SUPPRESSION OF THERMAL REACTIONS IN KAOLINITE

R. M. Gruver, E. C. Henry and H. Heystek,
The Pennsylvania State College, State College, Pennsylvania.

Abstract

Suppression of thermal reactions in kaolinite by fluxing impurities present in brick clays may cause considerable modification of thermal analysis results. Heat effects obtained by thermal analysis of complex mixtures may be misleading.

Introduction

In an investigation of brick clays from Pennsylvania by the techniques of x-ray diffraction and differential thermal analysis, the following observations were made:

1. After samples were tested in the differential thermal analysis furnace, many were slightly sintered and could be removed from the platinum bucket in one piece. The maximum temperature reached in the furnace on each run was 1050° C.
2. Although the x-ray diffraction patterns on many of the clays indicated the presence of an appreciable amount of kaolinite, it was not always possible to make the same deduction from the differential thermal curves.
3. In the case of a few clay samples that were more refractory than the others, no sintering was observed at 1050° C. The presence of a small amount of kaolinite in these was definitely indicated by the differential curves.

As a result of these observations, an attempt was made to simulate the sintering conditions occurring in the impure brick clays at low temperatures by adding small amounts of ferric oxide and sodium carbonate to Langley kaolin.

Materials and Methods

The thermal analysis apparatus used for this investigation has been described in a previous paper[1] along with the method by which the samples were run.

The samples to be tested were prepared by weighing the proper amounts of Langley kaolin and C.P. sodium carbonate, ferric oxide, or other materials to give a 2.500 gram batch. This batch was placed in an automatic mortar and pestle grinder, where the dry materials were ground for twenty minutes to obtain a uniform mixture.

From this mixture a 0.500 gram sample was taken for thermal analysis; an equal amount of calcined alumina was used for the standard reference

---

[1] Gruver, R. M., Precision method of thermal analysis: *Jour. Am. Ceram. Soc.*, **31,** 324–328 (1948).

TABLE 1

Composition of Samples, Weight Per Cent							Result of Thermal Analysis					
							Endothermic Reaction			Exothermic Reaction		
Sample No.	Kaolin	Na_2CO_3	Fe_2O_3	NaCl	$MgCl_2\cdot 6H_2O$	Calcined Kaolin	Area Under Curve	Depth of Peak	Peak Temp. (±3°)	Area Under Curve	Height of Peak	Peak Temp. (±3°)
1	100	—	—	—	—	—	7.7	3.1	595	0.6	4.75	976
2	98	2	—	—	—	—	7.4	3.0	597	0.75	4.25	973
3	96	4	—	—	—	—	7.3	2.9	598	0.7	3.1	975
4	94	3	3	—	—	—	7.0	2.9	598	0.7	3.3	974
5	94	6	—	—	—	—	6.8	2.8	598	0.5	2.1	976
6	94	—	6	—	—	—	6.7	2.9	599	0.8	4.8	975
7	90	4	6	—	—	—	6.6	2.8	600	0.6	2.2	976
8	94	—	—	—	—	6	6.6	2.8	599	0.7	4.8	976
9	90	—	10	—	—	—	6.3	2.65	590	0.75	4.4	976
10	90	6	4	—	—	—	6.3	2.5	587	0.45	1.5	972
11	90	10	—	—	—	—	6.2	2.3	590	0.4	0.85	974
12	94	—	—	—	6	—	5.7	2.5	592	0.6	2.15	965
13	94	—	—	6	—	—	5.4	2.3	583	0.35	1.05	973

material. These materials were heated at 400° C. per hour; the sensitivity of the recorder for the differential couple was set at 5 millivolts for a full scale deflection.

Results and Discussion

The mixtures tested by differential thermal analysis are listed in Table 1. For comparison, one sample diluted with calcined kaolin and two samples with materials which have melting points near that of sodium carbonate were included in the tests. Several of the differential thermal

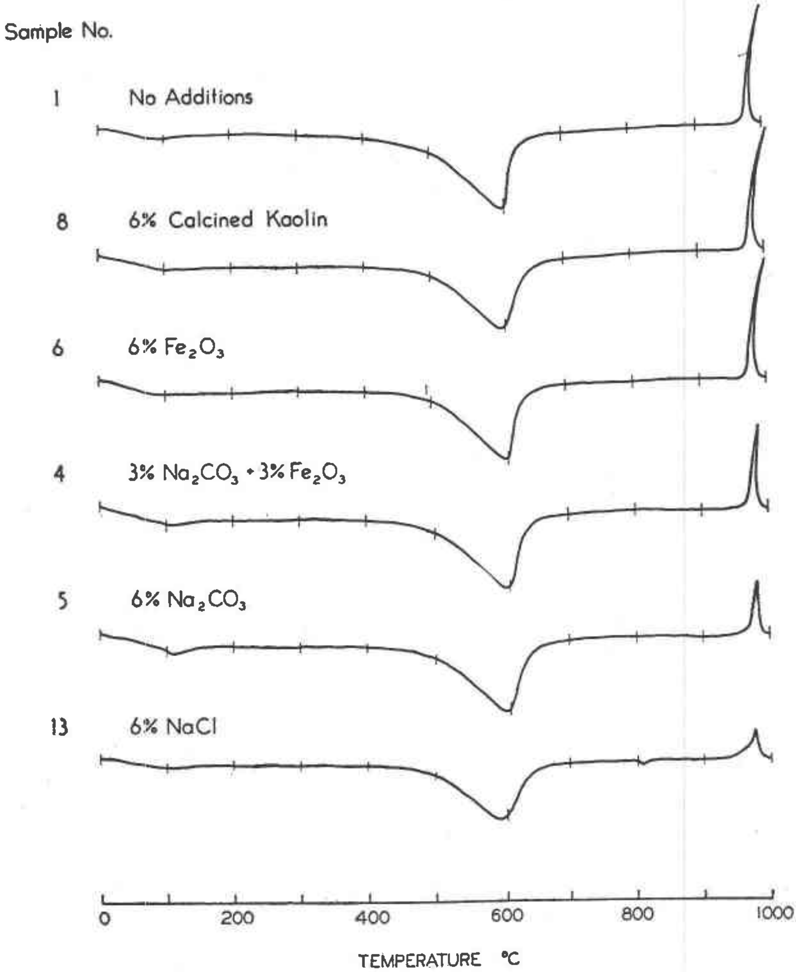

Fig. 1. Thermal analysis curves of Langley kaolin, showing the effects of various contaminants.

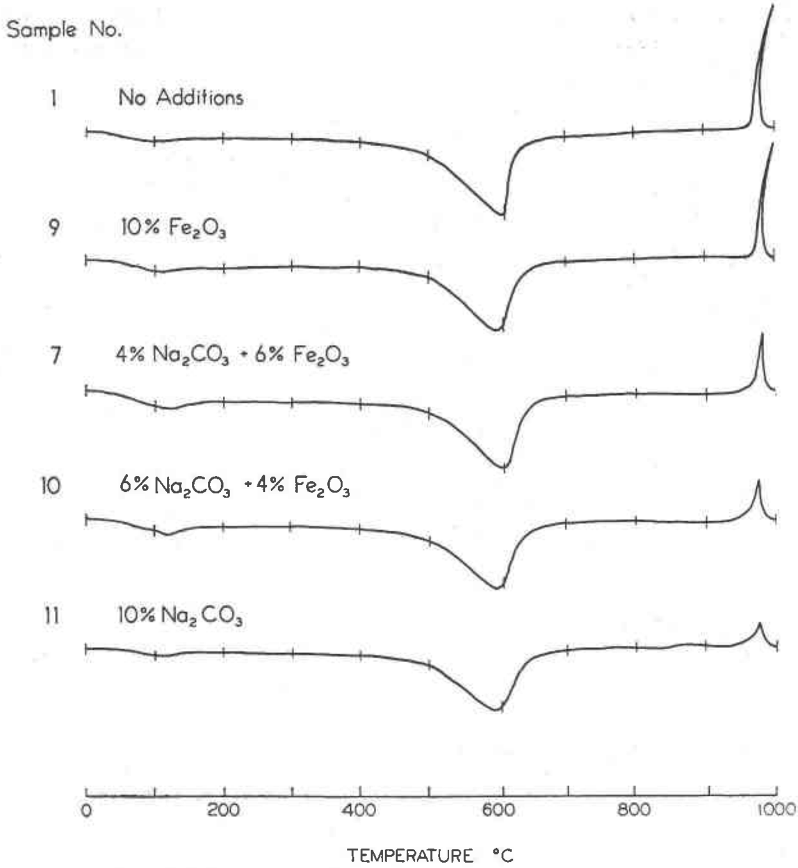

FIG. 2. Thermal analysis curves of Langley kaolin, showing effects of sodium carbonate and ferric oxide.

curves which portray the suppression of the thermal reactions are shown in Figs. 1 and 2.

As shown in Table 1, suppression of the heat effects of kaolinite is dependent on both the amount and type of contaminant present. The intensity of the exothermic reaction near 975° (transformation of amorphous alumina to gamma alumina) is affected more than that of the endothermic (dehydration) reaction at about 595°. Referring to Fig. 1, it appears that effective suppression is caused by fusible impurities in the kaolin. The peak is little affected by iron oxide or calcined kaolin alone, evidently because no fusion takes place. The curves in Fig. 2 seem to indicate that the presence of iron oxide in combination with a flux such as sodium carbonate does not suppress the formation of gamma alumina much more than does sodium carbonate alone.

The results indicate the possibility that impurities present in brick clays may react with the clay minerals and alter their normal heat effects. If a sample is sufficiently impure and reaction takes place while the material is being heated for differential thermal analysis, there is a good chance that one does not have mineralogically at elevated temperatures the same material which he had at room temperature. Thus, the heat effects due to kaolinite at 600° C. and 980° C. may reflect somewhat the amounts present at those temperatures, but should not be interpreted as indicative of the amount of kaolinite originally present.

From this picture, it seems apparent that observations of the magnitude and temperatures of heat effects obtained during the thermal analysis of complex mixtures may be misleading if one attempts thus to judge the amounts of various phases present in the mixture at room temperature.