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





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ENVIRON

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

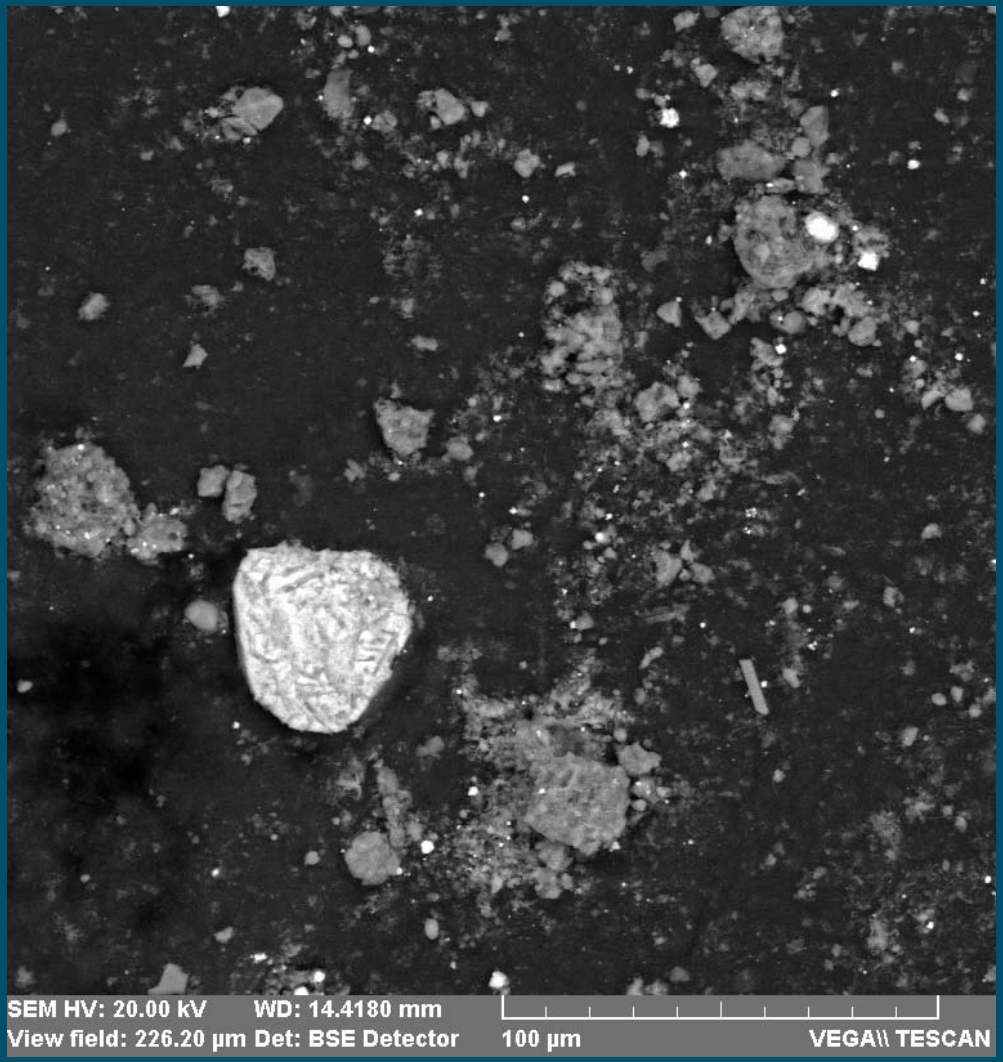
Materials Testing Program
The Beginning

- **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)

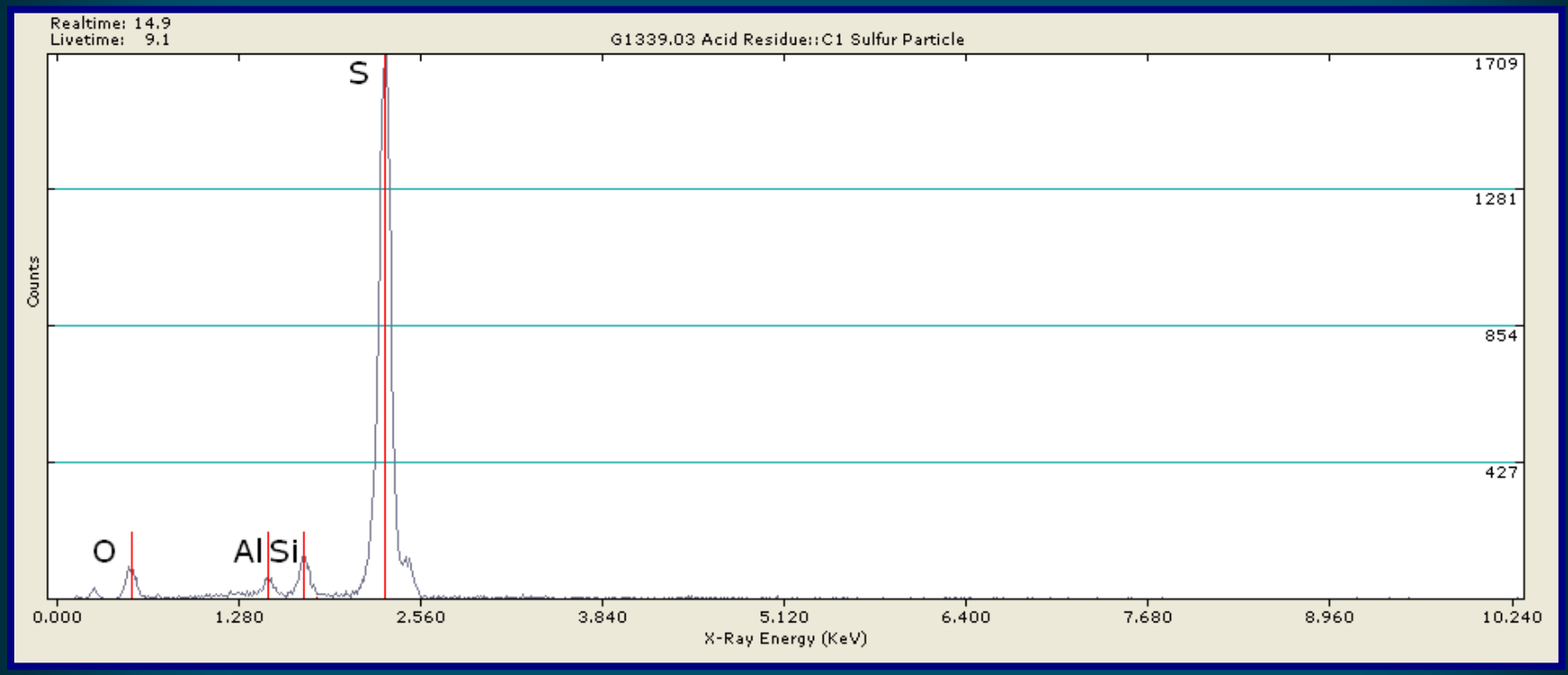
- Samples of Corrosive Imported Drywall and Domestic Brand Analyzed
- Gross analysis by EDX showed only calcium, sulfur, oxygen, silicon and aluminum.
- Individual particles were primarily aluminosilicates and silicates.
- Some iron/sulfur particles (pyrite) were found in both samples in small quantities.
- **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



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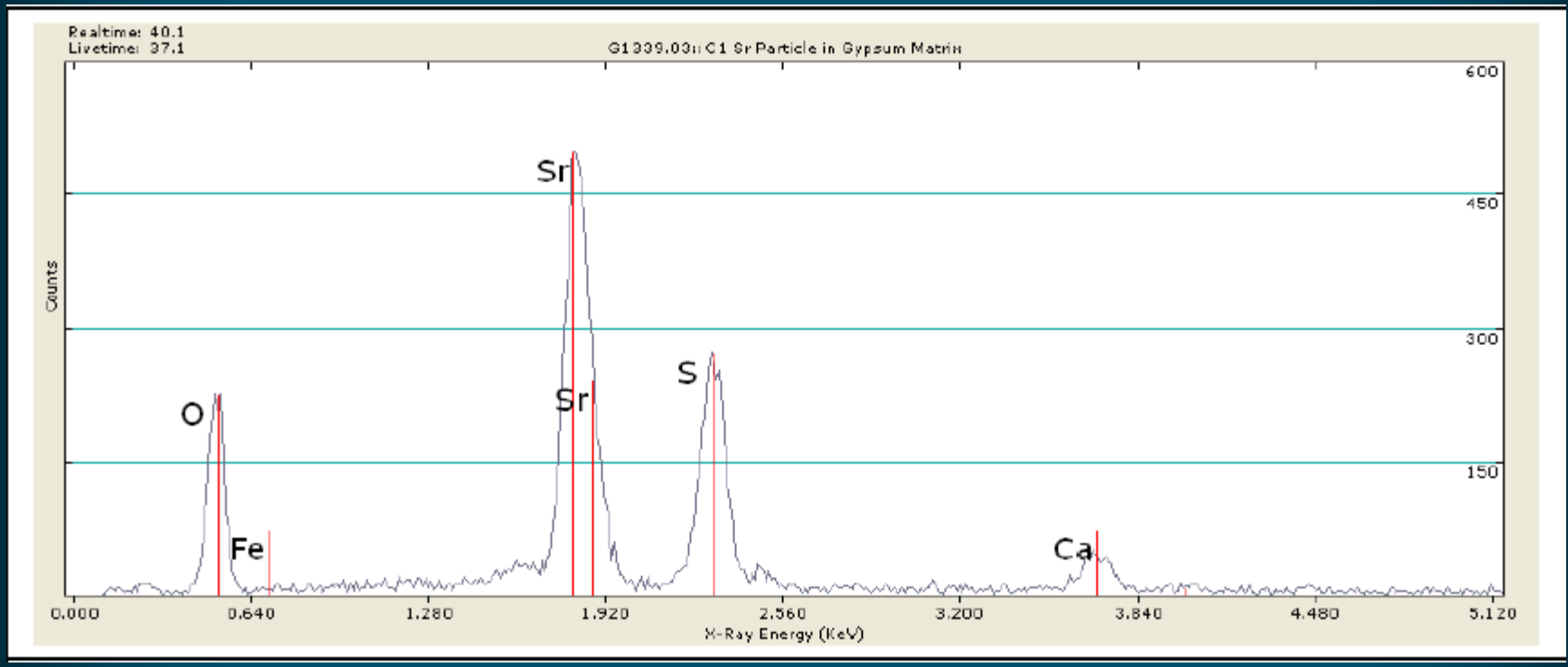
EDX Spectrum of Strontium Particle



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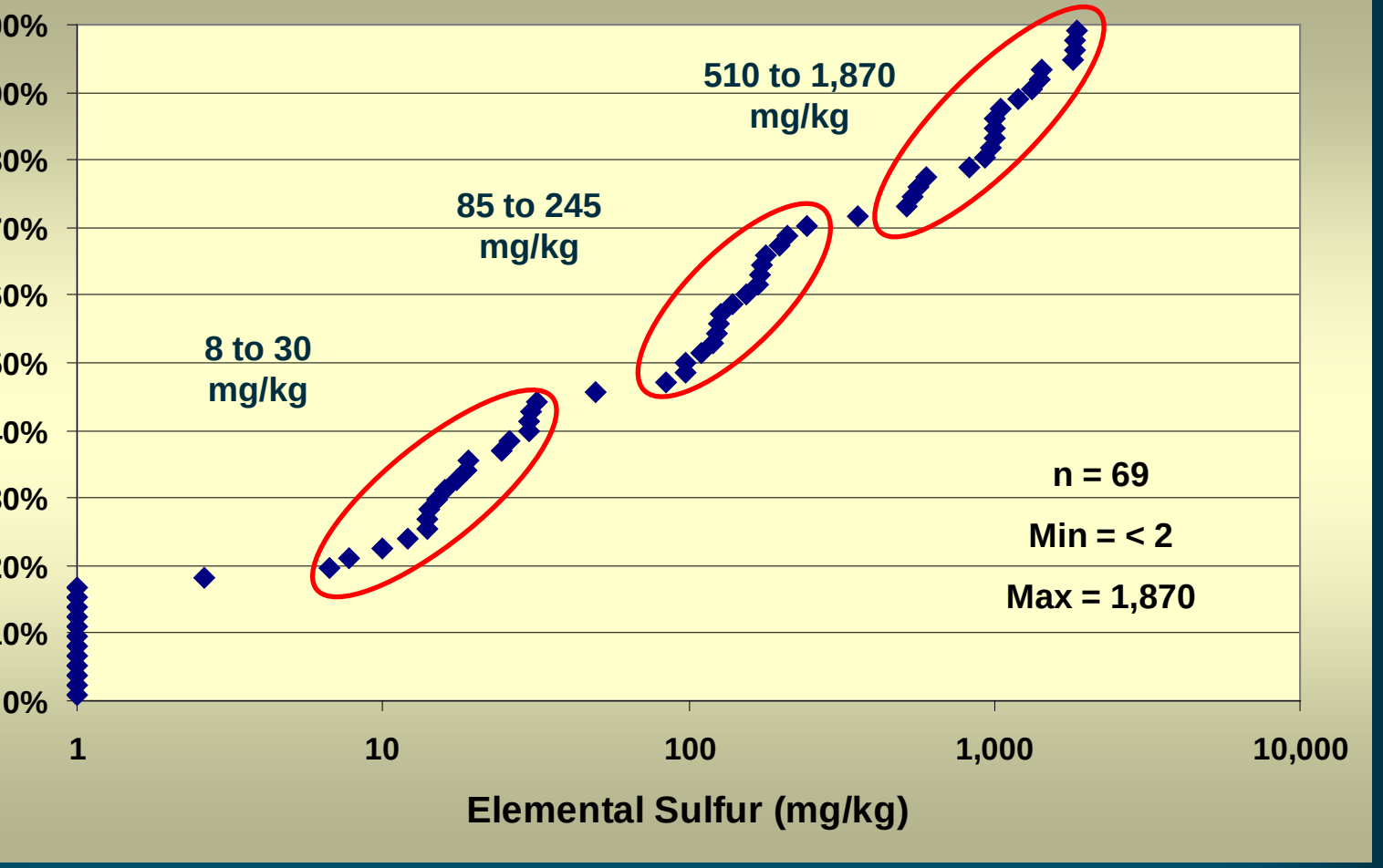
Determination of Elemental Sulfur

- 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.

McGuire, M.M. and R.J. Hamers. 2000. Extraction and quantitative analysis of elemental sulfur from sulfide mineral surfaces by high-performance liquid chromatography. *Environmental Science & Technology* 34:4651-4655.

Levels of Elemental Sulfur Detected in Chinese Wallboard

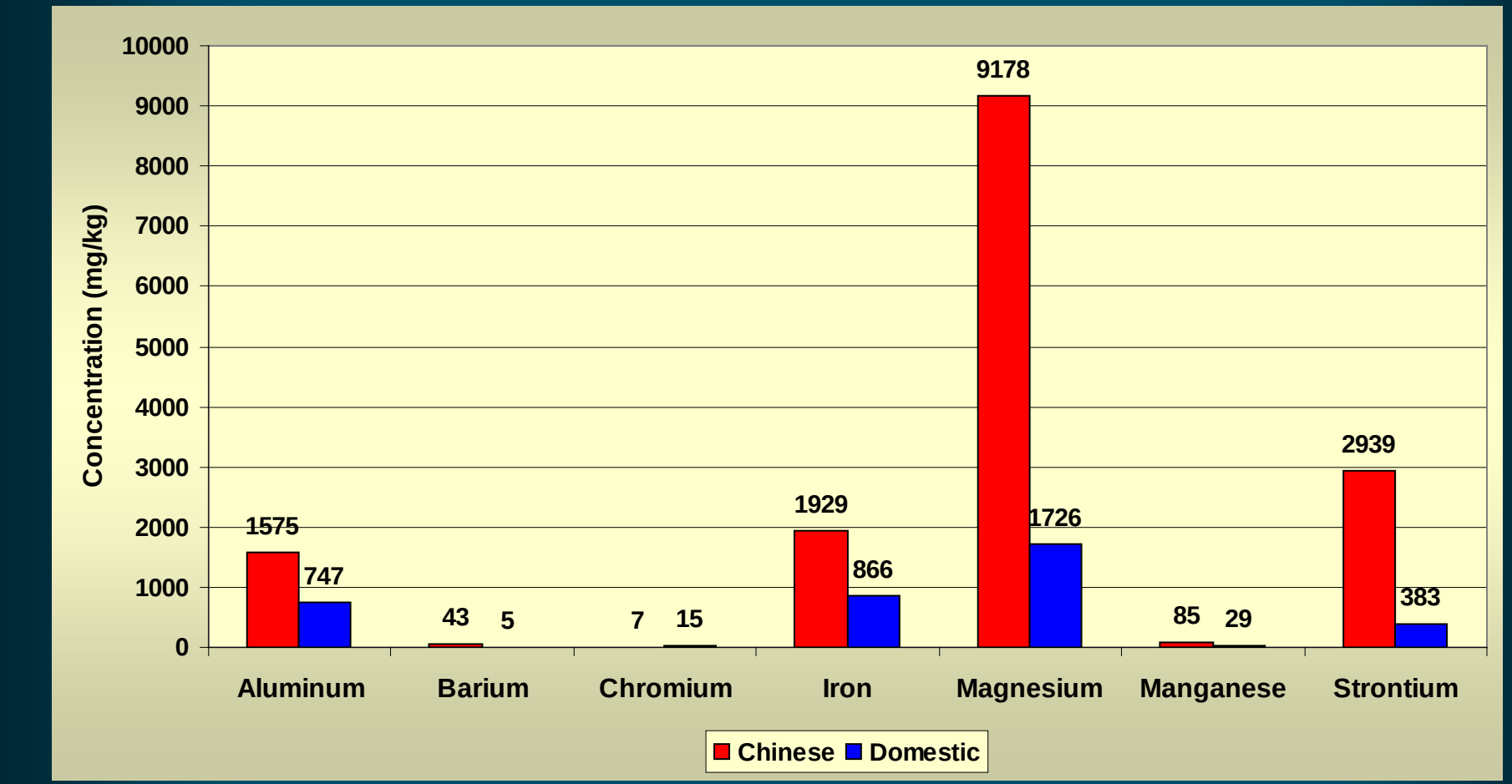


Trace Metals Analysis

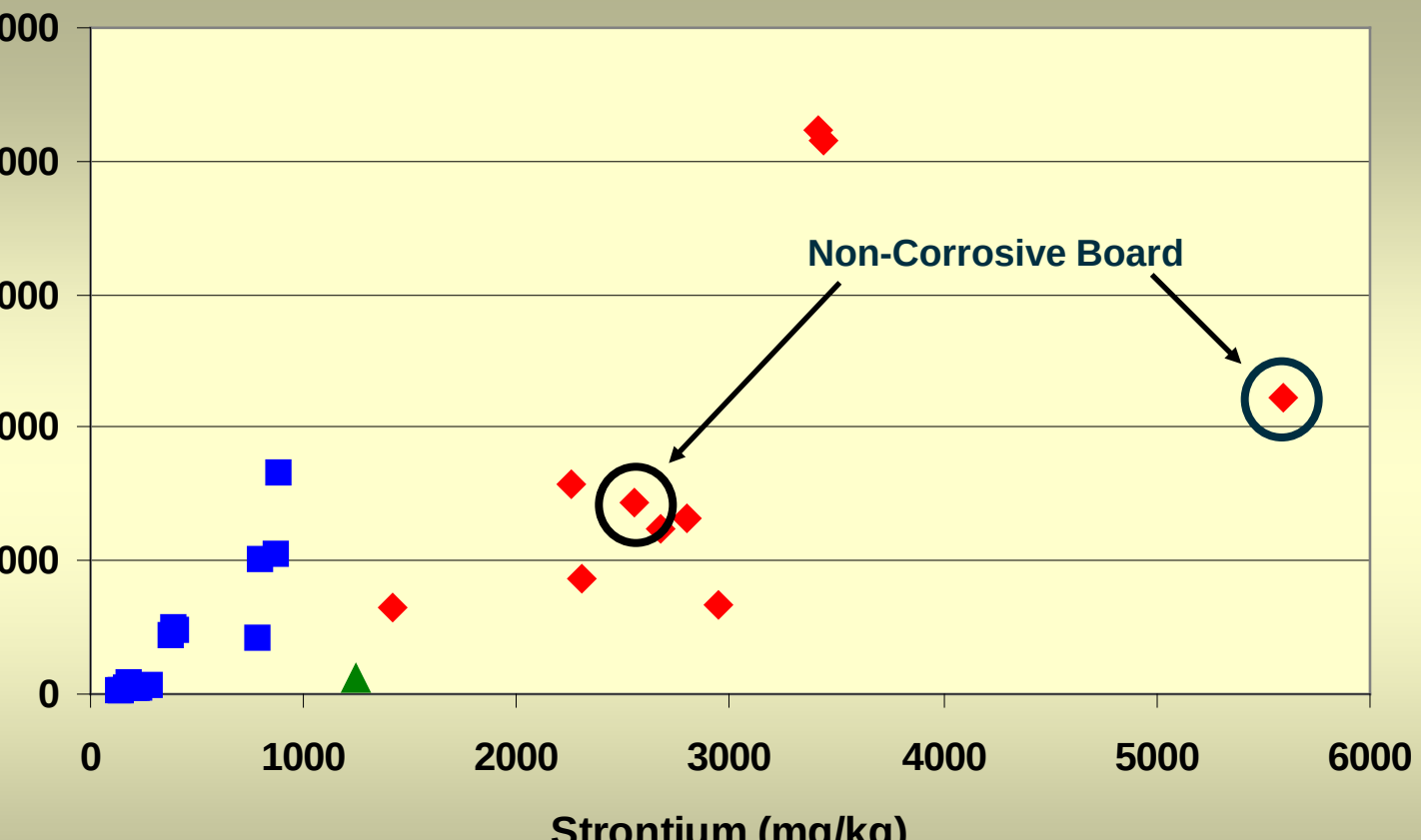
- Analyzed 10 samples manufactured in China*, 1 Canadian brand and 21 samples of domestic drywall for 23 metals.
- Al, ~~Sb~~, ~~As~~, Ba, ~~Be~~, B, ~~Cd~~, Cr, ~~Co~~, ~~Cu~~, Fe, ~~Pb~~, Mg, Mn, ~~Hg~~, ~~Mo~~, ~~Ni~~, ~~Se~~, ~~Ag~~, Sr, ~~Tl~~, ~~Ti~~, Zn
- Most were not detected or infrequently 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



Strontium and Magnesium Levels in Chinese and Domestic Drywall



No Difference Between Iron Pyrite Levels in Domestic and Corrosive Imported Drywall

Concentration of Iron Pyrite (mg/kg)		
Corrosive	Domestic	Domestic (FGD)
310	310	70
340	570	40
200	210	70
330	80	30
470	530	40
240	550	
250	90	
	180	
	320	
avg. = 310	avg. = 320	avg. = 50

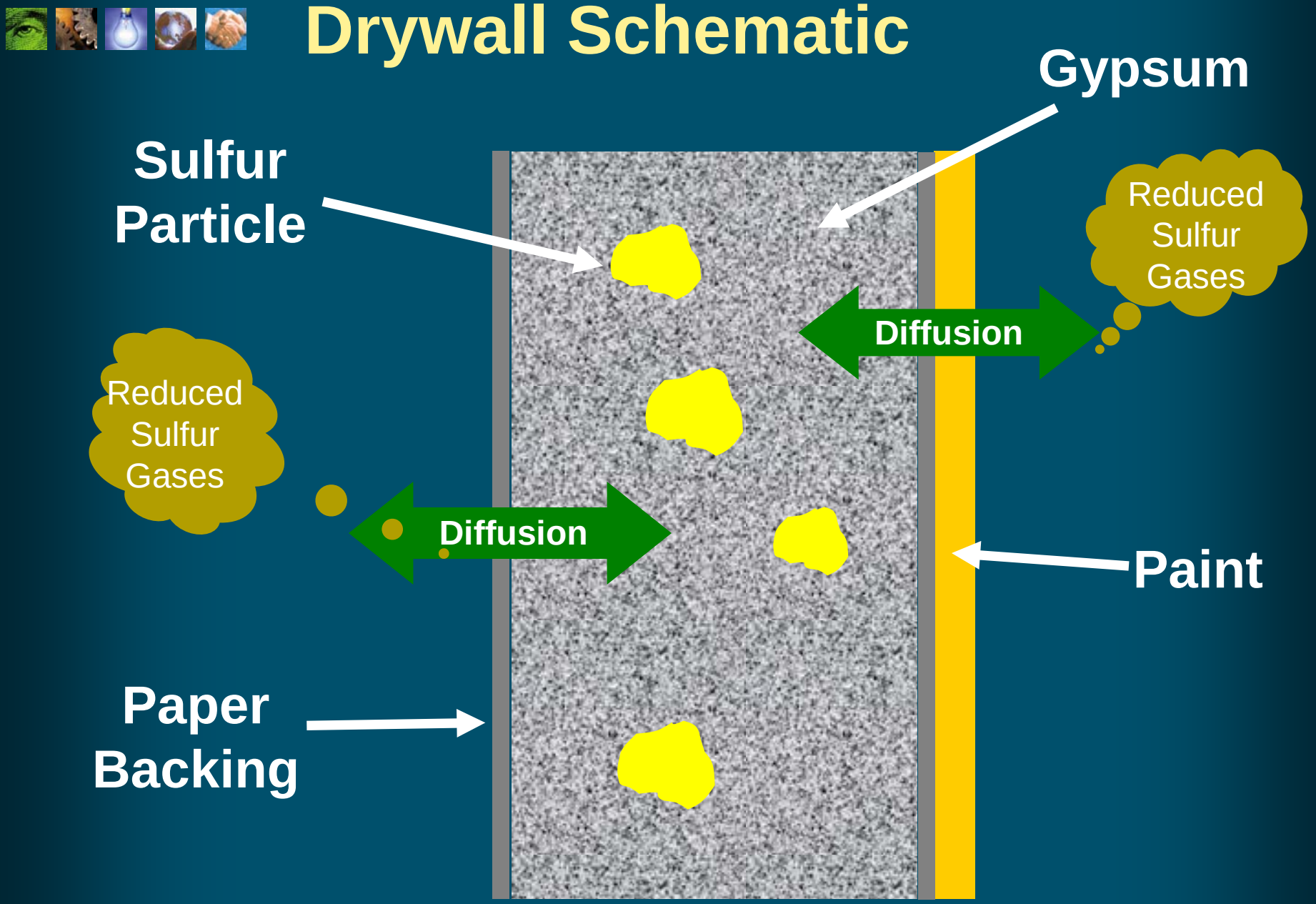
Indoor Air and Chamber Tests

- **Closed Chamber Tests**
  - **Hydrogen sulfide (H_2S), 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_2S detected**
  - **Dimethyl sulfide $(CH_3)_2S$ detected in one home at 18.7 ppbv**

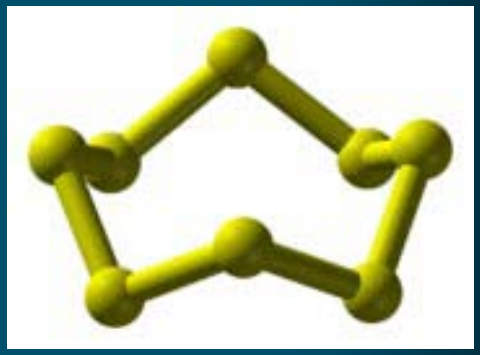
Primary Reactants and Products

- **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 H_2S, OCS and CS_2**

Drywall Schematic



Sulfur



- Solid at room temperature
- Very low vapor pressure (1.3 x 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)

Meyer, B. 1976. Elemental Sulfur. *Chemical Reviews, 76(3): 367 – 388.*

Curtis, M.E., P.R. Jones, O.D. Sparkman and R.B. Cody. 2009. *Journal of the American Society for Mass Spectrometry (in press).*

Proposed Reaction Mechanism

- **Carbon monoxide reacts with sulfur to form carbonyl sulfide**

Kcal/mole

$$CO_{(g)} + \tfrac{1}{2}S_{2(g)} \leftrightarrow OCS_{(g)} \qquad -34.2$$

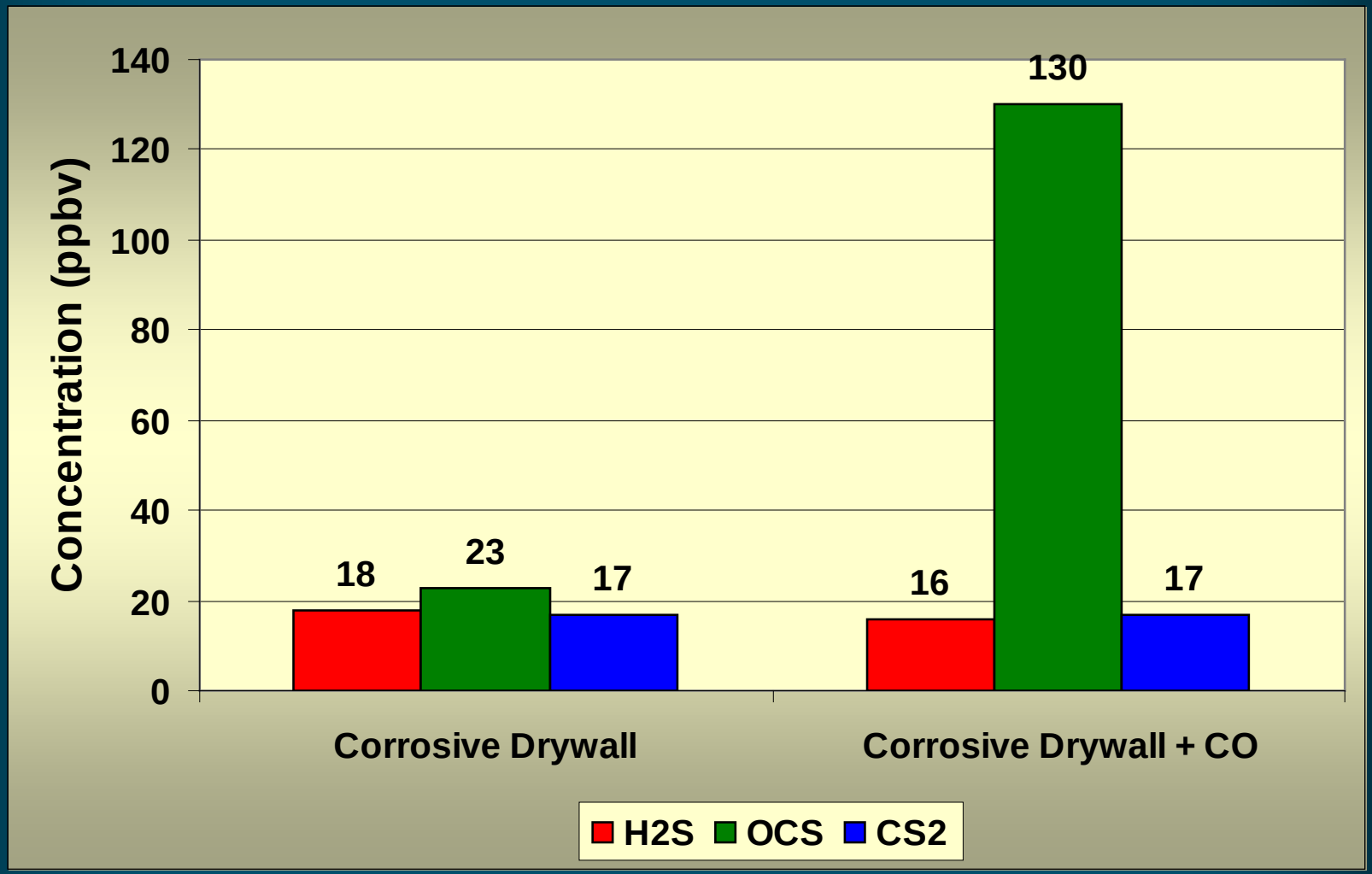
- **Carbonyl sulfide hydrolyzes to form hydrogen sulfide**

$$OCS_{(g)} + H_2O_{(g)} \leftrightarrow H_2S_{(g)} + CO_{2(g)} \qquad -7.1$$

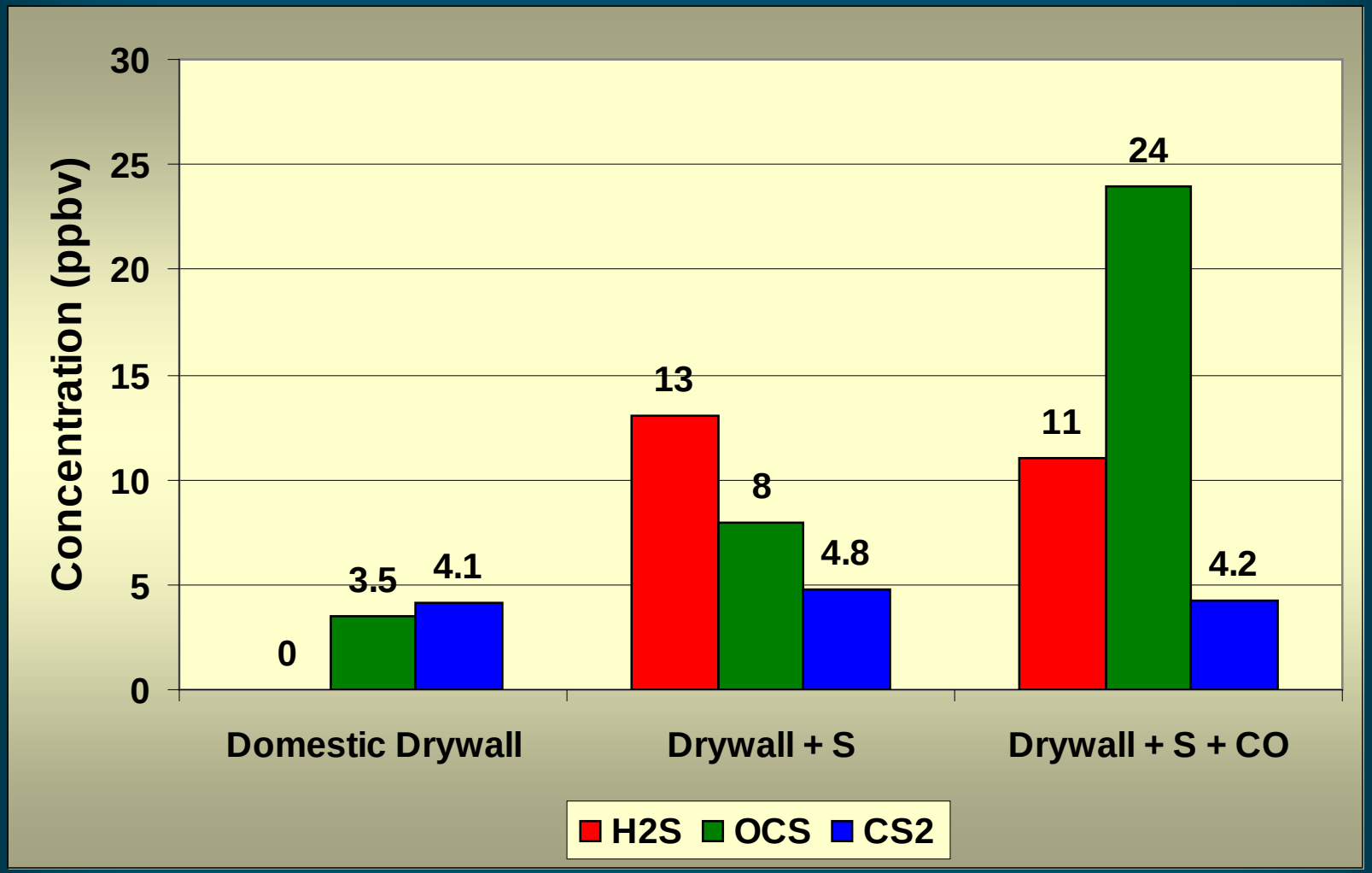
- **Competing reaction generates carbon disulfide**

$$2CO_{(g)} + S_{2(g)} \leftrightarrow CS_{2(g)} + CO_{2(g)} \qquad -32.0$$

Corrosive Imported Drywall
(24 Hours at 45-50 C in Humid Air)

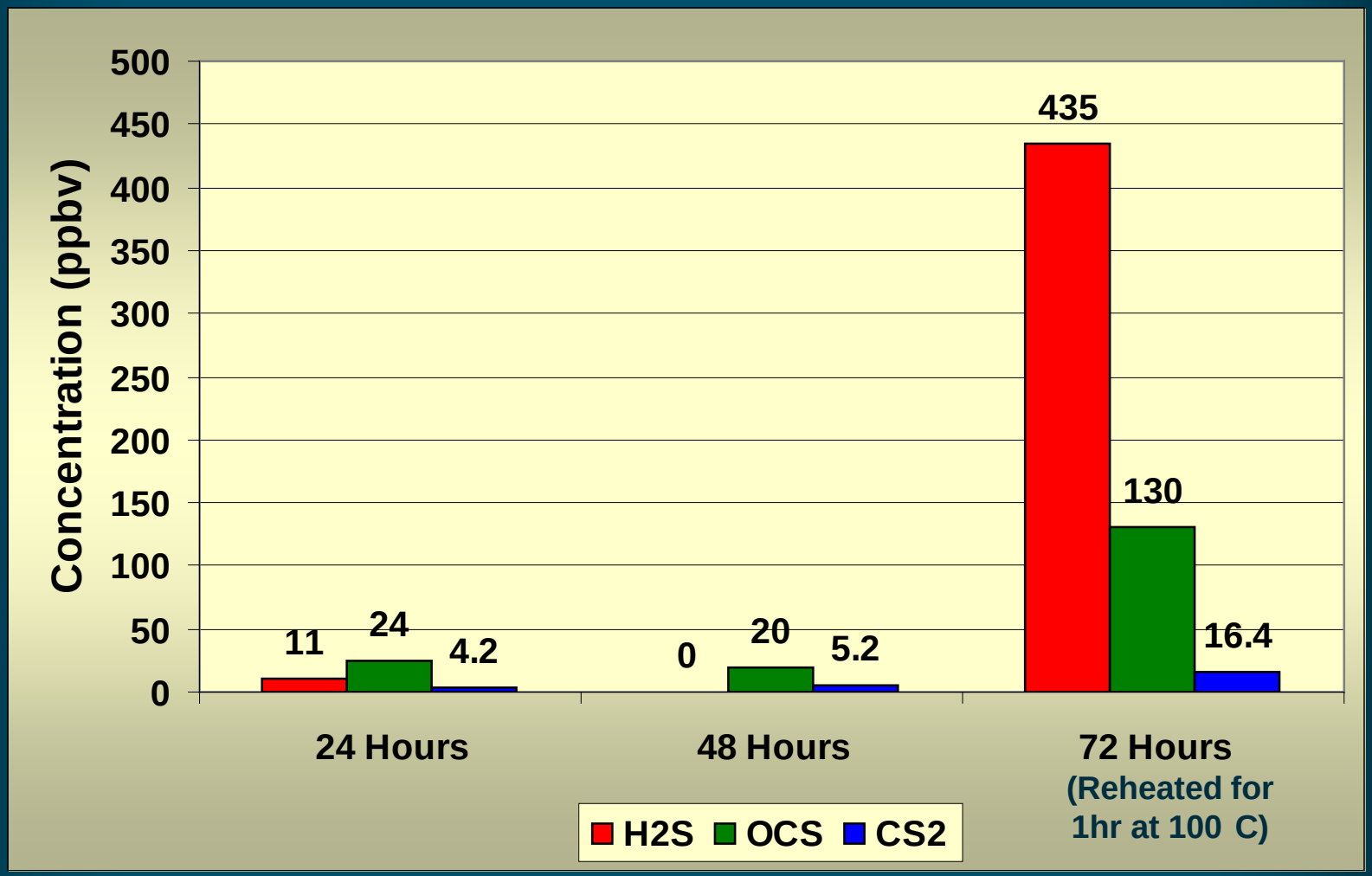


Domestic Drywall
(24 Hours at 45-50 C in Humid Air)

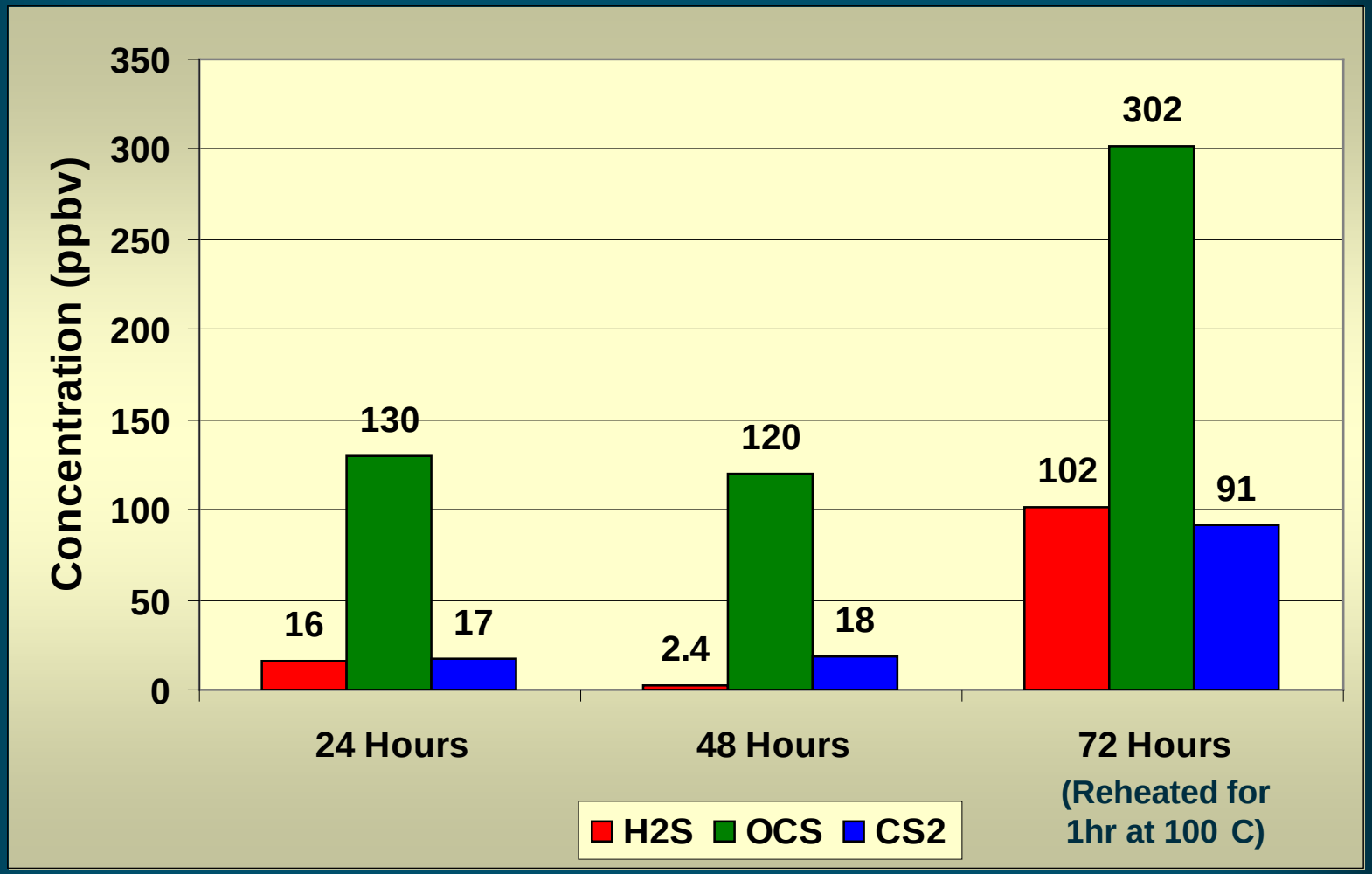


Domestic Drywall + S + CO

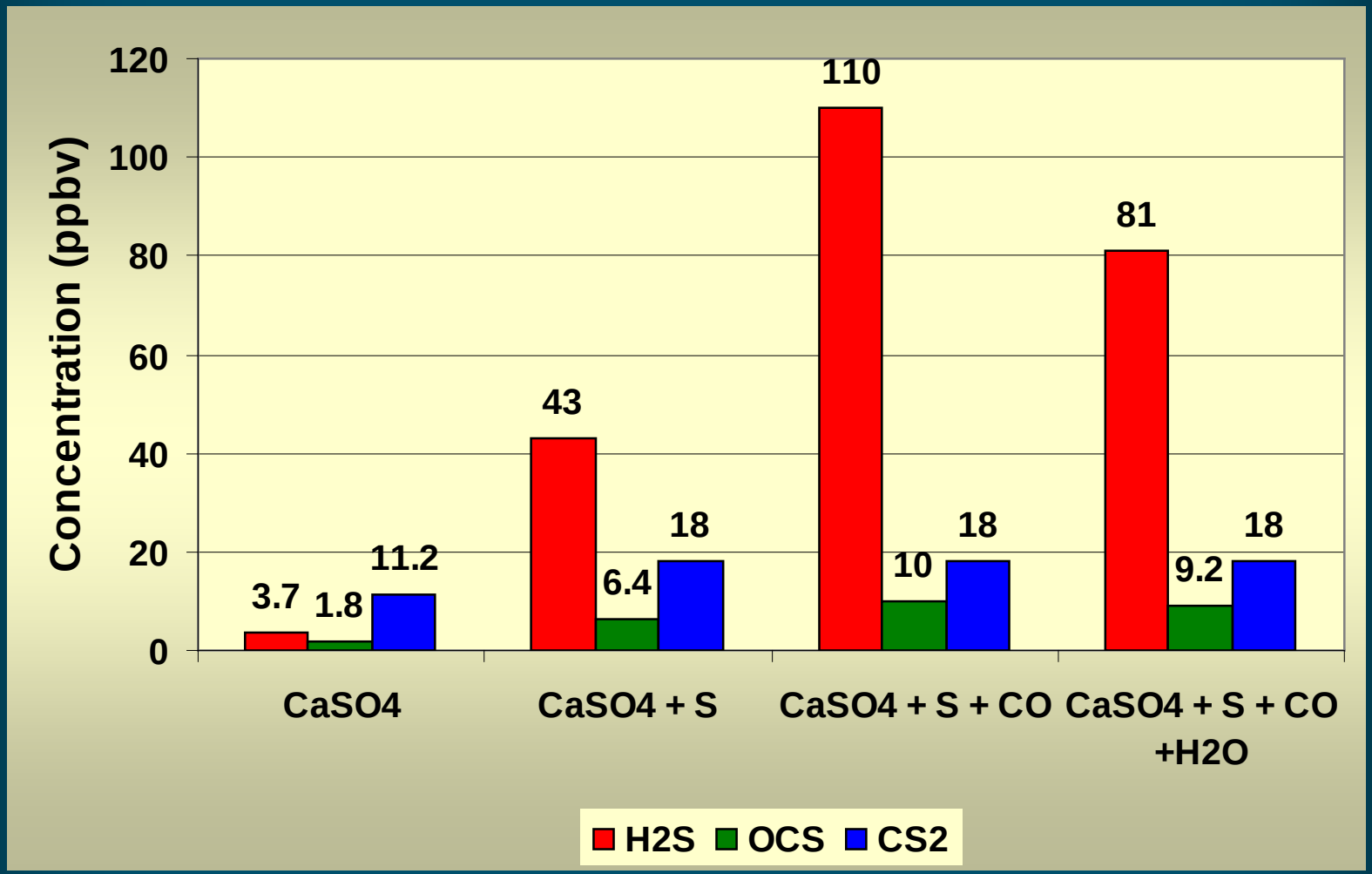
(24 Hours at 45-50 C in Humid Air)



Corrosive Imported Drywall with Added CO (24 Hours at 45-50 C in Humid Air)



Reagent Grade $CaSO_4 \cdot 2H_2O$ (1 Hour at 100 C in N_2 Atmosphere)



Other Reactions with Sulfur

Reaction	ΔG_f° (kcal/mol)
$S_{2(g)} + CH_2O_{(g)} \leftrightarrow H_2S_{(g)} + OCS_{(g)}$	-42.7
$H_{2(g)} + \frac{1}{2}S_{2(g)} \leftrightarrow H_2S_{(g)}$	-17.4
$2OCS_{(g)} \leftrightarrow CS_{2(g)} + CO_{2(g)}$	+2.2
$S_{2(g)} + 2H_2O_{(g)} \leftrightarrow 2H_2S_{(g)} + O_{2(g)}$	+74.5
$S_{2(g)} + CO_{2(g)} \leftrightarrow CS_{2(g)} + O_{2(g)}$	+90.8

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_2S, 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.

Acknowledgements

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Questions?