

Characterization of Two Different Clay Materials by Thermogravimetry (TG), Differential Scanning Calorimetry (DSC), Dilatometry (DIL) and Mass Spectrometry (MS) - 12215

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ABSTRACT

An illitic clay containing higher amounts of organic materials was investigated by dilatometry, thermogravimetry and differential scanning calorimetric. The evolved gases were studied during simultaneous TG-DSC (STA) and dilatometer measurements with simultaneous mass spectrometry in inert gas and oxidizing atmosphere. The dilatometer results were compared with the STA-MS results which confirmed and explained the reactions found during heating of the clay, like dehydration, dehydroxylation, shrinkage, sintering, quartz phase transition, combustion or pyrolysis of organics and the solid state reactions forming meta-kaolinite and mullite. The high amount of organic material effects in inert gas atmosphere most probably a reduction of the oxides which leads to a higher mass loss than in oxidizing atmosphere. Due to this reduction an additional CO₂ emission at around 1000°C was detected which did not occur in oxidizing atmosphere. Furthermore TG-MS results of a clay containing alkali nitrates show that during heating, in addition to water and CO₂, NO and NO₂ are also evolved, leading to additional mass loss steps.

INTRODUCTION

For the intermediate or long term storage of nuclear waste materials, different approaches have been considered by several countries. Under investigation are salt stocks (i.e. Germany), volcanite tuff formations (i.e. Yucca Mountain, USA) and clay formations (i.e. Switzerland).

Clay deposits are considered as nuclear repositories because of their low permeability to water and their good ability to retain radionuclides by physico-chemical adsorption [1]. Clay deposits can of course contain the appropriate clay minerals, like kaolinite or montmorillonite minerals, but other minerals like quartz, micas, etc. as well, along with organic material. Most of the thermal analysis investigations on clays were performed mainly because of interest in them for ceramic production [2, 3, 4]. Thermal analysis methods such as dilatometry, differential scanning calorimetry and thermogravimetry are very powerful tools for investigating the thermal behavior of such multi-mineral mixtures. Adding mass spectrometry for the analysis of the evolved gases during heating greatly increases the information acquired. These methods were applied to a western German illitic clay and a surrogate clay material impregnated with alkali nitrates.

ANALYTICAL APPROACH

The thermal expansion of the clay raw material was measured with a NETZSCH TMA 402 **F1 Hyperion**[®] in a synthetic air atmosphere with a flow rate of 60 ml/min. The powder sample was placed in a standard DSC alumina crucible (6 mm diameter). Placed on the top of the sample material an alumina plate was arranged which fitted in the crucible to support the push rod of the TMA. A heating rate of 5 K/min was applied. For the analysis of the evolved gases a NETZSCH Aeolos[®] QMS 403 mass spectrometer was connected via a heated capillary to the heated adapter head of the TMA outlet. The temperature of the transfer parts and the MS inlet was set to 300°C. The sample length was 2 mm.

The STA-MS measurements were performed with a NETZSCH STA 449 **F1 Jupiter**[®] coupled with NETZSCH Aeolos[®] QMS 403. The samples were measured in Pt crucibles with lids in the temperature range RT to 1200°C at a heating rate of 10 K/min. The sample weight was approx. 35 mg. The clay was measured in nitrogen and synthetic air atmospheres.

RESULTS and DISCUSSION

Illitic Clay

Figure 1 shows the TMA curve of the clay sample together with the intensities of mass number 18 and 44 representing water and carbon dioxide in the room temperature (RT) to 1000°C temperature range. After a small shrinkage at around 160°C the sample expands again until about 485°C (extrapolated onset) where a further shrinkage of 0.05% starts. After this the sample expands again due the low-high temperature transition at 575°C of the crystalline quartz amounts in the sample. The onset of sintering of the clay was detected at about 941°C (extrapolated). As can be seen, the shrinkage steps at 150°C and 500°C are correlated with the dehydration and dehydroxylation of the clay (MS water peaks at 149°C and 498°C). During the CO₂ emission at 337°C, which is due to oxidation of organic impurities, no corresponding shrinkage effect in the TMA curve was found.

Figure 2 shows the TG, TMA and DSC curves of the sample. The TG curve proves that the two shrinkage steps before 800°C were correlated with the mass loss of the sample. Also clearly seen is the burnout of the organics at about 310°C, which is combined with a mass loss of about 0.7 wt% and an exothermic enthalpy of about -85 J/g. The phase transition of the quartz is detected as an endothermic peak at 573°C with an enthalpy of 2 J/g. During sintering of the sample, the exothermic solid state reaction to meta-kaolinite/mullite also occurs (exothermic DSC peak at 964°C and approx. -32 J/g).

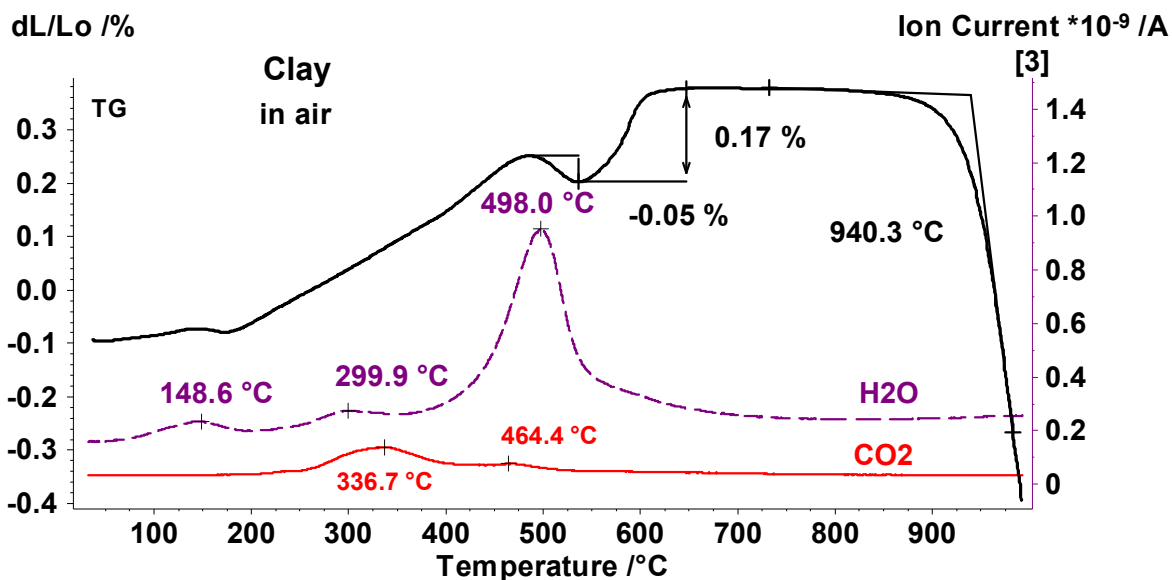


Figure 1. Thermal expansion curve and mass spectrometer curves of CO₂ and H₂O

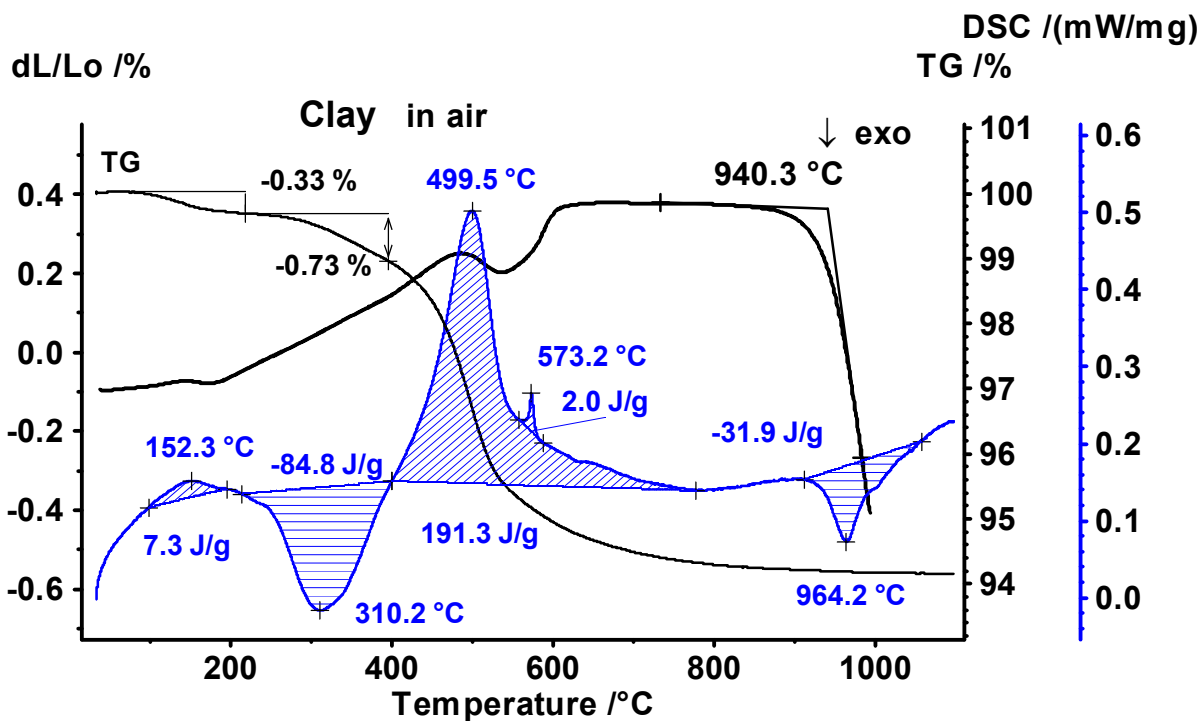


Figure 2. TG, DSC and thermal expansion curve of the illitic clay

Figure 3 depicts a comparison of the TG, DSC and mass spectrometer curves of CO₂ of the clay measured in air atmosphere (black curves) and nitrogen (red curves). Of course in inert gas atmosphere the organics only decompose and could not combust due to the lack of oxygen. Therefore the mass loss up to 800°C is 0.2 wt% less in nitrogen. During the solid state reaction at 942°C (extrapolated onset) a weight loss of 0.4 wt% was detected for the measurement in inert gas. Most probably some of the oxides were reduced by the remaining carbon from the pyrolysis of the organic impurities. The CO₂ formed during this reaction was detected by the mass spectrometer measurement.

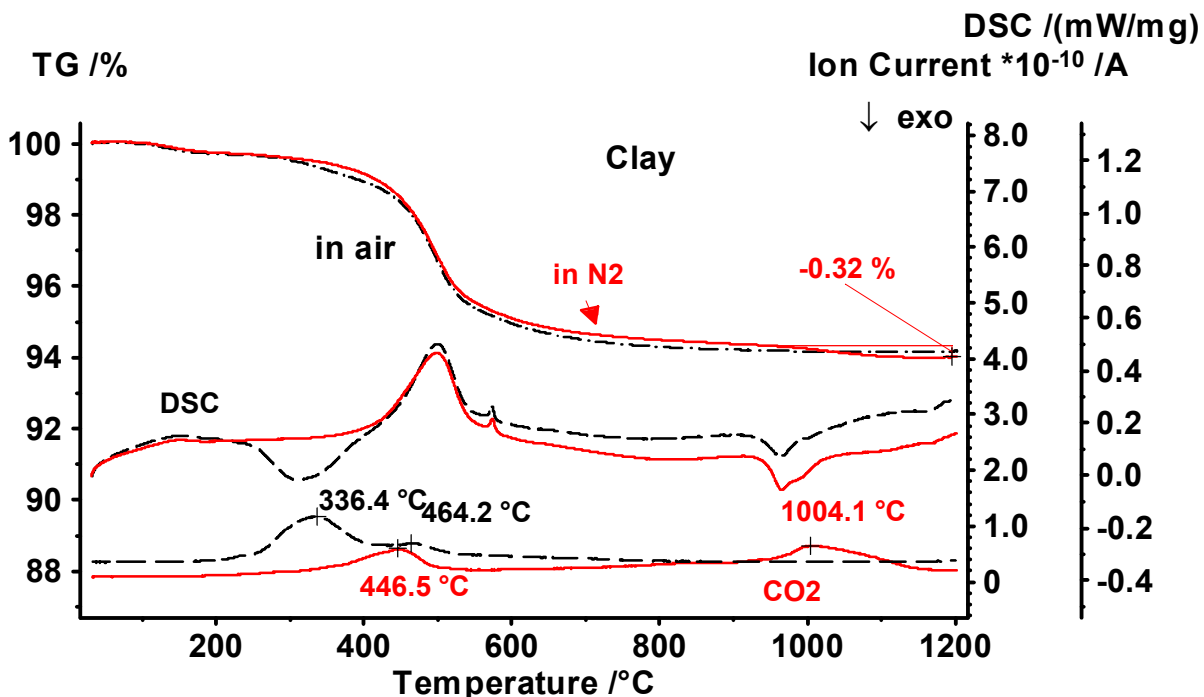


Figure 3. TG, DSC and mass spectrometer curves of CO₂ of the clay measured in air and inert gas atmosphere

Clay contaminated with alkali nitrates

The vermiculite rich clay used in this investigation contained alkali and earth alkali nitrates. During the linear heating at 10 K/min in He atmosphere water, nitrogen oxide, nitrogen dioxide and carbon dioxide were detected (Figure 4). The water was released between RT and about 400°C, and the nitrogen dioxide shows two intensity maxima at about 180°C and 497°C. The nitrogen oxide emission starts at around 300°C and shows maximum intensity at 658°C. The CO₂ amount is very small. Most probably there are some impurities of organic material, hydro carbonates or carbonates. Even during storage in an air atmosphere, some carbonates could be formed due to the small grain size of the material.

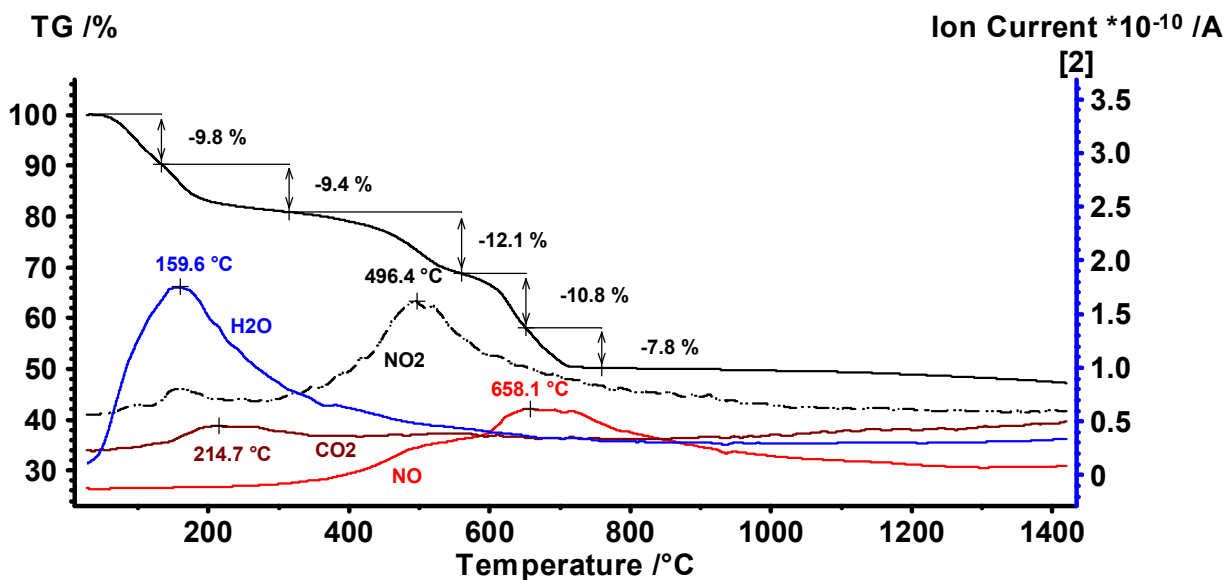


Figure 4. TG curve and mass spectrometer curves of H₂O, NO, CO₂ and NO₂

CONCLUSIONS

These types of clays showed water loss starting around 100°C or even earlier. This relative small mass loss affects only less shrinkage during the expansion of the sample. The dehydroxylation and the high crystalline quartz content result in considerable shrinkage and expansion of the clay. During the usual solid state reaction where the clay structure collapses, the remaining material finally shrinks down to a so-called clinker. With the help of MS the TG steps can be better interpreted as the evolved gases are identified. With the help of the MS it is possible to distinguish between CO₂ and water (carbonate decomposition, oxidation of organics or dehydration/dehydroxylation). The MS also clearly shows that mass number 44 is found during the TG step of the illitic clay at about 900°C in inert gas, which was interpreted as oxidation of pyrolytic carbon by reducing oxides. Additionally, without MS results, the mass loss steps of the nitrate contaminated clay could hardly be interpreted.

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