MINIMIZING BORATE EMISSIONS IN THE CERAMIC INDUSTRY

S. Sorlí, P. Benet, J. Calbo, M.A. Tena, G. Monrós.

Unit for Environmental Inorganic Chemistry and Ceramic Materials, Dept. of Inorganic and Organic Chemistry, Universidad Jaume I, Castellón (Spain).

1. INTRODUCTION

Borates are used in important quantities in ceramic glaze compositions as fluxes that do not raise the coefficient of thermal expansion, surfactants in fusion and promoters of the body-glaze bonding interface. In the fritting process, the borates added to the mill (borax, boric acid, ulexites, hydroboracites and colemanites) lose hydration water, forming a varied range of eutectics and glassy phases until the melt matures. In this process, borates are released between 140 and 300°C, which produce serious problems in baghouse filter operations that need to run above this temperature to avoid clogging by borate resublimates. The cleaning difficulties lead to solid borate deposition in fritting factory surroundings [1].

2. OBJECTIVES

The present study describes the monitoring of boron in the ceramic area of Castellón where, in the vicinity of the ceramic centres, the normal value of 1 mg/kg in soils is exceeded. In accordance with these data, the possible strategies for fixing boron are analyzed: (a) effect of the glaze composition on borate emissions, (b) study of borate leaching from the fritted material.

3. EXPERIMENTAL

The analysis of the boron content has been monitored in the soils of the Castellón ceramic district in the hydrological year 1999-2000 with three campaigns, in February, May and September. The soil collected in the non-farmed area at 5 cm depth was sieved at 1 mm and dried in air (STSA). This was subsequently mixed with water in a 1:5 proportion and analyzed for boron by means of the azomethine-H kinetic-colorimetric method. Table I details the results obtained in the three campaigns at 23 sampling points: it can be observed that there is a clear connection between the ceramic glaze environment and boron presence in the soil, exceeding the value of 1 mg/kg obtained in reference soil 23. The study of borate emission was followed by DTA-TG calorimetric analysis of the mixture to be fritted of a transparent frit of centesimal composition $B_2O_3(6.56)Al_2O_23(10.48)CaO(8.12)K_2O(7.74)MgO(2.50)Na_2O(2.26)SiO_2$ (57.27)ZnO(5.07) and of an opaque frit of centesimal composition $B_2O_3(6.48)Al_2O_2(6.24)CaO(9.01)K_2O(3.69)MgO(3.91)Na_2O(1.38)SiO_2$ (51.76)ZnO(8.42)ZrO_2(9.11). The frits obtained by fusion were subjected to leaching with a view to analyzing the frit borate fixing capacity in water [2]. The 1:16 frit:water ratio was held during stirring for different times measuring the leached boron.

4. RESULTS AND DISCUSSION

Figure 1 shows the DTA-TG (5°C/min) analyses of the samples of opaque glaze with and without the boron addition that was introduced as boric acid. When comparing both thermograms in the two frits, the losses are detected associated with the borates in the different thermal ranges: between 150 and 300°C for the opaque frit and between 240 and 300°C for the transparent frit. When analyzing these thermal ranges at rates of 1°C/min, borate weight loss was evaluated at 0.7% in the opaque frit and 0.2% in the transparent frit.

The boron leaching diagrams for the opaque and transparent frit indicate that in the opaque frit all the boron leaches in approximately 100 minutes, which means 13.3% of what was initially formulated in the frit. For the transparent frit the leaching was slower, eliminating all the leachable boron, which was only 2.4% of the initial boron, in 200 minutes.

Finally, 3 boron-containing frits of different types: (a) frit for transparent double firing, (b) frit for transparent porous single-fired wall tile and (c) frit for single-fired stoneware, were subjected to leaching by the foregoing procedure using 300 g frit [3]. The decanted leachates were cleaned using colloidal silica as an adsorbent (10%) and 200 ppm addition of mannitol as a borate sequestering agent, followed by 30 min stirring. The adsorbent was eliminated by centrifugation and the amount of boron present in the leachate before and after removal was measured, observing removal rates of the order of 20%.

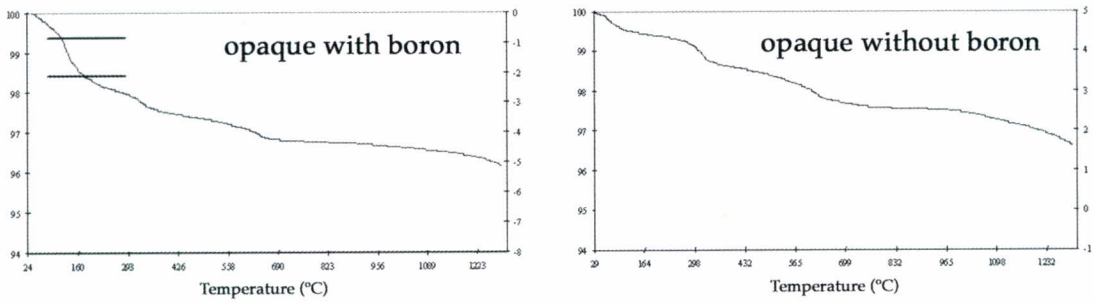

Figure 1. Thermograms (5°C/min) of the opaque frit showing borate-related losses.

Sample	Environment	1st Campaign	2 nd Campaign	3 rd Campaign
1	PR	3		
2	PR	3	2	7
3	PR	4		
4	PR	2		
5	PR*	3	9	9
6	PR*	4		
7	PR	2	3	6
8	PR*	3		
9	E+PR	6	6	6
10	PR	5		
11	E+PR	6	6	9
12	PR	6	4	7
13	PR	5	6	8
14	PR*	4		
15	PR*	4		
16	PR*	4		
17	PR	5	4	11
18	PR	4		
19	E	6	4	11
20	E	6	4	9
21	PR	6	4	13
22	E	5	4	14
23	E+PR	4		
Reference		1	1	1

Table I. Boron content (mg/kg) in soils of the Castellón ceramic district (1999-2000)

5. CONCLUSIONS

The boron levels in the Castellón ceramic area exceed the reference values and are related to depositions from the fritting industry. Borate fixing has been approached from the perspective of fritting emissions and frit leaching by water. The most fusible formulation (transparent) was shown to fix the borates best, while the borates were fixed worse in leaching of the less fusible frits (opaque). Finally, the strategy of borate removal from the leachates using colloidal silica as an adsorbent and mannitol as a sequestering agent only enabled eliminating 20% of the leached boron from the waters.

6. ACKNOWLEDGEMENTS

The authors thank Bancaja Foundation (Project P1-1B2001-23) for financing the study.

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