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Thermal behaviour of mixtures of an alunite ore with K_2CO_3, $CaCO_3$ and $Ca(OH)_2$

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Abstract

The thermal behaviour of alunite/K_2CO_3, alunite/$CaCO_3$ and alunite/$Ca(OH)_2$ mixtures has been established. DTA coupled with XRD analysis has allowed appraisal of the main reactions that occur when the mixtures are roasted up to about 1000°C. The main products of roasting are K_2SO_4, $CaSO_4$ and other sulphur compounds and aluminates which retain the SO_3 deriving from the alunite. The products are formed between 700 and 800°C. The aim of the work was to assess the feasibility of a thermal process for use in the case of certain kaolin deposits whose exploitation is impossible at the present time because they are contaminated with alunite ($KAl_3(SO_4)_2(OH)_6$). This mineral causes great difficulty when attempting to use these kaolin ores because kilning drives off SO_3 which corrodes the furnaces and is environmentally harmful. The K_2SO_4 and $CaSO_4$ produced by roasting the indicated mixtures can be leached with water and dilute HCl respectively and the former can be used as fertiliser. The leaching residue, with its reduced sulphur content, can then be employed by the ceramics and building industries. © 1997 Elsevier Science B.V.

1. Introduction

Alunite has been considered as an important alternative to bauxite for alumina production [1,2]. In alunite-kaolinite ores the alunite grade must be high enough to warrant an alumina-production process. The appropriate grade for this purpose is sometimes achieved by separating the kaolinite from the alunite by flotation and flocculation. However, when the grade of alunite in these ores is too low or its particle size is such as to prevent enrichment of either the kaolinite or the alunite, the latter detracts from the marketability of what would otherwise be a technically-acceptable kaolin, because it releases SO_3 when the contaminated clay is fired. This gas can damage kilns, pollute the environment and cause pin-holes on the surface of the ceramic product. The aim of the work reported in this paper was to investigate the thermal behaviour of K_2CO_3/alunite $CaCO_3$/alunite and $Ca(OH)_2$/alunite mixtures which react with the evolving SO_3 to form K_2SO_4 and $CaSO_4$, thus preventing its release into the environment. The following reactions probably occur during heating:

$$KAl_3(SO_4)_2(OH)_6 + \tfrac{3}{2}K_2CO_3 \rightarrow 2K_2SO_4 + 3H_2O\uparrow + \tfrac{3}{2}CO_2 + \tfrac{1}{2}Al_2O_3 \quad (1)$$

$$KAl_3(SO_4)_2(OH)_6 + \tfrac{3}{2}CaCO_3 \rightarrow \tfrac{3}{2}CaSO_4 + 3H_2O\uparrow + \tfrac{3}{2}CO_2 + 3Al_2O_3 + \tfrac{1}{2}K_2SO_4 \quad (2)$$

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$$\mathrm{KAl_3(SO_4)_2(OH)_6} + \tfrac{3}{2}\mathrm{Ca(OH)_2} \rightarrow \tfrac{3}{2}\mathrm{CaSO_4} + \tfrac{9}{2}\mathrm{H_2O}\uparrow + \tfrac{3}{2}\mathrm{Al_2O_3} + \tfrac{1}{2}\mathrm{K_2SO_4} \qquad (3)$$

According to the literature, the presence of SO_3 favours the decomposition of K_2CO_3 with formation of $K_2S_3O_{10}$ [3]. There is total miscibility between K_2CO_3 and K_2SO_4 as solids, and while the K_2SO_4 is in course of formation the liquidus temperature increases towards the melting point of the sulphate (1069°C) [4].

2. Experimental

2.1. Sample

The work was performed on an alunite ore from the Tolfa deposits in Lazio (Italy). This is a high-grade alunite with traces of potassium sulphate ($K_2S_2O_3$). The results of the chemical analysis, performed with a Perkin Elmer AAS, and of the particle-size analysis, performed with a laser analyser, are given in Table 1. All the salts used for the mixtures were analytical grade (Carlo Erba). Three mixtures were prepared: K_2CO_3/alunite (MIX1), $CaCO_3$/alunite (MIX2) and $Ca(OH)_2$/alunite (MIX3) at three different ratios: sub-stoichiometric 0.5 (MIXA), stoichiometric 1 (MIXB) and overstoichiometric 1.5 (MIXC) with respect to the amount of alunite present in the ore. Fig. 1 shows the XRD spectra of alunite, K_2CO_3 and the mixture subjected to thermal analysis. The mixtures were homogenized before thermal treatment by milling to minus 38 μm in an agate mortar. 20 g of each mixture at the highest stoichiometric ratio was roasted at 900°C and the residues subjected to X-ray analysis to support the interpretation of the thermal curves. The X-ray analysis was performed with a Siemens D500 X-ray diffractometer (CuKα) after the samples had been held for an hour in a desiccator.

Table 1
Chemical and particle-size analysis of alunite

Oxide	%	Size class (μm)	%
SO_3	42.25	103.0–73.0	3.3
Al_2O_3	31.32	73.0–51.0	8.3
K_2O	10.85	51.0–36.0	8.8
SiO_2	0.96	36.0–21.0	14.6
Na_2O	0.73	21.0–12.5	13.2
CaO	0.11	12.5–6.0	16.4
Fe_2O_3	0.11	6.0–3.1	12.9
CO_2	0.37	3.1–1.5	10.7
LOI [a]	13.59	<1.5	11.8
Total	100.29		100

[a] by TG; 24.27% after 1 h at 700°C in muffle. % Alunite: %Al/theoretical %Al content in pure alunite = 16.58/19.56*100=84.8%.

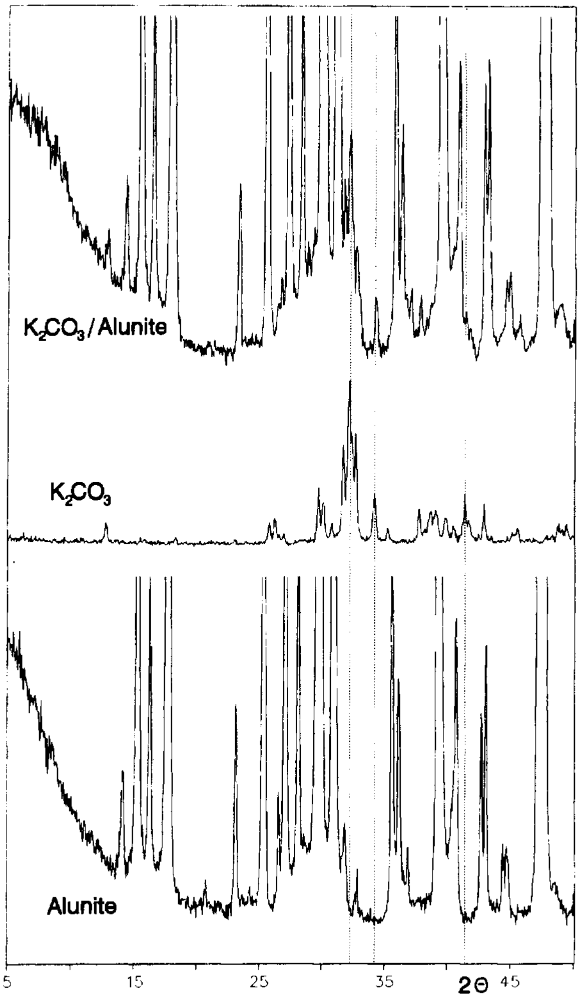

Fig. 1. X-ray spectra of alunite, K_2CO_3 and the alunite/K_2CO_3 mixture.

2.2. Thermal apparatus

The tests were performed in a stream of air using a Stanton Redcroft Model 1500 thermobalance having a sensitivity of 1 mg, temperature range of 20–1500°C and heating rates of 0.1–50°C/min. The furnace winding is platinum–rhodium and the thermocouple is located under the rhodium–platinum holder containing the sample. The instrument is interfaced with a computer for logging and processing the results. The sample was placed in the holder and heated in stream of air up to 1000°C at a rate of 20°C/min. Special care was taken always to maintain the same weight and the same sample geometry in the sample holder. DTA curves were standardized by dividing the DTA signal by the weight of the sample and multiplying the result by 84, namely the average in milligrams of the weight of all samples subjected to TG/DTA.

2.3. Thermal behaviour of alunite

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 aluminium atom lies in the centre (Fig. 2). The sulphate ions (tetrahedra) have three of the four oxygen atoms bonding directly to the aluminium octahedra thus forming the base of the tetrahedron. The potassium environment is likely to be octahedral [5]. The thermal behaviour of alunite on heating has been extensively studied [6–9]. 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 [9]:

First step:

$$2\mathrm{KAl}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6 \rightarrow 2\mathrm{KAl}(\mathrm{SO}_4)_2 + 2\mathrm{Al}_2\mathrm{O}_3 + 6\mathrm{H}_2\mathrm{O} \qquad (480\text{–}620^\circ\mathrm{C},\ \mathrm{W}\% = 13.05)$$

During this endothermic reaction alunite is transformed into crystalline $\mathrm{KAl(SO_4)_2}$ and amorphous $\mathrm{Al_2O_3}$.

Second step:

$$2\mathrm{KAl}(\mathrm{SO}_4)_2 \rightarrow \mathrm{K}_2\mathrm{SO}_4 + \mathrm{Al}_2\mathrm{O}_3 + 3\mathrm{SO}_3 \qquad (770\text{–}900^\circ\mathrm{C},\ \mathrm{W}\% = 28.99)$$

This second endothermic reaction refers to the loss of 75% of the sulphate present. The thermal curves of the alunite used for the mixtures are reported in Fig. 3. The dehydroxylation peak appears between 480 and 670°C, while the desulphuration peak occurs between 770 and 880°C. The small exothermic peak at about 760°C, could be associated with the crystallisation of either α or γ-$\mathrm{Al_2O_3}$ [11] or the decomposition of alum into separate phases [8] though decomposition should be accompanied by heat absorption. It ensues from the

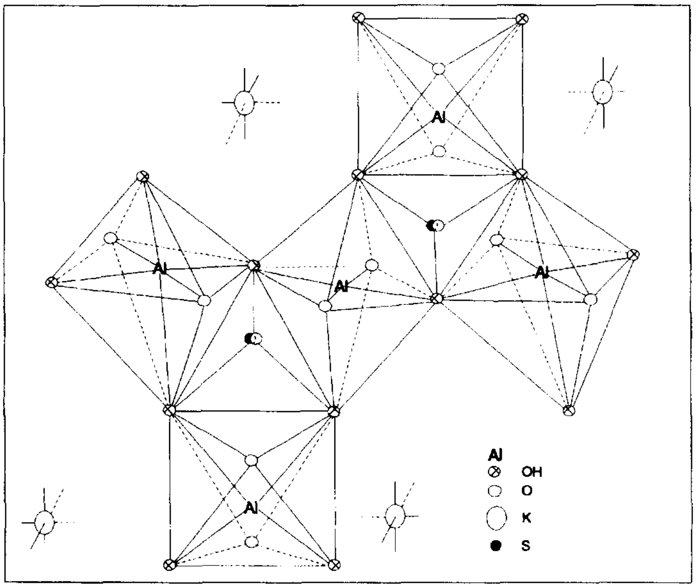

Fig. 2. Alunite structure. Bond angles and bond lengths not strictly respected.

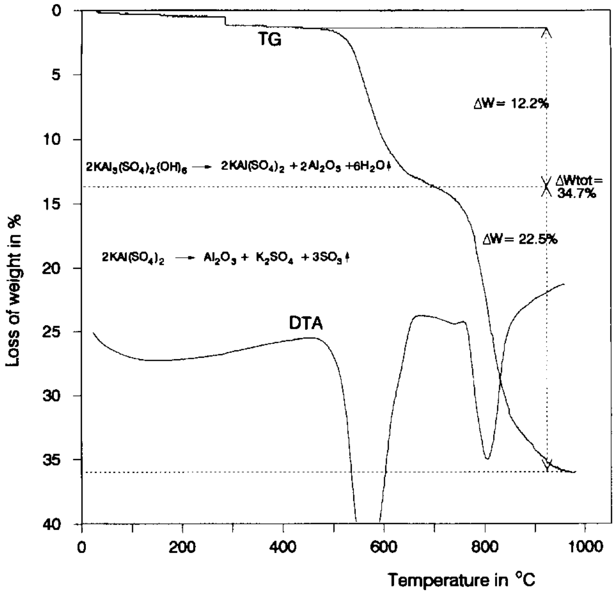

Fig. 3. Thermal curves (TG/DTA) of the alunite used for the mixtures.

total loss of weight of the TG curve (34.7%) that the grade of alunite was 82.6%, which is in good agreement with the grade calculated from the chemical analyses performed on the sample used to make the mixtures (Table 1).

3. Results and discussion

3.1. DTA evaluation

The DTA curves of the mixtures of alunite with K_2CO_3, $CaCO_3$ and $Ca(OH)_2$ in various stoichiometric ratios are reported in Figs. 4–6. The maximum of the alunite desulphuration peak shifts towards lower temperatures in all the mixtures as the amount of the mineral decreases. Fig. 4 clearly illustrates the effect of increasing the K_2CO_3/alunite ratio. As is evident, the area of the dehydroxylation peak (A) decreases with the increase in the K_2CO_3 content; the same effect is exhibited by the desulphuration peak (B) which ranges between 737 and 757°C depending on the composition of the mixture. As far as this last peak is concerned, the decrease is also attributable to the reaction between K_2CO_3 and SO_3 with the formation of K_2SO_4. In fact the ratio between the intensity of the dehydroxylation peak and the desulphuration peak increases as a function of the increase in the K_2CO_3 percentage. This could indicate that not all the SO_3 evolving from the decomposition of the alunite is released to the atmosphere but reacts with the K_2CO_3 (molten at the reaction temperature) as per Reaction (1). Table 2 reports the expected and the actual weight loss that occurs during the heating of the K_2CO_3/alunite mixtures (MIX1). It can be seen that the actual loss of weight due to SO_3 is always lower than that expected in the case of no reaction between alunite and K_2CO_3; this is due not only to the decrease in alunite from MIX1A to MIX1B. Indeed, the ratio between the evolving SO_3 and H_2O decreases from MIX1A to MIX1B, denoting that at least a part of the SO_3 has reacted with the K_2CO_3 to form K_2SO_4. The small exothermic peak at about 880°C in Fig. 4 is associated with the $\gamma \rightarrow \theta$ and $\chi \rightarrow \kappa$ transitions of Al_2O_3 [10]. In the DTA curves of MIX1A this effect is less evident, probably because the biggest desulphuration peak hides that peak. Fig. 5 shows the DTA curve of $CaCO_3$ with a decomposition peak (D) at about 842°C and also the curves for the $CaCO_3$/alunite mixtures. The exothermic peak (B) at about 738°C corresponds to Reaction (2) when $CaCO_3$ is substoichiometric with respect to the alunite. The next

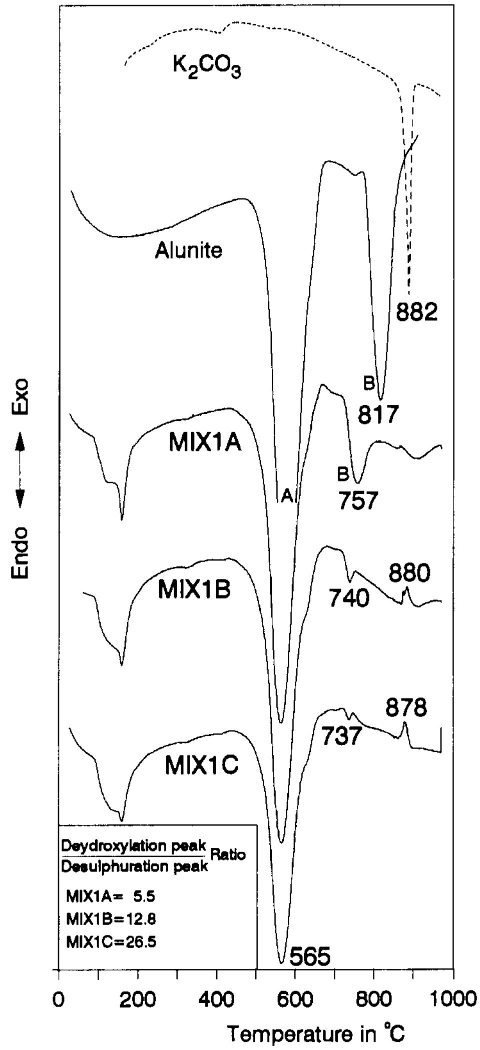

Fig. 4. Thermal curves (DTA) of the alunite/K_2CO_3 mixtures. Stoichiometric ratio alunite/K_2CO_3: MIXA = 0.5, MIXB = 1.0, MIXC = 1.5. The curves of pure K_2CO_3 and alunite are also reported.

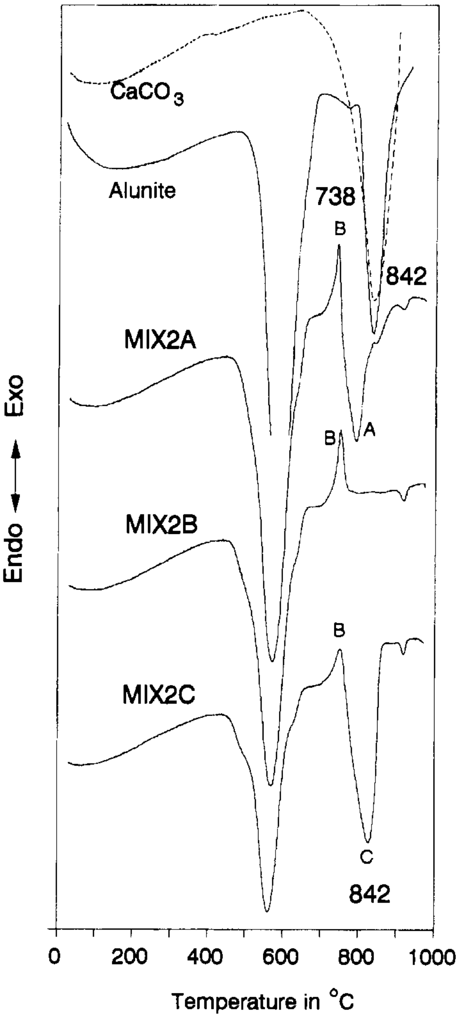

Fig. 5. Thermal curves (DTA) of the alunite/$CaCO_3$ mixtures. Stoichiometric ratio alunite/$CaCO_3$: MIXA = 0.5, MIXB = 1.0, MIXC = 1.5. The curves of pure $CaCO_3$ and alunite are also reported.

endothermic peak (A) at about 790°C is due to the SO_3 driven off from the unreacted alunite. While peak (B) is still present, endothermic peak (A) does not occur on the MIX2B curve for the increase in $CaCO_3$, up to the stoichiometric amount, that reacts completely with the SO_3 from the alunite. The complete absence of peak B could be due to the virtual parity of the formation and decomposition heats of $CaSO_4$ (−309.3 kcal/mol) and $CaCO_3$ (308.2 kcal/mol) respectively, calculated at the reaction temperature of 738°C. This is in agreement with the MIX2C curve which shows both peak B due to the reaction and an endothermic peak (C) at about 830°C due to the decomposition of the excess $CaCO_3$.

All the differential thermal curves of the $Ca(OH)_2$/alunite mixtures in Fig. 6 exhibit an initial endothermic peak (A) between 400 and 500°C due to the decomposition of the $Ca(OH)_2$, as clearly shown by

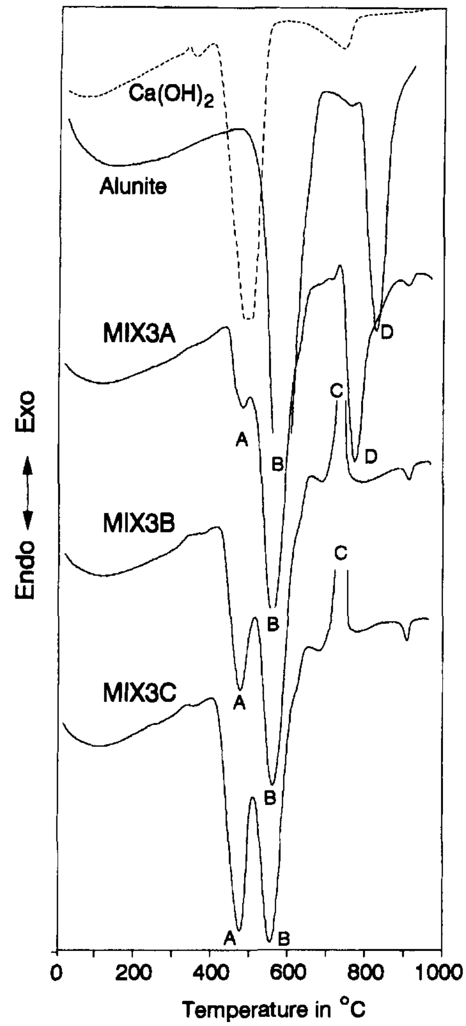

Fig. 6. Thermal curves (DTA) of the alunite/$Ca(OH)_2$ mixtures. Stoichiometric ratio alunite/$Ca(OH)_2$: MIXA = 0.5, MIXB = 1.0, MIXC = 1.5. The curves of pure $Ca(OH)_2$ and alunite are also reported.

the thermal curve of the pure salt. This peak increases in area with the increase in $Ca(OH)_2$ in the mixture, as is evident from comparison of the curves MIX3A, MIX3B and MIX3C. The following endothermic peak (B) at about 550°C is attributable to the dehydroxylation of alunite. The exothermic peak (C) between 730 and 745°C should correspond to Reaction (3) with the formation of $CaSO_4$. This peak increases in area with the increase in the amount of $Ca(OH)_2$ in mixtures MIX3B and MIX3C, in agreement with the disappearance of the desulphuration peak (D) that is absent in these last two mixtures.

Table 2
Expected and actual loss of weight of the mixture K_2CO_3/alunite

	Expected loss of weight (%) (no reaction)			Actual loss of weight		
	H_2O	SO_3	Ratio	H_2O	SO_3	Ratio
MIX1A	9.4	20.9	2.22	13.3	9.7	0.73
MIX1B	7.9	17.7	2.24	11.3	5.4	0.48
MIX1C	6.9	15.4	2.24	10.0	4.7	0.47

3.2. XRD evaluation

Fig. 7 reports the spectra of the three mixtures MIX1C, MIX2C and MIX3C after heating at 900°C. The spectrum of the unroasted K_2CO_3/alunite mixture is also given. The spectrum of the roasted K_2CO_3/alunite mixture shows the expected peaks attributable to K_2SO_4 in the form of arcanite (ASTM: 24-0703) but XRD analysis does not provide indications as to whether the sulphate comes only from decomposition of alunite or whether it is formed by the reaction between the K_2O and the evolving SO_3. The following phases are originated from the roasted $CaCO_3$/alunite mixture: $CaSO_4$ (ASTM: 6-0226), $Ca_4Al_6O_{12}SO_4$ (ASTM: 16-0335), $K_2Ca_2(SO_4)_3$ (ASTM: 20-0867) and free CaO (ASTM: 4-0777). Hence according to Eq. (2) Al_2O_3 and K_2SO_4 are missing, but the former could be amorphous and undetectable by means of XRD [8], while K_2SO_4 could have reacted with CaO to form the above phases. As far as the $Ca(OH)_2$/alunite mixture is concerned, the spectrum is almost the same as the previous one but the peaks of the free CaO and $Ca_4Al_6O_{12}SO_4$ are missing. This is probably because the reaction between the CaO, originated by decomposition of $Ca(OH)_2$, and the evolving SO_3 is more complete than the same reaction involving $CaCO_3$. This hypothesis is supported by the fact that the intensity of the $CaSO_4$ peaks is higher than that of the same peaks obtained on the $CaCO_3$/alunite mixture, and also by the absence of both free CaO and $Ca_4Al_6O_{12}SO_4$. Indeed, the formation of this compound requires a considerable amount of calcium that is mainly used to form $CaSO_4$.

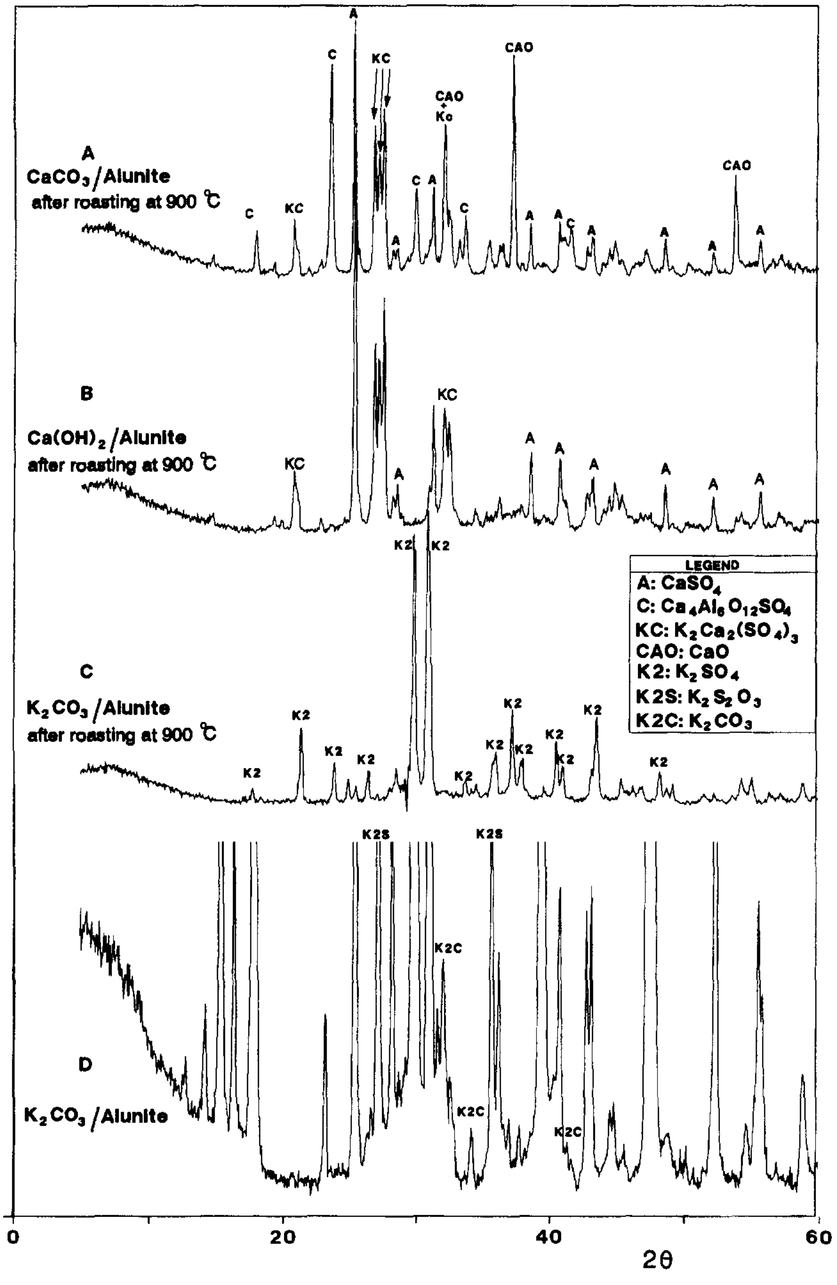

Fig. 7. X-ray diffraction analysis of the mixtures after thermal treatment at 900°C, 3 h (A,B,C). Analysis performed at the same sensitivity. D: before roasting at a higher sensitivity.

4. Conclusions

The roasting of mixtures of alunite with K_2CO_3, $CaCO_3$ and $Ca(OH)_2$ leads to the formation between 700 and 800°C of K_2SO_4 and $CaSO_4$ as main products and of other sulphur-bearing compounds as by-products. These reagents prevent the SO_3 contained in alunite being driven off from the ore. The formation of

$CaSO_4$ is most complete when the $Ca(OH)_2$/alunite mixture is used. After roasting, the soluble salts can be leached with water or dilute HCl to recover K_2SO_4 – which could be used as fertiliser – and $CaSO_4$. The purpose of the preliminary thermal study was to assess the feasibility of a thermal process to render alunite-polluted kaolin ores usable by the building industry. This has not been possible hitherto because alunite contains SO_3 – a gas that is harmful to furnaces and the environment – which is given off when such ores are roasted. Application of the proposed beneficiation process to these ores results in a roasted, leached residue suitable for use in the building industry.

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