Proposed Mechanism for the Release of Reduced Sulfur Compounds from Corrosive Imported Drywall

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Presentation Outline

- Materials Testing Results
  - SEM/EDX Analysis
  - Elemental Sulfur
  - Trace Metals Analysis
  - Iron Pyrite Content

- Identification of Key Reactants and Products

- Reaction Mechanisms

- Experimental Results

- Conclusions
Materials Testing Program
The Beginning

- **Volatile Compounds**
  - Crushed wallboard placed in heated Tedlar bags; TO-15 analysis of headspace
  - Methanol extraction, purge and trap, GC-MS analysis

- **Semi-Volatile Compounds**
  - Methylene chloride extraction; GC-MS analysis
  - Identified a number of TICs in both the imported corrosive drywall and domestic brands
  - **Elemental sulfur found in corrosive imported drywall but not domestic brand**
Scanning Electron Microscope/Energy Dispersive X-Ray Analysis (SEM/EDX)

- Samples of Corrosive Imported Drywall and Domestic Brand Analyzed
- Gross analysis by EDX showed only calcium, sulfur, oxygen, silicon and aluminum.
- Individual particles were primarily aluminosilicates and silicates.
- Some iron/sulfur particles (pyrite) were found in both samples in small quantities.
- The primary differences noted between the two drywall samples were the presence of numerous strontium-based particles and a few larger sulfur particles present in the corrosive drywall.
Scanning Electron Microscope Image of Elemental Sulfur Particle

Materials Analysis Group, Inc. Norcross GA
EDX Spectrum of Sulfur Particle

Materials Analysis Group, Inc. Norcross GA
EDX Spectrum of Strontium Particle

Materials Analysis Group, Inc. Norcross GA
Determination of Elemental Sulfur

- HPLC method for determination of elemental sulfur based on procedure reported by McGuire and Hamers (2000)

- **Chinese Brands (Corrosive and Non-corrosive)**
  - Elemental sulfur detected in 57 of 69 samples
  - Detected concentrations ranged from 3 to 1,870 mg/kg.

- **Domestic Brands**
  - Elemental sulfur not detected in 65 of 70 domestic samples (DL = 2 mg/kg).
  - Detected concentrations ranged from 3 to 4 mg/kg.

Levels of Elemental Sulfur Detected in Chinese Wallboard

- 8 to 30 mg/kg
- 85 to 245 mg/kg
- 510 to 1,870 mg/kg

- n = 69
- Min = < 2
- Max = 1,870
Trace Metals Analysis

- Analyzed 10 samples manufactured in China*, 1 Canadian brand and 21 samples of domestic drywall for 23 metals.

- Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Ag, Sr, Tl, Ti, Zn

- Most were not detected or infrequently detected at low levels.

- Distinct differences observed for some metals.

* Not all Chinese brands were determined to be corrosive
Differences in Average Metal Concentrations Between Chinese and Domestic Brands

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (mg/kg)</th>
<th>Chinese</th>
<th>Domestic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>1575</td>
<td>747</td>
<td>43</td>
</tr>
<tr>
<td>Barium</td>
<td>7</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Chromium</td>
<td>1929</td>
<td>866</td>
<td>7</td>
</tr>
<tr>
<td>Iron</td>
<td>9178</td>
<td>1726</td>
<td>29</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2939</td>
<td>383</td>
<td>85</td>
</tr>
<tr>
<td>Manganese</td>
<td>0</td>
<td>0</td>
<td>29</td>
</tr>
</tbody>
</table>
Strontium and Magnesium Levels in Chinese and Domestic Drywall

![Graph showing Strontium and Magnesium levels in different types of drywall]
No Difference Between Iron Pyrite Levels in Domestic and Corrosive Imported Drywall

<table>
<thead>
<tr>
<th>Concentration of Iron Pyrite (mg/kg)</th>
<th>Corrosive</th>
<th>Domestic</th>
<th>Domestic (FGD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>310</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>340</td>
<td>570</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>200</td>
<td>210</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>330</td>
<td>80</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>470</td>
<td>530</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>240</td>
<td>550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>320</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

avg. = 310 avg. = 320 avg. = 50
Indoor Air and Chamber Tests

- **Closed Chamber Tests**
  - Hydrogen sulfide (H$_2$S), carbonyl sulfide (OCS) and carbon disulfide (CS$_2$) detected in tests conducted with imported corrosive drywall.

- **Indoor Air Testing**
  - CS$_2$ detected in 20/79 residences; avg. = 7.1 ppbv; max = 13 ppbv
  - OCS detected in 7/79 residences; avg. = 8.6 ppbv; max = 23 ppbv
  - No H$_2$S detected
  - Dimethyl sulfide (CH$_3$)$_2$S detected in one home at 18.7 ppbv
Primary Reactants and Products

- **Elemental Sulfur** is the primary reactant involved in emissions from corrosive imported drywall.
  - No difference between iron pyrite levels in corrosive and domestic brands.
  - Strontium appears to be a good indicator for Chinese drywall – but not all Chinese drywall is corrosive.

- Primary products include $\text{H}_2\text{S}$, $\text{OCS}$ and $\text{CS}_2$
Sulfur

- Solid at room temperature
- Very low vapor pressure ($1.3 \times 10^{-8}$ atm at 39°C; Meyer, 1976)
- Prefers to exist as a ring structure ($S_8$)
- $S_2$, $S_3$ and $S_4$ ions detected in emissions from a “China Drywall” sample using DART (Direct Analysis in Real Time) mass spectrometry. Curtis et al. (2009)


Proposed Reaction Mechanism

- Carbon monoxide reacts with sulfur to form carbonyl sulfide
  \[
  \text{CO}_{(g)} + \frac{1}{2}\text{S}_2(g) \rightleftharpoons \text{OCS}_{(g)} \quad -34.2 \text{ Kcal/mole}
  \]

- Carbonyl sulfide hydrolyzes to form hydrogen sulfide
  \[
  \text{OCS}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{H}_2\text{S}_{(g)} + \text{CO}_2(g) \quad -7.1
  \]

- Competing reaction generates carbon disulfide
  \[
  2\text{CO}_{(g)} + \text{S}_2(g) \rightleftharpoons \text{CS}_2(g) + \text{CO}_2(g) \quad -32.0
  \]
Corrosive Imported Drywall
(24 Hours at 45-50 °C in Humid Air)
Domestic Drywall
(24 Hours at 45-50 °C in Humid Air)
Domestic Drywall + S + CO
(24 Hours at 45-50 °C in Humid Air)

Concentration (ppbv)

24 Hours 48 Hours 72 Hours
H2S OCS CS2

435
130
16.4

(Reheated for 1 hr at 100 °C)
Corrosive Imported Drywall with Added CO (24 Hours at 45-50 °C in Humid Air)

![Graph showing concentrations of H2S, OCS, and CS2 over 24, 48, and 72 hours.]

- **24 Hours**: H2S = 16 ppbv, OCS = 130 ppbv, CS2 = 17 ppbv
- **48 Hours**: H2S = 2.4 ppbv, OCS = 120 ppbv, CS2 = 18 ppbv
- **72 Hours**: H2S = 102 ppbv, OCS = 302 ppbv, CS2 = 91 ppbv

(Reheated for 1hr at 100 °C)

**Legend**:
- Red: H2S
- Green: OCS
- Blue: CS2
Reagent Grade CaSO$_4$·2H$_2$O (1 Hour at 100°C in N$_2$ Atmosphere)
Other Reactions with Sulfur

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G_f^\circ$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{S}_2(g) + \text{CH}_2\text{O}(g) \leftrightarrow \text{H}_2\text{S}(g) + \text{OCS}(g)$</td>
<td>-42.7</td>
</tr>
<tr>
<td>$\text{H}_2(g) + \frac{1}{2}\text{S}_2(g) \leftrightarrow \text{H}_2\text{S}(g)$</td>
<td>-17.4</td>
</tr>
<tr>
<td>$2\text{OCS}(g) \leftrightarrow \text{CS}_2(g) + \text{CO}_2(g)$</td>
<td>+2.2</td>
</tr>
<tr>
<td>$\text{S}_2(g) + 2\text{H}_2\text{O}(g) \leftrightarrow 2\text{H}_2\text{S}(g) + \text{O}_2(g)$</td>
<td>+74.5</td>
</tr>
<tr>
<td>$\text{S}_2(g) + \text{CO}_2(g) \leftrightarrow \text{CS}_2(g) + \text{O}_2(g)$</td>
<td>+90.8</td>
</tr>
</tbody>
</table>
Conclusions

- Elemental sulfur is the key characteristic distinguishing corrosive imported drywall from domestic brands.

- Elemental sulfur can react with CO in indoor air to yield reduced sulfur compounds (H$_2$S, OCS and CS$_2$).
  - Thermodynamically favored
  - Supported by experimental results

- Rate of reaction increases with temperature.

- Moisture (humidity) involved in the reaction.

- Reaction will proceed until sulfur is depleted.
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Questions?