AP42 Section:	11.3
Reference:	7
Title:	Monitoring For Hydrogen Fluoride Emissions D. A. Brosnan, " Ceramic Industry, July 1994.

Monitoring For Hydrogen Fluoride Emissions

Compliance monitoring is anticipated under the Clean Air Act, and the method required for monitoring hydrogen fluoride emissions remains in question

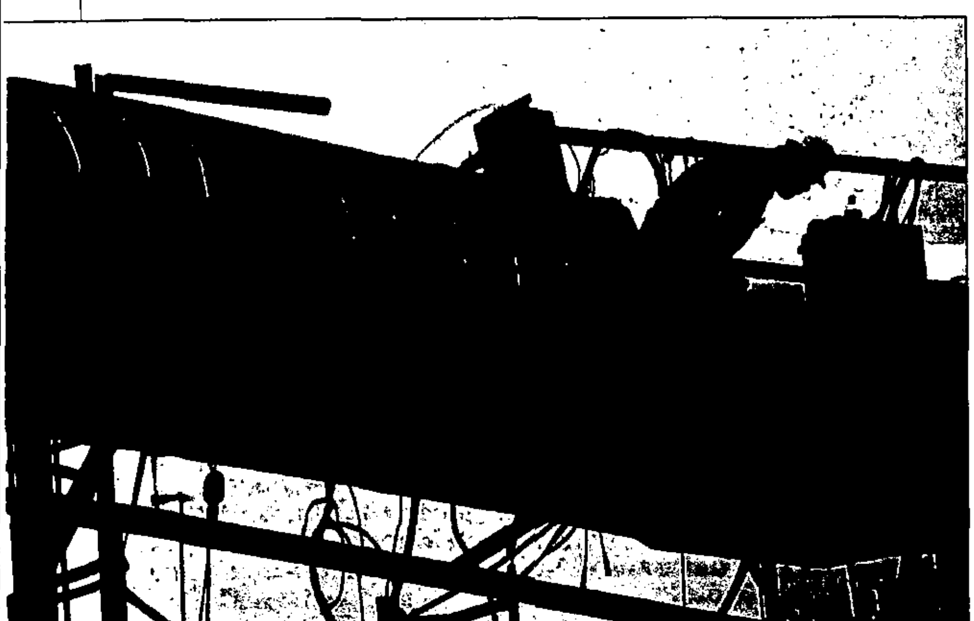
By: Denis A. Brosnan, Ph.D., PE, Director,
Center for Engineering Ceramic Manufacturing,
Clemson University, Clemson, S.C

Ceramic manufacturers have known for some time that hydrogen fluoride (HF) is a component of stack emissions from firing clay ceramics. Environmental effects include stunted vegetation around a few ceramic plants and rare reports of frosting of glass in plants, particularly during World War II when topaz minerals were calcined to produce mullite.

The reasons for emissions: most clays and shales contain 200 ppm to ≈800 ppm of fluorine (0.02-0.08% by weight) in isomorphous substitution for hydroxyl in the clay structure; fluorine is released as HF gas and possibly other fluorine species above ≈500°C (932°F) during dehydroxylation. Since fluorine content varies in different clay deposits, it is logical that HF emissions can vary from plant to plant. Therefore, plant specific test information may be appropriate in many cases to characterize emissions accurately.

HF is on the list of 189 hazardous air pollutants as regulated under the Clean Air Act and the 1990 Amendments. The implementation of the Clean Air Act is in progress, with most state agencies requiring detailed permit applications under Title V of the Act. These applications require information on a broad range of chemical species and particulate matter which are included in air emissions. Some of the species are those normally expected in stack emissions such as HF, NO_x and SO_x, but information on other trace emissions (e.g., metals and volatile organic compounds) is required.

The usual procedure for a manufacturer is to find a source of emission factor data (i.e., quantity of emissions per unit weight of product) and multiply production volume by the emission factor. The most widely used emission factor data pertinent to the ceramic industry are in the AP-42, Compilation of Air Pollution Emission Factors. Other data on emission factors are available.



Collecting stack test data at Pine Hall Brick, Madison, N.C., using a sample probe in a duct carrying kiln exhaust gases to the sawdust preheater. Photo courtesy Clemson University

The Clean Air Act will be fully implemented for the source category Clay Products Manufacturing in the year 2000. In preparation for implementation, EPA's Emissions Measurement and Emissions Inventory Branches have conducted source tests by stack testing at three brick companies in the United States during 1992-1993, with reports on these measurements recently becoming available.

EPA's objective is to update the AP-42 emission factors for HF and other species. Other important issues have yet to be resolved. For example, the method for compliance monitoring is of particular importance since the information used for compliance monitoring can be used in calculations of emissions levies or fees for manufacturers.

One low-cost possibility for compliance monitoring of HF emissions is the use of mass balance data, i.e., measuring the fluorine content of unfired and fired products and expressing the difference as the net fluorine released after converting the data to the same weight basis (usually fired weight). In fact, such procedures are in use in Germany, where practical regulations on inspection and compliance monitoring are used.

Data collected in the last year at brick plants in the United States indicate that mass balance will be both accurate and economical. This implies that many ceramic industries should be able to use the revised AP-42 emissions factors in calculations of emissions or use mass balance data if their emissions are lower than predicted using AP-42.

Mass balance by pyrohydrolysis

Pyrohydrolysis is a bench scale laboratory technique to determine fluorine content of a specimen by pulverizing the specimen, admixing an accelerator compound and heating the specimen in a flowing steam-air atmosphere for a sufficient time to remove all fluorine. The method was reported by Warf, et. al., in 1954, and it has been used in analyzing glasses.

Pyrohydrolysis has been shown to be clearly superior to conventional salt fusion techniques. Comparison of pyrohydrolysis data to mass spectrometry and use of NIST standards in calibration have demonstrated the precision and accuracy of the pyrohydrolysis technique with clay brick.

Facts on Pyrohydrolysis for Fluorine Determination

- Uses 500 mg of pulverized specimen mixed with 1000 mg V_2O_5 or other accelerator in a nickel combustion boat.
- Specimen heated to 850°C (1560°F) in 45 min and held for 1 hr in flowing steam (~2 mL/min condensate) in tube furnace employing a fused silica tube.
- Condensate diluted with buffer solution and measured for fluorine content using an ion specific electrode.
- Calibrate using NIST standards.

Analysis of raw materials from numerous brick plants across the United States has shown that raw materials can range in fluorine content from 141-1534 ppm. Fluorine contents in excess of ≈800 ppm may be found in illitic clays or those containing significant amounts of mica. Fluorine emissions, however, cannot be predicted from a raw material analysis alone, since a number of production factors influence the quantity of emissions.

Fluorine Analysis of Brick Clays by Pyrohydrolysis at Clemson

Raw Material	Average Fluorine [F] ppm	Range [F] ppm
Shale	527	324-876
Kaolin	362*	N/A
Illite	1099	760-1534
Fireclay	677	N/A
Alluvial clay	667	N/A

*Literature references suggest that some kaolins can contain substantially greater fluorine.

Mass balance is an acceptable method for estimation of fluorine emissions in Germany in the brick industry under the TA-Luft Regulations. Mass balance is used particularly in requests for permit change on introduction of a new product or upon exceeding permitted production rates. Because of its low cost, German manufacturers may use mass balance frequently in their own internal programs to ensure compliance.

Mass balance data for several U.S. brick plants show that the technique tends to over predict emissions as compared to stack tests for HF emissions. This is understandable since many factors which influence fluorine release vary from plant to plant. These factors include:

- Fuel type;
- Ramp rate to maximum firing temperature;
- Firing temperature;
- Time at peak temperature;
- Setting density;
- Exhaust temperature and dew point;
- Infusion of ambient air in kilns (leaks).

Comparison of Predicted HF Emissions by Mass Balance/Actual Stack Tests (EPA Method 26)

Plant (fuel)	Emission Rate (lb/hr) By Mass Balance	Emission Rate (lb/hr) By Stack Test	Over Prediction By Mass Balance % (Factor)*
A (gas)	3.3	3.1	[illegible]
B (gas)	6.5	5.0	30.0 (0.769)
C (gas)	9.2	[illegible]	[illegible]
D (sawdust)	15.7	8.0	96.2 (0.509)

* Stack test rate/mass balance rate prediction

The over prediction of HF emissions by mass balance for gas-fired plants is 6-33%. The key observation is that a factor can be assigned to each kiln which correlates actual emissions to predicted emissions using mass balance. If the factor is determined one time for each kiln by simultaneous stack and mass balance tests, then accurate predictions of emissions can be made for any product mix as long as mass balance data are available for each product.

The use of a correlation factor is plausible since it is known that ≈60-95% of fluorine in a brick body may be released depending on those variables in firing mentioned earlier. Since the pyrohydrolysis test was employed on top set brick products, the prediction does not account for temperature gradients in the kiln and other factors which may influence the total fluorine emissions. Statistically designed sampling methods could be expected to increase the factor closer to unity. However, the mass balance test cannot reach unity if there is excessive air leakage in kilns.

It is interesting that the mass balance method significantly over predicted the fluorine emissions in the case of the sawdust-fired brick plant. In a stack test series unrelated to the tests at the sawdust-fired plant, data were collected for another plant firing one brick product in both coal- and gas-fired kilns. The emission factor (lb/ton) for the coal-fired kiln was ≈45% of the factor for the gas-fired kiln for the same product. The differences were lower firing temperature in the coal-fired kiln (-50°F), significantly greater length and lower moisture content in the draft of the coal-fired kiln. Such differences among kilns also may explain the difference in predicted and actual HF emissions for the sawdust-fired plant (Plant D above).

Proper use of HF emission factors

Stack testing at brick plants during the period from 1993-1994 by the Center of Engineering Ceramic Manufacturing at Clemson University, Clemson, S.C., has shown that measured emission factors are usually below 1 lb of HF emitted per ton of product exiting the kiln. Tests have shown emission factors for shale-based brick mixes generally at 0.5-0.7 lb/ton, with some values in solid fuel-fired kilns as low as 0.2 lb/ton.

The current AP-42 value for HF emissions in brick manufacturing is 1 lb of HF emitted per ton of brick produced. Since this is the official emission factor, most states force companies to use it in filling out their air emissions inventories. But the case has been made that raw materials vary in fluorine content and processing affects emission rates.

Therefore, companies should have the choice of either:

- Accepting and using the AP-42 emission factor or,
- Presenting test data to show that actual emissions are less than those predicted using the AP-42 factor.

Implications on compliance monitoring

Compliance monitoring is anticipated under the Clean Air Act, and the method that will be required remains in question. The choices include:

- Mass balance predictions using a kiln correlation factor at a cost of ≈$100/test.
- Stack testing using Method 26 at a cost of $6000-$10,000/test.
- Stack testing using FTIR (Fourier Transform Infrared Spectroscopy) at a current cost in excess of $20,000/test.

Pyrohydrolysis furnace assembly showing condenser coil and collection flask. Photo courtesy Clemson University

It can be argued that the use of the mass balance method is essentially the same technical process as current use of AP-42 emission factors, i.e., use of an emission factor (lb/ton) multiplied by production volume (ton/hr) to predict emissions (lb/hr). Since this is true, requirements for stack tests in compliance monitoring would be unnecessary and an undue financial burden on industry. Therefore, industry should have the option to use either the AP-42 predictions or data based on the mass balance testing (which requires at least one stack test to develop a correlation factor).

Conclusions

HF emissions in ceramic manufacturing are a consequence of release of fluorine from clays as the products are heated in kilns. Fluorine contents of clays used in brick manufacture vary widely, and conditions in kilns influence actual emission rates of HF. Therefore, it is logical that emission rates can vary widely from plant to plant and from kiln to kiln.

Prediction of HF emissions can be accomplished using standard tabulated emissions data (AP-42) or by using actual test data. Manufacturers should be allowed to submit test data for emissions inventory or compliance purposes based on reasonably priced and sufficiently accurate test methods. Mass balance tests based on the pyrohydrolysis test offer the most economical means of emissions monitoring, and they essentially mimic current use of emissions factors using tabulated data. □

MIDWEST RESEARCH INSTITUTE
Suite 350
401 Harrison Oaks Blvd.
Cary, N.C. 27513
Telephone (919) 677-0249
Fax (919) 677-0065

FAX TRANSMISSION

TO: RON MYERS
FROM: R. MARINSHAW
TIME: 7:45
DATE: 7/20
CHARGE NO: ____________
(Task AND Subtask Nos.)

THIS FAX CONSISTS OF 4 PAGES (INCLUDING THIS PAGE)
RECEIVING FAX NUMBER: ____________
VERIFICATION PHONE NUMBER: ____________
COMMENTS:

HERE IS THE ARTICLE ON HF EMISSIONS.