

THE QUESTIONABLE KINETICS OF KAOLIN DEHYDROXYLATION

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Georgia Kaolin, an accepted "standard" kaolin, evolves carbon dioxide and carbon monoxide when heated to 4-500 °C. While the total amount is small, it is evolved more readily than the water and with a different temperature dependence than the water. Weight loss data are not satisfactory for studying the early stages of the dehydroxylation. Separate measurement of the water is necessary.

One of us [1, 2] has warned against the dangers of careless assumptions and experimentation, pointing out the fallacies in assuming, for example, that the nature of a quite complex reaction is known and only the kinetics remains for study or that if the temperature of a point in a specimen is known so is the temperature of the entire specimen. In particular, he has questioned the kinetic studies on kaolin on several grounds, one of which was the use of data under the least reliable circumstances. That is, the use of initial values of weight loss as observed by thermogravimetry, particularly when the experimenter must use very small absolute weight changes in his calculations, leads to uncertainties in the values found because of uncertainties in the values used. The uncertainties in the values used may not always be recognized because they arise partly out of problems in heat transfer and temperature homogeneity or blithe confidence that the nature of the reaction is precisely known. Thermogravimetry is such a useful tool where it is properly applicable that experimenters can easily forget its limitations.

Because of the greatly conflicting reports on kaolin [3-9] or kaolinite, and the conviction that none of the reports gave a satisfactory description, the present investigators undertook the study by repetitive gas chromatographic analysis of the evolved gases [10]. This method permits the dehydroxylation to occur under a known, reproducible and homogeneous environment. It also permits the accurate measurement of the submicrogram quantities of gases evolved in the initial stages. In both ways it presents advantages over thermogravimetry by extant techniques. The authors do not decry thermogravimetry as a technique; it is highly useful. It is not, however, the best technique for kinetic measurements, particularly for kaolin.

The non-homogeneity of reaction of kaolin has been recognized by virtually all observers. In general, limits have been placed on the applicability of the calcula-

tions. Koopman [11] used an empirical mathematical treatment of his data (by an analog computer curve resolver) to separate the dehydroxylation into three steps, but concluded that the three steps represented three different types of hydroxyl. The relative magnitudes of the peaks suggest that the number of peaks is fortuitous, merely giving the best fit to a curve which could not be expected to be truly the sum of a small number of gaussian peaks.

Since Georgia kaolin is a *de facto* standard in these studies, it, along with a relatively crude kaolin, was studied. Both the raw and the "treated" Georgia kaolin were obtained from the Georgia Kaolin Company [12]. Each material

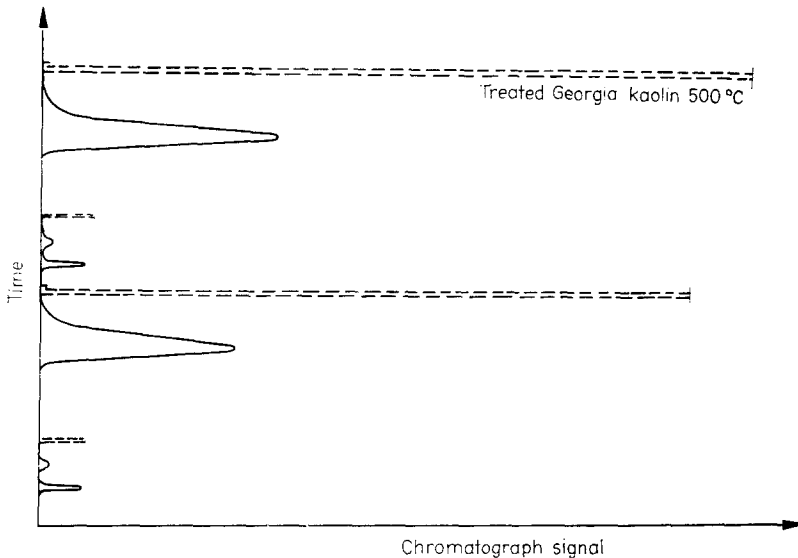


Fig. 1. Chromatograms from two successive samplings from Georgia Kaolin at 500°. The first peak is carbon monoxide, the second is carbon dioxide. The dotted line is an integration signal, measuring the sum of the two peaks. The large peak is water, followed by an integration signal for the water. While this signal is being recorded, the next sample is swept into the chromatograph

was dehydroxylated at a series of temperatures from 440 to 580° in the apparatus described. [10] Sampling was done automatically at five minute intervals. Even though sampling directly into a chromatographic detector alone (without a column) would give the sensitivity and accuracy needed, a Porapak P column at 70° was used to guard against just the sort of results found. Two chromatographic peaks (Fig. 1) prior to the water peak were observed; these were identified as carbon monoxide and carbon dioxide. In the treated kaolin carbon dioxide was, except for water, the predominant species while the raw kaolin gave roughly equal amounts of carbon monoxide and carbon dioxide. Since the total quantities

were small this might seem *prima facie* to be unimportant. However, these gases are evolved during the early stages of the decomposition so that they contribute disproportionately to the early data, precisely the data upon which kinetic data are heavily based.

The chromatographic detector gives a measure only of the molecular concentration, so the relative peak areas give an inadequate measure of the relative amounts; the relative amounts of carbon dioxide and carbon monoxide are greater by factors of 1.61 and 2.44 respectively. The actual weight fractions of water, carbon dioxide and carbon monoxide are given at two temperatures and two time intervals for untreated Georgia Kaolin in Table 1. Similar data are given for the

Table 1

Percentual weight fractions of water, carbon dioxide and carbon monoxide evolved from untreated Georgia kaolin during first and fourth ten-minute periods at several temperatures

Temperature	Gas	Interval	
		0-10 min.	30-40 min.
520°	Water	86.5	100
	Fraction of total water	(8.1)	(11.4)
	CO ₂	6.5	0
	CO	7.0	0
460°	Water	92.5	98.6
	Fraction of total water	(5.9)	(9.07)
	CO ₂	3.7	0
	CO	3.8	1.4

treated Georgia Kaolin and a Mexican kaolin in Tables 2 and 3. The data show very clearly that there is a very substantial quantity of other material evolved, bu

Table 2

Percentual weight fractions of water, carbon dioxide and carbon monoxide evolved from treated Georgia kaolin during first and fourth ten-minute periods at several temperatures

Temperature	Gas	Interval	
		0-10 min.	30-40 min.
520°	Water	88	100
	Fraction of total water	(5.8)	(12.5)
	CO ₂	8	0
	CO	4	0
460°	Water	94.0	96.3
	Fraction of total water	(3.7)	(7.24)
	CO ₂	4	1.7
	CO	2	2

Table 3

Percentual weight fractions of water, carbon dioxide and carbon monoxide evolved from Mexican kaolin during first and fourth ten-minute periods at several temperatures

Temperature	Gas	Interval	
		0-10 min.	30-40 min.
520°	Water	75	98.8
	Fraction of total water	(8.8)	(15.7)
	CO ₂	13	0.2
	CO	12	1
460°	Water	86	95.5
	Fraction of total water	(6.3)	(11.6)
	CO ₂	8	2
	CO	6	2.5

further, they show that the evolution of these other gases is neither constant nor proportional to the water evolution. Any calculations based upon the assumption that the entire weight loss is due to water will be in error by these amounts regardless of other uncertainties.

The present authors find it necessary to call into question the kinetic data and conclusions regarding the dehydroxylation of kaolin obtained by methods not specifically measuring the evolved water.

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RÉSUMÉ. — Le kaolin de Géorgie, choisi comme kaolin «étalon», perd du gaz carbonique et de l'oxyde de carbone s'il est chauffé à 400–500 °C. Tant que la quantité totale est faible, le départ de ces gaz s'effectue plus rapidement que celui de l'eau et dans un domaine de température différent. Les données relatives à la perte de poids ne suffisent pas pour l'étude des étapes initiales de la déshydroxylation. On doit faire un dosage séparé de l'eau.

ZUSAMMENFASSUNG — Georgia Kaolin, ein angenommener Standard-Kaolin, entwickelt Kohlendioxyd und Kohlenoxyd beim Erhitzen auf 400–500°C. Da die Gesamtmenge gering ist, entweicht es leichter und mit verschiedener Temperaturabhängigkeit als Wasser. Aus den Gewichtsverlustdaten kann deshalb nicht auf die ersten Stufen der Dehydroxylation gefolgert werden; es ist eine separate Messung des Wassers nötig.

Резюме. — Каолин Джорджии является стандартным каолином, из которого нагреванием при температуре 400–500 выделены двуокись углерода и окись углерода. До тех пор пока их количества малы, они образуются легче, чем вода и температурная зависимость их выделения иная, чем в случае выделения воды. Данные термогравиметрического анализа (ТГ) недостаточны для изучения ранних стадий дегидратации. Измерение воды ее отделением необходимо.