

MINIMISATION OF FLUORINE EMISSIONS IN THE CERAMIC INDUSTRY

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1. INTRODUCTION

Fluorine is released into the air in the form of different compounds (HF , F_2 , SiF_4 , H_2SiF_6 , etc.) in many industrial processes. In ceramics, fluorine is released on firing secondary clays, where it can replace the OH or H_2O of the formulable illite $(\text{K}, \text{H}_2\text{O})\text{Al}_2(\text{OH}, \text{H}_2\text{O}, \text{F})_2\text{AlSi}_3\text{O}_{10}$ pointing up the reticular relationship of F^- , OH^- and H_2O . F^- , OH^- and H_2O . The fluoride content in the red clays used in Castellón varies between 600 and 1200 ppm, while that of the white clays does not exceed 600 ppm. However, the defect of calcium carbonate in these inhibits retention in the form of CaF_2 : firing emissions in all the cases exceed 10 ppm and reach up to 80 ppm.

Although Spanish legislation (RD 547/79) limits total fluorine emission to 80 mg/Nm^3 , the European Ceramic Tile Manufacturers' Federation (CET) approved certain environmental requirements accepted by the Spanish Ceramic Tile Manufacturers' Association (ASCER) as CET associate, which restrict the total fluorine emission in firing to 10 mg/m^3 . At the present time, the ceramic industry meets the Spanish legal emission requirement of 10-50 mg/Nm^3 but not the CET agreement, or the limit emission values of

the mandatory report of 31/10/2001 to the EU Commission established by Directive 96/61 Integrated Prevention and Pollution Control (IPPC).

Fluorides are quickly absorbed by the vegetation, producing foliar damage and reduced growth, even at concentrations as low as 0.1-0.8 mg/Nm³. Cattle also suffers locomotor and dental (fluorosis) dysfunctions when food contains of the order of 40 or 60 ppm in fluoride. The practice of water fluoridation (1 ppm) for human tooth decay prevention, although confirmed by the reticular reinforcement of dental apatite with fluoride reticulation, is a source of scientific and political controversy due to the arising damage in the middle term caused by the exposure to fluorine. Inorganic fluorides such as NaF, BaSiF₆, Na₃AlF₆ and Na₂SiF₆ have been used as insecticides by ingestion; NaF fell into disuse owing to its toxicity in plants and high solubility, as the complexes slowly release fluoride which remains effective for long periods of time. The toxic action of fluoride is linked to the formation of complexes and, therefore to inhibition, of various biometallic enzymes (Fe,Ca,Mg).

2. OBJECTIVES

The present work sets out the monitoring of fluoride performed in the Castellón ceramic area, where in connection with the ceramic centres, the normal value of 2mg/kg is exceeded in soils. In accordance with these data, possible minimisation strategies are analysed regarding fluoride emissions: (a) chemical adaptation of the ceramic body, (b) adaptation of the kiln atmosphere for direct heat recovery.

3. EXPERIMENTAL

Fluorine content analysis was monitored in soils of the Castellón ceramic district in the hydrological year 1999-2000, with three campaigns in February, May and September. The soil collected in non cultivated areas at a depth of 5 cm was sieved to 1 mm and dried in air (STSA), then mixed with water in a proportion 1:5, analysing fluorine by the selective electrode method in a buffered medium. Table I presents the results obtained in the three campaigns at the 28 sampling points: it shows that there is a clear connection between the ceramic tile environment and the presence of fluorine in the soil, which widely exceeded the 2 ppm value considered normal in the literature, and finding a value of 23 in the reference soil. The study of fluorine emission produced by clay materials can be followed by mass spectroscopy adapted to a DTA-TG system of the gas emission of the fired material, which exhibits a two-step mechanism: (a) clay dehydroxylation by siloxane bridge formation $-\text{Si}-\text{OH} + \text{F}-\text{Si} \rightarrow -\text{Si}-\text{O}-\text{Si}- + \text{HF}(\text{g})$, this process occurs between 450 and 750°C with emission peaks around 2 mg HF/kg clay, (b) decomposition of the fluoridated compound arising at the clay particle surface by reaction with water $-\text{Si}-\text{F} + \text{F}-\text{Si}- + \text{H}_2\text{O} \rightarrow -\text{Si}-\text{O}-\text{Si}- + 2\text{HF}$. In general the Si-F bond is very stable and can remain in atmospheres without water at high temperatures. If the water concentration is less than 3% in the kiln atmosphere, emission can take place in the form of SiF₄, though this is not usual in ceramic batches. In this second step an emission peak was detected at 1100°C of around 4-5 mgHF/kg clay^[4].

Sample	Environment	1 st Campaign	2 nd Campaign	3 rd Campaign
1	PR	25		
2	PR	12	4	4
3	PR	24		
4	PR	14		
5	PR*	10	27	10
6	PR*	6		
7	PR	21	20	4
8	PR*	11		
9	E+PR	77	88	76
10	PR	23		
11	E+PR	28	20	32
12	PR	43	38	18
13	PR	14	27	32
14	PR*	14		
15	PR*	10		
16	PR*	3		
17	PR	11	32	67
18	PR	15		
19	E	6	3	1
20	E	15	5	4
21	PR	9	11	3
22	E	6	7	22
23	E+PR	21		
Reference		2	7	2
25	PR		44	42
26	PR		22	49
27	E		13	1
28	E		22	4

Table I. Fluorine content (ppm), Castellón ceramic district soils (1999-2000).

Environment: PR(Floor and wall tile industrial estate), E(Glazes),(*)outlying point in rural surroundings.

The first HF emission peak and SO₂ emission overlap between 400-600°C with a peak at 500°C of 0.5-1 mg/Nm³, the thermogram indicating two reaction steps: (a) pyrite oxidation $\text{FeS}_2 + \text{O}_2 \rightarrow \text{FeS} + \text{SO}_2$, between 400 and 600°C, (b) sulphurate oxidation to hematite $2\text{FeS} + 7/2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_2$ between 600-650°C; the SO₂ also reacts with the clay material producing sulphates that break down in the 850-950°C range with weaker emissions of 0.1-0.2 mg/Nm³ occurring. Both emissions form the acid emission of ceramic firings with emission factors ranging from 0,1-0,3 gHF/kg clay and 3-5gSO₂/kg clay. The solution to these emissions is the use of a bag filter or electrostatic abatement system with previously mixed alkaline neutralising agents such as CaO, NaHCO₃ or CaCO₃.

4. CONCLUSIONS

The fluorine levels in the Castellón ceramic area exceed the normal values and are related to the acid deposition of the ceramic tile industry. To reduce these emissions and to reduce the treatment cost two work strategies can be established: (a) adaptation of the raw materials in pyrite, sulphate and fluorine contents, particularly replacement of talc by clays with a low fluorine content and grog reuse or the addition to the body of active

calcite, (b) the emission analysis indicates that in the cooling stage after 1000°C in a single deck kiln, besides losing a considerable amount of recoverable energy (practically 250 Kcal/kg), 50% of the fluorine and SO₂ emissions could be avoided

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