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Technology and Regulatory Consequences of Fluorine Emissions in Ceramic Manufacturing

The ceramic industry in the United States faces fluorine regulation under the Clean Air Act and its Amendments of 1990. The industry as a whole can still influence aspects of the regulatory process. However, immediate action is required if any benefit to industry is to be realized.

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Recognition of the effect of fluorine emissions on animal life may have been initially recognized in England where cattle grazing on a farm near a clay brick plant were found to suffer from "fluorosis," but the effect of fluorine emissions from ceramic manufacturing on vegetation was probably known for a number of years prior to the cattle incident.[1] Fluorine emissions are known to occur from aluminum smelting operations, calcination of phosphate rock, production of steel, and ceramic plants.[2,3] Fluorine is present in ground and seawater with concentrations reaching 1.3 mg/L (Ref. 3) and in ceramic raw materials in the general range of 0.01%–0.2%.[1,3,4] Fluorine evolution was particularly noted when topaz was calcined in tunnel kilns during the Second World War.[1,5]

Since cases of fluorine poisoning in humans are rare, the regulation of emissions from ceramic plants has been driven by a desire to protect agricultural interests. Regulation has been relatively recent with initial measures published,[6] for example, in Germany in 1978, the United States in 1980, and England in 1983. Implementation of regulations was first accomplished in Germany with the Clean Air Guide or "TA-Luft" of 1986.[4] In the United States, implementation has followed measures in Europe and Canada. The Clean Air Act and its Amendments of 1990 are being implemented in the USA with regulation of the tonnage-scale for the ceramic industry progressing through the year 2000.[7,8] The ceramic industry as a whole has been very passive in its reaction to the Clean Air Act. Only the glass industry sought to remove its classification as a source category for fluorine emissions.[9] The U.S. Environmental Protection Agency (EPA) currently has efforts underway which will influence the ultimate form and cost of the regulations to the ceramic industry. It is clear that the industry can influence the regulatory process so as to achieve the best possible outcomes with respect to air pollution control technologies, fluorine detection methods, and permitting processes. Since the federal EPA actions have significant influence on state agencies, the industry should have incentive to act as soon as possible to influence both state and federal processes. However, timely actions are necessary, or the opportunities to influence the regulatory process will be lost.

Technology of Fluorine Emissions

Raw Materials

It is generally recognized that fluorine is incorporated in the structure of sheet silicates by substitution in lattice positions for hydroxyl

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Table 1. Survey of Fluorine Concentration (% F^-) in Ceramic Raw Materials

Raw Material	Source	F^- Concentration (%)
Shale	NC	0.04
Kaolinite	TN	0.03–0.09
Halloysite	TX	0.07
Illite	OK	0.07
Montmorillonite		0.1–0.14
Talc	TX	0.37–0.45
Pyrophyllite	NC	0.23–0.29
Muscovite mica		0.0–0.4
Biotite mica		1.9–2.3 (Maximum)

groups.[10] According to Robinson,[1] fluorite (CaF_2) can occur in rare cases as an accessory mineral in clay. Fluorine is present in kaolinite, talc, and pyrophyllite which are common raw materials for production of ceramic tile and sanitary ware.[11] A survey of fluorine concentration in raw materials used in traditional ceramic compositions is shown in Table I.

Robinson and Edgington[13] found some soil samples in the United States which exceeded 0.7% fluorine. In general, fluorine increases with increasing alkali, and/or lime, and/or magnesia, and/or alumina content in clays. The high fluorine content of high-magnesia raw materials is due to the presence of mica in the material. It is generally observed that the highest fluorine concentration is found in the finest particle-size fractions of raw clay materials. Data for a number of brick plants are shown in Table II, where the submicron fractions typically exhibit a slight to a significant elevation in fluorine content.

Evolution of Fluorine On Heating

Fluorine evolution is detected on heating during the period of dehydroxylation of clays, i.e., above 500°–600°C. As the fluorine is released it forms hydrogen fluoride (HF)[1] Studies using thermogravimetric analysis with evolved-gas analysis by mass spectrometry have suggested that HF and silicon tetrafluoride (SiF_4) are the evolved species.[11] The SiF_4 is a consequence of HF reaction with silica in raw materials or any other silica sources at elevated temperature. For example, HF can react with silica sources in a gas-sampling train to form SiF_4. The SiF_4 will be converted to fluorosilicic acid (H_2SiF_6) as exhaust gases cool below the dew point of water.[1]

Other fluorine species are possible. De Jonge suggests that gaseous species of ammonium silicon fluoride can be evolved.[6] Robinson suggests that reducing conditions in preheat can favor ammonium silicon fluoride formation with exhaust potentially as a particulate fume.[1]

Kolkmeier[4] states that gaseous HF will react with any lime present in the ceramic body to form calcium fluoride (CaF_2) thereby leading to only partial release of HF through the plant exhaust stack. Dehne[14] clearly shows the influence of lime content

Table II. Fluorine Concentration (% F^-) for Brick Mixes

Fraction	Plant A	Plant B	Plant C
Ground mix	0.067	0.065	0.021
>50μ	nd*	nd	0.019
3–50μ	0.024	0.019	nd
0.35–3μ	0.054	0.078	0.078
0.1–0.3μ	0.103	nd	0.066

nd* = not determined

with lime-poor raw materials evolving fluorine at low temperatures, i.e., about 600°C, and lime-rich raw materials evolving fluorine above 800°C. Lime-rich raw materials were found to contain CaF_2 and calcium fluorosilicate phases. Evolution of SO_x can interfere with capture of fluorine by lime.[15] Reducing the permeability of the body to provide additional time for reaction of HF with lime is one strategy for fluorine retention in the body. The duration of exposure of the ware above 700°C was directly related to the quantity of fluorine released.

If CaF_2 is formed within the ceramic body, it will partially decompose during the highest temperature exposure in the soak zone of the kiln. Evolution of fluorine is linked to the presence of water vapor in the kiln atmosphere. Use of high-hydrogen fuels provides for a greater concentration of water vapor and favors fluorine evolution.[4] Calcium fluoride has been found to undergo hydrolysis above ~1200°C.[16] Robinson states that mixtures of clay and calcium fluoride exhibit fluorine evolution starting at ~1060°C.[1] Providing a glass phase is one means of increasing retention of fluorine or "capture" in the body. Additions of limestone or other sintering aids which reduce vitrification temperatures lead to reduced emissions. German literature points to the use of "sintering powders" to reduce emissions.[4]

Reaction of HF with ware in the preheat zone of countercurrent tunnel kilns, i.e., recapture of fluorine, has been observed by Kolkmeier[4] suggesting the presence of a fluorine cycle in a tunnel kiln. Hauck, et. al.,[17] in extensive experiments showed recapture of fluorine to occur below 700°C and extending to below 300°C. A net decrease in fluorine emissions was observed using the "rebonding technology."

Extensive research[17] at the Brick and Tile Research Institute (IZF) in Essen has shown that the firing schedule is directly related to fluorine release. The three strategies to reduce fluorine emissions include the following: increasing the preheating rate above the dehydroxylation temperature, reducing the firing temperature to the minimum to achieve the required properties in the ceramic, and reducing the soak time drastically. Operating variables in commercial tunnel kilns and their relationship to fluorine release have been discussed by Storer-Folt.[18] Kiln draft and exhaust temperature should be kept to a minimum to achieve minimum fluorine emissions.

A summary of factors which influence fluorine

Table III. Factors Influencing Fluorine Emissions

Factor	Strategy to Reduce Fluorine Emissions
Body chemistry	Use of high lime raw materials or lime additions
Body and setting density	Employ higher density of body or setting pattern
Atmospheric water	Use of low hydrogen content fuels
Preheating rate	Increase above dehydroxylation temperature
Soak temperature	Reduce to a minimum
Vitrification	Increase through use of sintering aids
Soak duration	Reduce to a minimum
Kiln draft	Reduce to a minimum
Kiln exhaust temperature	Reduce to a minimum

emissions is presented in Table III. The technology of using limestone additions to retain fluorine in the body is viewed as undesirable by most brick producers in the United States since their raw materials usually exhibit <1% lime. The prevailing view is that higher lime contents could lead to problems in freeze–thaw durability or in efflorescence induced by capture of sulfur oxides during firing. Many companies, throughout the world, produce brick with high-lime contents, so U.S. producers may need to reconsider this option. Limestone additions have been commonplace in the U.S. to prevent vanadium staining, so limestone additions are not unusual for other purposes.

Fluorine Emissions Testing

Wilson and Johnson[19] performed the first survey of brick plants in the United States establishing some baseline numbers for fluorine emissions as shown in Table IV. Robinson[1] states that all of the raw materials used in the Wilson and Johnson studies contained <0.5% calcium oxide which explains, in part, the very low retention of fluorine in the brick. In 1972, Dobbins and Robinson[20,21] surveyed 46 stacks at brick plants across the Southeastern United States. Stack concentrations of flourine ranged from

Table IV. Initial Survey of Fluorine Emissions From Brick Plants

Plant	Fluorine in raw material (%)	Fluorine in fired brick (%)	Fluorine released (%)	Fluorine in stack mg/m3	Fluorine in stack (µlb/ft³)
A	0.0170	0.0003	98.3	30.4	(1.9)
B	0.0077	0.0003	96.2	99.3	(6.2)
C	0.0151	0.0026	82.8	100.9	(6.3)
D	0.0549	0.0023	95.8	161.8	(10.1)

1.0–215 mg/m³ (Fig. 1). The highest emission rate found for fluorine was 3.3 kg/h (7.3 lb/h), with most plants exhibiting below 3 kg/h as shown in Fig. 2. These emission rates generally represent less than 0.3 g/kg of fired brick (0.9 lb/ton).

Tile industry emissions in the United States may be similar or higher than those for brick plants because of the high fluorine concentration in tile raw materials (see Table I). Fluorine concentrations in exhaust from tile manufacturing may reach 128–202 mg/m³ (8–12.6 µlb/ft³) yielding total fluorine emissions up to about 42 kg/day (90 lb/day).

The fluorine emissions from U.S. plants can be compared to those reported in England. Data published by Amison[22] shows British brick-plant stack fluorine concentrations to reach a maximum, as tested, of about 230 mg/m³ (or about 100 mg/m³ with concentration corrected to 18% oxygen in the exhaust). The rate of fluorine emissions was found to vary in England from 0.1–4.4 kg/h (0.23–9.7 lb/h). The British data is in a similar concentration range and of a similar quantity for emissions as discussed previously for U.S. plants.

Fluorine Scrubbers

There were various attempts to scrub flue gases of fluorine by powder injection, condensation, and dry sorption in Germany as regulations developed.[23] The dry sorption units have evolved as the preferred method for scrubbing. These devices employ lime-

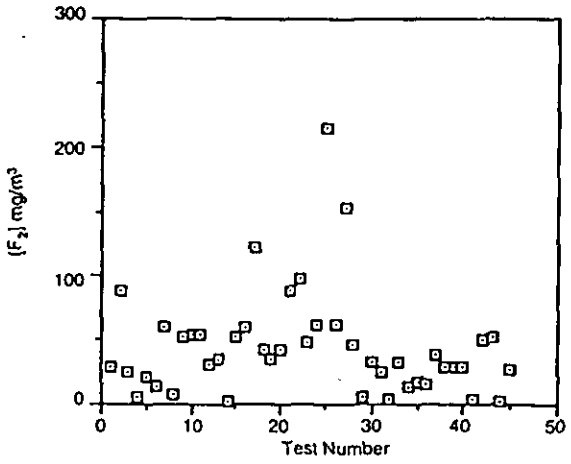

Fig. 1. Flourine stack concentrations.

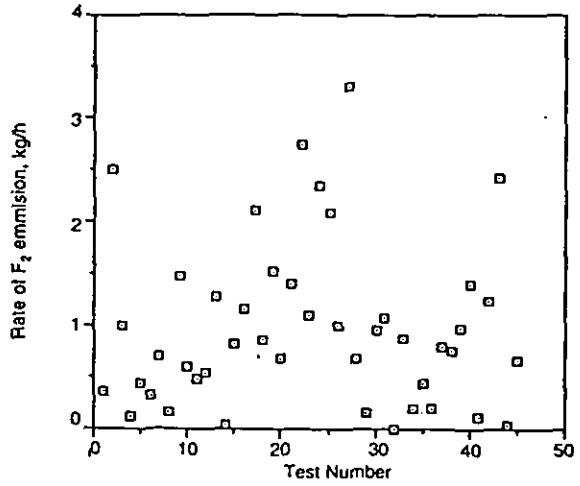

Fig. 2. Flourine emission rates.

stone as a sorption medium so that fluorine ions displace CO_2 on the limestone particle surface producing a coating of CaF_2 on the surface. This coating is typically removed using a rotating screen or drum. The residual calcium fluoride represents a disposal problem, and some work is reported on admixture of this product back into the brick body.[4]

Fluorine scrubbers are reported to exhibit 95%–99% efficiency for fluorine removal. There are three fluorine scrubbers currently operating on brick plants in North America. Actual efficiency numbers will be important as the EPA establishes maximum achievable control technology (MACT) as discussed below. Emissions of SO_x and volatile organic compounds (VOC) may drastically influence the performance of dry sorption scrubbers.

Regulatory Consequences in the United States

Requirements Under the Clean Air Act

The Clean Air Act (CAA) and its Amendments of 1990, in Title III—Hazardous Air Pollutants, provide for the following:

- Federal regulation of any industry emitting more than 10 tons/year of any single hazardous air pollutant (HAP) or 25 tons/year of any combination of HAP's. The 10 ton/year threshold can be changed in the future.
- A list of 189 chemical species classified as HAP's which includes hydrogen fluoride (HF), sulfur oxides (SO_x), and nitrogen oxides (NO_x). Particulate emissions are included in the CAA, but they are not included in Title III. The "Compilation of Air Pollutant Emission Factors," also known as "AP-42," contains data on particulate emissions.[24] This data is currently under dispute by the Brick Association of North Carolina.[25]
- A Title III "source list" was published in 1991, and the only ceramic industry to respond was the glass industry which petitioned to be removed from the source list for fluorine emissions on July 22, 1991. This request is still pending. It is possible for any industry to petition to be removed from the source list at any time, but successful removal of the brick industry is unlikely in view of regulations on HF and other HAP's in Germany, England, and elsewhere.
- A regulatory agenda or "schedule for standards" listing a timetable for implementation of standards by source and the initial regulatory limits was to be published in March of 1992, in the *Federal Register*. This appeared on September 24, 1992, with "Clay Products Manufacturing" scheduled in the last half of implementation of specific industries.[8]
- The initial maximum achievable control technology (MACT) regulations affecting the brick industry will be published in 1996 if the timetable given immediately above is followed. There will be a two-year period for public comment and revision.
- Permits under Title V will be due in late 1994, so ceramic companies will probably face producing extensive technical data as they did for National Pollution Discharge Elimination System (NPDES) permits.
- Draft regulations under Title IV (acid rain which affect NO_x and SO_x) are scheduled for issue during 1992 or early 1993 per EPA's schedule.
- State air regulatory agencies have either established their own regulations or they are writing them in anticipation of federal EPA regulations.

The ceramic industries have the opportunity to influence the regulatory process until about 1996 when regulations will be practically finalized. These opportunities are in the areas of air pollution control technologies, fluorine detection methods, and permitting processes. A proactive approach by the ceramic industry has been urged in the literature.[26]

Influencing MACT Criteria

The EPA will obtain information on scrubber performance to define the baseline all plants must meet. It is imperative that the EPA uses correct information in their determination of the baseline. This means that the plants in North America already equipped with fluorine scrubbers can be used as test sites for scrubber performance using testing methods and a testing protocol approved by the EPA. The industry should be proactive in obtaining their own certified test results so as to be prepared for public comment periods on MACT criteria. This will be the best and possibly the only chance the ceramic industry will have to insure that realistic MACT criteria are established.

Influencing Compliance Testing Methodology

Compliance testing will be a required activity once EPA regulation begins or as soon as any state environmental agency wishes to begin such activities. The issue of compliance testing methods is important, since it could add significant costs to manufacturing. The options include mass-balance methods, stack tests involving EPA's Method 13B or a modification thereof, and use of Fourier transform infrared spectroscopy (FTIR) devices for monitoring. The FTIR method could involve instrumental costs of about $100,000 per installation and annual costs for maintenance and operation. No information has been developed, for example, on how long mirrors in an FTIR sampling stack train will last in the presence of HF.

The EPA appears intent on a method which is selective for detecting HF since this is the only fluorine species included in the list of "Hazardous Air Pollutants." This intent to follow the law could end up requiring the industry to purchase FTIR instrumentation, since alternate methods usually reveal total fluorine in the effluent gases. In some parts of the world, mass-balance determinations (raw-material fluorine minus fired-product fluorine equals fluorine emitted) are considered sufficient for periodic

compliance monitoring. The cost of a mass-balance determination is <$100.

The ceramic industry has a significant opportunity to influence the compliance methodology by having data on alternative methods to present at public comment periods as regulations are developed by EPA. This will be the best and possibly the only chance the ceramic industry will have to insure that realistic compliance monitoring criteria are established.

Permitting

If the EPA follows its published timetable, the ceramic industry will experience significant costs on a plant-by-plant basis developing data to complete permit applications in 1994. The costs for fluorine stack emissions alone might total in excess of $10,000 per location. Therefore, any attempt to gather information to use in public comment periods as described above is money well-spent, since the money will necessarily be spent for permit applications.

Activities by CECM to Aid the Ceramic Industry

The Center For Engineering Ceramic Manufacturing (CECM) at Clemson University has ongoing programs to assist the ceramic industry as fluorine regulations develop. These programs include surveys of manufacturers with respect to emissions, evaluation of raw materials for fluorine content, and instrumental techniques for fluorine detection.

Summary

Fluorine emissions from manufacturing operations of traditional ceramics have been recognized as an environmental problem throughout the world for the last decade. The emissions arise from the occurrence of fluorine substituted in the crystal structure of clays and other sheet silicate minerals. On dehydroxylation above about ≈500°C, fluorine is evolved. There is a significant body of technology on fluorine emissions developed in Germany and elsewhere because regulations on emissions were implemented in other countries prior to the current implementation process in the United States.

The next decade will include finalizing the fluorine emission regulations with respect to permitting, compliance monitoring methodology, and maximum achievable control technology (MACT) criteria affecting the traditional ceramic industries. A window of only about three years duration exists for the ceramic industry to affect regulations. The regulations will be costly in terms of preparing permit applications, capital costs for scrubbers, and test fees or equipment and equipment operation for compliance monitoring. It is the option of the ceramic industry to be proactive and try to influence the regulations or to be passive and to bear the maximum future costs.

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