EMISSION AND ABSORPTION OF S-BASED GASES IN CERAMIC TILES

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ABSTRACT

The emission of sulphur-based gases during the firing process of red earthenware ceramic tiles, made of red clays from the Apennines, was investigated in detail.

Interesting and non-conventional data were found on analyzing the kiln stack atmosphere with an EGA analyzer and evaluating the S content in the tile bodies (both glazed and unglazed).

The presence of SO_2 was observed in the kiln atmosphere in the thermal range 500-1140°C, but no gas concentration was found in the neighbourhood of the kiln stack.

However, a large sulphur content was detected in the tile bodies in all the kiln sections during firing, and even at the end of the process.

The study proposes a new mechanism to explain these phenomena, based on sulphur re-adsorption in the tiles, depending on temperature and powder size in the pre-heating stage.

INTRODUCTION

Italian law on kiln emissions sets limits for the various pollutants. The limits for the SO_2 emissions are extremely low in view of the fact that this pollutant is very harmful. Elimination of the pollutant is therefore advisable. The techniques in this field are already consolidated and lead to higher production costs.

Sulphur-rich red clays from the Apennines are used in the production of floor and wall tiles (Sassuolo ceramic district). In this case, according to the Law of 12 July 1990, the limit for SO_2 concentrations in the emissions is 1500 mg/m^3. As the methane used in the plants has extremely low sulphur levels, the SO_2 content can only stem from the sulphur present in the raw materials used. The sulphur content produces undesired effects in fast firing (such as pinholes and increased black coring) [1], but it is not considered to be a hazardous pollutant owing to its low levels [2].

This report sets out a study of the sulphur and sulphur compounds that are released on fast firing Apennine red-clay mixtures with heat recovery from the flue gases.

EXPERIMENTAL

MATERIALS

Several Apennine red-clays were studied. Table 1 lists the analysis of the clays used and Table 2 gives some blend formulations with their corresponding sulphur content.

METHODS

In the first step of this investigation, different tiles were prepared and fired in an Explorer ERL 12-1200, thermal process analyzer. The heat-treatment cycle was the same as the industrial cycle. The emissions were determined by placing an emission gas capturing tube on the tile surface and reading the results with a detector.

In the second step, the gases were analyzed inside the industrial furnace, in each case extracting the gas and analyzing it with the same detector.

Clay	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	S	C	L.O.I.
1*	58.7	17.9	6.50	0.80	1.98	2.13	3.70	1.43	0.07	0.60	6.62
2**	52.3	19.1	6.80	0.75	2.65	3.15	2.41	0.92	<0.01	1.53	11.70
3***	63.7	16.4	6.75	0.69	0.31	1.88	3.02	1.34	<0.01	0.25	5.10

Table 1 – Chemical analysis of three red clays from the Apennines (wt %)

1 = Cavalieri clay 2** = S. Leo clay 3*** = Vallo clay*

	Clay 1*	Clay 2 **	Clay 3 ***
Blend no. 1	65	35	0
Blend no. 2	75	25	0
Blend no. 3	53	37	10

Table 2 – Typical blends for red single firing (wt %)

RESULTS

During firing in the laboratory furnace SO_2 levels were established as a function of the furnace temperature. In Fig. 1 (blend no. 3), the emissions peak at 900°C with a total content corresponding to the S level present in the blend as sulphides. No black core was found in the fired material.

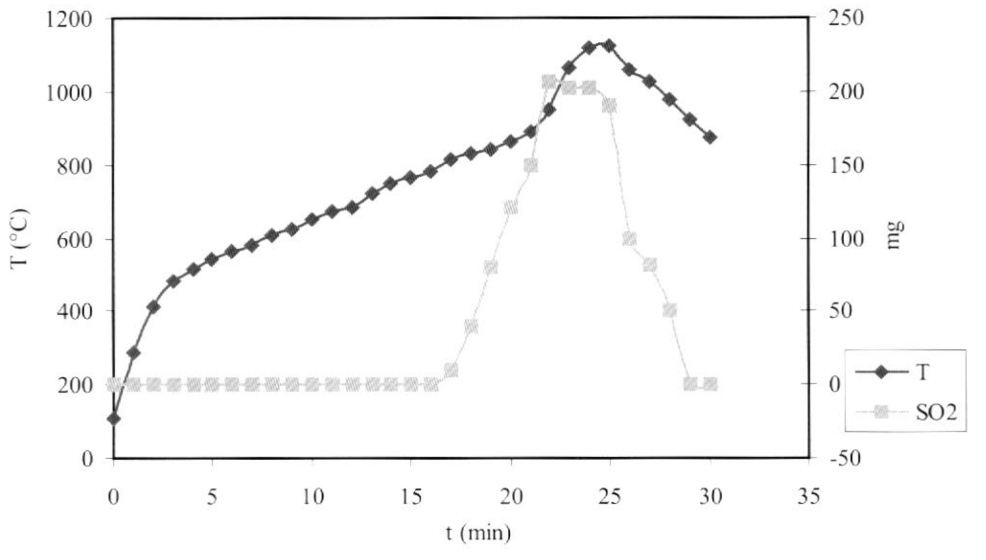

Figure 1 – Sulphur dioxide emissions in the laboratory furnace.

In the industrial kiln with flue gas recycling, gases were released at a temperature of almost 400°C, as recovered gas heat in counterflow is used to heat the product during firing. Flue gas analysis in the stack showed no presence of SO_2.

A close connection was found between the laboratory and industrial kiln emissions, in both cases with no SO_2 presence at the stack. To explain these data, two hypotheses were considered:

- A reaction between SO_2 and the furnace walls;
- A reaction between SO_2 and the material being fired.

The first hypothesis was discarded because no evidence was found of sulphate compounds on the furnace walls.

The second hypothesis was verified by analyzing the presence of sulphates in the fired materials.

The analyses were conducted on the powdered tiles treated with diluted hydrochloric acid and added to a $BaSO_4$ solution. The results were consistent with sulphur presence in the raw materials (see Table 3).

	S % in green body	S % in fired body	$SO_4^{=}$ % found	Calculated S %
Blend no. 1	0.048	0.053	0.1531	0.051
Blend no. 2	0.055	0.062	0.1826	0.060
Blend no. 3	0.042	0.046	0.1256	0.045

In view of the above data, the assumption was made that SO_2 reacts with the piece during the firing process, probably with the highly reactive products created by the break-up of the clay lattice at low temperatures (500-600°C). Moreover, a SO_2 reaction with Al_2O_3 can be suggested, owing to its strong basic characteristics.

CONCLUSIONS

The results can be summarized as follows:

- In the laboratory kiln, SO_2 was observed to develop in the 600-1000°C range;
- In the industrial kilns, the presence of SO_2 is comparable with the laboratory data;
- No presence of black cores was evidenced in the fired tiles;
- SO_2 was not present in the stack flue gases (about 400°C);
- Sulphates, which were absent in the raw materials, were found in the fired tiles, suggesting a reaction between flue gases and unfired tiles.

REFERENCES

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