discoloration Depth (mm)</td>
<td>1-2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Anhydrous Depth (mm)</td>
<td>1</td>
<td>2-3</td>
<td>3</td>
</tr>
<tr>
<td>Probe Depth (mm)</td>
<td>3.5</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Hemihydrate Depth (mm)</td>
<td>2-3</td>
<td>7</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 2: Summary of evaluation results of wall board specimens after progressive Cone exposure at 43 kW/m²

Figures 8 and 9 depict the cross sections of a single wall board sample exposed to 50 kW/m² for 143 seconds. The paper and paint from half of the exposed surface of this specimen was removed prior to cone exposure. Following cone exposure, the gypsum below the papered half (Figure 8) contained a dark band/discoloration to a depth of approximately 1-2 mm. The gypsum below the paperless half (Figure 9) had distinctly less discoloration at the top surface. It was possible the trace discoloration is due to combustion products from the papered half of the specimen. In both halves the 2.7 kg force probe penetrated 3.5 mm into the wall board. FTIR analysis of the papered cross section identified the first 1mm as anhydrous, 2-5 mm depths as the hemihydrate and depths greater than 6 mm as the dihydrate. FTIR analysis of the paperless half identified the surface as anhydrous, 1-4 mm depth as the hemihydrate and depths greater than 5mm as the dihydrate. In this exposure, the paper and paint provide both the fuel for the discolouration and the potential for additional heat to cause deeper dehydration. In this sample, the probe fell short in tracking the hemihydrate/dihydrate interface.

Specially prepared paperless wall board specimens tested at 43 kW/m² for progressive time intervals failed to produce the dark bands associated with papered wall board specimens. After suitable preparation, cutting and polishing an increase in porosity and a slight darkening was indicated proximal to the exposed surface by these changes were not definitive nor did they correlate to the more discrete bands of anhydrous and/or hemihydrate. The dehydration and probe depths were progressively deeper with increased exposure time in the Cone. At 43 kW/m² there was no indication of the formation of a lighter band near the exposed surface associated with the dehydration as noted in some of the literature. In no cases was there a change in the color of the wall board that could be confidently correlated to the hemihydrate/dihydrate interface.

In a separate experiment, paperless wall board was exposed for approximately 4 hours to a cool sooty fire as a “ceiling”; the maximum temperature of the exposed surface was approximately 66°C (150°F). Hemp, polyurethane foam and asphalt paper were used as the fuel to produce the smoke. Figure 10 depicts the resulting cross section of the ceiling wall board. No visible soot penetration was noted into the wall board. FTIR analysis of the calcium sulfate on the exposed surface showed it to be gypsum. No dehydration of the wall board occurred in this exposure. The lack of smoke penetration, despite a prolonged heavy smoke environment, and lack of dehydration of the exposed surface layer, suggest that calcination/formation of the hemihydrate is necessary before smoke can begin to penetrate the wall board.

One brand of type X (fire rated) 5/8” wall board was exposed in Cone testing. Fire rated wall board contains glass fiber reinforcement to help maintain the structural integrity of the product after it dehydrates on exposure to fire and can be used on interior
walls in residential construction. Type X wall board can be specified for fire-rated walls, ceilings and for party walls in apartments and condominiums.

Type X wall board samples produced similar results with the discolored band progressing through the wall board cross section with increasing time of heat exposure. These studies do not suggest that the glass reinforcing in fire rated wall board affect the diffusion of combustion products produced by heat exposure. (Refer to figure 11) Reproducible probing depths and corresponding verification of the hemihydrate/dihydrate interface by FTIR analysis demonstrated that the probing method is compatible with type X wall board and consistent with normal wall board.

In general, the exposure studies to date demonstrate that fire damage to wall board occurs progressively. This progression advances in the following manner:

- Soot coating of undamaged facing paper
- Discoloration/degredation of facing paper
- Facing paper burns away
- Partial dehydration and discoloration/soot staining of surface layer of gypsum
- Formation of anhydrous and hemihydrate layers with layers progressing through the cross section (discoloration correlates to soot penetration to the anhydrous/hemihydrate interface)
- Complete conversion of dihydrate to anhydrous and hemihydrate
- Anhydrous extends through the entire cross section
- Wall board becomes catastrophically heat damaged and lacks structural integrity

**Analysis of Wall Board Samples from Fire Scenes**

Samples from a few fire scenes were evaluated. Thorough analysis required careful collection technique and documentation. The clearest results were obtained when the recovered samples were dried for three days at 37°F (100°F), cross sectioned and polished. Such a practice is not recommended for normal fire investigation but was used in this case to complete our documentation and carry over laboratory data to the real world. Recovered field samples displayed a range of results, some of which were not produced in our laboratory experimentation.

Figure 12 depicts field samples from the north and south walls from the same bedroom. Color bands not seen in any of our laboratory prepared specimens were observed. Probing and FTIR analysis were conducted. Test results demonstrated that probing with 0.87 kg/mm² (6 lbs of pressure) accurately detected the hemihydrate/anhydrous interface as verified by FTIR. This interface was found to be at 4 mm in the south wall specimen and 7 mm in the north wall specimen. This interface was on the exposure side of the extra pinkish colored layer visible in both specimens. This extra band of color extends into the dihydrate layer. In this case, probing yielded a more accurate estimate of heat exposure than the visual assessment.
Conclusions

Gypsum used in the manufacture of wall board changes its state of hydration when exposed to elevated temperatures. Wall board exposed to a fire environment will convert to dehydrated forms that are stable and can remain in the dehydrated state despite exposure to humid conditions and/or liquid water. Gypsum that is completely dehydrated to form the anhydrous provides a permanent record of the heat exposure. Gypsum which is partially dehydrated can be re-hydrated after contact with water.

The complete dehydration of gypsum to form the anhydrous form begins on the exposed surface and progresses into the wall board cross section in incremental steps. This dehydration most likely changes the porosity/density of the wall board sufficient to allow combustion products to diffuse into the wall board up to the anhydrous/hemihydrate interface. The visible smoke layer in both laboratory and field samples correlate well to the anhydrous/hemihydrate interface, especially in the initial stages of heat exposure.

FTIR analysis is an effective laboratory method to verify the degree of dehydration of a gypsum wall board specimen. The formation of the hemihydrate precedes the anhydrous and creates a layer of less cohesive wall board that is easily probed using fairly simple instrumentation. The porosity of this hemihydrate layer is sufficient to allow rapid diffusion of combustion products. The hemihydrate/anhydrous layer was not readily visualized in these studies.

Probing wall board using simple tools and consistent pressure can yield results that find the depth of total dehydration (the anhydrous layer). However, the use of inconsistent pressure, too much pressure or inconsistencies in the wall board (voids) will produce unreliable results. Both regular and type X wall board yield similar results. Proper utilization of a proper probing procedure is not necessarily straightforward at a typical fire scene.

Visual interpretation of the banding in wall board at fire scenes can be misleading. It has been documented that colored bands within fire scene samples are not necessarily related to the degree of dehydration of the gypsum. Some multiple bands within recovered samples have not been fully explained by laboratory experimentation. The presence of water vapor, higher pressures and other unrecognized factors within an involved room may result in the unexplained visual artifacts.

Acknowledgements

The authors would like to thank Mr. Brian Fitz for FTIR analyses. Mr. Keith Cline and Mr. Michael Fitz are thanked for their thoughtful comments, discussions and input to this project.

Bibliography


DALE MANN earned his Bachelor of Science degrees in chemistry and oceanography from the University of Washington in 1976. After four years in private industry, Dale spent the next 17 years working for the Washington State Patrol Crime Laboratory. He joined MDE, Inc. as a principal in 1998 where he currently heads the Forensic Laboratories Division. He is certified by the American Board of Criminalistics and is a Certified Fire Investigator.

Dale has performed chemical and physical analyses in thousands of investigations involving fire, explosives, drug manufacturing, product tampering and product failure. He has also been the principle researcher, author and lecturer in numerous topic areas involving forensic chemistry and fire investigation.

NOEL PUTAANSUU is President of the IAAR Washington Chapter 21. Noel is a IAAR-CFI. Noel started at MDE in 2002, he serves as a technical specialist working in the field of laboratory sciences, fire scene investigation, fire modeling and forensic analysis. He also consults in fire scene reconstruction, ASTM test methodology, developing fire test equipment, fire litigation, Noel has worked in the field of fire science and reconstruction since 1982.