<table>
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<th>AP42 Section:</th>
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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 realised.

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Recognition of the effect of fluorine emissions on animal life may have been initially recognised 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. Fluorine emissions are known to occur from aluminum smelting operations, calcination of phosphate rock, production of steel, and ceramic plants. 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%. Fluorine evolution was particularly noted when topaz was calcined in tunnel kilns during the Second World War. 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, 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. 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. 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. 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...
groups. According to Robinson, fluoride (CaF₂) 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. A survey of fluorine concentration in raw materials used in traditional ceramic compositions is shown in Table I.

Robinson and Edgington 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 (H₂F) and silicon fluoride (SiF₄) are the evolved species. The SiF₄ is a consequence of H₂F reaction with silica in raw materials or any other silica sources at elevated temperature. For example, H₂F can react with silica sources in a gas-sampling train to form SiF₄. The SiF₄ will be converted to fluorosilicic acid (H₂SiF₆) as exhaust gases cool below the dew point of water.

Other fluorine species are possible. De Jonge suggests that gaseous species of ammonium silicon fluoride can be evolved. Robinson suggests that reducing conditions in preheat can favor ammonium silicon fluoride formation with exhaustion potentially as a particular fume. Kolkmeier states that gaseous H₂F will react with any lime present in the ceramic body to form calcium fluoride (CaF₂) thereby leading to only partial release of HF through the plant exhaust stack. Dehne clearly shows the influence of lime content 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 CaF₂ and calcium fluorosilicate phases. Evolution of SO₂ can interfere with capture of fluoride by lime. Reducing the permeability of the body to provide additional time for reaction of H₂F 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 CaF₂ 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. Calcium fluoride has been found to undergo hydrolysis above 1200°C. Robinson states that mixtures of clay and calcium fluoride exhibit fluorine evolution starting at 1060°C. 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.

Reaction of H₂F with lime in the preheat zone of countercurrent tunnel kilns, i.e., recapture of fluorine, has been observed by Kolkmeier suggesting the presence of a fluorine cycle in a tunnel kiln. Hauke, et al., 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 at the Brick and Tile Research Institute (ZIE) 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. Kiln draft and exhaust temperature should be kept to a minimum to achieve minimum fluorine emissions.

A summary of factors which influence fluorine

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**Table I. Survey of Fluorine Concentration (% F⁻) in Ceramic Raw Materials**

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Source</th>
<th>F⁻ Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale</td>
<td>NC</td>
<td>0.04</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>TN</td>
<td>0.03-0.09</td>
</tr>
<tr>
<td>Halloysite</td>
<td>TX</td>
<td>0.07</td>
</tr>
<tr>
<td>Illite</td>
<td>OK</td>
<td>0.07</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td></td>
<td>0.1-0.14</td>
</tr>
<tr>
<td>Talc</td>
<td>TX</td>
<td>0.07</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>NC</td>
<td>0.23-0.29</td>
</tr>
<tr>
<td>Muscovite mica</td>
<td></td>
<td>0.0-0.4</td>
</tr>
<tr>
<td>Biotite mica</td>
<td></td>
<td>1.9-2.3 (Maximum)</td>
</tr>
</tbody>
</table>

**Table II. Fluorine Concentration (% F⁻) for Brick Mixes**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Plant A</th>
<th>Plant B</th>
<th>Plant C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground mix</td>
<td>0.067</td>
<td>0.065</td>
<td>0.021</td>
</tr>
<tr>
<td>&gt;50µ</td>
<td>nd</td>
<td>nd</td>
<td>0.019</td>
</tr>
<tr>
<td>3-50µ</td>
<td>0.024</td>
<td>0.019</td>
<td>nd</td>
</tr>
<tr>
<td>0.35-3µ</td>
<td>0.054</td>
<td>0.078</td>
<td>0.078</td>
</tr>
<tr>
<td>0.1-0.3µ</td>
<td>0.103</td>
<td>nd</td>
<td>0.066</td>
</tr>
</tbody>
</table>

nd = not determined
MANUFACTURING

Table III. Factors Influencing Fluorine Emissions

<table>
<thead>
<tr>
<th>Factor</th>
<th>Strategy to Reduce Fluorine Emissions</th>
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</thead>
<tbody>
<tr>
<td>Body chemistry</td>
<td>Use of high lime raw materials or lime additions</td>
</tr>
<tr>
<td>Body setting density</td>
<td>Employ higher density of body or setting pattern</td>
</tr>
<tr>
<td>Atmospheric water</td>
<td>Use of low hydrogen content fuels</td>
</tr>
<tr>
<td>Preheating rate</td>
<td>Increase above dehydration temperature</td>
</tr>
<tr>
<td>Soak temperature</td>
<td>Reduce to a minimum</td>
</tr>
<tr>
<td>Verification</td>
<td>Increase through use of sintering aids</td>
</tr>
<tr>
<td>Soak duration</td>
<td>Reduce to a minimum</td>
</tr>
<tr>
<td>Kiln draft</td>
<td>Reduce to a minimum</td>
</tr>
<tr>
<td>Kiln exhaust temperature</td>
<td>Reduce to a minimum</td>
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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\textsuperscript{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\textsuperscript{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\textsuperscript{20,21} surveyed 46 stacks at brick plants across the Southeastern United States. Stack concentrations of fluorine ranged from 1.0–215 mg/m\textsuperscript{3} (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/m\textsuperscript{3} (8–12.6 lb/ft\textsuperscript{3}) 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\textsuperscript{22} shows British brick-plant stack fluorine concentrations to reach a maximum, as tested, of about 230 mg/m\textsuperscript{3} (or about 100 mg/m\textsuperscript{3} 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.\textsuperscript{23} The dry sorption units have evolved as the preferred method for scrubbing. These devices employ lime-

![Fig. 1. Fluorine stack concentrations.](image)

![Fig. 2. Fluorine emission rates.](image)
stone as a sorption medium so that fluorine ions displace CO₂ on the limestone particle surface producing a coating of CaF₂ 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.¹

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 SO₂ 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 tons/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 (SOₓ), and nitrogen oxides (NOₓ). 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.² This data is currently under dispute by the Brick Association of North Carolina.³

• 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 HAP’s in other countries 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.⁴

• 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 NOₓ and SO₂) 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.⁵

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 <s100.
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 ensure that realistic
compliance monitoring criteria are established.

Permitting
If the EPA follows its published timetable, the cerami-
c 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 manu-
facturers with respect to emissions, evaluation of raw
materials for fluorine content, and instrumental tech-
niques 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 pro-
cess in the United States.

The next decade will include finalizing the fluorine
emission regulations with respect to permitting, com-
pliance monitoring methodology, and maximum
achievable control technology (MACT) criteria affect-
ing the traditional ceramic industries. A window of
only about three years duration exists for the cerami-
c industry to affect regulations. The regulations will
be costly in terms of preparing permit applications,
capital costs for scrubbers, and test fees or equip-
ment and equipment operation for compliance moni-
toring. 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.

References
1. Gilbert C. Robinson, "Fluorine and Brick—Past, Present,
and Future," Report for the Center for Engineering Ceramic
Manufacturing, Clemson University, August, 1992.
3. R. C. Rieger, R. T. Vanderbilt Company; personal
communication.
4. H. Kolkmeier, "Emission Control In The Brick and Tile
5. O. J. Whittenburg, personal communication.
6. L. S. de Jonge, "Atmospheric Pollution by the Brick and Tile
7. Implementation Strategies For The Clean Air Act Amendments
8. R. H. Hunley, U.S. Environmental Protection Agency; personal
communication.
9. J. Raney, Monarch Tile Company; personal communication.
10. H. Hübner, "Geochronische Interpretation von
14, 1-15.
11. (a) L. S. Shahidi, "Fluoride Emissions From Brick and Tile Raw
Materials," in an Abstract to D. L. Bish, Los Alamos National
Laboratory, August, 1991. (b) S. J. Chipera and D. L. Bish, "The
Nature of Fluorine in a Partially Ordered 8V Clay," Earth and Space
Sciences Division, Los Alamos National Laboratory, Los Alamos,
NM, October, 1989.
12. Dennis A. Hennan, "The Brick Industry's Aggressive Program On
Fluorine", presented at the Southeastern Section Meeting of the
14. G. Dehne, "Relationship Between Fluorine Emission During
Firing of Ceramic Products and the Firing Temperature and the
16. L. Dendere, J. S. Macdonald, and A. W. Allen, "Stability of
Inorganic Fluorine-Bearing Compounds: Binary Metallic
17. H. Hübner and E. Hübner, "Possibilities For The Reduction of
Fluorine Emission In The Firing of Bricks and Tiles," ZI Ziegeliind.
18. J. Winter-Folte, D. Cooper, and E. Bocc, "Fluorine Release In a
20. W. S. Dobbs, "Stack Emission From Southeastern Brick
21. P. G. Robinson, "Fuel Consumption In Southeastern Brick
Plants in 1972," Report to the Glad Health Committee, Clemson
University, Clemson, SC, July, 1974.
GMBH, Wiesbaden, Germany, 1982.
Environmental Protection Agency, Research Triangle, NC 27711.
25. R. E. Stolfa, Brick Association of North Carolina; personal
communication.