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CHARACTERISTICS OF FLUORIDE EMISSION FROM FIVE CLAY MINERALS AS AFFECTED BY TEMPERATURE, HEATING TIME AND ADDITION OF CALCIUM COMPOUNDS*

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Abstract: Characteristics of fluoride emission from five clay minerals (montmorillonite, kaolinite, vermiculite, geothite, and allophane) as affected by temperature, heating time and addition of calcium compounds were studied. Marked increase of the fluoride emission rate was noticed with increase of temperature. The fluoride release, began at 500 ℃ - 600 ℃, and the main bulk of the fluoride emission occurred at the temperature of about 800 ℃. The loss of crystalline water was primarily responsible for the increase of fluoride emission. When minerals were heated at 800 ℃, The fluoride emission rate from the clay minerals reached the highest after heating for 1 hour. The samples treated by CaO, $CaCO_3$, $Ca(OH)_2$, $Ca_3(PO_4)_2$, and $CaSO_4$ had 55.45%, 59.58%, 46.45%, 54.31%, 31.25% reduction in the fluoride emission from montmorillonite at the temperature of 800 ℃, respectively. $CaCO_3$ had the highest fluoride fixing capacity compared to other calcium compounds.

Key words: fluoride emission, clay minerals, high temperature
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INTRODUCTION

The sericulture ecosystem of the Hang-Jia-Hu district in Zhejiang Province has been seriously polluted by fluoride since 1982. Widely distributed silicate industries, such as brick, ceramic, fireproof material, and cement processing industries which make their products using various clays and clay minerals, are the main pollution source. High temperature is indispensable during the processing in these industries. As a result, there exist desirable physicochemical and mineralogical reactions, such as dehydration, paramorphic transformation, lattice collapse, and crystal generation (Ying, 1983) in clay minerals. Fluoride is emitted from minerals thereby in the gaseous forms of HF and SiF4, which results in fluoride pollution of the air and toxicity to animals (Xie et al., 1999).

However, there is little information on the behavior of fluoride at high temperature and our knowledge on how to fix fluoride is limited. The objective of this study was to examine the influence of high temperature and calcium compounds as factors determining fluoride emission from minerals so that effective measures could be devised to fix the fluoride into clay and thus to control fluoride pollution in the atmosphere.

MATERIALS AND METHODS

Materials preparation

Table 1 lists the minerals used and their basic properties. Kaolinite was obtained from Yangshang, Jiangsu Province, and montmorillonite and vermiculite from Lin-an, Zhejiang Province. Geothite was synthesized according to the methods of Aktinson et al. (1967). X-ray diffraction indicated that the kaolinite was a nearly pure sample, and the contents of SiO_2 and K-$(AlSi_3O_8)$ in montmorillonite were low.

The fluoride concentration of kaolinite, allophane, vermiculite, and geothite was regulated with NaF solution (F, 1000 $kg \cdot kg^{-1}$) solution

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so that the four minerals had fluoride contents equivalent to that of montomorillonite. After being kept for 20 days at room temperature, when the moisture content of the samples was about 3%, the samples were ground to pass through a 100 mesh sieve and stored.

Table 1 The basic properties of the mineral samples

Properties	Montmorillonite	Kaolinite	Allophane	Vermiculite	Geothite
pH(H_2O)	10.15	5.69	9.89	5.12	8.71
Crystal level(%)*	100	89	–	98	85
Total fluoride(mg/kg)	452	280	10	350	10
Specific surface area(m^2/g)	620	18	88	620	120

* crystal level(%) = 100% − $\frac{Fe_o}{Fe_t}$ or $\frac{Al_o}{Al_t}$(%)

$\frac{Fe_o}{Fe_t}$ or $\frac{Al_o}{Al_t}$(%) = Concentration of Fe or Al extracted by Tamm reagent/total Fe or Al in sample

Experimental layout

Effect of temperature on fluoride emission

Five g of mineral samples placed in a nickel crucible inside a muffle furnace were heated under temperatures of 300 ℃, 400 ℃, 500 ℃, 600 ℃, 700 ℃, 800 ℃, 900 ℃, and 1000 ℃ for 2 hours, respectively.

Effect of heating time on fluoride emission

Five g of another group of the above 5 mineral samples were heated for 0.5, 1, 1.5, 2, 2.5 hours, respectively, at 800 ℃ in a muffle furnace to study the influence of heating time on fluoride emission.

When cooled down, the samples were ground to pass through a 100 mesh sieve. All the samples treated were stored in clean, dry, tightly closed polyvinyl bottles.

Effect of calcium compounds on fluoride emission

Five aliquots of montmorillonite samples were weighed and placed in 100 ml plastic containers, into which the following calcium containing compounds (chemical grade) were added, respectively: 0.4612 g of $CaSO_4$, 0.3938 g of $CaCl_2$, 0.2689 g of $CaCO_3$, 0.1985 g of $Ca(OH)_2$, and 0.8308 g of $Ca_3(PO)_4$, so that there was 1.5 % calcium in the form of CaO in the montmorillonite samples. After being stirred with deionised water, the samples were dried at room temperature.

Measurements and calculation

Direct determination of fluoride in minerals was made using a NaOH fusion-selective ion electrode technique by a method of standard additions (Baker, 1972; Villa, 1979).

After accurately weighed, 0.25g of samples transferred to a 50 ml nickel crucible were moistened slightly with distilled water, 3.0 ml of 16.75 mol/L NaOH solution was added into the crucible. After being dispersed uniformly in the NaOH solution, the crucible with samples was placed in an oven at 150 ℃ for 1 hour until the sodium hydroxide had solidified, and then the crucible with sample was placed in a muffle furnace set to 300 ℃. The temperature was raised to 600 ℃. The samples were fused after 30 min at this temperature. After the samples were removed from the muffle furnace and allowed to cool, before 5 ml of de-ionised water was added. Then, about 4 ml of concentrated HCl was slowly added, with stirring, to adjust pH to 8 – 9 (checked with pH test paper). The cooled acidified sample was transferred to a 50 ml volumetric flask, diluted with distilled water to volume, and then filtered through dry filter paper. A 5 ml aliquot was taken with pipette and placed in a 50 ml plastic beaker, to which 50 ml of 0.1 mol/L perchloric acid was added and the mixture was stirred magnetically, the fluoride electrode and calomel reference electrode were then inserted into the solution. A reading E_1 was taken after the potential was stable. After 0.1 ml of the fluoride standard solution (2000 mg/L) was added from a microburette, a stable reading E_2 was taken after 5 minutes. The content of fluoride in the sample was obtained from the equation:

$$C_F = \frac{M}{m(10^{\Delta E/S} - 1)}$$

Where m is dry mass of sample in grams, M is mass of fluoride added; $\Delta S = E_2 - E_1$; S is electrode slope or Nernst factor, the theoretical value at 22 ℃ being 58.5 mV per decade of change in activity.

Fluoride emission rate was described by the following equation:

$$Y_s(\%) = (C_0 - C_1)/C_0 \times 100\%$$

Where C_0 is the content of fluoride in the mineral before heating; C_1 is the fluoride content after heating.

Mineral pH was measured in a 1:5 soil/water suspension. Specific surface area was determined with the Ethylene Glycol Monoethylether (EGME) technique (Heilman, 1965).

RESULTS AND DISCUSSIONS

Effect of temperature on fluoride emission

Temperature greatly affected the rate of fluoride emission from five minerals (Fig. 1). Marked increases of the fluoride emission rate were noticed with increase of temperature, as expected from reaction thermodynamics. The fluoride release, began at 500 ℃ – 600 ℃, and the main bulk of the fluoride emission occurred at the temperature of approximately 800 ℃.

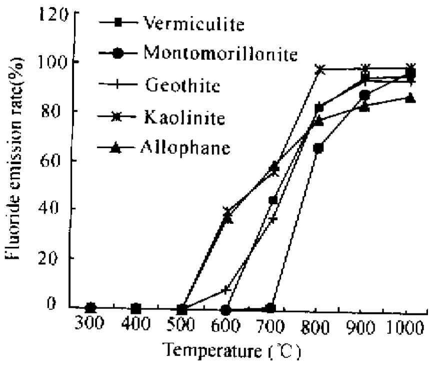

Fig. 1 **Influence of temperature on fluoride emission rates of five minerals**

There were some differences among fluoride emission from minerals, however. It was 500 ℃ when fluorides began to release from kaolinite, while it was 700 ℃ when fluorides began to release from montmorillonite. Fluoride emitted from kaolinite at the temperature of 600 ℃ was 39.7%, while only 15.5% fluoride released from montmorillonite at the temperature of 700 ℃. The hysteretic fluoride emission from montmorillonite was possibly attributable to physicochemical changes of minerals at high temperature. Kaolinite lost 11% (on weight basis) crystalline water at 450 ℃ – 600 ℃ (Yin, 1983; Lin et al., 1989), and montmorillonite began to lose crystalline water [OH] at 700 ℃. The temperature at the turning point of the curve shown in Fig. 1 was close to the temperature at which the mineral disintegrated. It could be concluded that there was a close correlation between fluoride emission and the change of crystalline water content. Some reactions occurred when the crystal lattice of a mineral collapsed and the crystalline water was lost at high temperature:

$$OH^- + F^- \longleftrightarrow (F^-)^* + (OH^-)^* \rightarrow HF\uparrow + O^{2-} \quad (1)$$

$$H^+ + F^- \longleftrightarrow (H^+)^* + (F^-)^* \rightarrow HF\uparrow \quad (2)$$

Then

$$HF + SiO_2 \rightarrow SiF_4 + H_2O \quad (3)$$

$(F^-)^*$, $(OH^-)^*$, $(H^+)^*$ in Eqs (1) and (2) represent activated forms. We inferred that the loss of crystalline water was primarily responsible for the increase of fluoride emission.

Fluoride emission from vermiculite at different temperatures was identical to that from montmorillonite, so it seemed that fluoride emission from 1:1 phyllosilicates was easier than from 2:1 phyllosilicates. For allophane and kaolinite, the curve of fluoride emission was similar. However, The rate of fluoride emission from kaolinite was 12 % higher than that from allophane as allophane was noncrystalline substance.

Effect of heating time on fluoride emission

Heating time also affected fluoride emission from the five minerals (Fig.2). Fluoride emissions increased greatly in an hour and slightly later. The rate of fluoride emission from montmorillonite increased from 37.8% to 73.6% as the time increased from 0.5 hour to 2 hours at the temperature of 800 ℃. Minerals would sinter, however, when heated too long. If minerals were heated for more than 2 hours, fluoride emission rates would decrease slightly. Therefore, heating time was also an important factor affecting fluoride emission from minerals.

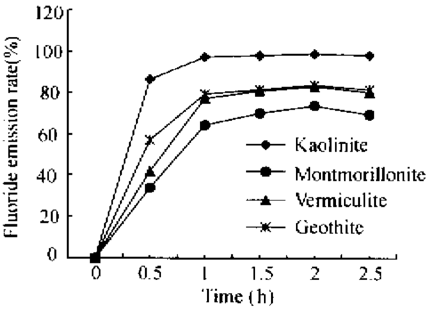

Fig.2 Influence of heating time on fluoride emission rates

Effect of calcium compounds on fluoride emission

Based on the fact that fluoride could react with calcium to form calcium fluoride, which had higher thermal stability, calcium compounds were considered as available materials that could fix fluoride at high temperature in the forms of CaF_2 and $CaSiF_6$ (Dehne, 1987). Five calcium compounds including CaO, $CaCO_3$, $Ca(OH)_2$, $Ca_3(PO_4)_2$, and $CaSO_4$ were thereby selected to study their fluoride-fixing efficiency.

Results showed that the samples treated with CaO, $CaCO_3$, $Ca(OH)_2$, $Ca_3(PO_4)_2$, and $CaSO_4$ had 55.45%, 59.58%, 46.45%, 54.31%, 31.25% reduction in the fluoride emission at the temperature of 800 ℃ (Table 2), respectively. Amongst the calcium compounds, $CaCO_3$ had the highest fluoride-fixing capacity. This might be due to the following chemical reactions by which the fluoride-fixing mechanism of $CaCO_3$ can be elucidated.

$$CaCO_3 \xrightarrow{800-900\ ^\circ C} CaO^* + CO_2 \uparrow \tag{4}$$

$$CaO + 2HF \rightarrow CaF_2 \downarrow + H_2O \tag{5}$$

$$2CaO + 3SiF_4 \rightarrow 2CaSiF_6 \downarrow + SiO_2 \tag{6}$$

Table 2 Effect of calcium compounds on fluoride emission from montmorillonite(%)

Temperature (℃)	Control	CaO		$CaCO_3$		$Ca(OH)_2$		$Ca_3(PO_4)_2$		$CaSO_4$	
		A	B	A	B	A	B	A	B	A	B
600	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
700	1.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
800	66.70	11.25	55.45	7.12	59.58	20.25	46.45	15.39	51.31	35.45	31.25
900	88.50	41.55	46.95	39.55	48.95	72.70	15.80	51.03	37.47	88.35	0.15
1000	98.10	83.58	14.52	83.27	14.83	92.49	5.61	82.47	15.63	93.61	4.49

A = rate of fluoride emission from montmorillonite to which was added calcium compounds (%)
B = difference of fluoride emission rate between treatment and control (%).

The reaction (1) made the CaO^* have more poles and pole surface area, and have stronger reaction activity than before. Consequently, it was easier for HF and SiF_4 to be fixed by passing through holes and reaching the inner surface.

When temperature reached 900 ℃ – 1000 ℃, some of the CaO were sintered, making the activity of CaO lower as a result of decrease of pole surface area. And there was a reaction which decreased the CaO content: $2CaO + SiO_2 \rightarrow 2CaO \cdot SiO_2$. It could be elucidated that $CaCO_3$ had stronger fluoride fixing capacity than CaO at 800 ℃, while having similar capacity at 1000 ℃. 15.63% reduction of fluoride emission rate was found when treated by $Ca_3(PO_4)_2$ at 1000 ℃. But wholly speaking, the reaction between fluoride and $CaCO_3$ was easier.

Some experiments were made to study the effect of $CaCO_3$ on fluoride emission from other minerals (Table 3). The result was analogous to that obtained from montmorillonite. At 800 ℃, $CaCO_3$ could fix most of fluoride in the minerals. That is, the effect of $CaCO_3$ was the most significant at this temperature.

CONCLUSIONS

This study indicated that fluoride emission rate varied with temperature, heating time; and that $CaCO_3$ could fix most of the fluoride into the clay minerals at 800 ℃. Therefore, some measures should be taken to reduce the fluoride emission into the atmospheric environment during the processing of brick, ceramic, and fireproof material. The suggested measures could be (1) to reduce the fire temperature, (2) to shorten the heating time, and (3) to add materials containing $CaCO_3$ to clay and clay mineral.

Table 3 Effect of $CaCO_3$ on fluoride emission rate from clay minerals (%)

Temperature (℃)	Kaolinite			Vermiculite			Geothite		
	Control	*A*	*B*	Control	*A*	*B*	Control	*A*	*B*
500	15.70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
600	39.70	29.80	9.90	4.80	0.00	0.00	8.30	5.30	3.00
700	56.70	28.86	27.84	45.50	25.98	19.52	37.40	30.00	7.40
800	98.50	53.23	45.27	82.80	61.44	21.36	83.60	45.44	38.16
900	99.40	88.93	10.47	95.70	94.23	1.47	94.30	86.76	7.54
1000	100.00	96.01	3.99	96.10	96.13	−0.03	94.30	91.90	2.40

A = rate of fluoride emission from mineral to which was added $CaCO_3$ (%)
B = difference of fluoride emission rate between treatment and control (%).

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