Contaminated Drywall Compared with American-Made Drywall as Determined by Materials Characterization

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Contaminated Drywall Compared with American-Made Drywall as Determined by Materials Characterization

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ABSTRACT
One of the most important problems with building materials experienced in the United States, primarily in the southeastern states, has been drywall suspected of reacting with moisture in houses. During the construction boom that ensued after nine hurricanes hit Florida and the Gulf Coast states in 2004–2005, including Hurricane Katrina in 2005, more than 6,000 homes (and others estimate 60,000 to 100,000 homes; Herman et al., 2011) that were either built or remodeled between 2004 and 2008 were affected by defective drywall imported from China, according to estimates from the U.S. Consumer Product Safety Commission (CPSC). By October 13, 2011, the CPSC had received more than 3,900 complaint reports from 42 states, the District of Columbia, American Samoa, and Puerto Rico regarding the corrosion of metal components in their homes or negative health symptoms suspected to be related to problematic drywall (CPSC 2011a,b). Since 2009, the CPSC has engaged several major national laboratories and government agencies in determining the source of the reaction causing metal corrosion and any potential hazards associated with this reaction, which is believed to be related to problematic drywall. This paper briefly reviews some theories proposed and describes a materials characterization study conducted by the author (Hagni, 2011) that were lacking in the problematic drywall. Entrained air voids were a distinguishing feature in American-made (uncontaminated) drywall that were lacking in the problematic drywall. The chemistry was similar in all samples and was not a distinguishing characteristic.

INTRODUCTION
The Atlantic hurricane season in 2004 included Hurricanes Alex, Charlie, Frances, Gaston, Ivan, and Jeanne. The 2005 Atlantic hurricane season was even more catastrophic for the southeastern United States, with three major hurricanes: Hurricane Wilma, which affected Florida, and Hurricanes Katrina and Rita, which devastated much of the southern portions of Florida, Alabama, Mississippi, Louisiana, and Texas. The rebuilding boom in 2006 and 2007 found building materials in short supply because of the significantly increased demand. As builders and remodelers exhausted the supply of American-made drywall, they began utilizing drywall imported from China (drywall had first been imported from China in 2001). Approximately 60% of the imported Chinese drywall passed through ports in Florida during the 2006–2007 rebuilding boom (Henning and Shoeburg 2009). Imports through the Port of Miami accounted for 85,273 metric tons of Chinese drywall in 2006, and those through the Port of Tampa accounted for 68,927 tons, representing 70.7% of Chinese drywall imports into the United States through Florida ports in 2006 (Crangle 2009). Of the 3,082 cases of problematic building materials reported to the U.S. Consumer Product Safety Commission (CPSC) as of April 2, 2010, 59% were located in Florida, 20% were in Louisiana, 6% were in Mississippi, and 5% were in Alabama, with the remaining 10% in 28 additional states and Puerto Rico (CPSC 2011a,b).

Many of the new homes and newly remodeled homes began exhibiting symptoms unusual for new homes. These symptoms included corrosion of certain metal components (typically copper in air conditioner coils, appliances, electrical fixtures, and plumbing), a rotten egg odor, and reported health concerns [Centers for Disease Control and Prevention (CDC) 2011]. The CDC (2011) separated these health concerns into three categories:

1. issues related to indoor air
   a. a rotten egg smell
   b. the smell of matches or fireworks
2. issues related to metal inside homes
   a. blackened metal components
   b. corroded metal components
   c. frequent replacement of metal components in air conditioning units
3. health symptoms
   a. irritated and itchy eyes and skin
   b. difficulty breathing
   c. nasal irritation
   d. recurrent headaches
   e. sinus infections
   f. exacerbation of asthma

The corrosion and reported health issues led to extensive studies comparing American-made drywall with imported drywall, in particular the drywall made in China (Glass et al. 2011; Maddalena 2011; Matheson et al. 2011). Since 2009, the CPSC has engaged the Lawrence Berkeley National Laboratory (LBNL), Environmental Health & Engineering Inc. (EH&E), Sandia National Laboratories (SNL), the National Institute of Standards and Technology (NIST), and the U.S. Geological Survey (USGS) in studying the problematic drywall to determine the cause of the metal corrosion from the potentially problematic drywall and any potential hazards associated with it (CPSC 2011a, Release...
Table 1  Typical drywall composition

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum (calcium sulfate)</td>
<td>CaSO₄·2H₂O</td>
<td>70–90</td>
</tr>
<tr>
<td>Calcite (calcium carbonate)</td>
<td>CaCO₃</td>
<td>60–65</td>
</tr>
<tr>
<td>Cellulose</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>0–10</td>
</tr>
<tr>
<td>Crystalline silica (quartz)</td>
<td>SiO₂</td>
<td>0–2</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>(Mg,Fe,Al)₃(Al,Si)O₁₀(OH)₂</td>
<td>0–10</td>
</tr>
<tr>
<td>Potassium sulfate</td>
<td>KSO₄</td>
<td>0–5</td>
</tr>
<tr>
<td>Starch</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>0–5</td>
</tr>
<tr>
<td>Fiberglass (continuous filament)</td>
<td>SiO₂</td>
<td>0–5</td>
</tr>
<tr>
<td>Mica</td>
<td>K(Mg,Fe)₃(Si₂Al)O₁₀(OH,F)₂</td>
<td>2–3</td>
</tr>
<tr>
<td>Paraffin wax (fume)</td>
<td>C₄H₁₀O₂</td>
<td>0–2</td>
</tr>
<tr>
<td>Boric acid</td>
<td>H₃BO₃</td>
<td>0–1</td>
</tr>
</tbody>
</table>


Drywall, also known as gypsum board, wallboard, or plasterboard, is a noncombustible panel board made primarily of gypsum covered with paper on the front and back sides (Gypsum Association 2015d). Gypsum is calcined to remove about 75% of the bound water. Mined gypsum (CaSO₄·2H₂O) is crushed, ground to a powder, and heated to approximately 150°C (300°F) to remove most of the chemically combined water. The calcined gypsum, also known as hemihydrate (CaSO₄·½H₂O), is combined with additives of starch, paper pulp, emulsifier (thickening agent), and water to form a gypsum paste or slurry. The slurry is fed 3/8 to 3/4 inch thick (9.5 to 19.0 mm thick) between two pieces of continuous manila paper, at which time the slurry adheres to the paper and recrystallizes to gypsum through hydration. The board is heated to approximately 260°C (500°F) for about 30 minutes to remove any excess moisture, and then cut to designated sizes. Synthetic gypsum is increasingly being used in place of natural mined gypsum (Crangle 2009; USG 2011; American Gypsum 2015; Gypsum Association 2015d). The former is a by-product of coal-fired power plants through fossil-fuel flue gas desulfurization (Gypsum Association 2015c; Lafarge North America 2011). Over time, air entrainment was added to the processing to decrease the weight and increase the durability (decrease the brittleness) of the drywall (Gypsum Association 2015b).

The typical drywall composition, as indicated in the Lafarge North America Material Safety Data Sheet for drywall (Lafarge North America 2015; see Table 1), shows 70 to 90% gypsum, 60 to 65% calcite, 2 to 3% mica, and a possibility (0 to 10%) of eight other phases. Advantages of drywall include its fire resistance, sound attenuation, durability, economy, and versatility. In North America, the United States and Canada manufacture more than 20 billion square feet (1.9 billion square meters) of drywall per year (Gypsum Association 2015b; USGS 2015).

REACTION THEORIES

Theory 1: Strontium Sulfide Chemical Reaction

Originally, one theory was that the problematic Chinese-made drywall might contain higher levels of strontium (Sr) than the American-made drywall.
The Chinese-made drywall was postulated to be reacting with humidity (and possibly formaldehyde and other aldehydes) to form hydrogen sulfide ($\text{H}_2\text{S}$) gas, creating a rotten egg odor and causing the corrosion of metal (CPSC 2009a,b; EH&E 2010; Bischel 2011). Strontium in the Chinese drywall was speculated to be present as strontium sulfide (SrS; Bischel 2011), which, in moist air, slowly released $\text{H}_2\text{S}$ (Cameo Chemicals 2015). It is possible that in China, manufacturers apply a coating to drywall they expect to be placed in humid environments, such as bathrooms and kitchens. Thus, drywall reactions with moisture typically are not evident or are not an issue in China (personal communication, 2011). One source of SrS was speculated to be coal fly ash (ChineseDrywall.com 2011). In North America, the Gypsum Association has indicated its members are allowed to use synthetic gypsum in the production of drywall, but not fly ash. Fly ash cannot be used as a substitute for gypsum because it has a different composition (Gypsum Association 2009, 2015a). The Gypsum Association makes this distinction because drywall produced in China might include coal fly ash.

**Theory 2: Pyrite Inclusions**

Another theory suggests that relatively greater levels of pyrite (FeS$_2$) are present in imported drywall compared with American-made drywall and that this pyrite may react with moisture to form $\text{H}_2\text{S}$ gas, causing odor and corrosion (ChineseDrywall.cc 2011). The pyrite inclusion theory, however, does not seem applicable in this particular case study because iron (Fe) was not detected in the crushed powders by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS; Table 2), pyrite was not detected by quantitative X-ray diffraction (QXRD; Table 3), and only a few small (<1-µm) grains of pyrite were observed in Drywall B and Drywall C by reflected light optical microscopy (RLM) and SEM-backscattered electron imaging (BSI).

**Theory 3: Sulfur-Reducing Bacteria**

A third theory suggests sulfur ($\text{S}$) reducing bacteria caused the reaction in Chinese drywall, forming $\text{H}_2\text{S}$ gas that created odors and corrosion (ChineseDrywall.com 2011; Tardi 2011). Some researchers have identified the Fe- and S-reducing bacteria *Thiobacillus ferrooxidans* as present in larger concentrations in Chinese drywall and as not identified (below detection levels) in American-made drywall (Defendorf 2010; Tardi 2011). Some researchers have identified the Fe- and S-reducing bacteria *Thiobacillus ferrooxidans* as present in larger concentrations in Chinese drywall and as not identified (below detection levels) in American-made drywall (Defendorf 2010; Tardi 2011). *Thiobacillus ferrooxidans* are the same bacteria used in metal extraction and acid mine drainage to convert sulfides to oxides, a reaction that creates unpleasant odors (Power et al. 2010; Andrews et al. 2013). Tardi (2011) speculated that one source of *T. ferrooxidans*

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**Table 2** Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) semiquantitative oxide by difference (%) results for crushed drywall$^{1,2}$

<table>
<thead>
<tr>
<th>Oxide by difference</th>
<th>Drywall A</th>
<th>Drywall B</th>
<th>Drywall C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>ND</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>ND</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.6</td>
<td>1.4</td>
<td>2.7</td>
</tr>
<tr>
<td>FeO</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>37.4</td>
<td>36.7</td>
<td>32.2</td>
</tr>
<tr>
<td>CaO</td>
<td>61.9</td>
<td>61.2</td>
<td>63.2</td>
</tr>
<tr>
<td>SrO</td>
<td>0.1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Normalized total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.1</td>
</tr>
</tbody>
</table>

$^1$ND = not detected (below the SEM-EDS detection limit of approximately 0.1%).

$^2$Oxide by difference indicates oxygen is not quantified (because oxygen quantification by SEM-EDS is typically not accurate), and oxygen is therefore calculated for each cation.

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**Table 3** Rietveld quantitative X-ray diffraction (QXRD) results (%) for crushed drywall$^1$

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>Drywall A</th>
<th>Drywall B</th>
<th>Drywall C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum</td>
<td>CaSO$_4$·2H$_2$O</td>
<td>63.9</td>
<td>78.2</td>
<td>75.0</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO$_4$</td>
<td>20.5</td>
<td>1.3</td>
<td>ND</td>
</tr>
<tr>
<td>Bassanite</td>
<td>2CaSO$_4$·H$_2$O</td>
<td>6.5</td>
<td>9.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO$_3$)$_2$</td>
<td>8.9</td>
<td>9.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>ND</td>
<td>ND</td>
<td>10.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>0.2</td>
<td>2.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>(Na, Ca)(Al, Si)$_2$O$_8$</td>
<td>ND</td>
<td>ND</td>
<td>1.9</td>
</tr>
<tr>
<td>Celestine</td>
<td>SrSO$_4$</td>
<td>ND</td>
<td>ND</td>
<td>1.7</td>
</tr>
</tbody>
</table>

$^1$ND = not detected (below the QXRD detection limit of approximately 0.1%).
bacteria might be from contaminated water used in processing the Chinese drywall.

The CPSC has dismissed this bacteria theory based on a study conducted by the USGS, in which four methods were used and no S-reducing bacteria were identified (CPSC 2011a, Release #11-327; Matheson et al. 2011). The four methods used by Matheson et al. (2011) in the USGS study were epifluorescent microscopy, quantitative polymerase chain reaction, enrichment culture followed by quantitative polymerase chain reaction, and genetic sequencing.

**DRYWALL SAMPLES SPECIFIC TO THIS STUDY**

In this study, three samples obtained in the first half of 2009 were analyzed: (1) Drywall A, from a residence exhibiting no symptoms; (2) Drywall B, American-made drywall purchased from a Midwestern hardware store on March 30, 2009; and (3) Drywall C, from a residence in Florida with the problematic drywall symptoms of a rotten egg odor and copper wire corrosion. Figure 1 shows a cross section of the drywall samples as received.

**SEM-EDS Semiquantitative Chemistry of Whole-Sample Crushed Drywall Powder**

A portion of each of the three drywall samples was crushed to a powder and analyzed by SEM-EDS for semiquantitative bulk analyses. The SEM-EDS method does not detect hydrogen (H) and typically does not quantify carbon (C). Energy dispersive spectroscopy chemistry results were quantified as oxides [oxygen (O) by difference] and normalized to 100% (Table 2), which is the typical presentation of SEM-EDS results.
Scanning electron microscopy results for the crushed drywall showed similarities across all three samples in calcium (Ca), and slightly less S in Drywall C (the problematic drywall sample) compared with Drywall A (the drywall sample with no symptoms) and Drywall B (the locally purchased drywall sample with no symptoms). Drywall B and Drywall C had the same amounts of Sr.

**Drywall Sample Preparation for Microscopy**

Polished thin sections of each drywall sample were prepared. The drywall samples were embedded in epoxy, mounted on a glass slide, and ground to 30 µm thick, and the surfaces were polished. Oil, rather than water, was used as a grinding medium to prevent oxidation during preparation of the polished thin sections. The polished thin sections provided 30-µm-thick cross sections of the drywall samples for transmitted light optical microscopy (TLM), as well as polished surfaces for RLM and SEM. A Hitachi S570 scanning electron microscope equipped with a lanthanum hexaboride (LaB$_6$) filament, silicon (Si) drift detector (SDD), and 4pi EDS system was utilized.

**SEM Study of Polished Thin Sections**

Drywall C had Sr in the form of strontium sulfate (SrSO$_4$), as determined by SEM-BSI and SEM-EDS (Figure 2). The particle probed by SEM-EDS shown in Figure 2 was bright white, with approximately 1% silicon dioxide (SiO$_2$), confirming that it was not a Si-rich particle, which would be darker) and approximately 66% strontium oxide (SrO) and 33% sulfur trioxide (SO$_3$). Although the EDS results were not stoichiometrically SrSO$_4$, which would have been 56% SrO and 44% SO$_3$, a strong O peak was quite clear (Figure 2b), and this phase was not SrS. If this particle had originally been SrS and had already oxidized (by the addition of water), one would expect the oxidized particle to be strontium hydroxide [Sr(OH)$_2$], with the S combining with moisture, forming H$_2$S gas and leaving no S remaining (MacMillan et al. 2002; Cameo Chemicals 2015).

**Quantitative X-ray Diffraction**

Rietveld QXRD was applied to crushed powders of the three samples in this study by utilizing a Scintag X-ray diffractometer (at 40 kV and 30 mA) and RIGAS Rietveld quantitative software from Materials Data, Inc. (MDI; Table 3). The results showed that the main phase in all three samples was gypsum (64 to 78%) and that anhydrite was a significant phase in Drywall A only (21%). Bassanite (2 to 9%) and dolomite (8 to 9%) were present in all three samples, as was quartz (<2%). Calcite (10%) and plagioclase (2%) were present in Drywall C only. Celestine (SrSO$_4$, also known as celestite) was also identified in Drywall C only (<2%). Celestine occurs naturally mostly in sedimentary rocks, often in association with gypsum, anhydrite, and halite (Mindat.org 2011). Strontium sulfate was not detected in any of the three samples. A small hump (shoulder) existed at the main S peak (23.1° 2θ) in Drywall C, which overlapped with a secondary calcite peak. This peak also overlapped with anhydrite in Drywall A and did not exist in the Drywall B XRD pattern. Although it was possible that elemental S was present in Drywall C based on XRD results, it would have been approximately <0.5%, and another technique would have been required to verify the presence of elemental S.

Although the amount of celestine determined by QXRD in Drywall C was greater than would be calculated from the amount of SrO determined by SEM-EDS, the results by both QXRD and SEM-EDS were too close to their detection limits to accurately quantify celestine (QXRD) and SrO (SEM-EDS). Even though celestine and SrO could not be quantified, they were positively identified as being present in Drywall C.

Identifying celestine in the crystalline form by QXRD in Drywall C confirmed the Sr–S–O result in a polished thin section by SEM-EDS. The absence of celestine and any other phase containing Sr in Drywall B by QXRD, which had the same amount of Sr in the crushed powder as Drywall C, was indicative that Sr was noncrystalline (amorphous) in Drywall B. Thus, although the forms of Sr were different in the nonproblematic drywall compared with the problematic drywall (amorphous compared with SrSO$_4$ in the respective drywall samples), celestine is an essentially stable phase and only very slightly soluble in water (Mindat.org 2011). In this study, SrS was not identified in either the problematic or the nonproblematic drywall. Although SrSO$_4$ was identified in the problematic drywall, it is a relatively stable phase.

**Textures**

Cross-sectional views of the drywall samples in this study showed that Drywall A and Drywall B were air-entrained, with essentially uniform and spherical voids (Figure 3a,b). Air-entrainment refers to material (drywall, in this case) in which small air bubbles have purposely been introduced into the drywall during production. The practice of air-entrainment originated in drywall production decades ago to reduce the weight, and thus the expense, of transporting drywall. Air-entrainment is also a common practice in the production of concrete. In this study, Drywall C showed entrapped air only (Figure 3c), which is air that had been trapped during the mixing of drywall and not intentionally created or added during production. Entrained air is typically nonuniform, with distorted (nonspherical) shapes. The distinction between air-entrained drywall (Figures 4a,b) and entrapped-air drywall (Figure 4c) can clearly be observed at a higher magnification.

For this study, drywall samples were prepared expressly to observe cross sections, which proved beneficial in distinguishing between problematic and nonproblematic drywall. For the three drywall samples examined, entrained-air versus entrapped-air textures clearly distinguished the nonproblematic drywall with entrained air (Drywall A and Drywall B) from the problematic drywall with only entrapped air (Drywall C). Although the air bubble textures did not indicate the source or cause of the reactions, the air bubble textures were inherent to the problematic drywall. It appears from this preliminary study of the three samples that air-entrained drywall is most likely American made...
Figure 2 Scanning electron microscopy (SEM) of Drywall C, showing (a) a backscattered electron image (BSI) with the circled white particle probed in (b), and (b) energy dispersive spectrometry (EDS) of the white particle in (a) showing Sr–S–O peaks (red lines indicate gold peaks used to coat the polished thin section to prevent charging).
Figure 3 SEM-BSI of polished thin sections showing cross-sectional views of drywall: (a) Drywall A, with entrained air; (b) Drywall B, with entrained air; and (c) Drywall C, with entrapped air. 60× magnification.

Figure 4 SEM-BSI of polished thin sections showing cross-sectional views of drywall: (a) Drywall A, with entrained air, (b) Drywall B, with entrained air, and (c) Drywall C, with entrapped air. 120× magnification.
and not problematic, whereas drywall with entrapped air only (with no entrained air) is most likely Chinese made.

Additional samples of known origin (Chinese made and American made) and the reaction state (unreacted and reacted) are required to validate this observation of entrained versus entrapped air. An effort was made to obtain samples of known origin from the CPSC, with the aid of U.S. Representative Jo Ann Emerson and her very helpful staff; however, such samples were not obtainable because of the controlled nature of those samples (they were unable to be released) in May of 2010.

SUMMARY AND CONCLUSIONS

Much effort and expense has been expended by many researchers, scientists, national laboratories, independent laboratories, government agencies, and consulting firms to study the problematic drywall. Several theories have been suggested as to the cause and possible reactions, and three of these theories are briefly addressed here. One area of drywall study that appears to have been overlooked is air void textures. This study demonstrated clearly that the nonproblematic drywall samples contained entrained air, whereas the problematic drywall samples did not, but rather contained only entrapped air. Additional drywall samples of known origin are required to validate this textural feature as being consistent in contaminated versus uncontaminated drywall. By identifying entrained air voids (indicating the drywall was American made and thus uncontaminated) versus entrapped air voids only (indicating the drywall was most likely Chinese made and possibly contaminated), the manufacturing source of American-made versus Chinese-made drywall might be determined, which would aid in determining uncontaminated versus possibly contaminated drywall.

ACKNOWLEDGMENTS

The author thanks an anonymous colleague for providing two of the drywall samples (Drywall A and Drywall C). Thanks to Winton Cornell, Applied Associate Professor at The University of Tulsa, for the Rietveld QXRD analyses and for his patience in fine-tuning and reevaluating the XRD as additional information was made available through chemistry, microscopy, and other studies. The author thanks former U.S. Representative Jo Ann Emerson and staffer Melanie Bell for their persistent effort to obtain drywall samples of known origin. Their efforts were an encouragement to the author that the U.S. government is truly “of the people, by the people, for the people” (Abraham Lincoln, Gettysburg Address, November 19, 1863).

REFERENCES


