

## TG/DTA-INVESTIGATIONS OF SYNTHETIC MINERALS

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### ABSTRACT

TG/DTA investigations for synthetic Ba-hollandite, perovskite and zirconolite individually and collectively were performed. Phase development of these minerals was studied by X-ray diffraction methods as function of temperature. Addition of simulated high level radioactive waste calcine to the mixture of the aforementioned three mineral phases shows complicated TG/DTA curves due to the multi-phase, multi-components behaviour, reduction of some of HLW oxides to metallic states e.g., Rh, Pd and Mo by the reducing Ar-4 % H<sub>2</sub> sintering atmosphere and decomposition of some residual nitrates from HLW components is starting at about 600°C. The reaction temperature for building up the mineral phases is lowered by the addition of the simulated waste components. Volatilization of some compounds with high vapor pressure e.g., Cs, MoO<sub>3</sub>, RuO<sub>x</sub>, Se, Te could be detected at temperatures higher than 800°C. \*(HLW).

### INTRODUCTION

Fixation of high level radioactive waste, generated from the reprocessing of nuclear spent fuel of light water reactors, in a durable and chemically stable solid matrix is the ultimate goal of any waste management scheme. Glass and its derivatives, e.g., glass ceramics, high silica glass, and borosilicate glass have been studied for the last three decades.<sup>1,2,3</sup> The chemical stability of glass and glass ceramic against water or brine attack, especially under high pressure (150 bar) and temperature (200°C) conditions, i.e. similar to the deep geologic disposal environment, has shown unsatisfactory and undesirable behaviour. Devitrification during long term storage of millions of years due to its amorphous structure and no great resistance of silicate phases against leaching attack calls up the scientific community to look for better products. Therefore attention has been paid to develop crystalline mineral-like phases, which can incorporate the high level radioactive waste species in a chemically more stable, radiation resistant and thermomechanically integrable assemblage which prevent the introduction of the radioactive waste species into the biosphere through the movement of groundwater.<sup>4,5</sup>

Synthetic rocks or SYNROC waste forms have been investigated for the last five years.<sup>6,7,8,9,10</sup> Hot pressing or hot isostatic pressing was proposed to be the processing scheme of SYNROC waste form due to the high melting point of the mineral assemblages. Subsolidus sintering has been developed as an alternative

process because of its convenience especially under remote operations in high gamma irradiation conditions.<sup>8</sup>

The stabilizing phases of SYNROC-B waste form are Ba-hollandite, perovskite and zirconolite.<sup>7</sup> The stoichiometry of Ba-hollandite has been recently identified by X-ray powder diffraction technique and it was found to be  $Ba Al_2 Ti_5 O_{14}$ .<sup>11</sup> The three synthetic mineral phases are mutually compatible to one another, thermodynamically stable and can accommodate within their crystal structures a wide range of the high level radioactive elements.

During SYNROC-B waste form processing one should investigate, besides the development and changing of the different phases, the volatilization behaviour of the volatile fission products (VFPs), which exist in high level radioactive waste mixture. This is an important factor in evaluating the safety aspects of the processing scheme.<sup>12</sup> Thermogravimetric and mass-spectrometric investigations have to be carried out to study the volatilization rate of the fission product components during the formation of SYNROC as function of temperature. Besides high temperature mass-spectrometry, radiotracer techniques are used to measure elements volatilized during the waste form processing quantitatively.

#### EXPERIMENT AND DATA ANALYSIS

The mineral phases investigated in this study are Ba-hollandite,  $Ba Al_2 Ti_5 O_{14}$ , perovskite,  $Ca TiO_3$  and zirconolite  $Ca Zr Ti_2 O_7$ . In addition to these three pure phases, assemblages or mixtures of the three phase pure or doped with 10 % simulated high level radioactive waste have been investigated. Tab. 1 shows the composition of the products.

TABLE 1

Composition (oxide wt %) of Modified SYNROC-B and the individual mineral phases

	Ba-hollandite	Perovskite	Zirconolith	SYNROC-B	SYNROC-B+10 % HLW**
Al <sub>2</sub> O <sub>3</sub>	15.56	-	-	8.79	8.18
BaO	23.27*	-	-	13.22*	10.31*
CaO	-	41.24*	16.54*	10.58*	8.25*
TiO <sub>2</sub>	61.17	58.76	36.34	60.74	57.16
ZrO <sub>2</sub>	-	-	47.12	6.67	6.10
HLW	-	-	-	-	10.00

\* Introduced as BaCO<sub>3</sub> and CaCO<sub>3</sub> respectively

\*\*Calculations are based upon random ion substitution scheme for the partitioning of HLW elements between SYNROC-phases. HLW = High level radioactive waste.

The starting materials for the individual phases of modified SYNROC-B assemblages were CaCO<sub>3</sub>, BaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>. The simulated HLW used in this study is a mixture of oxides and nitrates of about thirty elements which

represent most of the fission product elements based upon ORIGEN-Code.<sup>13</sup> Actinides were omitted. The preparation procedure of the simulated waste is summarized in the following chemical steps:

- As the fuel elements are dissolved in  $\text{HNO}_3$ , mixing of the appropriate compositions of the nitrates respectively oxides of the waste elements in 5 m  $\text{HNO}_3$ .
- Denitration step of the solution to destroy the nitric acid and the nitrates of most of the waste components using formaldehyde,  $\text{HCHO}$  or formic acid  $\text{HCOOH}$ .
- Drying and calcination at  $500\text{--}600^\circ\text{C}$  to assure complete decomposition of the nitrates of the alkalis and alkaline earth elements.

More details about sample preparation and the heat treatment steps are described elsewhere.<sup>8</sup>

#### Ba-hollandite phase: $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 5 \text{TiO}_2$

The Ba-hollandite phase is considered to be the host phase for radioactive waste ions like  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Mo}^{4+}$  and corrosion products like  $\text{Fe}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ . Therefore it was synthesized corresponding to the amount of these ions in HLW from the mixture of  $\text{BaCO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . Fig. 1 shows the TG/DTA-curves of the mixture  $\text{BaCO}_3 + \text{Al}_2\text{O}_3 + 5 \text{TiO}_2$ . It is to be mentioned, that the decomposition

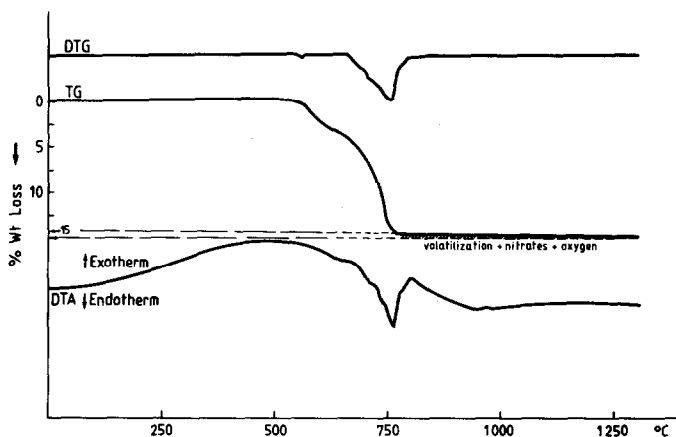
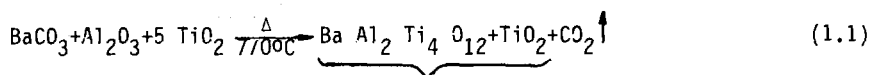


Fig. 1. TG/DTA-curves of the mixture  $\text{BaCO}_3 + \text{Al}_2\text{O}_3 + 5 \text{TiO}_2$

of  $\text{BaCO}_3$  starts at  $\sim 550^\circ\text{C}$  with complete decomposition at  $\sim 910^\circ$ . At point A, i.e.  $770^\circ\text{C}$ , the X-ray diffraction analysis has revealed a major phase which has been identified as  $\text{Ba Al}_2 \text{Ti}_4 \text{O}_{12}$  plus minor unknown plus rutile,  $\text{TiO}_2$ . At point B, C and C',  $980$ ,  $1220$  and  $1250^\circ\text{C}$  respectively, there were no minor phase and the phase  $\text{Ba Al}_2 \text{Ti}_5 \text{O}_{14}$  was identified.<sup>11</sup> The calculated weight loss due to

$\text{CO}_2$  was equal to the measured weight loss from TG data, i.e., there is no volatilization of Ba or BaO. The chemical reaction which can describe the phase formation of  $\text{Ba Al}_2 \text{Ti}_5 \text{O}_{14}$  is as follows:



#### Ca-perovskite phase: $\text{CaO} \cdot \text{TiO}_2$

The Ca-perovskite phase is considered to be the <sup>\*</sup>most phase for radioactive waste ions like  $\text{Sr}^{2+}$ ,  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ,  $\text{Np}^{3+}$ ,  $\text{REE}^{3+}$  and small amounts of  $\text{Ac}^{3+}$ . The amount of the synthesizing materials of  $\text{CaCO}_3$  and  $\text{TiO}_2$  corresponds to the content of these ions in HLW. Fig. 2 shows the TG/DTA data of the mixture  $\text{CaCO}_3 + \text{TiO}_2$ . At point A, i.e.  $810\text{--}850^\circ\text{C}$  the complete decomposition for  $\text{CaCO}_3$  is achieved. The chemical reaction of the formation of Ca-perovskite may be

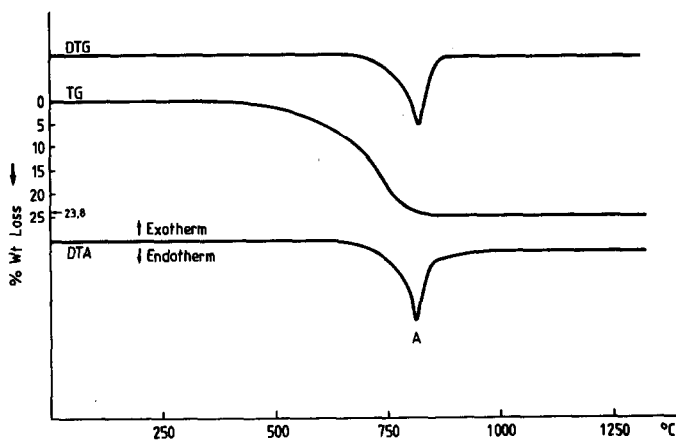
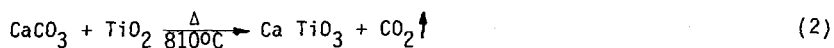


Fig. 2. TG/DTA curves of the mixture  $\text{CaCO}_3 + \text{TiO}_2$

described by the following equation:



The resultant phase has been identified by X-ray diffraction analysis.

\* REE = Rare earth elements

### Zirconolite: $\text{CaO} \cdot \text{ZrO}_2 \cdot 2 \text{TiO}_2$

The zirconolite phase is considered to be the host phase for the radioactive waste ions like  $\text{U}^{4+}$ ,  $\text{Th}^{4+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Cm}^{4+}$ ,  $\text{Am}^{4+}$ ,  $\text{Np}^{4+}$  and in small amounts  $\text{Ac}^{3+}$ ,  $\text{REE}^{3+}$  and  $\text{Sr}^{2+}$ . The starting materials for this phase were  $\text{CaCO}_3$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$ . Fig. 3 shows the TG/DTA data of the mixture  $\text{CaCO}_3 + \text{ZrO}_2 + 2 \text{TiO}_2$ . At point A, i.e.  $810^\circ\text{C}$ , more than 95 % of the calculated weight loss due to  $\text{CaCO}_3$  decomposition has been achieved and the resultant phase is  $\text{CaTiO}_3$  as mentioned before. X-ray diffraction analyses revealed the existence of perovskite,  $\text{ZrO}_2$

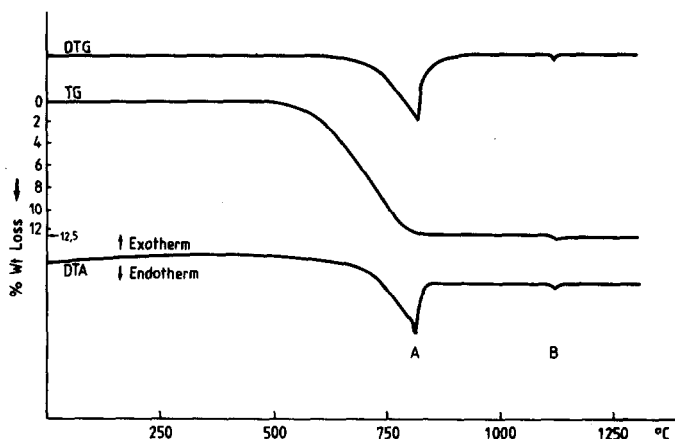
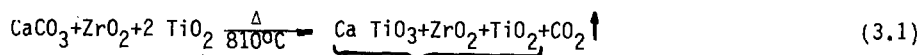


Fig. 3. TG/DTA curves of the mixture  $\text{CaCO}_3 + \text{ZrO}_2 + 2 \text{TiO}_2$

and  $\text{TiO}_2$  (rutile). At point B, i.e.  $1120^\circ\text{C}$ , Zirconolite phase was identified and there were no unreacted  $\text{ZrO}_2$  or  $\text{TiO}_2$  or  $\text{ZrTiO}_4$  detected by X-ray diffraction analyses.

The chemical reaction can be given by



### Undoped SYNROC-B

Several mixtures of Ba-hollandite (H), perovskite (P) and zirconolite (Z) phases were investigated. Modified SYNROC-B is a mixture which has H-P-Z ratios (60:20:20) in proportion to an ion substitution scheme based on the most probable substitution of HLW ions in the three phases.<sup>7</sup> Subsequently a phase-composition calculation was achieved by Computer programs.<sup>5,7</sup> Fig. 4 shows

typical TG/DTA-curves for undoped SYNROC-B assemblage. It is to be noted that the endothermic reaction, i.e. point A, represents a complex or an overlapped peak for two reactions indicated by equations 1, 2 and 3.1. The endothermic reaction at B represents the formation of zirconolite phase as indicated by

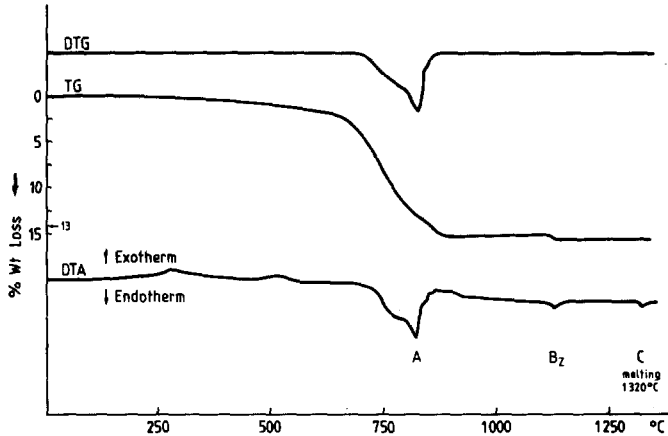


Fig. 4. TG/DTA curves for undoped SYNROC-B

equation 3.2. The melting temperature of this assemblage is indicated by point C, i.e., at  $\sim 1320^{\circ}\text{C}$ .

#### Modified SYNROC-B + 10 wt. % HLW

By adding simulated HLW to the assemblage of mineral phases it has to be considered, that in the wastes mixture besides the cations there are some mineral matrix producing compositions, i.e.,  $\text{ZrO}_2$  and  $\text{BaO}$ . Therefore, new phase-compositions calculations for different types of waste and SYNROC-B like mineral phases have to be performed as to be seen in Tab. 1.<sup>7</sup> The TG/DTA investigations of this modified SYNROC-B + 10 wt % simulated HLW and the interpretation of the resulting data are a rather complicated problem due to several reasons:

- a) The multicomponents and multiphase simulated HLW calcine must react with SYNROC-B constituents to end up with the desired 3-phase host system at different reaction temperatures.
- b) The decomposition of some residual nitrates, in particular the alkaline elements, e.g. Cs and Rb.
- c) The reduction reaction of some of the HLW oxides into a metallic state as a result of the reducing atmosphere ( $\text{Ar-4 \% H}_2$ ), especially Mo, Rh and Pd.<sup>15</sup>
- d) The volatilization of some of the volatile compounds and/or elements of HLW, e.g. As, Se,  $\text{MoO}_3$ , Cd, Te and Cs.<sup>12</sup>

Fig. 5 shows TG/DTA-curves of SYNROC-B with 10 wt % simulated HLW calcine. It is to be noticed that the addition of HLW calcine to SYNROC-B constituents lowers the reaction temperature and enhances the stabilization of HLW elements in SYNROC-B matrix. The figure of merit of volatilization of Cs and Mo are 5 and 6,9 % per g of sintered product.<sup>12</sup> Scanning electron microscope provided with energy dispersive analysis of X-ray, SEM/EDS, has been utilized to investigate the microstructure and phase-microanalysis of the sintered products. Presence of metallic inclusions of Ru, Rh, Pd and Mo was confirmed indicating the reduction of their oxides into a metallic state and subsequently loss of oxygen has occurred.

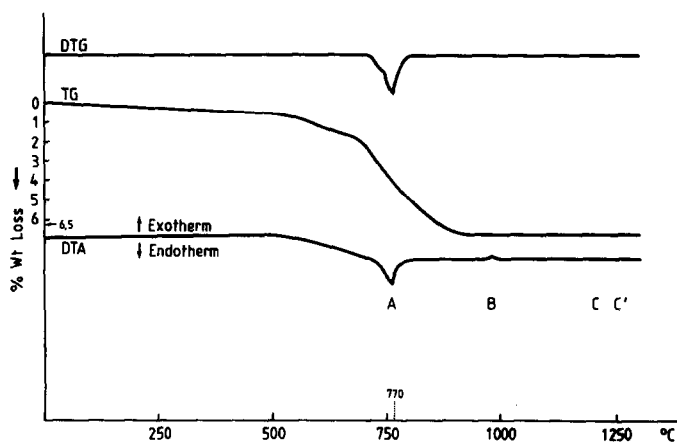


Fig. 5. TG/DTA-curves of SYNROC-B with 10 wt % simulated HLW

## CONCLUSIONS

TG/DTA-MS investigations for the solidification of high level radioactive waste in synthetic mineral waste form are an important parameter to evaluate the process technology including the off-gas treatment. The parameters which can minimize the reaction temperature and the volatilization rate of the compounds during subsolidus sintering of SYNROC-B waste form are:

- High degree of homogeneity between the radioactive waste components and the matrix additives, i.e., the distance between the particles should be in the range of the diffusion path in order to activate a solid state reaction (particle size  $\leq 1 \mu\text{m}$ ).
- The type of reducing atmosphere (Ar-H<sub>2</sub> mixture).

Preliminary investigations showed a significant reduction in the volatilization rate with increasing H<sub>2</sub>-content in the reducing atmosphere. The sintered products had a density  $\geq 96$  % of the theoretical value without any water absorption. The phase formation as function of temperature has been

investigated by X-ray powder diffraction technique indicating that Ba-hollandite, perovskite and zirconolite are formed at 970, 810 and 1120°C respectively. The addition of 10 wt % of simulated HLW lowers the reaction temperatures. The volatilization of the most volatile fission products Cs and MoO<sub>3</sub> is reduced to about 6 % in the temperature range up to 1210°C. Further studies are required to evaluate the optimal composition and process.

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