ENVIRONMENTAL REGULATIONS AND THEIR EFFECT ON CERAMIC MANUFACTURING IN NORTH AMERICA

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ABSTRACT

While the Clean Air Act was enacted in the United States in 1970, the implementation of measurements and air pollution controls did not start for the traditional ceramic community of brick, tile, and whiteware producers until about 1990. By contrast, implementation of like regulations began in Canada at least one decade earlier so that installation of air pollution control equipment was largely complete in Canada before the regulatory process even began in the United States.

The focus of regulatory activity for ceramic producers in North America has been hydrogen fluoride (HF) emissions. Because of earlier implementation of emissions controls in Europe, there has been a great deal of published information on HF emissions; however, regulations developed in a different manner in the United States necessitating additional research. As emissions of sulfur oxides or SOx represent potentially larger quantities of emissions for many ceramic manufacturers, more recent attention has been directed to the origin and control of SOx. In addition, particulate matter emissions have come under increased scrutiny due to changes in the allowable ambient concentrations in the United States.

These regulatory considerations have forced many ceramic producers to purchase scrubbers, and others have reformulated their bodies to minimize air emissions problems. Now a low fluorine content "calcined" talc is available for use in the tile industry, and at least three tile producers in the United States have switched from talc based wall tile bodies to conventional clay-flint-feldspar bodies. Much greater attention has been recently directed to the sulfur content of ball clays.

INTRODUCTION TO REGULATIONS IN THE UNITED STATES

Under the Clean Air Act as amended in 1980, categories of air emissions were established as follows:

1) Criteria Pollutants - those listed under the National Ambient Air Quality Standards (NAAQS) which include particulate matter, sulfur oxide or SOx, lead, and ground level ozone all of which represent an immediate concern for public health according to the federal government. Some original criteria in the NAAQS were SO_2 (annual mean of 80 $\mu g/m^3$ and 24-hr. average of 365 $\mu g/m^3$), PM<10μ (annual mean of 50 $\mu g/m^3$ and 24-hr. average of 150 $\mu g/m^3$), and O3 (0.12 $\mu g/m^3$ 24-hr. average).

2) Hazardous Air Pollutants or "HAP's" - those listed as having an important, but secondary or less serious effect on public health which include hydrogen fluoride or HF and hydrogen chloride or HCl.

If an area in the United States did not "attain" the levels of ambient concentrations given under the NAAQS, the area was classed as "Non-Attainment". Ceramic manufacturers in Non-Attainment areas, such as Atlanta, GA, or Dallas, TX, were subject to greatly increased regulatory scrutiny which included installation of air pollution controls and greater difficulty in obtaining or changing their air emissions permits.

With respect to HAP's, much effort has been expended, since 1990, in developing emission factors, i.e. expression of emissions in terms of the quantity in pounds (lb.) or kilograms of emissions per unit weight of fired product produced with the product weight expressed in short tons (St) or metric tons (Mt). For convenience in this paper, only the metric quantities will be used.

It is important for ceramic producers which may be considering expansion into the United States to know two facts about the regulations:

1) The federal regulations are based on quantities rather than concentrations. For example, above a threshold of nine Mt per year of HF emissions, the facility is then regulated under the federal regulations which will dictate requirements for total controlled emissions in the year 2002.

2) Individual states may impose more stringent restrictions or a more accelerated schedule for implementation of controls than those in the federal regulations (imposed by the Environmental Protection Agency or "EPA"). Notable examples are the States of Texas, Connecticut, Maryland, and South Carolina which have more stringent or more accelerated compliance schedules for some segments of the ceramic community.

The federal regulatory agency (EPA) is currently developing Maximum Achievable Control Technology (MACT) standards. The form of these standards will be a maximum emission for a plant in terms of kg/Mt or lb./ton, and it will be the responsibility of the ceramic manufacturer to install controls to meet these MACT standards by the year 2002. There are many issues to be settled in the process including compliance monitoring procedures which will have a cost impact on manufacturers.

The President of the United States announced more stringent ambient concentrations for particulate matter and ozone on June 25, 1997. The new regulations change the 24-hr. ozone standard from 0.12 mg/m^3 to 0.08 mg/m^3 and institute a new standard for PM-2.5 (particulate matter < 2.5μ) with a 24 hr. mean of 15 $\mu g/m^3$. The effect on ceramic manufacturing will be seen beyond 2005, and it is difficult to predict the consequences of these new regulations.

HYDROGEN FLUORIDE EMISSIONS IN CERAMIC MANUFACTURING

It is well understood that fluorine occurs in most clay minerals in the range of about 200-800 ppm occupying hydroxyl sites in the clay crystal structure. Non-clay minerals such as

pyrophyllite and talc can exhibit fluorine contents as high as 1000-3000 ppm with the highest concentration of fluorine in raw materials which are more basic in character or which contain mica as an accessory mineral. It is also understood that fluorine is generally released during dehydroxylation, and it immediately reacts with water vapor forming HF in the kiln draft.

Stack testing data reported by Robinson[1] showed that most U.S. brick plants were emitting up to the equivalent of 1.6 kg of HF per hour with the maximum emission rate of about 3.7 kg of HF per hour. Work by Wilson and Johnson[2] surveying brick plants apparently led to adoption of the current emission factor used by the Environmental Protection Agency[3]. After 1992, the EPA conducted survey activities at brick plants and compiled data for other ceramic industries[4]. The results of these activities are presented in Table 1.

	Clay Brick Tunnel Kiln	Glazed Brick Tunnel Kiln	Quarry Tile Tunnel Kiln	Wall Tile Roller Hearth Kiln
HF	0.185	0.32	0.16	0.036
CO_2	200	180	70	100
NOx	0.175	N/A	0.47	0.14
SO_2	0.325	3.9	2.4	0.51
PM	0.50	0.14	0.59	0.028

Table 1. *EPA Emission Factors (kg/Mt) For Traditional Ceramic. Manufacturing with Gas Fired Kilns.*

The EPA emission factors given in Table 1 are obviously specific to the particular raw materials used by the ceramic producer. For example, the glazed brick data in Table 1 is from one ceramic manufacturer using fireclays and the clay brick data is from shale based plants. It is necessary for each ceramic manufacturer to obtain data specific to a certain plant. This is usually obtained by stack testing methods or by mass balance techniques using the pyrohydrolysis test[5].

The work of Hill[6] and that of Sanders[7] has been particularly important in the understanding of acid gas emissions. Using FT-IR to detect evolved gases during heating clay specimens, Hill found two regimes of HF evolution in the ranges 450-750°C and above about 900°C (Figure 1). The initial period of HF release was attributed to release of fluorine during dehydroxylation and the second period of HF release was attributed to decomposition of fluorine compounds formed temporarily on residual particle surfaces during and after dehydroxylation. Sanders similarly found two sulfur release regimes (as discussed below).

Storer-Folt has added to the understanding of fluorine emissions on firing[8]. Using thermodynamic calculations, he has shown that HF is the only stable fluorine species in a combustion environment, and this has been confirmed by Hill who found SiF_4 evolved on firing only if the combustion atmosphere contained less than about 3% water vapor.

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[1]. GILBERT C. ROBINSON, *"Fluorine and Brick - Past, Present, and Future,"* Report For The Center For Engineering Ceramic Manufacturing, Clemson University, August, 1992.

[2]. H. H. WILSON AND L. D. JOHNSON, *"Characterization of Air Pollutants Emitted From Brick Plant Kilns,"* Ceramic Bulletin, 54 (11)990-994 (1975).

[3]. *"Compilation of Air Pollution Emission Factors, AP-42,"* Fifth Edition, United States Environmental Protection Agency.

[4]. *"Ceramic Products Manufacturing, Emission Factor Documentation For AP-42, Section 11.7, Draft Report,"* United States Environmental Protection Agency, Research Triangle Park, NC (June, 1995).

[6]. *"Detection, Measurement, and Control of Gaseous Hydrogen Fluoride Emissions Produced When Firing Traditional Ceramics"* J. K. HILL, M. S. THESIS, Clemson University, December, 1995.

[7]. *"Measurement and Control of Fluorine Emissions From Ceramic Manufacturing"*, JOHN P. SANDERS, M. S. THESIS, Clemson University, December, 1993.

[8]. *"Techniques to Minimize Emissions,"* JOHN STORER-FOLT, CMC Workshop 8A on "Monitoring Emissions", Charlotte, NC, September 25, 1996.

Storer-Folt further revealed an equilibrium between clay particles and fluorine containing gases explaining that high fluorine partial pressure during dehydroxylation favor formation of fluorine-clay compounds which will not decompose until higher temperature regimes are experienced during preheat or soak.

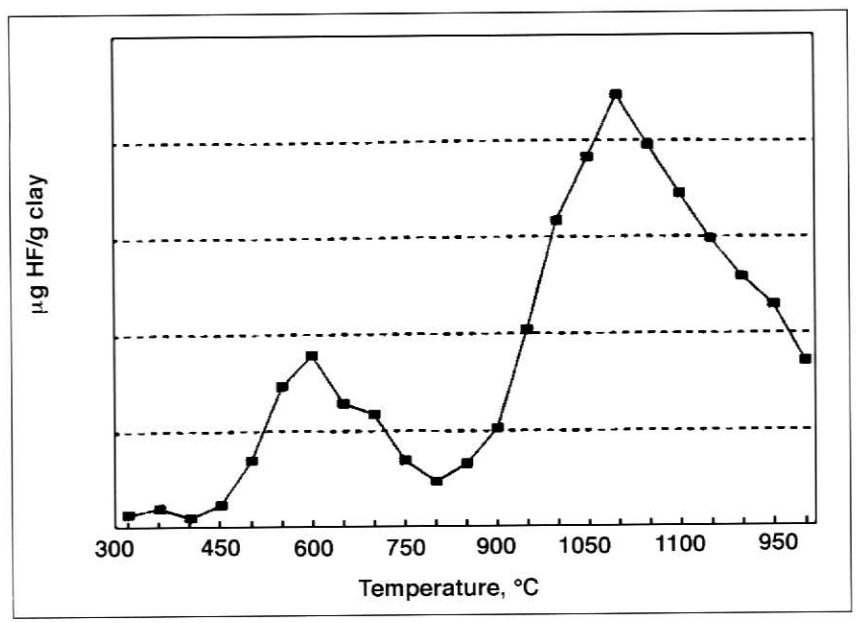

Figure 1. HF Evolution In A Water Vapor Containing Atmosphere.

SOx EMISSIONS IN CERAMIC MANUFACTURING

The data in Table 1 shows SOx emissions from the red clay body (brick and quarry tile) plants and the glazed brick plant all of which used raw materials containing traces of pyrite as an accessory mineral. The tile plant used ball clay containing natural sulfate minerals. Oxidation of the pyrite and/or decomposition of the sulfate led to the SOx emissions.

As mentioned above, Wilson and Johnson reported on emissions of SOx from ceramic plants in 1975, and their data shows SO_2 as the major sulfur oxide species in the stack emissions representing about 85 - 98% of the sulfur species present with the balance as SO_3[9]. This is no surprise since the equilibrium for the reaction:

$$SO_2\,(g) + 1/2O_2\,(g) = SO_3\,(g)$$

severely limits the amount of SO_3 formed above 500°C even in the presence of catalysts. Junge points out that while SO_3 formation may be thermodynamically favored at low temperatures, SO_2 formation is kinetically favored[10]. Therefore, sulfur emissions, primarily as SO_2 with some SO_3, arise in preheat from combustion of sulfur species, from decomposition of pyrite, or from removal of sulfur bearing conditioners/binders such as liganosulfonates.

In the heavy clay industry, most sulfur emissions result from the oxidation of pyrite (FeS_2) entrained in the raw material[10]. Using FT-IR analysis of evolved gases on heating by quantitative analysis of SO_2 (using the 1360 cm-1 absorption band and employing a 20

[9]. Reference 2.
[10]. *"Transport of Internally Generated SO2 Through Porous Clay Ceramics,"* JOHN P. SANDERS, Ph.D. Dissertation, Clemson University, December, 1995.

meter gas cell), Sanders found this oxidation to occur in the realm of 400-600°C for finely divided pyrite as shown in Figure 2.

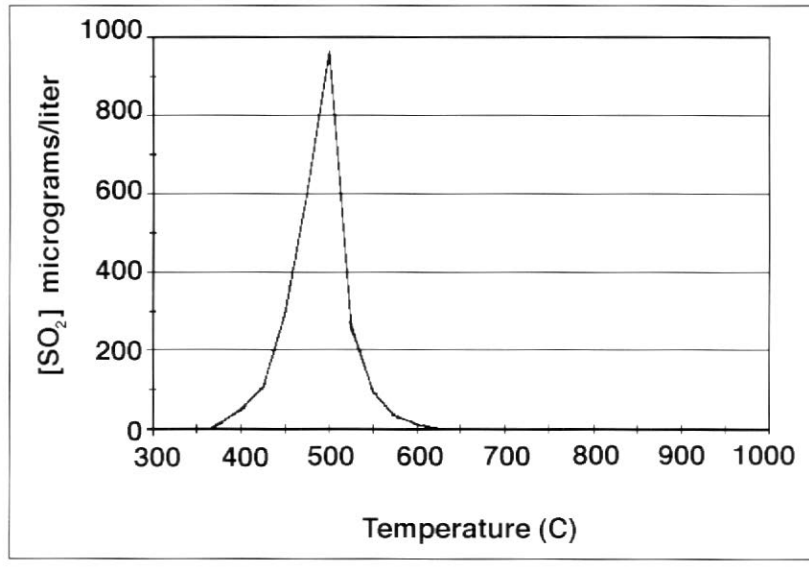

Figure 2. Emission of SO_2 For Pyrite (-325 Mesh).

Brownell[11] has stated that pyrite can decompose in two steps where[1] an initial step involves oxidation of FeS_2 to FeS and[2] a second step involves oxidation of FeS to Fe_2O_3. Thermogravimetric analysis of decomposition of -325M pyrite by Sanders appears to confirm Brownell's observations as two regimes of weight loss are observed of the same magnitude expected for the two stage oxidation (Figure 3). Since pyrite occurs as an accessory mineral in particle sizes up to several millimeters in clays, higher temperature sulfur emissions may be expected with coarser pyrite.

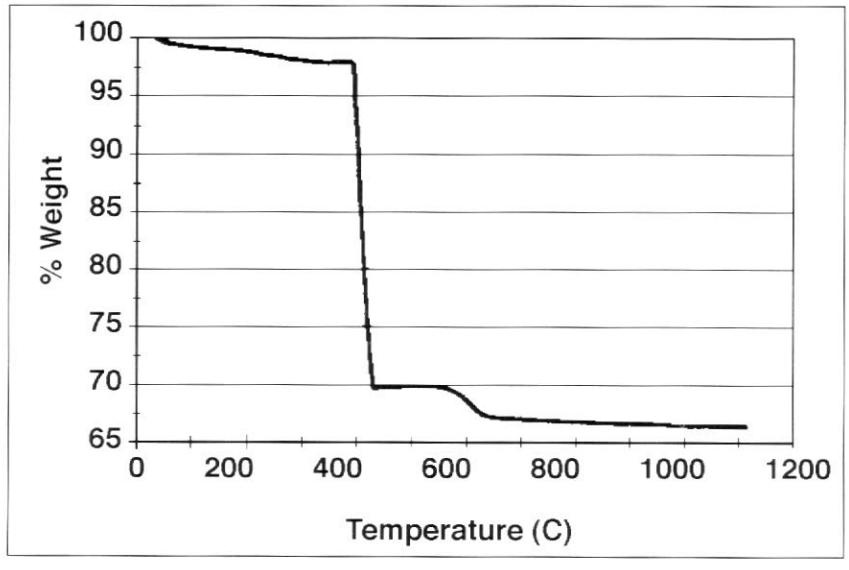

Figure 3. Thermogravimetric Analysis of Pyrite (-325M) Heated In Air.

[1]. Gilbert C. Robinson, *"Fluorine and Brick - Past, Present, and Future,"* Report For The Center For Engineering Ceramic Manufacturing, Clemson University, August, 1992.

[2]. H. H. Wilson and L. D. Johnson, *"Characterization of Air Pollutants Emitted From Brick Plant Kilns,"* Ceramic Bulletin, 54 (11)990-994 (1975).

[11]. W. Brownell, Structural Clay Products, Springer-Verlag, New York (1976). See also J. Blachere, *"Desulfurization of Pyrite"*, J. Am. Ceram. Soc., 49 (11) , 590-593 (1966).

In order to investigate release of SO_2 during firing due to pyrite oxidation, Sanders[12] made cylindrical specimens of a clay-shale raw material containing 0.4% pyrite (-325 M) additions which were fired in a tube furnace employing a flowing air atmosphere with heating at 3°C/min. The raw material used by Sanders did not contain natural pyrite.

The pyrite doped clay specimens were found to exhibit two regimes of SO_2 evolution as shown in Figure 4. The initial regime of SO_2 evolution corresponds to the oxidation of the pyrite in the range 400-600°C. The second regime of SO_2 evolution arises from the adsorption of sulfur bearing gases on the pore walls leading to the formation of surface sulfates that only decompose at higher temperatures releasing SO_2.

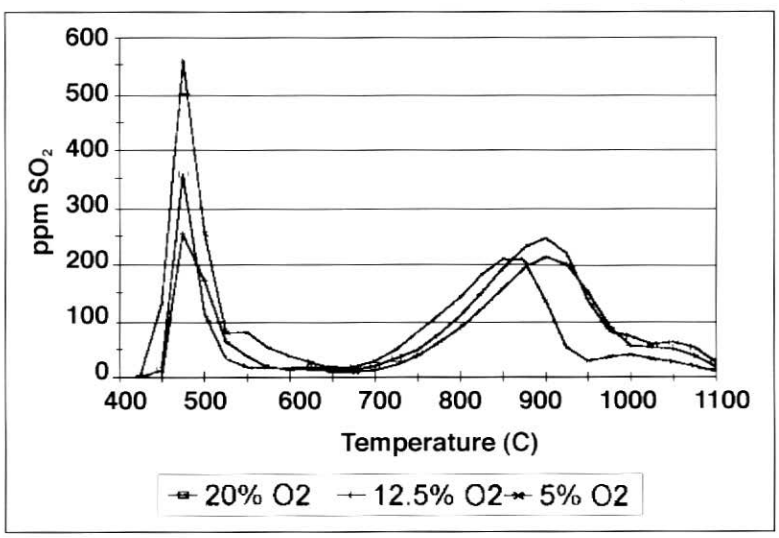

Figure 4. SO_2 Evolution Over Pyrite Doped Clay Specimens.

Since the raw material employed in this study contains a total of 5.2% of basic oxides (MgO, CaO, Na_2O, and K_2O), the temporary partial adsorption of SO_2 by the body seems plausible. Junge states that $CaSO_4$ begins to decompose at 950°C in clay systems[13]. Brownell found in clay systems that $MgSO_4$ decomposes above 750°C, Na_2SO_4 decomposes between 650°C and 700°C, and K_2SO_4 decomposes between 500°C and 600°C[14]. Adsorption of acid species by clays has been recently discussed by Storer-Folt, and Brownell states that even pure kaolinites can absorb SO_2.

The influence of oxygen content of the atmosphere (Figure 3) also supports the idea of temporary formation of sulfates. At higher oxygen contents, the emission of SO_2 is lower during the pyrite decomposition regime possibly because sulfate formation on the pore walls is favored.

A final possibility for SO_2 emissions due to accessory minerals concerns natural sulfate minerals such as gypsum in the raw material. While clay producers typically avoid clay deposits with significant gypsum content, some deposits contain finely divided and variable quantities of gypsum. The emission of SO_2 over such a material (primarily kaolinite-mica-montmorillonite) is shown in Figure 5. In this experiment, the furnace was heated and held at 1100°C for forty minutes until all SO_2 had been liberated.

The fact that sulfur emissions can result from decomposition of sulfates in clays

[12]. Reference 10.
[13]. K. JUNGE, *"Reduction of Sulfur Emissions In The Thermoreactor"*, ZI-Annual, 32-46 (1992).
[14]. Reference 11.

hasrecently become of concern in some traditional ceramic industries. Ball clays can range in sulfur content from a trace quantity of about 200 μg/g (or ppm) up to 2800 μg/g representing

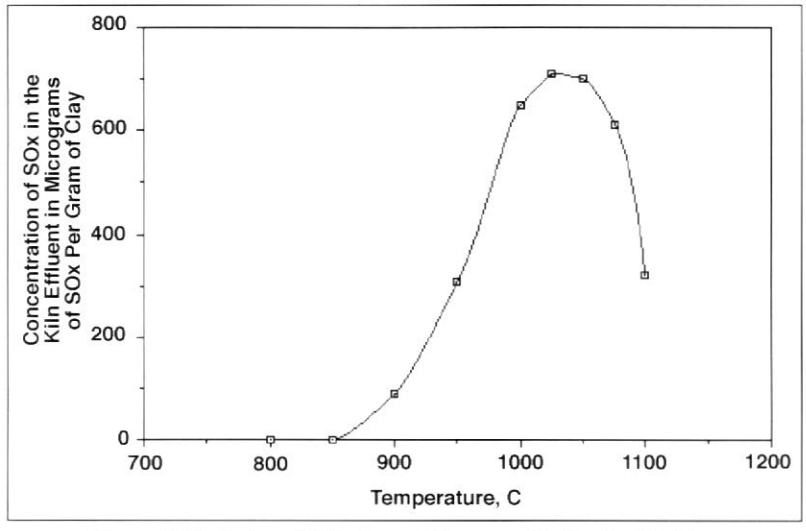

Figure 5. Emission of SO_2 From A Gypsum Contaminated Clay.

potential emissions in the range of 0.1-2.8 kg/Mg, and Wyoming bentonite can contain up to 1900 μg/g representing a potential emission of up to 1.9 kg/Mg[15]. Some ceramic tile producers have instituted sulfur content specifications in response to regulatory activities on SOx emissions.

PARTICULATE MATTER EMISSIONS

The particulate matter emissions for tunnel kilns (Table 1) all show emission rates of the same order of magnitude. The lower value for the glazed brick plant may reflect lower kiln cross sections and different setting patterns. The lowest value for the roller hearth kiln is not surprising.

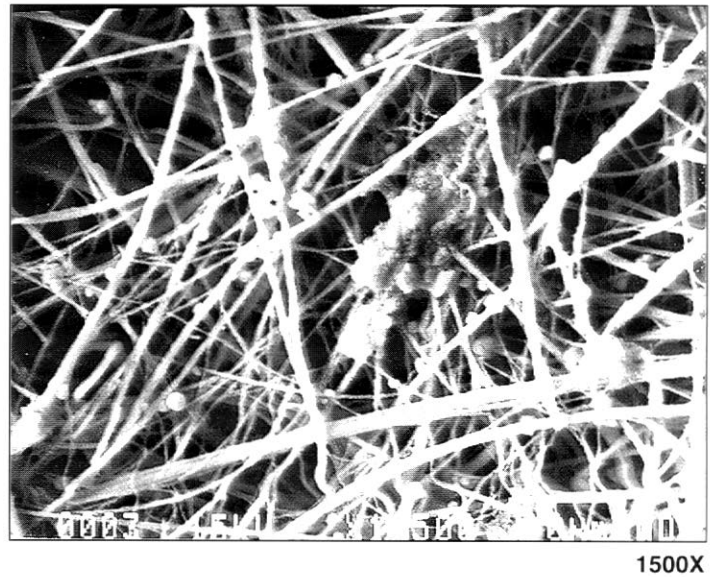

Figure 6. Brick Plant Stack Particulate On A Filter Pad.

[15]. H. SALMANG, Ceramics, Butterworths, London, p. 78 (1961).

Particulate matter found in kiln exhaust consists of condensable particulate and mineral matter. This is illustrated in Figure 6 for particulate matter found in the exhaust of a California brick plant near the seacoast. The particulate lying on the filter pad is generally about 1-3μ in size, and there is evidence of condensed salt on the filter. The salt was found to contain sulfur by Energy Dispersive X-ray analysis, and colorant particles (iron chromite) were likely present along with clay particles.

Particulate matter emissions from several brick plants have been determined to have stack emission rates from gas fired plants in the range 0.5-0.7 kg/hr. Measurements have shown generation of 2.4-4.8 kg/hr. of airborne particulates within a grinding/screening area of a brick plant without a dust collection system. This suggests environmental emissions of about 0.1-0.2 kg/hr. assuming 95% retention of particulate matter in the plant building. In a brick plant with dust collection, the generation of particulate matter in grinding and screening within the plant buildings was in the range 0.002-0.003 kg/hr. This information suggests that stack emission rates for particulate matter are more significant than other plant operations especially if the plant has dust collection equipment.

There is very little information on the particle size distribution of particulate matter in kiln stacks. Some brick plant data shows the largest percentage of 2.5 micron particulates in a tunnel kiln fired with wood flour (~48% <2.5 microns). One coal-fired kiln exhibited 23% of particulate matter <2.5 microns.

In the United States, regulatory agencies consider particulate matter to be "metals emissions" since the particulates consist of species containing metals. These emissions consist both of species carried into the kiln draft by various processes, and they consist of species that volatilized during firing. The latter species include the volatile metals shown in Table 2.

Pb	0.00042
Cd	0.000027
Cr	0.0001
Mn	0.0004
Ni	0.00006

Table 2. *Gas Fired Brick Plant Emissions of Volatile Metallic Species, kg/hr.*

These emissions can reach a significant level in a year's time. For example, the emission rate for Pb shown above can reach a total of 4 kg/year. This Pb emission is a regulated level in many areas in the United States classifying the manufacturer as a "major source". Many experts believe that metals emissions represent an area where future regulations will be developed for the ceramic industry.

SUMMARY/THE EFFECT ON THE CERAMIC INDUSTRY

Acid gas emissions including HF and SOx emissions are currently forcing ceramic producers to install acid gas scrubbers in the United States. There are currently at least four dry sorption scrubbers, four lime injection/baghouse scrubbers, and two wet scrubbers at North American ceramic plants, and it is reasonably expected that another 20 scrubbers will be added per year until 2002. This is costing ceramic plants an average of $1 million per plant and adding operating costs of at least $10/ton (in brick plants).

In order to avoid installing a scrubber, some tile plants have switched from talc

based bodies to clay/flint bodies or to the use of "calcined" talc. However, SOx content of ball clays continues to be an area of concern.

Regulations in the United States are expected to become increasingly stringent. The effect of new regulations on PM-2.5 and ozone generating chemicals is yet to be apparent. New announcements on greenhouse gases may further have an impact on the ceramic industry.