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ESTIMATION OF FLUORINE EMISSION DURING FIRING OF SOME POLISH CLAYS

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Abstract: The fluorine content in some Polish ceramic clays, representing different ages from Carboniferous to Quaternary, was determined using PIGE method. It varies from about 330 *ppm* up to 1300 *ppm* in raw material. Firing of clays at 1200 °*C* causes significant reduction of fluorine content - usually below 100 *ppm*. The total emission of fluorine related to the Polish brick industry, consuming the highest amounts of clays in comparison to other branches of ceramics, was estimated. It is significant (e.g. 3.19 thousand *Mg* in 1989, 1.64 thousand *Mg* in 1990) and comparable with the fluorine emission of such pollutants of the natural environment as: the aluminum metallurgy, chemical (mainly production of phosphate fertilizers), glass and enamel industries.

Key words: air pollution, clays, fluorine, PIGE.

Introduction

In the ceramic industry, depending on mineral composition and technological properties, clay raw materials are widely applied. During the firing process of clays, the emission of many volatiles, e.g. F, Cl, B, Br, NO_2 , SO_3 , takes place (Keller 1986; Heller-Kallai et al. 1988). First of all, it is caused by the decomposition of clay minerals, micas, organic matter and also iron sulphides (pyrite, marcasite), occurring in subordinate amounts. The majority of these volatiles has a definitely harmful influence on the natural environment. It is a general opinion that the ceramic industry is mainly emitting sulphur oxides and - to a lesser degree - nitrogen oxides. The threats related to the emission of fluorine during the firing process of ceramic clays were noticed on a large scale in Italy in the early 1970s (Palmonari & Timellini 1989).

This problem is also intensely studied in other European countries such as: West Germany (e.g. Grätz 1980; Hauck & Hilker 1986; Dehne 1987; Eckhardt et al. 1990) and Great Britain (Amison 1989). In this process, fluorine is liberated first of all in the form of hydrofluoric and fluorosilicic acids, as well as silicon tetrafluoride - all very dangerous for the natural environment (Blank & Klemm 1983; Palmonari & Timellini 1989). Up to now, the fluorine emission in Poland has been considered to be connected mainly with aluminum metallurgy and with the activity of chemical (particularly the production of phosphate fertilizers), glass and enamel industries (Paluch & Szalonek 1970; Nowicki 1986). A negative influence concerning fluorine in ceramic clays has been neglected up to now.

It is supposed that the analytical difficulties were one of the causes of the lack of studies concerning the fluorine content in Polish ceramic clays and its emission during firing. It is well known that the determination of this element using classical methods, even after modifications proposed for silicate materials by Fabbri & Donati (1981), is rather complicated. Considerable progress in this respect was noted by introduction, into analytical practice, of the PIGE (proton induced gamma-ray emission) method which was just applied in this study.

Experimental

The determination of fluorine content by means of the PIGE method, was carried out in the Institute of Nuclear Physics in Cracow. This method is particularly useful for the determination of light elements. The beam of protons, accelerated to the energy of 2.6 *MeV* in the cyclotron C-48, strikes analysed samples, prepared in the form of pressed pellets (diameter of 8 *mm*, thickness of about 1 *mm*); protons are completely absorbed causing excitation of atomic nuclei of some light elements. Gamma radiation of characteristic energy of each transition between nuclear shells is detected. The reaction leading to excitation of fluorine is as follows:

$$^{19}F(p,\ p'\gamma)\ ^{19}F$$

We observe two main analytically usable lines of energy: 110 and 197 *keV*. For precise quantitative analysis of fluorine in clay samples three standards as reference materials were used: Soil-5, Soil-7 (International Atomic Energy Agency, Vienna, Austria) and KK kaolin (Institute of Mineral Raw Materials, Kutná Hora, Czecho-Slovakia). The fluorine contents in them are as follows: 628 *ppm*, 480 *ppm* and 880 *ppm*, respectively. The detection limit for fluorine during our measurements has been improved (from initially 100 $\mu g/g$ to 30 $\mu g/g$). This improvement is due to geometrical optimization of measurements and better energetical stabilization of beam of protons.

Results and discussion

The clays from different deposits in Poland, ranging in age from Carboniferous to Quaternary, were studied (Tab. 1, Fig. 1). These rocks display considerable variability of mineral composition. Kaolinite and illite are the commonest components whilst mixed layer illite/smectite and smectite occur rarely. They are accompanied by quartz, micas and subordinate amounts of other minerals (e.g. feldspars). The samples were delivered

Table 1: Localization and age of studied clays.

Age	Deposit	Age	Deposit
Quaternary: Pleistocene	Grabów Leczcki Lebork Lezany Piastowo Pilitowo Plecewice Rumaki Sagnity		Zielonki, Kraków
		Oligocene	Turów II
		Eocene	Trepcza
		Cretaceous	Wawal
		Jurassic	Grójec Jakubów Stara Góra Zapniów Zarnów
Tertaiary: Miocene	Bonarka, Kraków Gozdnica Jaroszów Leknica Pawłów Słowiany Trzcianka Wola Rzedzinska Zebrzydowa Zeslawice, Kraków	Triassic	Baramów
		Permian	Slavków
		Carboniferous	Jaworzno Kozlowa Góra Mikołów

mainly from active open pits, working, among others, for the brick industry. The production of raw clays from different places is presented in Fig. 2. They vary significantly - from the largest Polish fireclay deposit in Jaroszów (699 thousand *Mg*/year in 1989) to small ones, as e.g. brick-clay deposits in Zielonki near Kraków and Rumaki. Their production amounts to about 10 thousand *Mg*/year.

The content of fluorine in the raw ceramic clays studied is presented in Tab. 2 and in Fig. 3. It varies within the limits from about 330 *ppm* (Jaworzno) up to 1300 *ppm* (Zebrzydowa); whereas usually it amounts to 500 - 900 *ppm*. These values are comparable with the data reported for other clays e.g. with fluorine contents in brick-clays of Lower Saxony in Germany (Eckhardt et al. 1990). For the calculations presented in this paper it was accepted that the mean content of this element in ceramic clays occurring within the Polish territory amounts to 700 *ppm*.

Fig. 1. Sampling sites of ceramic clays from the Polish deposits studied.

Table 2: Fluorine content in raw clays studied.

Deposit	F[*ppm*]	Deposit	F[*ppm*]
Baranów	540	Sagnity	830
Bonarka, Kraków	720	Slawków	970
Gozdnica	950	Slowiany	760
Grabów Leczycki	610	Stara Góra	570
Grójec	570	Trepcza	790
Jakubów	730	Trzcianka	380
Jaroszów	550	Turów II[1]	800
Jaworzno	330	Turów II[2]	710
Kozlowa Góra	680	Turów II[3]	1020
Lebork	665	Wawal	830
Leknica	760	Wola Rzedzinska	660
Lezany	740	Zapniów	540
Mikolów	670	Zebrzydowa[4]	1300
Pawlów	690	Zebrzydowa[5]	920
Piastowo	440	Zeslawice	780
Pilitowo	690	Zielonki, Kraków	710
Plecewice	920	Zarnów	600
Rumaki	750		

[1] borehole SP-3, depth 3 - 4 *m*; [2] borehole SP - 3, depth 7.3 - 8.3 *m*; [3] bed B; [4] STANDARD-1 sort; [5] STANDARD-2 sort (with pyrite admixture).

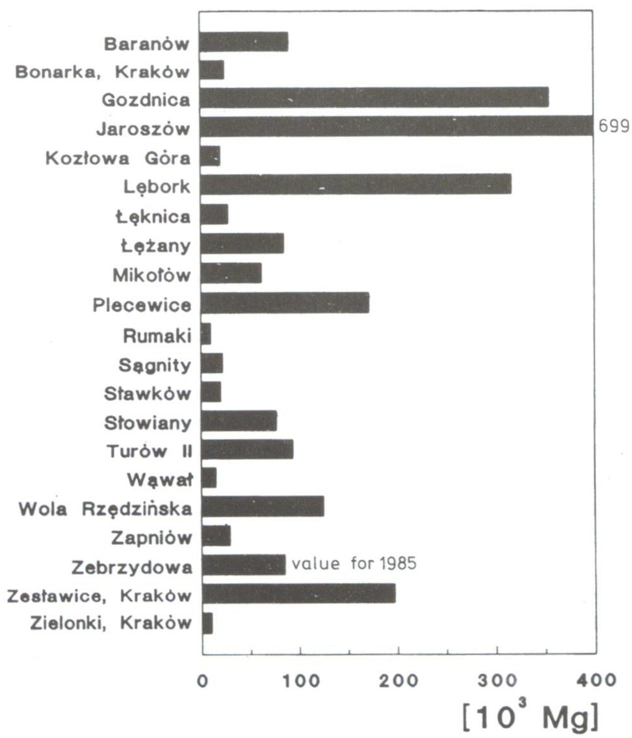

Fig. 2. Production of some ceramic clays studied in 1989.

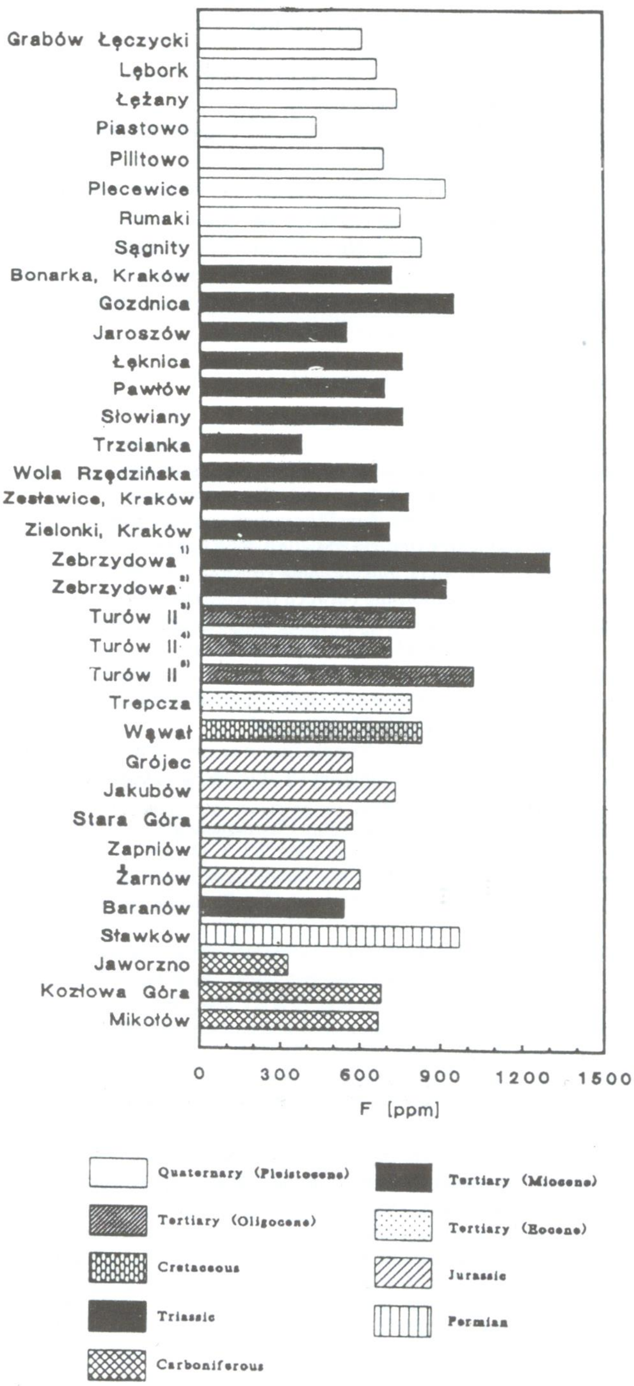

Fig. 3. Fluorine content in raw clays studied.
[1)]borehole SP-3, depth 3.0-4.0 *m*,
[2)]borehole SP-3, depth 7.3-8.3 *m*,
[3)]bed B.

During firing of clays at 1200 °*C* the fluorine content considerably diminishes (Tab.3). Generally, it is below the detection limit of this element. Only in some cases is it 100 *ppm* (Zielonki near Kraków) and sporadically increases up to 200 *ppm*, as in the case of stoneware clay from Zebrzydowa. It should be emphasized that such high fluorine content after firing is characteristic only in the case of clay characterized by the highest concentration of this element in the raw material.

Table 3: Fluorine content in selected clays after firing (1200 °*C*/2*h*).

Deposit	F[*ppm*]
Bonarka, Kraków	<DL*
Grójec	<DL
Jakubów	<DL
Kozlowa Góra	<DL
Leknica	<DL
Mikolów	<DL
Slawków	<DL
Stara Góra	<DL
Turów II	<DL
Wola Rzedzinska[1]	170
Zebrzydowa[2]	200
Zebrydowa[3]	250
Zeslawice, Kraków	<DL*
Zielonki, Kraków	100
Zarnów	<DL

Explanations: [1]firing temperature - 960 °*C*, [2]STANDARD-1 sort, [3]STANDARD-2 sort, DL - detection limit in earlier analyses (100 *ppm*), DL* - detection limit of analyses carried out under improved conditions (30 *ppm*).

Taking into account the content of fluorine before and after firing as well as the data on consumption of clays in Poland it was possible to evaluate annual emission of this element. Approximate data on total emission of fluorine related with to activity of the brick industry in the whole country for 1980, 1985, 1989 and 1990 were computed (Fig. 4). When compared with other branches of ceramic industry, the brickyards consume the highest amounts of clay raw materials. Consequently, total emission related to the latter is significant. In the years 1980, 1985, 1989 and 1990 this branch of ceramic industry consumed 13.082, 11.500, 22.120 and 11.375 million *Mg*, respectively. The fluorine emission was computed by assuming: 20 wt.% moisture in raw clays, 700 *ppm* F in clays after drying, 100 *ppm* F in clays after firing at 1200 °*C*. Taking into account that the firing temperature of bricks is lower and usually does not exceed 1000 °*C* this amount should be reduced to 30%. The data estimated in this manner concerning the total emission of fluorine related to the firing of these materials are as follows: 1980 - 1.88, 1985 - 1.66, 1989 - 3.19 and 1990 - 1.64 thousand *Mg*. The values obtained are consistent with the data reported by Eckhardt et al. (1990) for the temperature of 1000 °*C* and also with the results of our control determination of fluorine content in selected samples of domestic bricks. As already mentioned, the presented evaluation does not take into account the emission connected with the activity of other branches of the ceramic industry (whiteware, fireclay refractories). By way of example it was calculated that the annual emission of fluorine during firing of raw material from the largest deposit of fireclays in Jaroszów (Lower Silesia) amounted to about 250 *Mg*.

The emission connected with the activity of brick industry is relatively high and can be compared with the total emission of this element by the aluminum metallurgy, chemical industry (mainly the production of phosphate fertilizers) as well as the

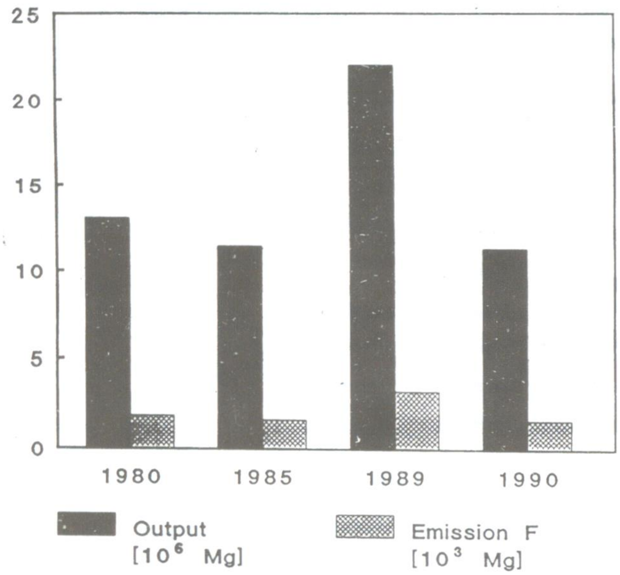

Fig. 4. Estimated total fluorine emission in Poland caused by brick industry in the years 1980, 1985, 1989, 1990.

glass and enamel industries. In Poland, until recently, these industries were commonly considered to be the main sources of pollution of the natural environment by fluorine. There are different data on emission of this element by these industries: from 2 thousand *Mg* - through 7 thousand *Mg* - up to 17 thousand *Mg* (Wieczorek 1985). As follows from the results of the studies presented here, the ceramic industry is also one of the important emitors of fluorine in Poland. This refers, first of all, to the brick industry, consuming the highest amounts of clay raw materials. Moreover, it was shown that PIGE was a very convenient method for mass estimation of trace amounts of hardly determinable fluorine in mineral raw materials.

Table 4: Fluorine emission (in thousands *Mg*) during firing of brick-clays.

Emission \ Year	1980	1985	1989	1990
Hypotetical emission of fluorine at 1200 °*C*	6.28	5.52	10.62	5.46
Estimated total emission of fluorine during firing of brick-clays	1.88	1.66	3.19	1.64

Conclusions

1 - The fluorine content in Polish ceramic clays varies from about 330 *ppm* up to 1300 *ppm*.

2 - Firing of clays at 1200 °*C* usually causes the reduction of fluorine content below 100 *ppm*.

3 - The total emission of fluorine related with the brick industry in Poland is significant (1980 - 1.88, 1985 - 1.66, 1989 - 3.19 and 1990 - 1.64 thousand *Mg*) and can be compared with that caused by such pollutants of the natural environment as: aluminum metallurgy, chemical (mainly production of phosphate fertilizers), glass and enamel industries.

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