Elemental Sulfur and Trace Metal Content in Chinese and Domestic Brands of Gypsum Wallboard

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ABSTRACT

Testing more than 100 examples of Chinese and domestic brands of gypsum wallboard has shown that the single characteristic distinguishing Chinese wallboard producing effects in homes from unaffected Chinese and domestic brands is the presence of elevated levels of elemental sulfur in the gypsum. A high performance liquid chromatography technique for analysis of elemental sulfur in rock matrices was adapted for determination of elemental sulfur in gypsum wallboard. Elemental sulfur concentrations in defective Chinese wallboard ranged from a low of about 8 mg/kg to as high as 1900 mg/kg; whereas, elemental sulfur was detected in only 5 of 70 samples of domestic brand wallboard at concentrations of 3 to 4 mg/kg; concentrations in all other samples of domestic wallboard were below the reporting limit (~ 2 mg/kg). We also performed trace metal analysis of 10 samples (7 brands) of Chinese wallboard and 21 samples (5 brands) of domestic wallboard. Strontium levels in Chinese wallboard samples ranged from 1400 to 5600 mg/kg compared to levels of 150 to 890 mg/kg in domestic brands. The highest level of strontium was found in a Chinese brand of wallboard that was determined to be non-defective (i.e., does not affect copper and does not contain elemental sulfur). A wallboard sample manufactured in Canada contained 1240 mg/kg strontium, but no elemental sulfur. We also estimated levels of iron pyrite in Chinese and domestic brands of wallboard and found no significant difference between the two groups. Further evaluation of within-board variability will be useful for refining a threshold value of elemental sulfur for identifying defective wallboard, however, via this method, concentrations as low as 8 mg/kg may reflect a potential to affect copper components in homes.

INTRODUCTION

When samples of corrosive imported wallboard and domestic wallboard were observed under scanning electron microscopy, unusual particles showing a distinct spectrum of elemental sulfur were noted uniquely in corrosive wallboard. Since the corrosion related to such wallboard is characteristic of reduced sulfur (sulfide) gases, which can be produced readily from elemental sulfur, but not, in the presence of oxygen, from oxidized forms such as calcium sulfate (i.e., gypsum), this observation identified a viable chemical source for the corrosive properties of the wallboard.

Elemental sulfur is associated with certain gypsum deposits and we hypothesized that corrosive wallboard contained elemental sulfur derived from the source mine. Elemental sulfur and trace metals were subsequently analyzed in over 100 wallboard samples to characterize the concentrations present and consistency of these potential chemical fingerprints. We also evaluated the hypothesis that iron pyrite (iron disulfide) was a unique reduced sulfur characteristic for imported wallboard.

The presence of elemental sulfur, which cannot survive combustion, along with the trace metal content, also definitively ruled out synthetic flue-gas derived gypsum as the basis for corrosive imported wallboard.

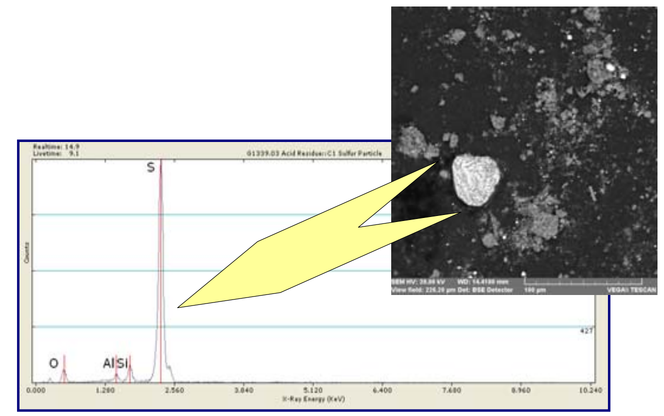
MATERIALS AND METHODS

Elemental sulfur was measured using a High Performance Liquid Chromatography (HPLC) method developed for rock matrices (McGuire and Hamers, 2000 *Environmental Science & Technology* 34:4651) and adapted for gypsum wallboard. Samples were extracted with tetrachloroethylene for 0.5-18 hours at room temperature and analyzed on an Agilent Model 1200 HPLC fitted with a UV detector operating at 254 nm. An Econosphere 5μm C18 reverse phase column (4.6 x 250 mm) was used at a flow rate of 1 mL/min and a 95/5 methanol/water eluent.

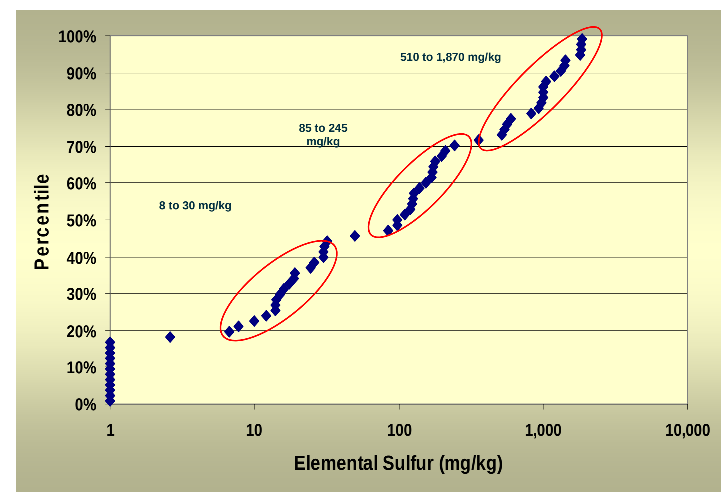
Concentrations of metals were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; U.S. EPA Methods 3050/6010B). Wallboard was digested in concentrated nitric acid, hydrochloric acid, and hydrogen peroxide at a temperature of 95 °C followed by filtration of the cooled digestate using a 2-micron propylene filter. The filtrate was then analyzed using ICP-AES.

Pyrite (iron disulfide) was measured using an energy-dispersive X-ray spectroscopy (EDX) method. After separating gypsum from paper and any other surface applications on the wallboard, approximately 1.5 to 4.5 grams were crushed into a coarse powder, placed in a clean glass beaker with 150 mL of dilute hydrochloric acid and heated to 70 °C until bubbling stopped and no gypsum particles were visible. The solution was filtered through a pre-weighed 0.45 micron mixed cellulose ester filter and the residue was rinsed, dried and weighed. The residue and filter were ashed for several hours at 500 °C to remove elemental sulfur. Ash residue was analyzed by EDX to determine the mass of sulfur as pyrite in the sample.

Particles of Elemental Sulfur via Scanning Electron Microscopy, EDX Uniquely Observed in Corrosive Imported Wallboard



Elevated Elemental Sulfur Concentrations in Chinese Wallboard Match Corrosivity

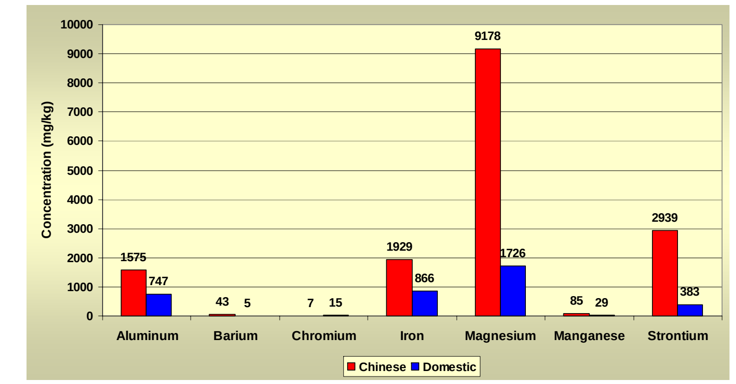


- Elemental sulfur detected in 57 of 69 samples, known corrosive samples around 10 mg/kg and higher
- Elemental sulfur detected in only 5 of 70 domestic samples, max.concentration 4 mg/kg (DL = 2 mg/kg)
- Elemental sulfur similarly low in domestic board and non-corrosive Chinese board

Iron Pyrite in Different Types of Gypsum Wallboard – No Difference Between Corrosive Imported and Domestic

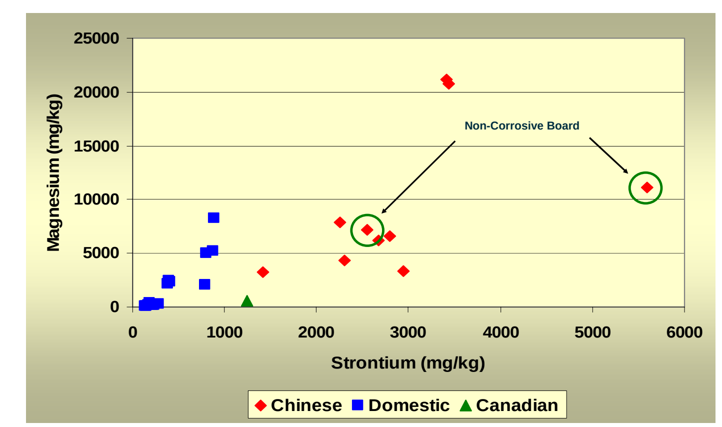
Corrosive Imported	Domestic	Domestic - Synthetic
310 mg/kg	310 mg/kg	70 mg/kg
340 mg/kg	570 mg/kg	40 mg/kg
200 mg/kg	210 mg/kg	70 mg/kg
330 mg/kg	80mg/kg	30 mg/kg
470 mg/kg	530 mg/kg	40 mg/kg
240 mg/kg	550 mg/kg	
250 mg/kg	90 mg/kg	
	180mg/kg	
	320 mg/kg	
Avg – 310 mg/kg	Avg – 320 mg/kg	Avg – 50 mg/kg

Trace Metal Content Differences Between Chinese and Domestic Wallboard



- Differences in several trace metals substantial, potentially useful for source fingerprinting
- Average levels of magnesium, strontium, and iron distinctly higher in Chinese board
- Chromium higher in Domestic board, but very low concentrations

Elevated Strontium Characteristic of Chinese Source, Not Corrosivity



- Strontium levels elevated in both corrosive and non-corrosive wallboard from China
- Useful marker of geological source of gypsum, but not the source of corrosive gas formation

CONCLUSIONS

- **Elevated elemental sulfur content is the single distinguishing characteristic of corrosive imported wallboard.**
  - ***This form of sulfur is a ready source for reduced sulfur gases causing corrosion.***
  - ***Sulfates (e.g., gypsum) are not readily reduced in presence of oxygen.***
  - ***The threshold level of elemental sulfur for wallboard that demonstrates corrosivity is around 10 mg/kg.***
- **Trace metals, especially strontium, can be useful for source location fingerprinting, but are not related to corrosivity – beware “false positives.”**
- **Pyrite not useful marker for corrosive wallboard, but distinguishes synthetic gypsum.**