Environmental Issues And Structural Clay Products

Jim Frederic
National Brick Research Center
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Topics For Discussion

- NO_x Emissions
- CO/CO_2 Emissions
- Measurement of Crystalline SiO_2
- Defining Carbon and Sulfur Contents
- Fluorine Content of Raw Materials

Overview of NO_x Emissions

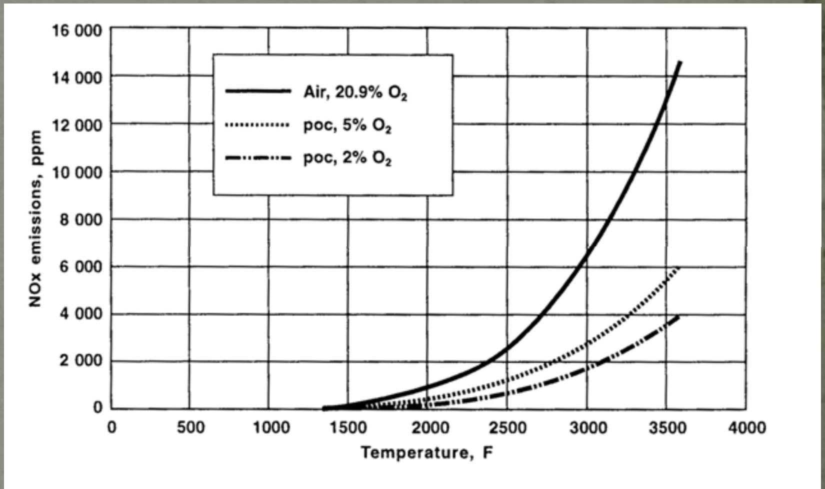
- Sources of NO_X Emissions
- Survey Plant Measurements of NO_X Emissions
- Lab Measurements of NO_X Emissions
- Conclusions on NO_X Emissions

What is NO_x

- The term NO_X is used to describe the most common oxides of nitrogen, NO, and NO_2.
- NO_X emissions occur when nitrogen (N_2) and oxygen (O_2) combine at high temperature.
- There are three recognized mechanisms for the formation of NO_X from combustion processes.
  - Thermal NO_X
  - Prompt NO_X
  - Fuel NO_X

Thermal NO_X

- Thermal NO_X is formed when Nitrogen (N_2) and Oxygen (O_2) dissociate at high temperature and react to form NO_x at high temperature.
- The rate of thermal NO_X formation is affected by:
  - Peak Temperature
  - Oxygen Concentration
  - Time at Temperature



North American Combustion Handbook, Volume II, North American Mfg. Co., Cleveland OH, 1997

Other NO_x Mechanisms

- Prompt NO_X
  - Prompt NO_X is produced at low temperature by the reaction of N_2 and partially burned hydrocarbons (VOCs).
  - This is a very minor source of NO_X.
- Fuel NO_X
  - Fuel NO_X is produced by the oxidation of nitrogen compounds in the fuel.
  - Natural gas has a very low nitrogen content which means that the amount of Fuel NO_X that is produced is negligible.
  - Other fuels that have a higher nitrogen content may produce more Fuel NO_X.

Overview of Plant Emission Measurements

- NO_X emissions were measured at several plants using an Enerac hand held emission monitor.
- The monitor measures both NO and NO_2, but only NO was measured in our plant measurements.
- Excellent correlation was found between the Enerac and a continuous emission monitoring system at one of the plants.
- All measurements were taken on a dry basis.

Overview of Lab Measurements of NO_X Emission

Conclusions on NO_X Emissions

- NO_X emissions are a consequence of the combustion process, but are influenced by kiln temperature and oxygen content in both lab measurements and plant measurements.
  - Exhaust flow rate, production rate and energy consumption rate were also found to influence NO_X emissions based on statistical analysis of plant measurements.
- Based on these measurements, it appears that the AP-42 emission rate for NO_X is too high and deserves further consideration.
- In the lab, NO_2 emissions were observed first, but as the temperature increased, NO emissions predominated.

Overview of CO/CO_2 Emissions

- Sources of CO/CO_2 Emissions
- Lab Measurements of CO/CO_2 Emissions
- Plant Measurements of CO/CO_2 Emission
- Comparison of Total Carbon Emissions and Carbon Emissions from the Raw Materials (by Mass Balance)

Sources of CO/CO_2 Emissions

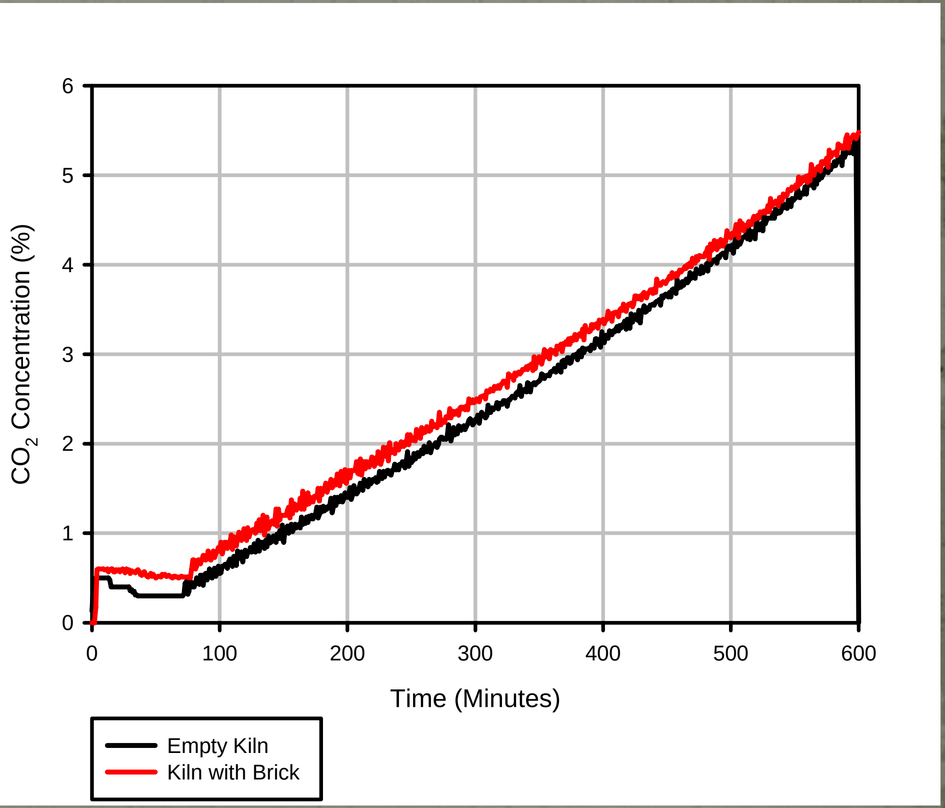
- Combustion process
  - The ratio of CO to CO_2 is determined by the available oxygen and the temperature where combustion takes place.
- Oxidation of organics in the raw material
- Inside the brick, CO is generated as the organics burn, but depending on the temperature and availability of oxygen, may oxidize to CO_2 once it migrates out of the pores of the brick.
- In extreme cases where oxygen is extremely limited, volatile organic compounds (VOCs) may be generated.

Observations on Lab Kiln CO/CO_2 Measurements

- CO and CO_2 emissions were measured on an empty lab kiln to understand the combustion process.
- CO emissions were measured as soon as the pilots were lit.
- CO emissions began to decline at 1000°F due to the auto-ignition of CO.
- CO appears to take oxygen from NO_2 above 1000°F to make NO and CO_2.
- CO_2 emissions increased with increasing kiln output and closely mirrored the oxygen content of the kiln exhaust.

Lab Kiln CO_2 Emission Comparison

- CO_2 emissions were compared on the empty lab kiln, and the lab kiln containing 200 lbs of brick using the same heating schedule.
- The CO_2 output was only slightly increased for the run with brick.
    - A small increase in kiln output was also required to heat the brick.



Conclusions on CO/CO_2 Emissions

- Based on these measurements, it appears that the AP-42 emission rate for CO_2 is too high for some kilns and deserves further consideration.
  - We found the highest CO_2 emissions for the plant with the highest energy consumption.
- CO emissions were highest for the plant with the highest carbon content in the raw material.
- It appears that the carbon content of the raw material contributes only a fraction of the total CO_2 emissions.
  - For the plant with the highest carbon content in the raw material, up to 20% of the total CO_2 emissions could be coming from the carbon in the raw material.
  - For the other plants, 10% or less of the CO_2 emissions could be attributed to carbon in the raw material.

Measurement of Crystalline Silica- A Comparison of XRF and XRD

XRF = X-Ray Fluorescence

- Provides the chemical oxide analysis of raw materials
- Identifies and determines the quantity of <u>most</u> elements
- Most results reported as oxides using molecular weight conversions (thus, Si reported as SiO_2)
- SiO_2 is TOTAL silica

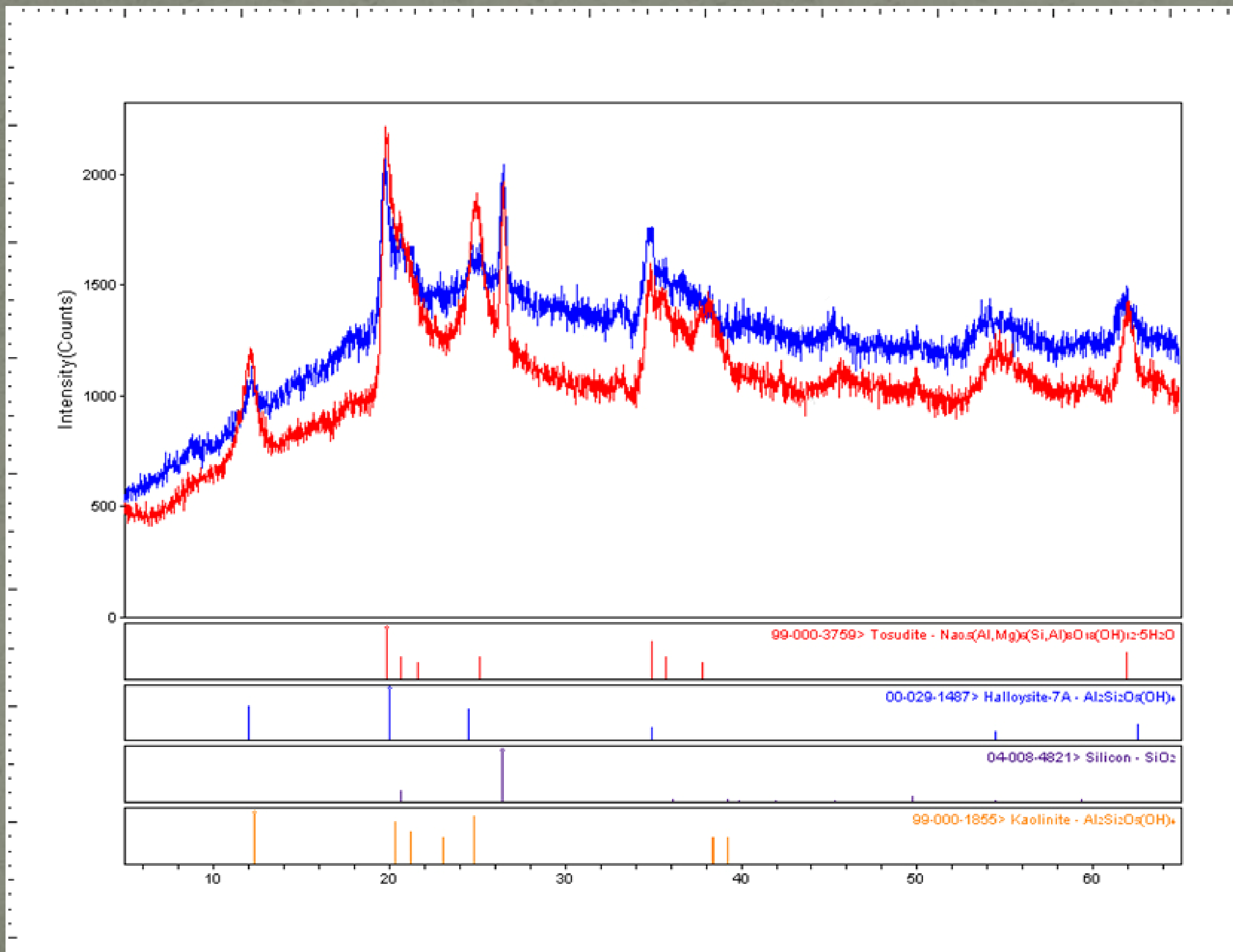
Typical XRF Chart

RESULTS			
Major Constituents	**Unit**	***Blend #1 (base mix. plant)*** *As Received 3/12/2008*	***Blend#3 (base mix, lab)*** *As Received 3/12/2008*
Al_2O_3	%	18.72	18.54
SiO_2	%	64.12	65.61
Na_2O	%	0.61	0.51
K_2O	%	1.72	1.61
MgO	%	1.62	1.23
CaO	%	1.48	1.39
TiO_2	%	0.91	0.93
MnO	%	0.04	0.04
Fe_2O_3	%	4.71	4.22
P_2O_5	%	<0.018	<0.018
S	%	0.31	0.31

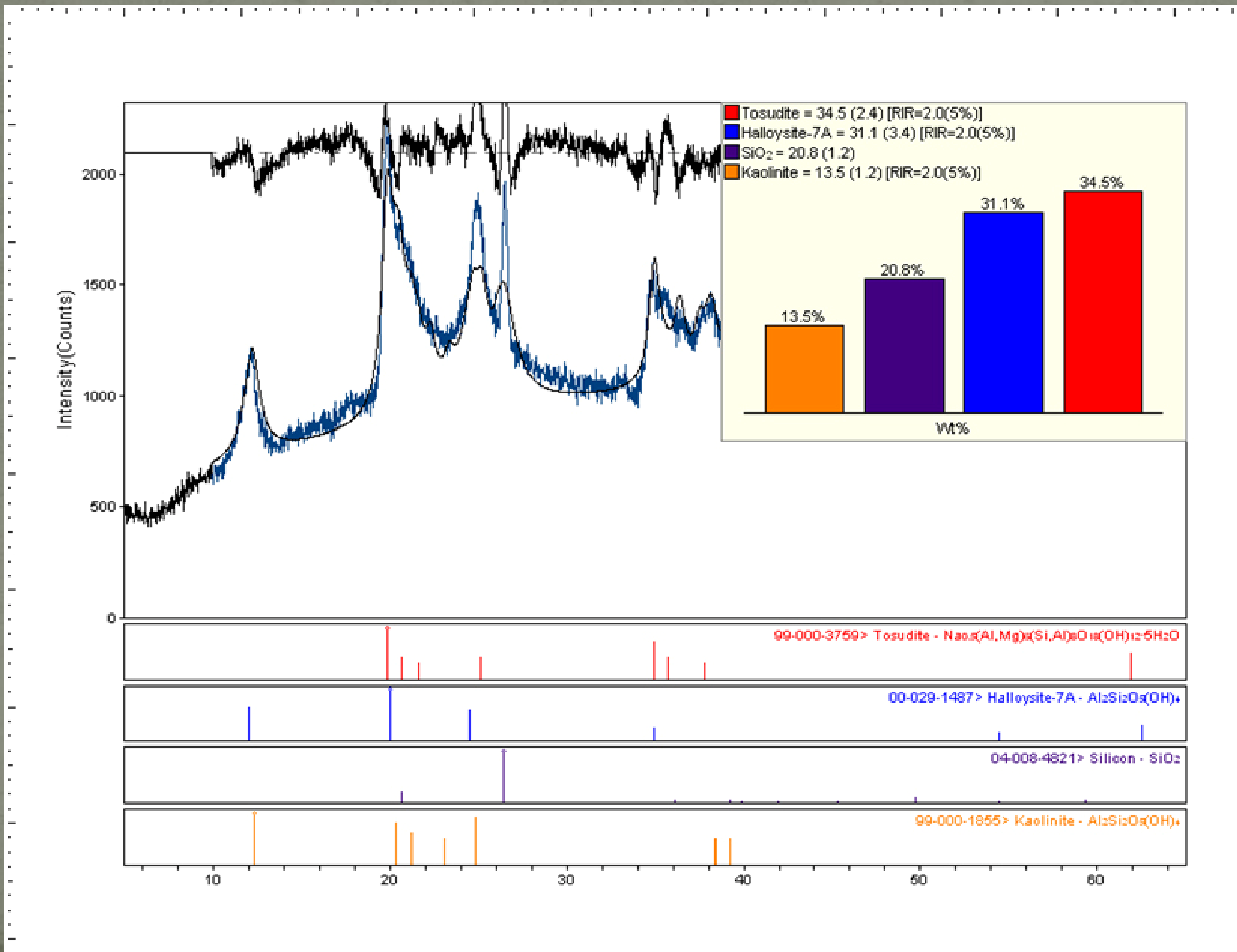
XRD = X-Ray Diffraction

- Provides the identity of minerals or crystalline phases
- Also quantifies the minerals or crystalline phases
- Results reported by mineral name, not by elements
- SiO_2 is clearly identified as either “Combined” or “Crystalline”

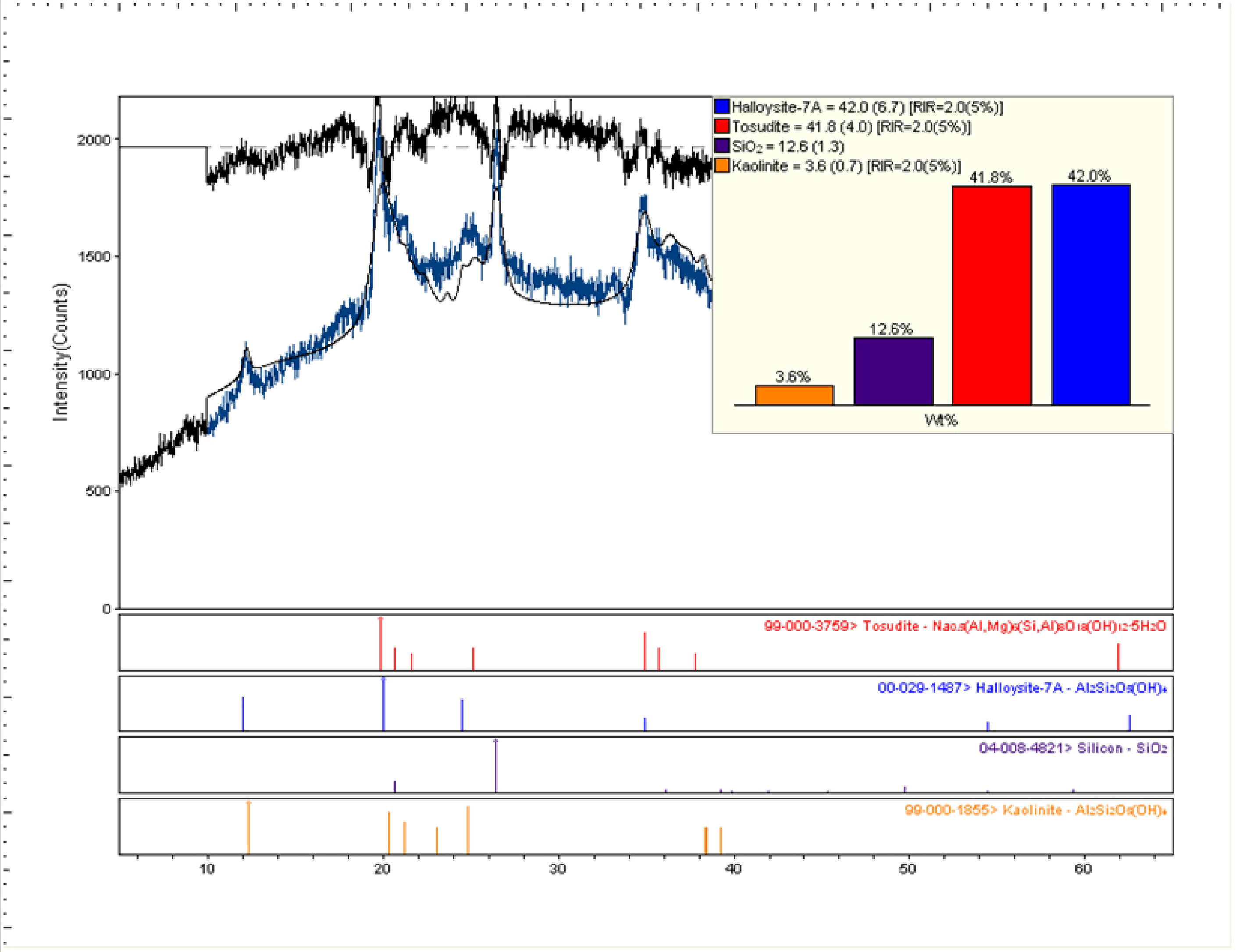
Typical XRD Charts



Typical XRD Charts



Typical XRD Charts



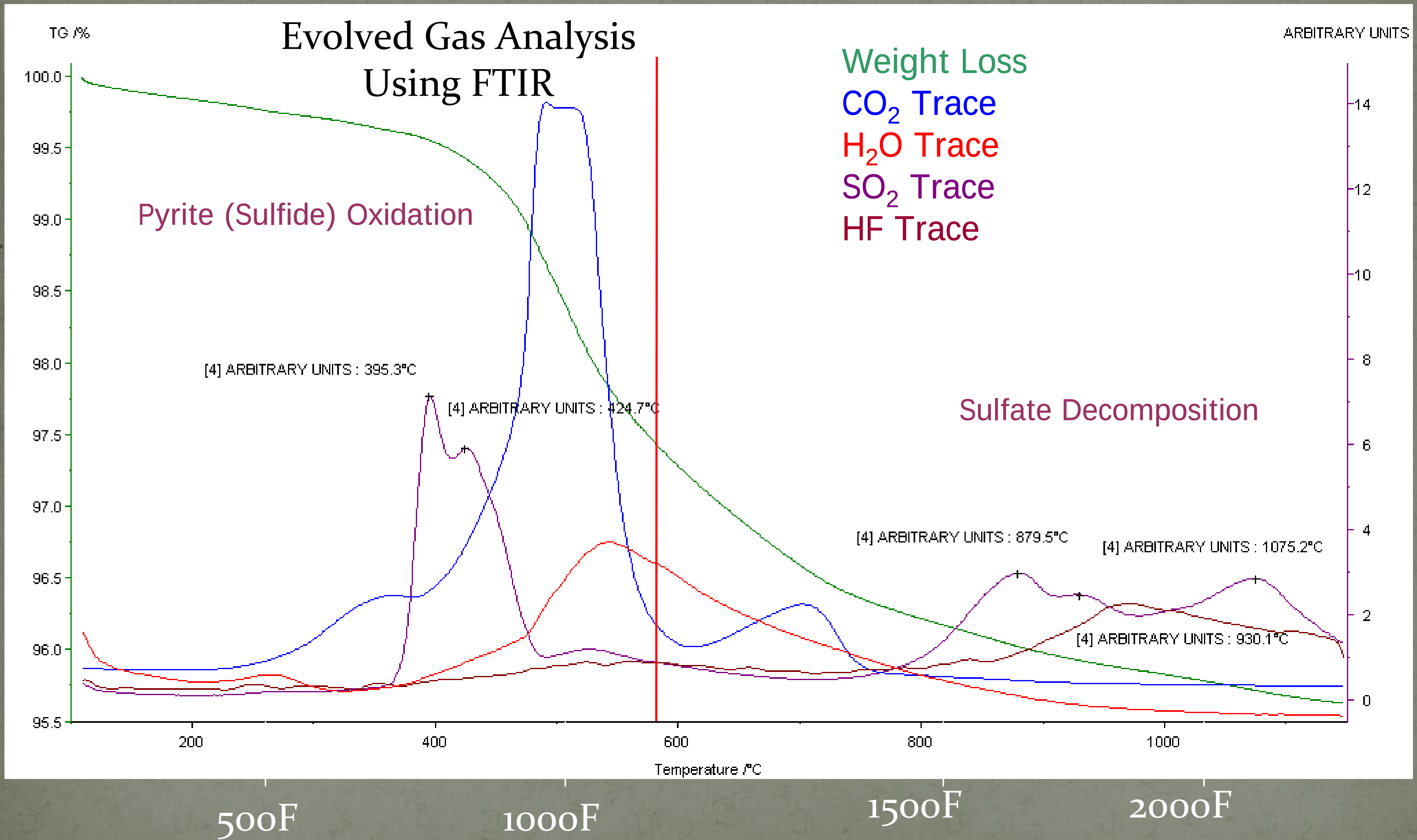
Defining Carbon and Sulfur Contents
(for Potential Burnout and Emissions Problems)

- Organic carbon versus inorganic carbon (for example, carbonates)
- Sulfides versus sulfates
- Basis in ASTM E-1915
- Test Method is LECO
  1. Total carbon and sulfur, as received
  2. Heat samples to 550°C
  3. Total carbon and sulfur, pyrolyzed/calcined samples

Sample	Sulfur		Carbon	
Dry	0.134		0.864	
Fired (to 550° C)	0.125	(Sulfates)	0.289	(Inorganic)
Difference	0.009	(Pyrites)	0.575	(Organic)

All results in weight %

Raw Material Selection
Shale with a tendenancy to efflorescence



Fluorine Content of Raw Materials

- "Content" only (pyrohydrolysis)
- "Mass Balance" (pyrohydrolysis) for potential emissions
- Use of HF information by various states
  - Relation to MACT status
  - Examples