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Thermochimica Acta 265 (1995) 177–187

thermochimica
acta

Thermogravimetry of a kaolinite–alunite ore

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Received 17 January 1995; accepted 29 March 1995

Abstract

An ore containing kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), feldspar (KAlSi_3O_8) and quartz (SiO_2) was analysed by TG/DTA to determine the mineralogical composition of samples considered representative of concentrates and tailings likely to be obtained from physical treatments designed to produce a kaolin concentrate as low as possible in alunite. The ore was divided into various particle-size fractions each of which was subjected to TG/DTA analysis. A knowledge of the reactions and the decomposition temperatures of the minerals present permits the application of a system of equations that provides the composition of each size fraction, thus circumventing difficulties due to the overlapping of weight-loss curves during execution of the thermal curve. The alunite results provided by TG are in good agreement with those obtained via standard calculation starting from elemental chemical analysis. The kaolinite results are less accurate but as they follow the same trend as those obtained by chemical analyses, except for the finest fractions, they can be used for relative comparison of samples obtained during a physical treatment testing campaign.

Keywords: Alunite; DTA; Kaolinite; TA; TG

1. Introduction

Thermogravimetry provides an alternative method to the standard calculation usually adopted for determining the composition of a mixture of minerals; this often requires titrimetric determination of numerous elements, is time-consuming and calls for the support of a chemical laboratory which generally handles all the analyses for teams performing the physical treatment tests. The physical processes adopted in such tests (flotation, magnetic separation, selective milling, cycloning, etc.) are designed to concentrate the desired component of an ore without altering its chemical composition.

Where the products of such treatments are clays they can often be analysed by thermogravimetry. In spite of apparent disadvantages [1], such as the overlap of phenomena, temperature shifts due to dilution effects and particle size distribution, or chemical composition, and the difficult choice of analytical conditions when the components exhibit contrasting thermal behaviour, thermogravimetry gives immediate results and is precise enough to be used for the control of a beneficiation process. This paper reports the results of thermogravimetric analysis applied to a kaolin ore containing kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), feldspar (KAlSi_3O_8) and quartz (SiO_2). The mineralogical composition had to be determined in view of beneficiation testing in order to obtain a kaolin concentrate low in alunite, as the presence of this mineral prevents the marketing of the untreated ore and, hence, commercial exploitation of the deposit.

Of the four minerals present in the ore, only kaolinite and alunite decompose on heating, water being released in the case of the former, and water and sulphur trioxide in the latter. Consequently, knowing the formula weights of the minerals and thus the weight losses, as well as the temperature range within which they decompose, the quantities of these two components can be determined. Quantitative differential thermal analysis has already been used on samples containing different amounts of alunite [2], while thermogravimetric analysis has also been employed for quantitative determination on alunite ores of diverse origin [3]. However, in the reported cases, the amount of alunite was much higher (40–50%) than in the samples studied here and, moreover, the heating rate proposed in Ref.[3] (1°C min^{-1}) and the isothermal periods necessary to separate the weight-loss steps are not really suitable for routine analysis of the numerous samples obtained during physical treatment testing. Hence a heating rate of $20^\circ\text{C min}^{-1}$ has been adopted for the kaolin ore and the separation between the two weight losses on the thermogram has been taken as the mid-point between the two DTG peaks, i.e. the inflection point on the relevant curve.

2. Sample

The kaolin ore comes from the Piloni-Torniella deposit in Tuscany (Italy). The kaolin is the product of hydrothermal alteration of rhyolitic volcanics located near an important NW/SE-oriented fracture line. The clay was transported by waters at the margin of the volcanic outcrops where well-developed sedimentary structures may be discerned [4].

The sample was divided into thirteen particle-size fractions by a cyclosizer operated in such a way as to simulate the products obtained from physical treatments which yield concentrates that can differ considerably from tailings as regards particle-size. The classification resulted in samples containing different quantities of kaolinite, alunite, feldspar and quartz. About 300 g of the ore were divided into the following fractions: +1000 μm , 1000–710 μm , 710–500 μm , 500–355 μm , 355–250 μm , 250–90 μm , 90–63 μm , 63–42 μm , 42–30 μm , 30–21 μm , 21–15 μm , 15–12 μm and –12 μm . Prior to thermogravimetric analysis, samples coarser than 63 μm were ground to minus 50 μm to ensure homogeneity. The moisture content of the samples differed depending on the particle size.

3. X-ray diffractometry investigation

A Siemens D500 X-ray diffractometer ($\text{CrK}\alpha$) revealed the presence of kaolinite, quartz, feldspar and alunite. Traces were obtained for each particle-size fraction; those for the four particle-size fractions given in Fig. 1 show that the amount of kaolinite and alunite increases steadily as the particle size decreases from 1000 to $-12\ \mu\text{m}$, at which point quartz and feldspar were barely detectable. The behaviour of the latter two minerals is precisely the opposite of the first two, the amount present increasing in the coarser fractions ($+1000$ and $355\text{--}250\ \mu\text{m}$) and decreasing in the finer ones ($63\text{--}42$ and $-12\ \mu\text{m}$). This happens because aggregates of kaolinite and alunite break down readily and thus tend to concentrate in the finer fractions.

4. Thermal apparatus

The tests were performed in a stream of air using a Stanton Redcroft Model 1500 thermobalance with sensitivity of $1\ \mu\text{g}$, temperature range of $20\text{--}1500^\circ\text{C}$ and heating rates of $0.1\text{--}50^\circ\text{C}\ \text{min}^{-1}$. The furnace winding is platinum–rhodium and the thermocouple is located under the rhodium–platinum crucible containing the sample. The heating rate in the tests was $20^\circ\text{C}\ \text{min}^{-1}$ from 25 to 1000°C . Special care was taken to maintain the same sample geometry in the sample holder.

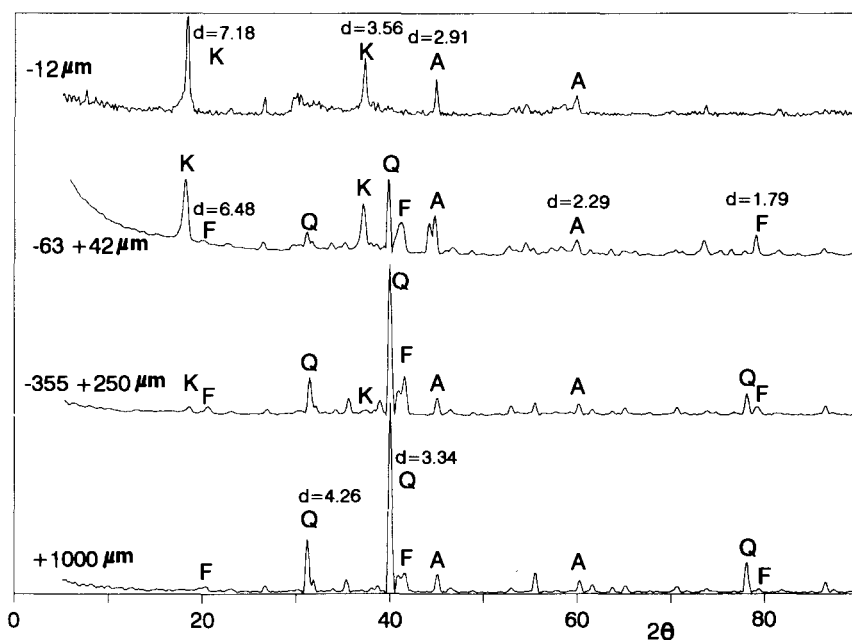


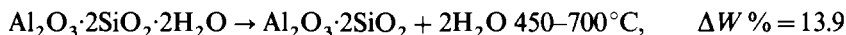
Fig. 1. X-ray diffraction pattern ($\text{CrK}\alpha$, radiation) of some particle-size fractions of the kaolin ore; A, alunite; F, feldspar; K, kaolinite; Q, quartz.

DTA curves were standardized by dividing the DTA signal by the weight of the sample and multiplying the result by 45, the average in milligrams of the weight of the samples subjected to TG/DTA.

5. Thermal decomposition of kaolinite and alunite

5.1. Kaolinite ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$)

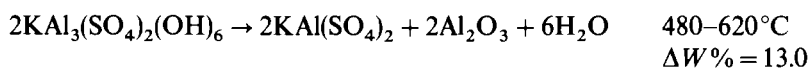
Kaolinite is a two-layer phyllosilicate whose structure consists of a tetrahedral sheet containing silicon and an octahedral sheet containing aluminium. The reaction and dehydroxylation temperature range of kaolinite are as follows:



The reaction is accompanied by an endothermic DTA peak. It leads to destruction of the octahedral sheet and the formation of metakaolinite. The area of the dehydroxylation peak, when only kaolinite is involved, can be used for quantitative determinations in most cases [5]. Another two exothermic peaks at about 1000 and 1200°C [6–8] refer to products forming from metakaolinite.

5.2. Alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$)

Alunite is a potassium aluminium sulphate whose structure takes the form of sheets of octahedra formed by four hydroxyl groups and two oxygen atoms; the sulphate ions (tetrahedra) have three of the four oxygen atoms forming the base of the tetrahedron [9]. The behaviour of alunite on heating has been extensively studied [10–12]. Dehydroxylation occurs first at a lower temperature, with complete destruction of the structure; sulphur trioxide is then lost at a higher temperature. The reactions and decomposition temperatures of alunite are as follows. First step:



During this endothermic reaction alunite is transformed into crystalline $\text{KAl}(\text{SO}_4)_2$ and amorphous Al_2O_3 . Second step:



This second endothermic reaction refers to the loss of 75% of the sulphate present. However, it is known [3,13,14] that solid state reactions occur when alunite is diluted with kaolinite and quartz leading to the loss of all the alunite sulphate. This being the case, the loss of all the sulphate content in the second step leads to a weight loss of 38.6%. Alunite is called natroalunite when sodium replaces potassium; in this form the weight losses in the two steps are respectively 13.6% and 40.2%. As microprobe analysis of a number of alunite grains in the sample under investigation revealed a ratio between sodium and potassium of about 1, it is assumed that the weight losses of the phase are the average between those due to the two types of alunite (13.3% and 39.4%).

6. Method of calculation

The formula correlating weight loss with the quantity of mineral in a mixture can be expressed in the following way

$$\% \text{ Phase} = \frac{\Delta W}{(TW \times W)} 10^4$$

where

ΔW = weight loss of mineral considered (mg).

TW = theoretical weight loss just for the mineral to be determined (%)

W = original weight of sample (mg).

The TG and DTA curves of the sample of kaolin ore is shown in Fig. 2. The beginning of the first step was considered to occur after the weight loss due to moisture and was determined experimentally for each sample. In fact, depending upon the particle size, the temperature considered was that at which the departure of physically adsorbed water occurs; this varies between 224°C (+1000 μm) and 317°C (−12 μm). As dehydroxylation of kaolinite and alunite takes place in the same temperature range, both contribute to the weight loss of the first step of the thermogram. The problem of the overlapping weight losses of kaolinite and alunite has been tackled by means of

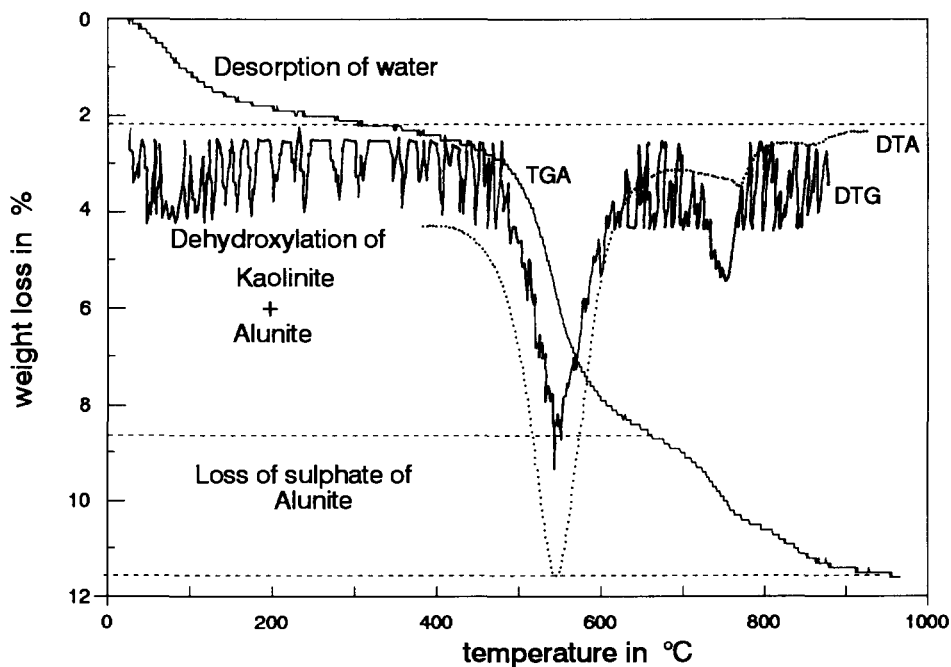


Fig. 2. TG and DTA curves for untreated kaolin ore. Sample ground to less than 50 μm. Heating rate: 20°C min⁻¹. Performed in a stream of air. Sample weight: 65.9 mg.

a system of equations

$$\left\{ \begin{array}{l} (\text{mg } L_1 - 1/4 \text{ mg } AL) \times \frac{1}{W \times WTKA} \times 10^4 = KA \\ (\text{mg } AL_1 + \text{mg } AL_2) \times \frac{1}{W \times WTAL} \times 10^4 = AL \\ \text{mg } AL_1 + \text{mg } AL_2 = \text{mg } AL \\ \text{mg } AL_1 = 1/3 \text{ mg } AL_2 \end{array} \right. \quad (1)$$

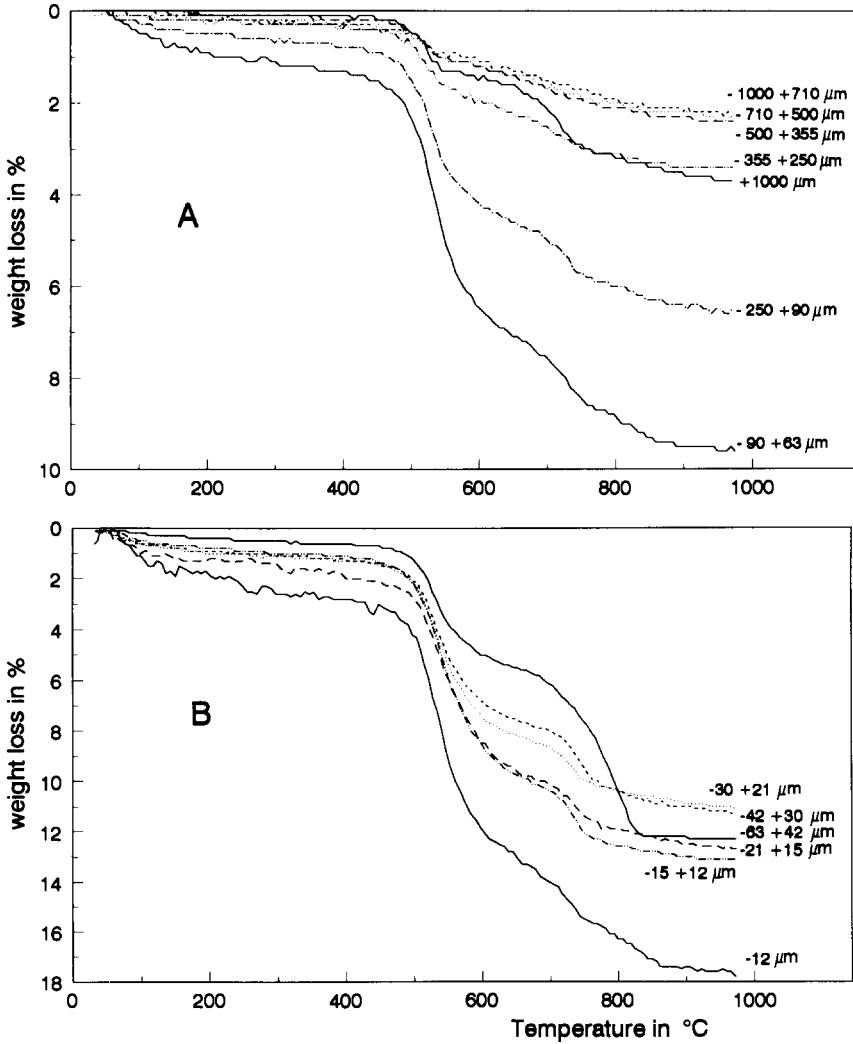


Fig. 3. A. TG curves of the coarser particle-size fractions of the kaolin ore. Samples ground to less than 50 μm. B. TG curves of the smaller particle-size fractions of the kaolin ore. Heating rate: 20 °C min⁻¹. Performed in a stream of air.

where the unknowns are AL and KA and the symbols have the following meanings:

- $\text{mg } L_1$ = First step on curve (mg).
 $\text{mg } AL_1$ = Alunite loss of weight in the first step of curve (mg).
 $\text{mg } AL_2$ = Alunite loss of weight in the second step of curve (mg).
 $\text{mg } AL$ = Sum of contributions of steps L_1 and L_2 of the alunite weight loss (mg).
 AL = Percentage weight of alunite in sample analysed (%).
 KA = Percentage weight of kaolinite in sample analysed (%).
 W = Sample weight (mg)
 $WTAL$ = Weight loss of alunite (52.7%).
 $WTKA$ = Weight loss of kaolinite (13.9%).

7. Results

The TG curves for the thirteen particle-size groups are reported in Fig. 3 while the total weight losses of the samples examined are reported in Fig. 4. The alunite grade in the +1000 μm fraction is higher than in the other coarse fractions, probably because alunite grains are occluded in rock fragments so, despite their softness, they are not able to concentrate in the finer fractions. The weight loss increases in these finer fractions, which, as already shown by XRD examination, means that alunite, and especially kaolinite, concentrate there. The corresponding DTA curves are reported in Fig. 5. The curve of the 63–42 μm fraction reveals a significant concentration of alunite and

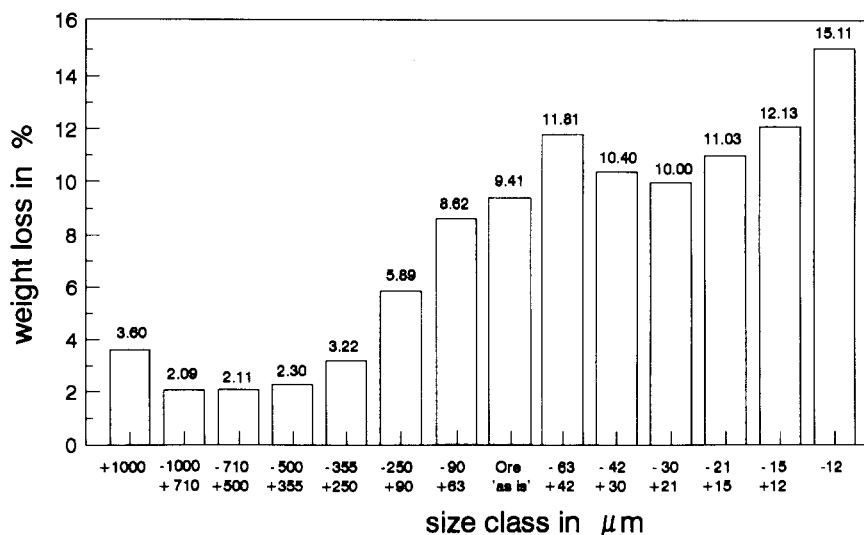


Fig. 4. Total weight losses (%) of the thermal curves executed on the selected particle-size fractions of the kaolin ore. Physically adsorbed water not included.

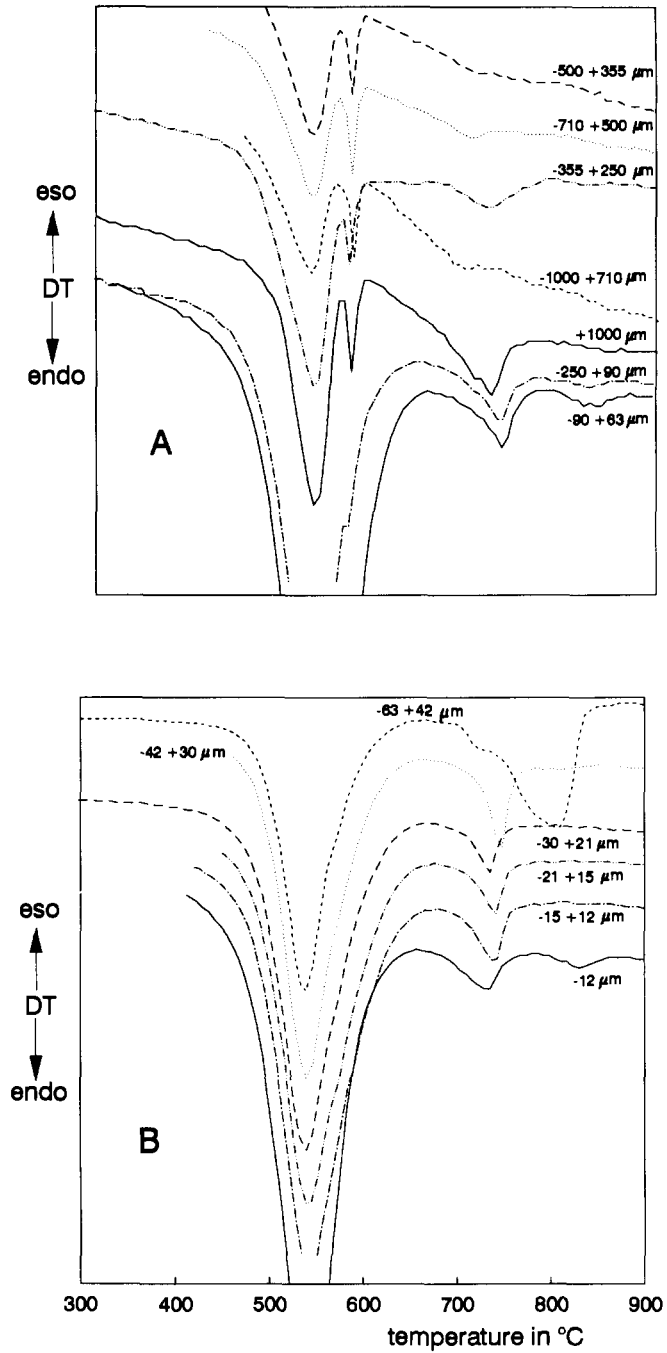


Fig. 5. DTA curves of kaolin ore. A. Coarser particle-sizes. B. Finer particle-sizes.

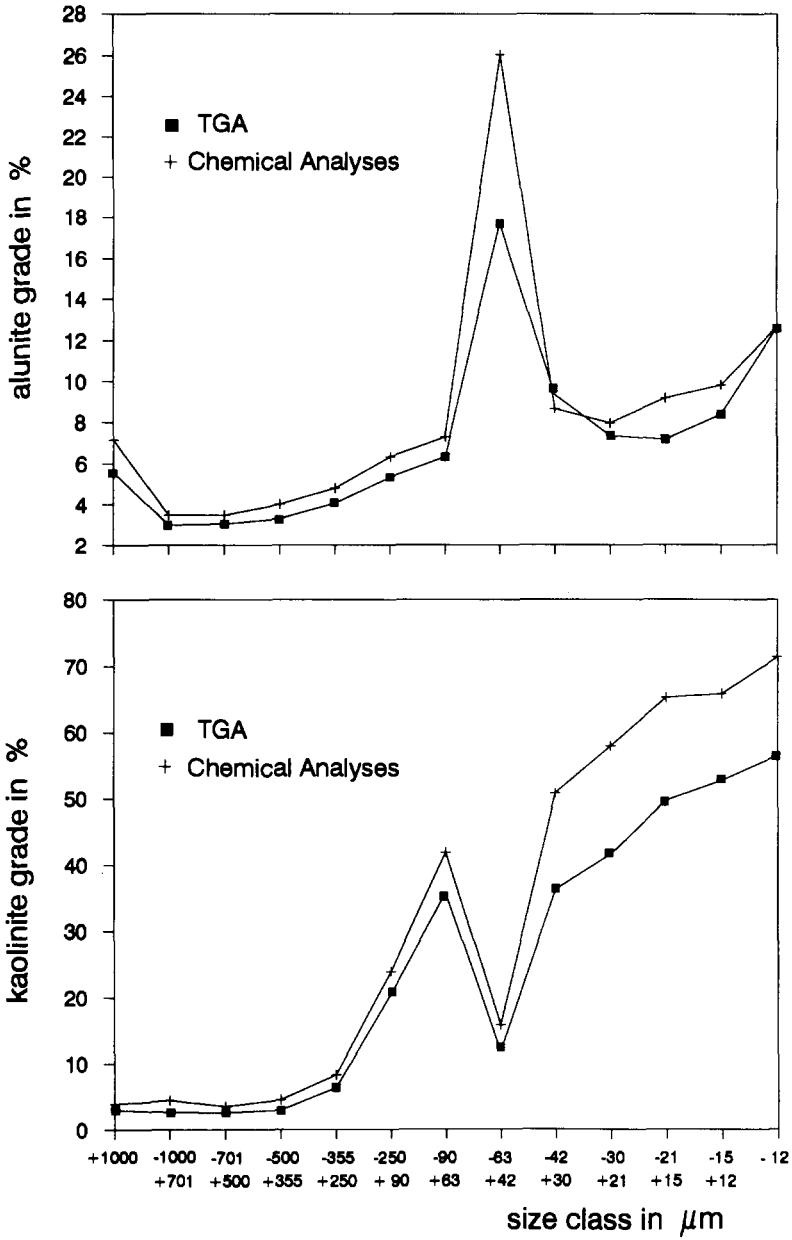


Fig. 6. Alunite and kaolinite grades obtained by TG analysis compared with those obtained by chemical-standard analysis.

a consequent decrease in the kaolinite grade. The desulphuration peak of alunite is in fact larger than the others and is shifted to a higher temperature; this is probably due to the relatively high heating rate adopted which may not have allowed all the SO_3 to be driven off at its proper decomposition temperature. The TG curve of the same fraction (Fig. 3) also shows a higher weight loss at high temperature (alunite) than at low temperature (kaolinite). In the upper curves of Fig. 5, relative to the coarser fractions, the peak of the $\alpha \leftrightarrow \beta$ inversion of quartz is evident at about 580°C . The peak disappears in the smaller fractions where the amount of quartz decreases, as already revealed by XRD examination. The mineralogical estimate, carried out by standard calculation starting from elemental chemical analyses and utilized as reference, was executed in the following manner: the % alunite was determined by sulphur analysis. Since only alunite and feldspar contain potassium, it is possible to calculate feldspar from total potassium minus the potassium contained in alunite whose amount is already known. Kaolinite was calculated from total aluminium minus the amount contained in the alunite and the feldspar.

Fig. 6 illustrates the results obtained for the samples analysed. In the case of alunite there is good agreement between the thermogravimetric and chemical methods. In fact the differences in absolute values between the two analyses range from 0.03% (+ 12 μm sample) and 0.45% (710–500 μm sample) to 8.35% (63–42 μm sample). Apart from the 42–30 μm sample, the results supplied by TG are consistently lower than those obtained by chemical analysis. The results obtained for kaolinite follow the same trend but are less accurate and are consistently lower than those obtained by chemical analyses. There could be two reasons for this: kaolinite is the third mineral to be determined by chemical analysis after alunite and feldspar, therefore it suffers more from errors due to chemical analysis than does alunite; and the weight loss of kaolinite is calculated as the difference between the weight loss of the first step as a whole and that of the second step which is due entirely to alunite. Finally, the error between the chemical and the thermogravimetric calculations is higher for the finest fractions because in this case it was more difficult to separate the two steps of the thermogravimetric curve. Nevertheless, the results can be used for relative comparison of the tests carried out during a physical treatment campaign.

8. Conclusions

The thermogravimetry of the particle-size fractions obtained by classifying a kaolin ore gives results in good agreement with those obtained via standard calculations starting from elemental chemical analysis. The adoption of a system of equations avoids the need for matching weight-loss curves as a function of temperature obtained from the thermal curve. The results achieved for the alunite grade of the samples are more accurate than those for kaolinite owing to the method of calculation adopted. When samples of different mineralogical composition are involved, thermogravimetric analysis thus provides a quicker method of mineral analysis for this type of ore than does chemical analysis. TG/DTA also indicates how kaolinite and alunite are distributed among the various particle-size fractions investigated. In the case considered,

alunite is concentrated in the 63–42 μm and 42–30 μm particle-size fractions while in the coarser fraction (+ 1000 μm), it is occluded in rock fragments of feldspar and quartz and so is unable to concentrate in the finest fractions. As far as kaolinite is concerned, thermogravimetric analysis gives less accurate results. Nevertheless, these follow the same trend as those obtained via chemical analysis thus providing a useful relative estimate for the content of the products obtained from physical treatment tests. It is not so easy to perform a reliable mineralogical analysis on the smaller particle-size fractions owing to the difficulty of separating the two weight-loss steps on the thermogravimetric curve.

Acknowledgement

The author thanks Mr. G. Marruzzo for XRD analysis and Mr. R. Massidda for sample preparation.

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