Reaction path of a way of synthetis of nepheline NaAlSiO4

Françoise Valdivieso, Michèle Pijolat, Olivier Fiquet

REACTION PATH OF A WAY OF SYNTHESIS OF NEPHELINE $NaAlSiO_4$

F. VALDIVIESO, M.PIJOLAT, O. FIQUET (*)

Centre SPIN, Ecole des Mines, 158 Cours Fauriel, 42023 Saint-Etienne Cedex 2, FRANCE

(*) DESD/SEP/LEMC, C.E.N. Cadarache, 13108 St Paul lez Durance, FRANCE

Abstract :

The transformation of a simulated nuclear waste into nepheline $NaAlSiO_4$ has been studied, using thermogravimetry, mass spectrometry and X-ray diffraction. Several mixtures have been used, which were elaborated from a simulated waste (containing mainly sodium nitrate), alumina and silica. Considering the various mass losses observed, the phases obtained after each mass loss (identified by X-ray diffraction) and the gases released, a reaction path for the transformation has been proposed.

1. Introduction

Sodium nitrate is a common waste of both chemical and nuclear industry, resulting of neutralization of nitric acid by soda. Its transformation into nepheline $NaAlSiO_4$, a stable silicoaluminate mineral is studied in this work.

The reaction path from precursors to nepheline has been investigated. Several mixtures elaborated from a simulated waste, oxalic acid, silica and alumina have been supplied by the C.E.N. Cadarache. They have been characterized by X-Ray diffraction (XRD) and calcined in a thermobalance up to 1300°C. Considering the mass losses, the evolved gases and the phases obtained at different temperatures, a reaction path has been proposed to account for the transformation of the mixtures into nepheline.

2. Experimental

The precursors have been prepared by the atomization of mixtures containing a simulated waste (or pure sodium nitrate), oxalic acid, silica and alumina (or aluminium hydroxide). The components of the initial mixtures are indicated in the second column of Table 1, and the phases identified by XRD measurements in the studied samples (diffractometer Siemens D5000, Cu Kα) are reported in the third column.

Sample	initial mixture (before atomization)	Identified phases
sample A	simulated waste, alumina	α-Al_2O_3, $NaHC_2O_4,H_2O$ mainly $NaNO_3$, $Na_2C_2O_4$
sample B	simulated waste,aluminium hydroxide	$Al(OH)_3$
sample A1	sodium nitrate, alumina	α-Al_2O_3, $Na_2C_2O_4$ mainly $NaNO_3$, $NaHC_2O_4,H_2O$
sample B1	sodium nitrate, aluminium hydroxide	$Al(OH)_3$, $NaNO_3$

Table 1 : Preparation and XRD characterization of the studied samples.

The diffractograms of samples A and B (see Table 1) are given in Figure 1a and 1b.

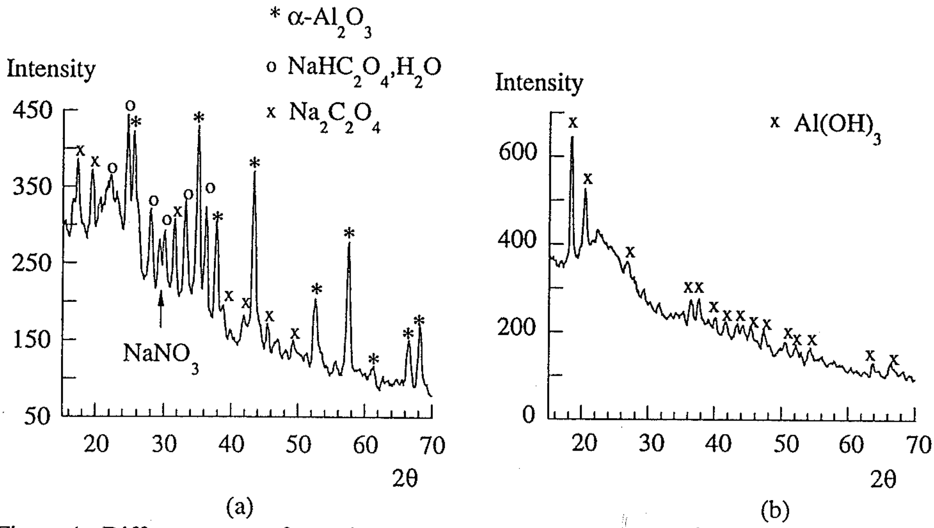

Figure 1 : Diffractograms of samples A(a) and B (b), (see Table 1).

The samples were calcined in a thermobalance SETARAM TAG24, in a flowing helium-oxygen (25%) atmosphere, the total flow rate being $2l.h^{-1}$. The temperature was raised up to 1300°C (5°C/min), the DTA signal was followed simultaneously with the mass loss, and the gases evolved were analysed by a mass spectrometer BALZERS QMG 420C.

2.1. Samples containing α-alumina

Successive mass losses have been observed between 100 and 500°C, as shown in Figure 2a (which corresponds to sample A). The evolved gases detected by mass spectrometry are reported in Figure 2b, 2c and 2d.

Water vapour (m/e=18) and carbon dioxide (m/e=44) can be observed, as well as nitrogen monoxide (m/e=30) and dioxide (m/e=46) in a smaller extent, coming from the decomposition of nitrate ions. The different maxima on the curve of rate of mass loss can be related to these gaseous evolving.

The mass loss curve and the corresponding evolved gases obtained with sample A1 (elaborated from sodium nitrate, see Table 1) are indicated on Figure 3. The results are quite similar to those obtained with sample A (prepared from a simulated waste), although the mass loss which occurs before 350°C is smaller in the case of sample A1 than for sample A.

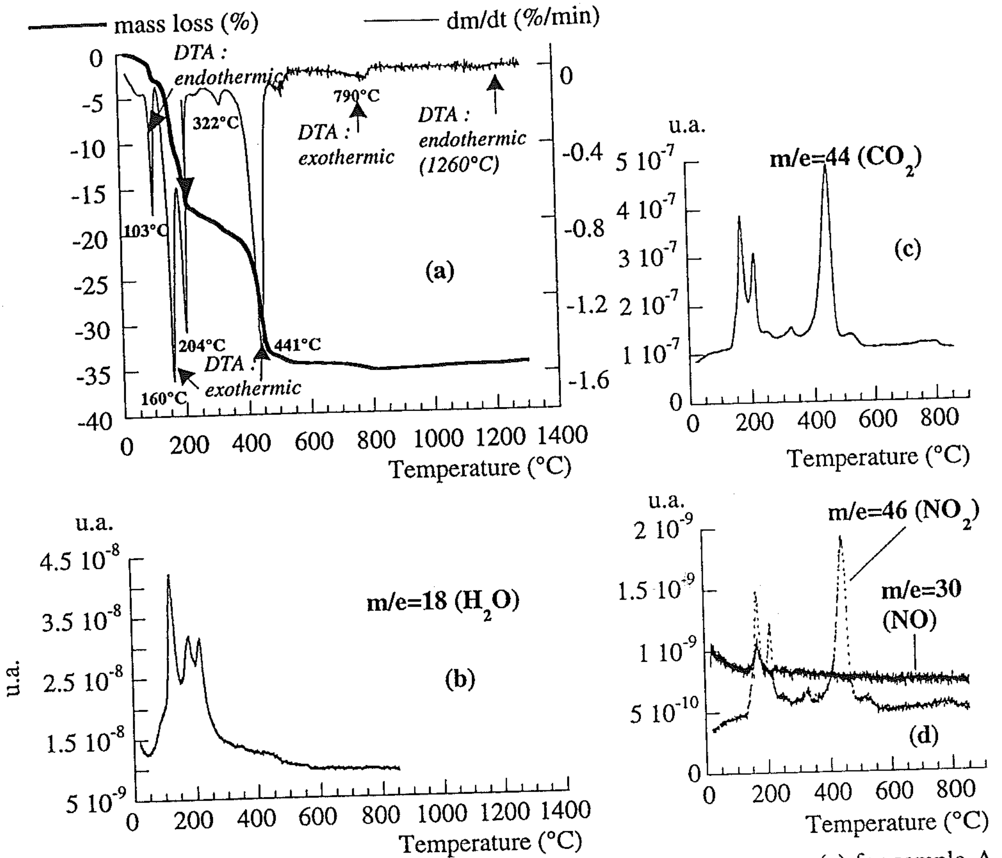

Figure 2 : Curves of mass loss and rate of mass loss versus temperature (a) for sample A, and the evolved gases (water vapour (b), carbon dioxide (c), nitrogen oxides (d)).

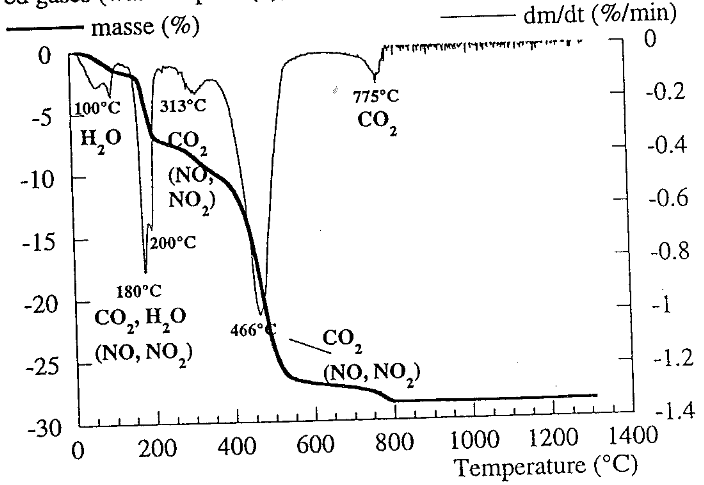

Figure 3 : Curves of mass loss and rate of mass loss versus temperature for sample A1, and the corresponding released gases.

Various samples were prepared by calcination of sample A in the same conditions as previously described, but up to different temperatures corresponding to the successive mass losses, and they were analysed by XRD. The temperatures and the identified phases are indicated in Table 2.

temperature (*)	**gaseous evolving (**)**	**identified phases**
125°C	H_2O	Al_2O_3, $NaHC_2O_4,H_2O$ $Na_2C_2O_4$
180°C	CO_2, H_2O, (NO, NO_2)	Al_2O_3, $NaHC_2O_4,H_2O$ ↘ $Na_2C_2O_4$ ↗
235°C	CO_2, H_2O, (NO_2)	Al_2O_3, $Na_2C_2O_4$
340°C	CO_2, (NO_2)	idem
485°C	CO_2, (NO_2)	Al_2O_3, $Na_2C_2O_4$ (minor)
590°C	CO_2, (NO_2)	Al_2O_3 (quite badly crystallized sample)
825°C	CO_2, (NO_2)	Al_2O_3, $NaAlSiO_4$ (nepheline)
1300°C		$NaAlSiO_4$ (carnegeite)

Table 2 : Phase identification by XRD measurements (sample A).
(*) temperature at which the programmation was stopped (after each peak on the DTG curve)
(**) gaseous evolving observed for the DTG peak corresponding to each temperature

2.2. Samples containing aluminium hydroxide

The curves of mass loss obtained for the samples prepared from a simulated waste or pure sodium nitrate are quite similar.

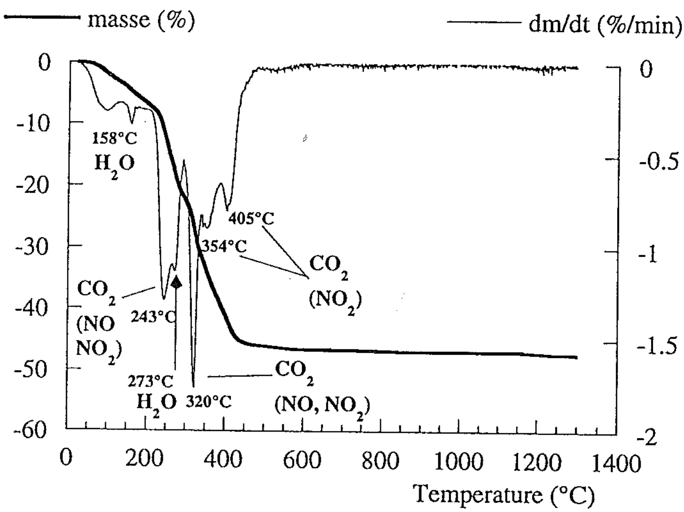

Figure 4 : Curves of mass loss and rate of mass loss versus temperature for sample B, and the corresponding released gases.

The thermograms and the gaseous evolving corresponding to sample B are given in Figure 4 : the gases are the same as those observed for the samples containing α-alumina (water vapour, carbon dioxide and nitrogen oxides).

An experiment carried out with an aluminium hydroxide sample has shown that the DTG peak at about 270°C, which is associated with a strongly endothermic release of water, corresponds to the decomposition of $Al(OH)_3$.

The other mass losses are more difficult to explain, since all the samples prepared at different temperatures are amorphous, so the phases could not be identified by XRD, excepted at 760°C, where crystallized nepheline is observed.

3. Interpretation

Considering the experimental results obtained for samples containing α-alumina (the mass losses, the phases obtained after each mass loss, as well as the evolved gases), a reaction path for the transformation of the precursors into nepheline can be proposed :

- up to about 350°C, the reaction of sodium hydrogen oxalate with oxygen leads to sodium oxalate, according to :

$$2\ NaHC_2O_4,H_2O + \tfrac{1}{2}\ O_2 = Na_2C_2O_4 + 2\ CO_2 + 3\ H_2O \qquad (1)$$

- then, two reaction paths are possible : either sodium oxalate reacts directly with alumina and silica to give nepheline at about 440°C (exothermic reaction), according to:

$$Na_2C_2O_4 + Al_2O_3 + 2\ SiO_2 + \tfrac{1}{2}\ O_2 = 2\ NaAlSiO_4 + 2\ CO_2 \qquad (2)$$

or sodium carbonate Na_2CO_3 is formed as an intermediate phase :

$$Na_2C_2O_4 + \tfrac{1}{2}\ O_2 = Na_2CO_3 + CO_2 \qquad (3)$$

and $$Na_2CO_3 + Al_2O_3 + 2\ SiO_2 = 2\ NaAlSiO_4 + CO_2 \qquad (4)$$

But an experiment carried out with sodium oxalate, in the same conditions as previously described, has shown that sodium oxalate is decomposed into sodium carbonate between 500°C and 600°C. Therefore, as the mass loss occurs for the mixtures between 400 and 500°C, sodium oxalate may react directly with alumina and silica (reaction (2)), but XRD reveals only the crystallized alumina phase.

So, amorphous nepheline is obtained at 500°C, which crystallises at about 800°C (an exothermic peak is observed on the DTA curve, associated with a slight mass loss). Nepheline is transformed into $NaAlSiO_4$ carnegeite at 1260°C (cubic structure above 1250°C, whereas nepheline has an hexagonal structure) (endothermic DTA peak).

The theoretical mass loss for the transformation of sodium oxalate into nepheline (due to reaction (2)) is 20.2% (assuming that the mixture of sodium oxalate, alumina and silica is in stoichiometric proportions). Despite the fact that the studied mixtures contain several phases that can react simultaneously (even the samples prepared from sodium nitrate), we can try to compare the theoretical and experimental mass losses : for sample A1, if we suppose that the mixture obtained at about 250°C is composed of sodium oxalate, alumina and silica in stoichiometric proportions, the mass loss is 21.7% (considering the mass of the sample at 250°C). So, the agreement between the experimental and theoretical mass losses for reaction (2) is quite correct.

4. Conclusions

The transformation into nepheline of various precursors elaborated from a simulated waste (or sodium nitrate), alumina (or aluminium hydroxide) and silica has been studied using thermogravimetry, mass spectrometry and XRD. Whatever the mixture is, the reaction path is nearly the same :

1) decomposition of sodium hydrogen oxalate up to about 350°C. As far as the samples containing aluminium hydroxide are concerned, an additionnal step of decomposition of aluminium hydroxide occurs at about 275°C.

2) formation of amorphous nepheline between 400 et 600°C, probably from a direct reaction between sodium oxalate and alumina and silica.

3) crystallisation of nepheline at about 800°C (as soon as 740°C for samples containing aluminium hydroxide).