

The Air Pollution Potential for Brick Making Materials and Additives

by

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Introduction:

Regulation of air emissions from brick manufacturing facilities started in developed countries over thirty years ago. In response to the regulations, there was a significant amount of early research to discover the fundamental causes of air emissions and the effect of process variables on the quantity of emissions in brick manufacturing. This early research usually considered acid gas emissions because of the initial regulatory interest in these species.

More recent research has focused on other species using bench scale techniques, including thermal analysis with evolved gas analysis coupling, to evaluate the potential for emissions. Coupled thermal analysis provides a powerful and convenient method for evaluating the emission potential of raw materials and additives used in brick making. Examples of these analyses are described, including new research on the effect of additives on acid gas emissions, the emission of organics, and the potential emission of metals. The use of coupled thermal analysis in evaluating the efficiency of adsorbent materials for acid gas control devices is described.

Literature Review:

Hydrogen Fluoride

It is well known that trace quantities of fluorine are situated in clay crystals with fluorine ions located in place of some hydroxyl (OH) ions. Dehne and Kolkmeier described the relationship between fluorine atoms in brick making clay and emission of hydrogen fluoride (HF) [1,2]. There are several early papers that deal with the quantity of HF that is contained in clays, shale, and other brick making materials. For example, Robinson found that many brick plants emitted approximately 1.6 kg HF/hr. [3]. Wilson and Johnson performed similar surveys of brick plant emissions that were used to establish emission factors expressed as weight of HF emitted per unit weight of fired brick products [4].

Despite the fact that the fluorine is released locally during dehydroxylation, the actual release from the brick into the kiln atmosphere can occur at higher temperatures due to retention of the fluorine "in the brick body" by active species. Therefore, the emission range for HF can begin at about 320°C and continue through the remainder of the firing cycle. Hill has described two periods of emission of HF, with the first corresponding to the dehydroxylation of the clay mineral, and with a second higher temperature emission due to temporary retention of the fluorine in the body and subsequent release of all or part of the fluorine [5]. When the fluorine is released, it reacts with water vapor locally to form HF, which is the major emission product, but in extremely dry atmospheres, SiF₄ can also be formed [5,6]. Emission of other fluoride species, including condensable salt species, is possible if certain cationic species are in the effluent gases [2].

Several articles describe the potential for retaining or "capturing" fluorine in the brick during firing by reacting fluorine with selected additives to the clay

raw material. In particular, alkaline additions including calcium carbonate have been used to provide a reduction in the emission of HF [1,5,6].

Sulfur Oxides

The emission of sulfur oxides in brick making has received considerable attention [4,7,8,9]. The term SO_x is a generic term describing emissions of SO_2 and SO_3 . In practice, SO_2 is the primary emission in brick making [9].

In a similar fashion as the case of HF emissions, the emission of SO_2 takes place in two periods [9,10]. The first emission of SO_2 occurs around 450°C, it and is attributed to the oxidation of pyrite (FeS_2) within the brick making raw material. This oxidation takes place in a stepwise fashion with an initial release of SO_2 during pyrite oxidation and with a higher temperature emission due to temporary retention of sulfates and with subsequent release of all or part of the sulfur as SO_2 [9,10,11]. Sulfur dioxide can also be released during oxidation of sulfur-containing carbonaceous matter at low temperature [12].

The second emission of SO_2 begins above 750°C and can continue through the firing cycle. This emission is due to the decomposition of “sulfates” formed on “active sites” on clay crystals or on particle surfaces. These “sulfates” are temporarily present until higher local temperatures cause their decomposition. This latter decomposition exhibits a low rate of reaction, and the rate is limited by the closing of pores within the body due to vitrification. If the sulfates are not completely removed during firing, it is well known that a potential for efflorescence exists [13,14].

Hydrogen Chloride and Nitrogen Emissions

Hydrogen chloride (HCl) emissions in brick making have received less attention in the literature. Amison has reported results from stack testing at brick plants including HCl emissions [8]. Due to the ionic size of the chloride ion, it is unlikely that chlorine is directly substituted into the clay mineral (as was the case with fluorine). Inorganic species (salts) and chlorine-containing organic compounds present with the clay are potential sources of HCl emissions.

Nitrogen oxide (NO_x) emissions in brick making mainly originate from the oxidation of nitrogen in the combustion atmosphere [8,13]. There can be emissions of NO_x during the oxidation of nitrogen-containing organics [13]. In several studies, the emission of NO_x in brick making has not been found to be significant [2,8,13].

Organic Emissions

Trace quantities of organic emissions in brick making originate from the incomplete combustion of fuels and from oxidation of organics naturally existing in the raw material. Because of the heating schedule in tunnel kilns, the oxidation of natural organics has been called “smoldering combustion” or “flameless combustion”, and the process leads to emission of molecules and molecular fragments in a process called “depolymerization”. It is well known that additives used to increase porosity (polymer powder or sawdust) also lead to organic emissions [2].

Organic emissions from raw materials or additives occur in the range of 200°C to 450°C [2,7]. Trace quantities of species such as benzene, formaldehyde, acetaldehyde and phenol have been detected in kiln emissions [2,13]. Organic emissions are reduced by altering kiln design and by controlling the kiln atmosphere when polymers are added to clay to increase porosity [13].

Particulate Matter

Particulate matter emissions in brick making consist of mineral matter, i.e. dust entrained in process gases, and condensable particulate matter. Condensable particulate matter theoretically can contain metals that have been volatilized during firing. While levels of particulate matter in brick plant exhaust are known, there is little bench scale work on these emissions due to the differences between bench scale and production scale processes [15,16].

Experimental

In bench scale studies to identify and quantify emissions, brick making raw materials were heated using traditional thermal analysis coupled with evolved gas analysis. For the study of acid gases and some organic emissions, a Netzsch STA 449C coupled to a Bruker Vector 22 FTIR (Fourier Transform Infrared Spectrometer) at The National Brick Research Center (USA) was used. Kaisersberger and Post and Kaisersberger, Post, Opfermann and Emmerich have described these instruments [17,18].

For the study of metals emissions, organics and nitrogen oxide emissions, a Netzsch STA 409C coupled to a Balzers MS (Mass Spectrometer) employing "skimmer coupling" was used at GSF (The Institute of Ecological Chemistry, Munich) and at Netzsch (Selb). Kaisersberger and Emmerich have described these instruments [19].

Thermal analysis experiments were conducted with a specimen size ranging from 100 milligrams up to about 30 grams. With full size brick units, heat transfer effects and large mass of bricks often produce emissions at higher ambient temperatures in kilns.

Acid Gases Emissions

Acid gas and other emissions from alluvial clay with sawdust added on heating with air atmosphere in the STA 409C with MS coupling are shown in Figure 1 (Range 108 to 638°C). For convenience, the carrier gas species have been electronically subtracted from the total MS output to reveal the emissions from the specimen. A compilation of evolved species in the mass range 0-60 atomic mass units is given in Table 1.

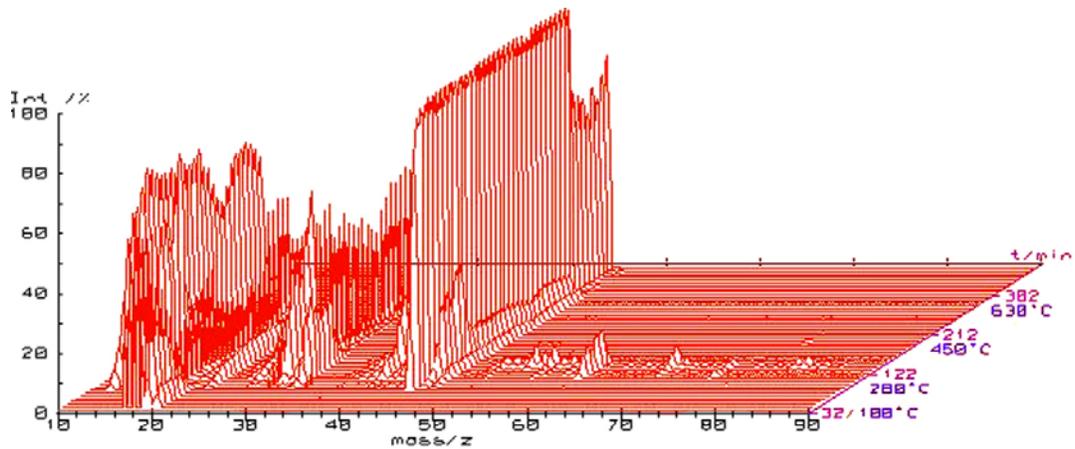


Figure 1: Emissions From an Alluvial Clay With Sawdust Added

Table 1: Emissions of Selected Species on Heating Alluvial Clay With Sawdust Added

Mass/Charge(z)	Species	Temperature Range, °C
12	C (fragment from CO ₂)	180°C+
18	H ₂ O	200-500°C
20	HF	200°C+
44	CO ₂	180°C+

The emissions from the alluvial clay mainly consist of carbon dioxide, water vapor, and hydrogen fluoride. The HF emission initially occurs during dehydroxylation and continues throughout the range of normal firing temperature. There is a suggestion of a nitrogen emission (mass/z = 28) in the range of about 180-500°C possibly originating from an organic form of nitrogen in the clay. There is a trace sulfur emission [mass/z = 28 (sulfur), 48 (SO), and 64 (SO₂)] with the first two species detected due to fragmentation of SO₂ in the MS detector. Emissions of organic species are visible above mass/z of 50.

A similar analysis using FTIR coupling on a blend of shale and fireclay raw materials containing pyrite is shown in Figure 2. As discussed earlier, the emission of SO₂ takes place in two regions with a low temperature emission due to the oxidation of sulfide (pyrite) and a higher temperature emission due to the decomposition of sulfates. The relatively small emission of HF is also seen in Figure 2. The measurement of HF by FTIR is difficult as it is present in the clay in minute quantities, and HF is a weak absorber of infrared. Additionally, there is some overlap in absorption with water vapor (labeled in Figure 2 as water vapor interference). The weight loss and water vapor traces are included in Figure 2. Emissions are summarized in Table 2.

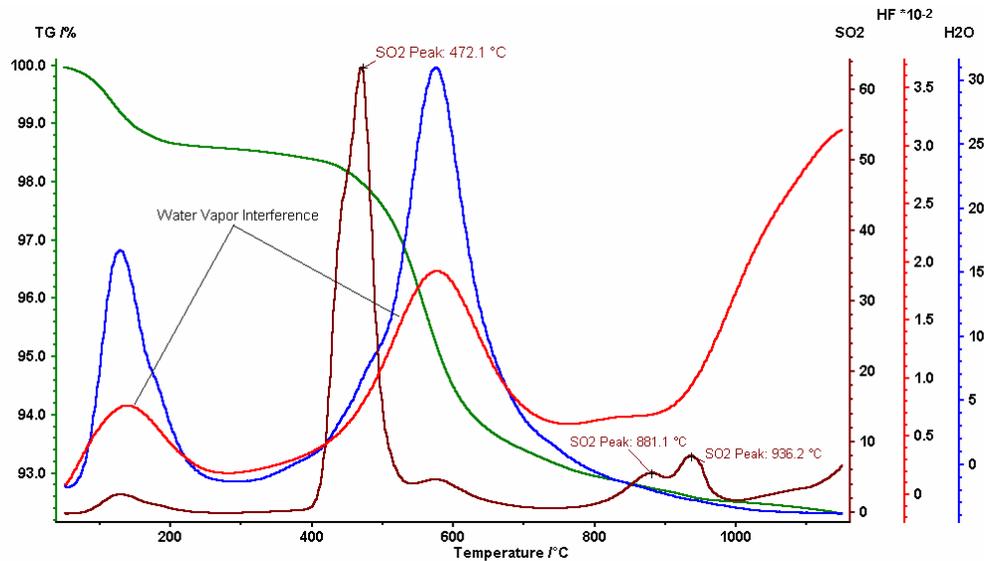


Figure 2: Acid Gas Emissions from a Fire Clay and Shale Blend

Table 2: Emissions From The Fireclay and Shale Blend

Trace For	Color of Trace in Figure 2	Approximate Temperature Range, °C
Weight Loss (TG)	Green	20-1150
SO ₂	Brown	400-520 and 800-960
H ₂ O	Blue	70-200 and 320-800
HF	Red	320-720 and above 920

With a basic emission assay from the raw material described in Figure 2, predictive experiments show how additives or process variables potentially influence emissions. In Figure 3, the emissions from the fireclay and shale blend are compared to emissions from the same blend with the addition of limestone to the mixture using FTIR. With the limestone addition, there was a small decrease in the amount of SO₂ due to pyrite oxidation, and there was a substantial decrease in the SO₂ released due to sulfate decomposition. The HF emissions were also significantly reduced due to the additive.

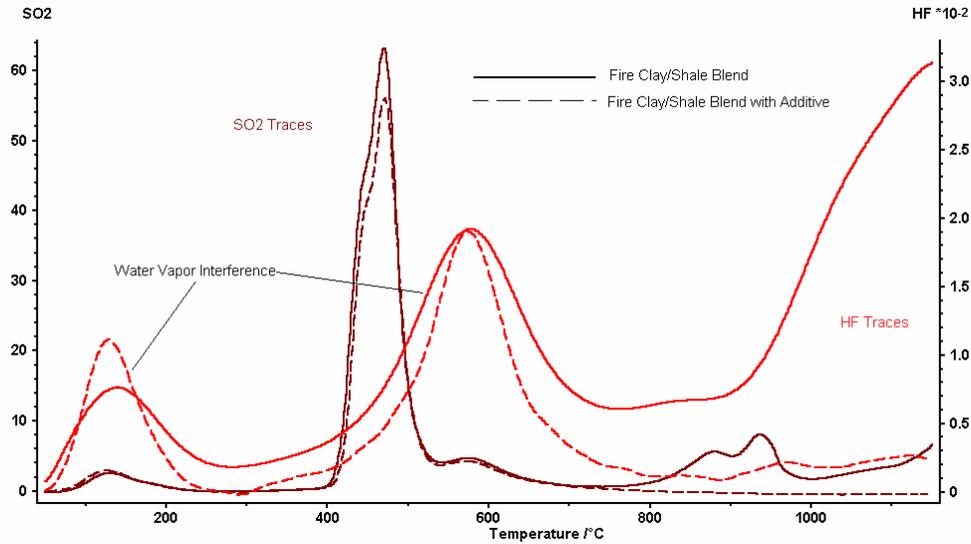


Figure 3: Comparison of the Effect of a Limestone Addition to the Acid Gas Emissions From a Fireclay/Shale Blend

An example of HCl emissions from a shale raw material, detected using FTIR coupling, is shown in Figure 4. The brick plant using this material was experiencing a corrosion problem with metal drying trays. The analysis revealed that the material emitted both HCl and SO₂ at high temperatures suggesting that carryover of acid gases into the dryer was a problem in the plant. Emissions are summarized in Table 3.

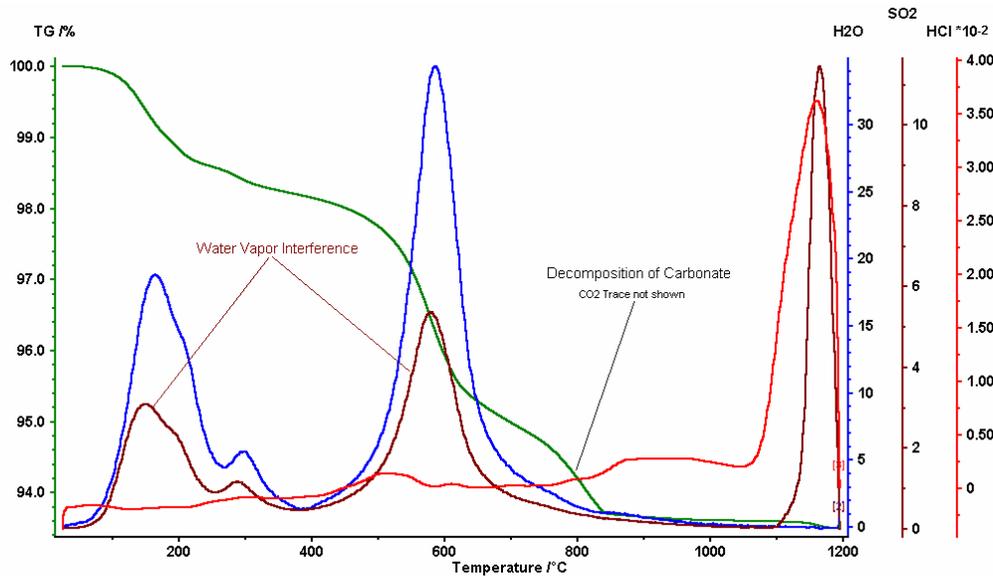


Figure 4: HCl and Other Emissions from a Shale Material

Table 3: Emissions from Shale in Figure 4

Trace For	Color of Trace in Figure 2	Approximate Temperature Range, °C
Weight Loss (TG)	Green	20-1200
SO ₂	Brown	400-520 and 800-960
H ₂ O	Blue	70-200 and 320-800
HCl	Red	450-560 and above 840

Emission of Organics:

In Figure 1, the MS instrument coupled to the STA 409 detected trace quantities of species with mass/z greater than 50 in brick making clay with admixed sawdust. The species detected from the same raw material mixture with mass/z greater than 90 are shown in Figure 5. The organic compounds or fragments detected on heating typically have mass/z equal to or greater than 58. It is clear from Figures 1 and 5 that these organic emissions are seen above 200°C.

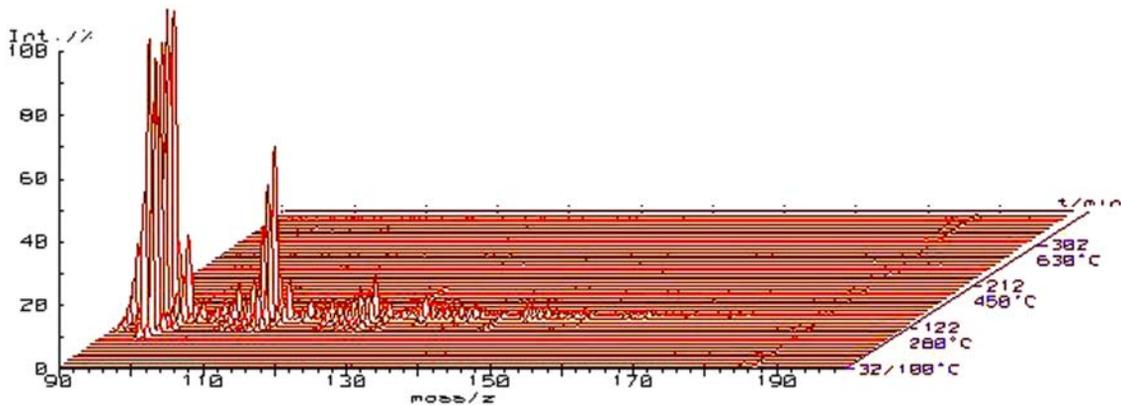


Figure 5: Emissions in the High Mass/Z Region For the Alluvial Clay Containing Sawdust

Other representations of this data for a given temperature (~310°C) are given in Figures 6 and 7. A listing of possible organic compounds in the emissions on heating is given in Table 4.

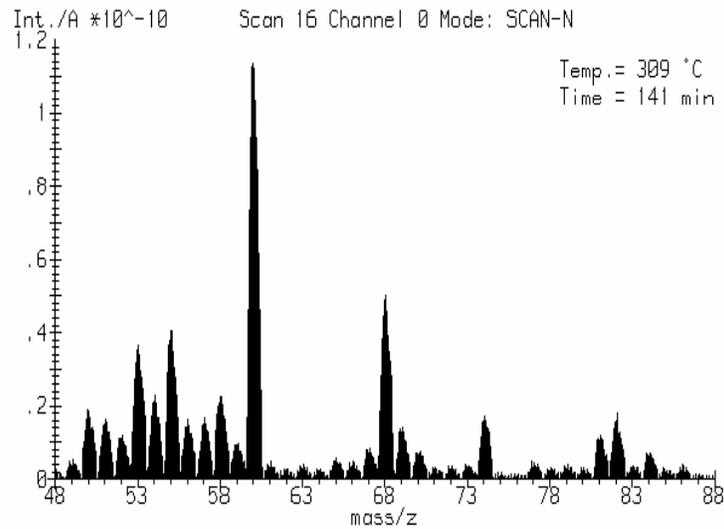


Figure 6: Profile of Emissions for Mass/z of 48-88

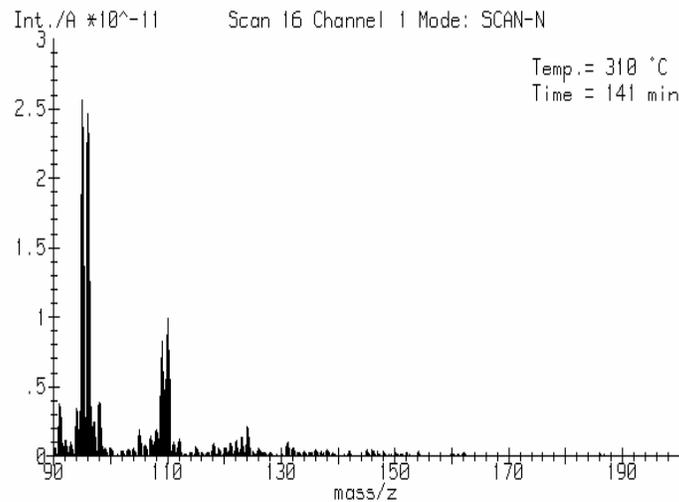


Figure 7: Profile of Emissions For Mass/z Greater Than 90

With substances such as acetone and phenol strongly suggested, it appears that “smoldering combustion” of the sawdust led to the emissions seen. In numerous tests of brick making raw materials that did not have sawdust added, only minor organic peaks in the same mass/z range were seen. Therefore, the examples shown were selected because of the nature of the emissions, but these examples do not represent the normal or typical situation for clays that do not contain sawdust.

Table 4: Organic Emissions Suspected in the Alluvial Clay With Sawdust Added at ~310°C

Mass/Charge(z)	Species
58-60	acetone
91-92	toluene
94-96	phenol
106-110	xylene

Organic emissions can also originate from hard forms of carbon, such as coal, that are entrained in fireclay or other materials. To study this case, additions of hard coal (anthracite) at one and three percent levels were made to low-carbon shale, and the emissions were observed on heating using FTIR coupling. The addition of coal generated two major exothermic peaks (350°C and 550°C). The material with no coal dust added exhibited an endothermic peak at 550°C due to the dehydroxylation of the clay mineral.

The comparison of the emission of volatile organic compounds (VOC's) in a neutral atmosphere (helium) is given in Figure 8. All three formulations exhibited low temperature emissions of VOC's. The specimens with coal added exhibited a large evolution of VOC's around 500°C due to the pyrolysis of the coal in the neutral atmosphere. The IR spectrum of the VOC emissions observed in this analysis is shown in Figure 8. The adsorption in the range shown is typical of carbon-hydrogen bonds.

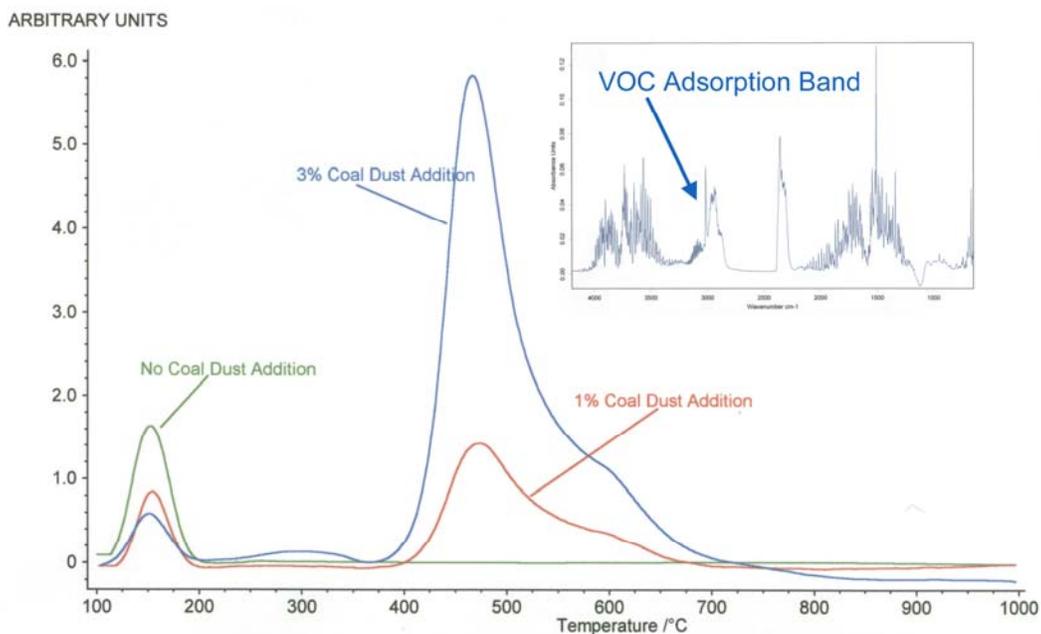


Figure 8: Comparison of VOC Emissions From the Oxidation of Coal Dust Mixed With Low Carbon Shale

Emission of Metals:

To check for volatilization of metals during firing of a brick with colorant oxides applied to the face, specimens of manganese oxides (MnO_2 and Mn_3O_4) and iron chromite were heated in an oxidizing atmosphere with observation of emissions using the MS "skimmer" coupling system. An example of the results for MnO_2 colorant (78.5% MnO_2) is shown in Figure 9 with evolved species identified in Table 5.

The largest weight loss with MnO_2 is seen in the range of 550-650°C associated with an endothermic reaction peaking at 594°C. During the endotherm, there is a large evolution of oxygen and a smaller evolution of CO_2 . A trace of "SO" is detected starting with the onset of the endotherm and continuing through the heating period suggesting the presence of SO_2 emanating from a trace impurity of sulfate. A second endotherm, associated with a smaller weight loss, occurs in the range of 825-1025°C. Oxygen is also evolved during this second endothermic reaction. An exotherm is seen above 1025°C suggesting oxidation of the colorant. It is significant that neither manganese nor manganese oxide species were detected during heating below 1200°C.

Experiments of the same type were conducted with a colorant grade of Mn_3O_4 (95.8% Mn_3O_4). In this case, a trace of CO_2 was noted at 356°C, and endotherms were seen at 1132 and above 1200°C. Evolution of MnO (mass/z = 71) was suggested above 1200°C, but this temperature is well above the normal firing temperature in brick kilns.

In a like manner, an iron chromite colorant (FeCr_2O_4 with 46% Cr_2O_3) was heated with an analysis of evolved gases. No metallic species were observed; however, a weight loss began above 1200°C. Regardless of the reason for the weight loss, there was no volatilization of constituents in the iron chromite at brick making temperatures (<1200°C).

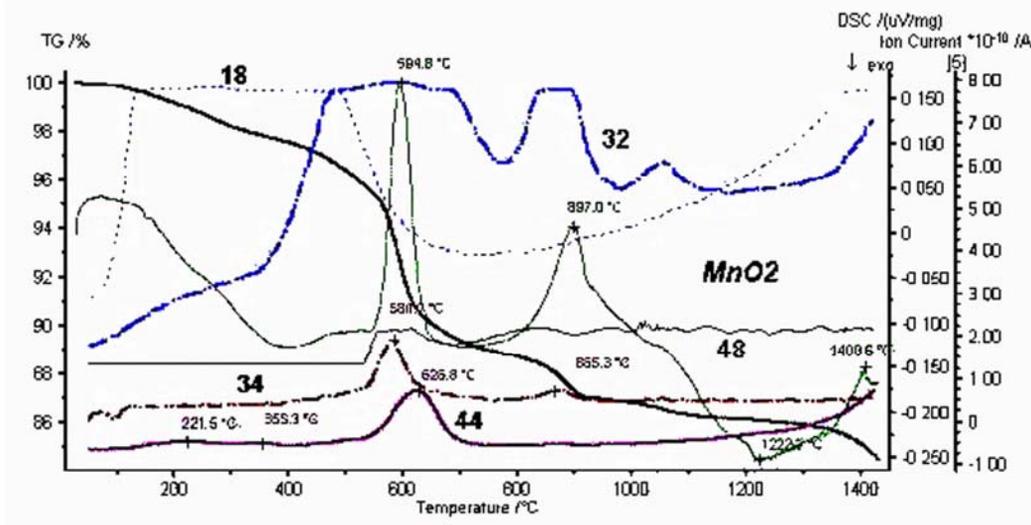


Figure 9: Evolution of Species Over MnO_2 Colorant on Heating

Table 5: Species Evolved on Heating MnO₂

Mass/Charge(z)	Species
18	H ₂ O
32	O ₂ (isotope 16)
34	O ₂ (Isotope 17)
44	CO ₂
48	SO

Comparison of Adsorbent Materials:

A novel application of thermal analysis with evolved gas analysis is comparing the relative efficiencies or adsorption rates of natural and synthetic materials for packed bed, dry adsorption scrubbers. To perform this evaluation, adsorbent granules were placed on a platform in the STA 449C and an acid gas of known composition was passed over the granules. The concentration of the acid gas was then monitored as a function of time by the coupled FTIR.

To determine how much acid gas was adsorbed during the experiments, the difference between the initial gas concentration (with no sample in the STA) and the gas concentration after flowing across the sorbent was used. This comparison allows observation of the adsorption rate, and it allows calculation of relative adsorption rates that could be used in the design and operation of scrubbers.

For this study, three adsorbent materials were compared including limestone of marine origin and two synthetic adsorbent materials. A summary of the physical properties of these materials is given in Table 6. The synthetic materials have higher porosity, higher surface area, and a smaller median pore size.

Table 6: Comparison of Adsorbent Physical Properties

Adsorbent	Porosity (%)	Surface Area (m ² /g)	Median Pore Size (μm)	Packed Bulk Density (g/cc)	Apparent Density (g/cc)
Limestone	19.3	2.9	0.539	1.17	2.71
Synthetic 1	38.1	40.7	0.036	0.78	2.20
Synthetic 2	27.6	7.5	0.060	1.05	2.58

To compare these materials, HF, HCl and SO₂ in dry nitrogen were individually injected into the STA. The HCl and SO₂ used were calibration gases, and the HF was generated using a permeation tube. The relative steady state adsorption for each adsorbent is given in Figure 10 at 200°C.

To calculate adsorption rates a linear approximation was made after the initial adsorption period. Further, these rates are reported as mass of acid gas per volume of adsorbent per minute. The volume of the adsorbent was taken as a loose-packed bulk density to simulate how these granules fill a packed bed scrubber. As can be seen in Figure 10 for HF, all of adsorbents had the same approximate adsorption rates while for both HCl and SO₂ the limestone had little adsorption.

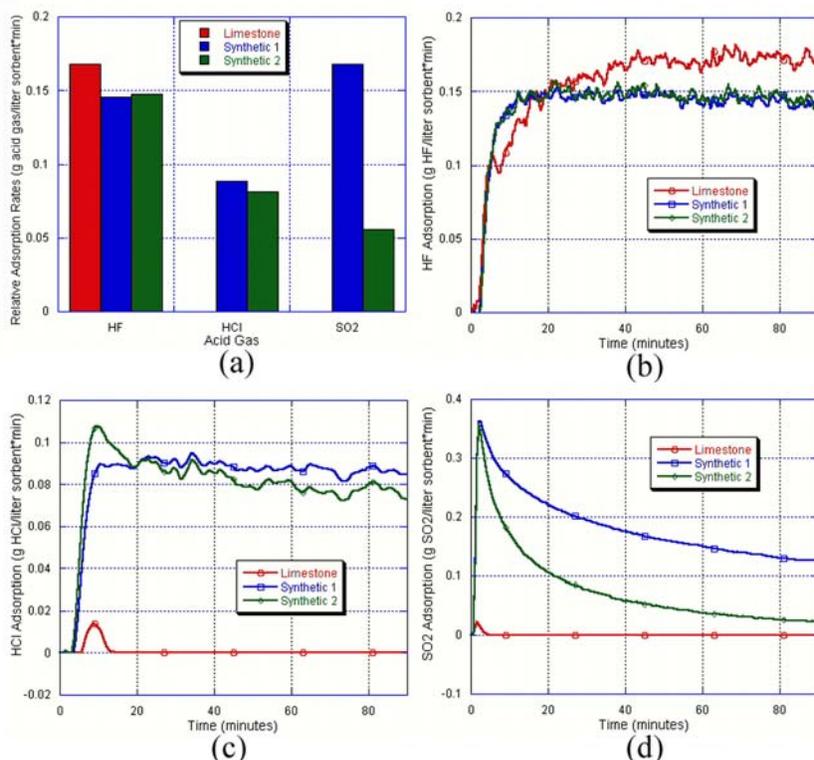


Figure 10: Comparison of Adsorption Rates

The adsorption rates as a function of time for HF, HCl and SO₂ are given in Figures 10b through 10d respectively. The initial period of the adsorption tests reflects the time needed for the acid gas dilution to fill the sample chamber of the STA and reach the gas cell of the FTIR. For the adsorption of HF (Figure 10b), after the initial period the adsorption rate was approximately constant for the duration of the test. With the adsorption of HCl (Figure 10c), the synthetic adsorbents were similarly effective, but after a brief initial adsorption, the limestone did not continue adsorption. A similar trend for limestone was observed for the adsorption of SO₂ (Figure 10d), and the synthetic adsorbents showed a higher initial adsorption rate followed by a declining rate period. This data suggests that this adsorption process for synthetic sorbents was controlled by diffusion of the acid gas through the pore phase and into the adsorbent grains. In the case of HF, with a relatively small molecular size, the adsorption rate was nearly constant. For SO₂, a larger molecule, the adsorption rate declined as a function of time.

Conclusions:

Bench scale studies using thermal analysis apparatus coupled to either MS or FTIR evolved gas analysis equipment has been used to study emissions and predict emissions of pollutant species from brick making raw materials and additives. The following was typically observed in numerous studies:

1. Acid gases evolve in characteristic patterns with an initial release due to a particular process and a secondary or continuing release due to a second

process. In the case of HF, the initial release occurs during dehydroxylation with HF typically detected in the range of 320-720°C, and the secondary release is detected above 920°C due to decomposition of temporary fluoride species. In the case of SO_x (or SO₂), the initial release occurs in the range of 400-520°C due to oxidation of pyrite, and the secondary release occurs in the range 800-960°C+ due to decomposition of temporary sulfate species. In the case of HCl emissions, a release may occur in the range 450-560°C due to oxidation of chlorine containing organic matter, and another release may occur above about 840°C due to decomposition of salts containing chlorine. In actual size bricks, temperatures of evolution of acid gases are influenced by size and heating rates so that somewhat different periods of evolution can be expected in practice.

2. Organics emissions occur due to smoldering combustion of natural organic matter in clay in the general range of 200-300°C, but hard forms of carbon such as coal entrained in clay may cause organic emissions in the general range of 400-700°C. In the case of clay with admixed sawdust, suggested emissions include acetone, toluene, phenol, and xylene as well as numerous molecular fragments due to depolymerization. Clay without sawdust additions emits only trace quantities of organics.

3. Studies with manganese oxide (Mn₂O₃ or MnO₂) and iron chromite (FeCr₂O₄) colorants revealed no metal oxide or "suboxide" species evolved on heating below 1200°C.

4. Thermal analysis with evolved gas analysis has been employed to study the relative absorption rates of acid gases by natural and synthetic sorbents used in packed bed scrubbers used by the brick industry.

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