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A NEW HIGH-TEMPERATURE COUPLING SYSTEM FOR TG/DTA-MS

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ABSTRACT

To get a better interpretation of weight loss curves for multicomponent systems, the knowledge of the volatile species is of great interest. Coupling systems TG/DTA-MS seem to be the best combination for this investigation . As the measurements with the mass-spectrometer are performed in high vacuum, the pressure of one atmosphere in the sample room must be reduced by a two stage gas inlet system. A metallic coupling system for temperatures up to 1250°C was developed, which forms a molecular beam by which even condensable gas species are measurable with a mass-spectrometer.

INTRODUCTION

For the final storage of high level radioactive waste (HLW) generated from nuclear power plants fuel reprocessing in deep geologic formations the liquid wastes have to be solidified. The reference concept in Germany considers to solidify the fission products in a glass matrix.

The sodium-borosilikate-glasses have a remarkably high solubility for all of the 40 fission products.[1] The fixation of this HLW in a glass matrix needs melting temperatures of about 1200°C. This will imply, that some of the fission products will vaporize due to their high partial pressures at this temperature.[2] Some of the thermogravimetric results of this vaporization studies are shown in Fig. 1.

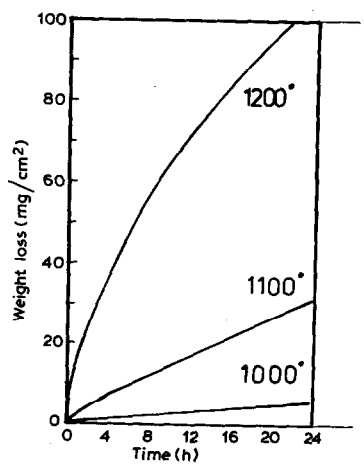

Fig. 1. Weight-loss studies of glasses containing simulated waste

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But results of TG/DTA investigations give only rough informations about the overall weight loss and can not clarify the thermal behaviour of the different elements in this multicomponent system.

To get more precise data about the behaviour of the volatile components, the TG/DTA-system 429 of Netzsch company was coupled with a mass-spetrometer Q 511 of Balzers. With this equipment it should be possible to investigate the physico-chemical reactions during the melting process and the vaporization rate.

Gasdynamic considerations

The melting process of the glasses is going on at normal pressure in air. As the measurements with the mass-spectrometer are performed in high vacuum, the pressure of one atmosphere in the sample room must be reduced to high vacuum by differential pumping, so that the gaseous species are directed by a molecular beam towards the electron impact source.

Actual used two-stage-inlet-systems for MS to investigate gaseous species consist of two Al_2O_3-tube-apertures.[3] By the first orifice with a diameter of 0.1 mm and the suction capacity of the rotation pump of 4 m^3/h the pressure of 10^3 mbar is reduced to 1-5 mbar. This implies a viscous gas inlet into the intermediate vacuum. The viscous gas streaming quantity is largely independent of the molecular weight in contrast to the molecular flow, which has to be formed from this intermediate vacuum by the second aperture. In this molecular flow the gaseous species don't exert an alternating effect on each other, because the average free path of the molecules is large in relation to the dimensions of the tubing and constrictions, i.e. Knudsen-number (Kn) = $\frac{\text{mean free path}}{\text{orifice}}$ $(\frac{\lambda}{d})>1$ at which $\lambda \sim \frac{1}{p}$.

This indicates for an orifice of 0.1 mm in the second aperture, that the pressure at the opening of the orifice must be smaller than 0.35 mb. Therefore the suction capacity of the intermediate vacuum pump or the aperture size are to be chosen such, that the pressure in the first stage is about 10^{-4} mb under the gas load from the source. At this pressure those molecules traveling along the axis of the system can reach the second aperture without suffering collisions and enter the second differentially pumped vacuum chamber as a molecular beam traveling in high vacuum ($< 10^{-4}$ mb). The expansion of the gaseous stream at the orifice outlet occurs according to the cosinus distribution. Due to the gasdynamic the effusion rate of the particles N which arrive at the orifice per time unit is

$$N = \frac{1}{4} \frac{n_i}{n} \cdot \bar{u} \cdot A$$

where

$\frac{n_i}{n}$ = the amount of species n_i in n

$\bar{u}$ = mean thermic velocity of the particles

A = area of the orifice

The intensity of these particles in the ion source of the mass-spectrometer is $I = \frac{N}{\pi x^2}$, if the dispersion is not considered.

The dispersion reduces the intensity $I^* = I \cdot e^{(-x/\lambda)}$

x = distance 2. orifice-ion source

There is a second reduction of the intensity by those molecules, which are reflected by the inner walls of the second pressure reducing tube. This disturbance of the molecular beam can be calculated from

$$I^{**} = I^*(k + \frac{\text{arc tan } (4,5/l)}{90^0})$$

k = equipment specific constant

l = length of the inner tube

EXPERIMENTAL RESULTS

By calculating the value for the old Al_2O_3-tube-system, it could be found, that 97 % of the species, which enter the high vacuum chamber, will touch the walls. If the walls are heated, they will desorb and reflect by which the molecular beam is destroyed.

This can be seen in the following pictures (Fig. 2).

From these results it seems to be necessary to shorten the total two stage coupling system. By intensive investigations and calculations it could be pointed out, that according to the extention of the expansion zone of the gaseous stream after the first aperture, the optimal distance between the two apertures should be about 5 mm.

The different parts of the new short two stage coupling system are shown in the following pictures (Fig. 3).

For the heating of this system a new short furnace with an unsymmetrical temperature profile was developed.[4] The new equipments were tested with six elements with different vapour pressure [I_2(RT-183^{0}C), Hg (80^{0}C-357^{0}C), Se (270-685^{0}C), Te (705-1087^{0}C), Pb (835-1200^{0}C), Ag (1150-1250^{0}C)].

All these elements could be detected with the mass-spectrometer according to their isotope ratio. An increase of the temperature magnified the intensity of the registrated vapour pressure.

DISCUSSION AND CONCLUSIONS

The new developed short two-stage coupling system for TG/DTA-MS equipments is made from chromium-nickel-steel 1.4841 (25,50 CrNi). This system can be used up to 1250^{0}C and is able to reduce the pressure of a gaseous stream of condensable products and to form a molecular beam for investigations with a

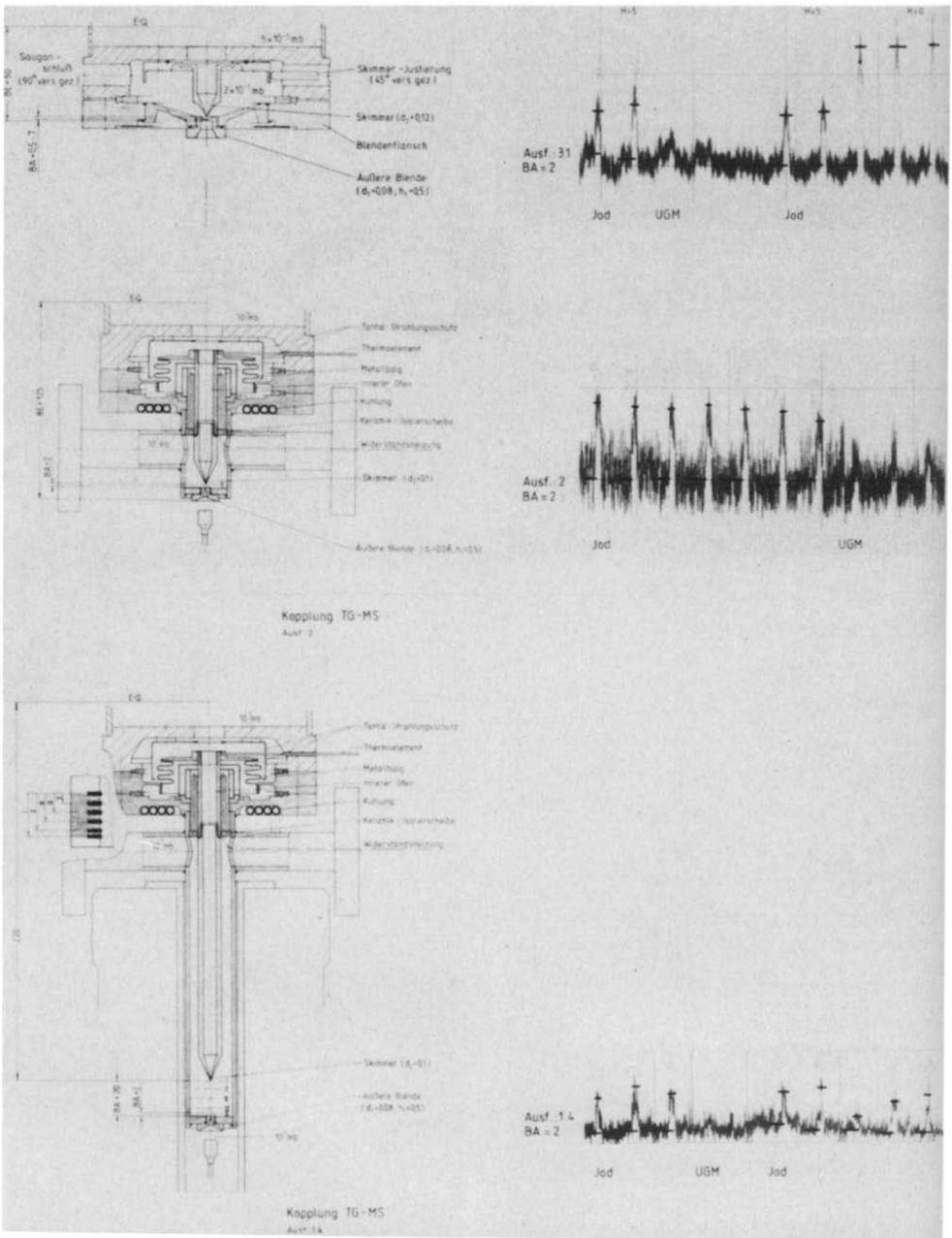
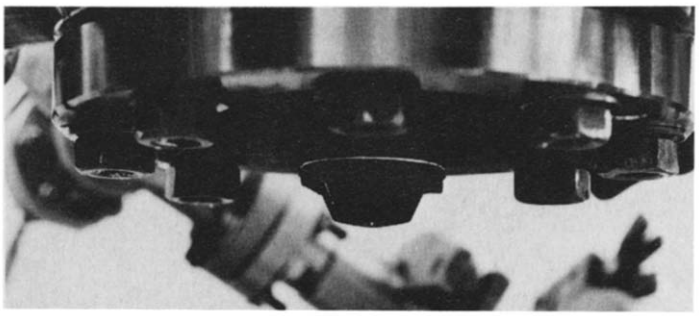
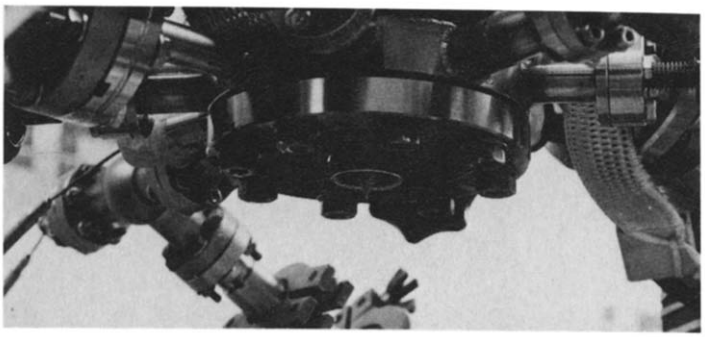


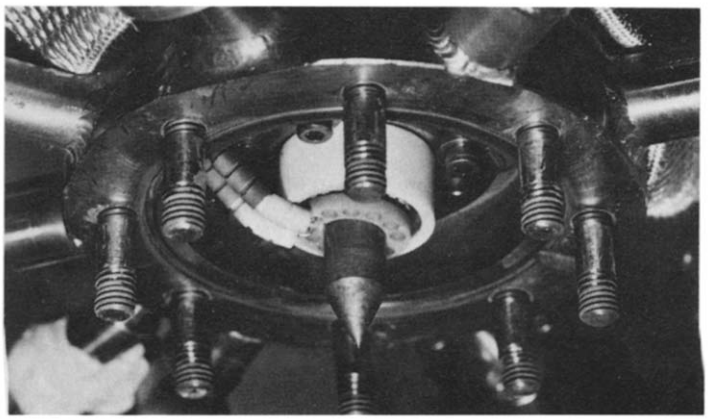
Fig. 2. Mass-spectrometric registration of Iodine with coupling systems of diverse length



3.1 Divergent-nozzle of the first aperture after adjustment with a laser-beam (light point in the middle of the flange)



3.2 After removing the first aperture the skimmer is to be seen (laser-beam as light point at the tip of the skimmer)



3.3 After removing the flange of the first aperture to heating furnace for the skimmer is to be seen

Fig. 3. Optimized short coupling system in different setting up situations

mass-spectrometer.

Through the shortening of the whole two-stage-system from 280 mm to 60 mm, there was an increase of the intensity of a factor of about 20. The short inner aperture avoids reflexion and condensation of gas species.

To measure samples with a low vapour pressure, the first aperture has to have the form of a laval-nozzle or of a divergent-nozzle; the second aperture that of a skimmer. The distance between this two orifices should be about 4-5 mm.

For the heating of the optimized coupling system a new developed resistance furnace was used. An additional inner furnace was placed around the skimmer. A schematic design of the new coupling system is shown in Fig. 4.

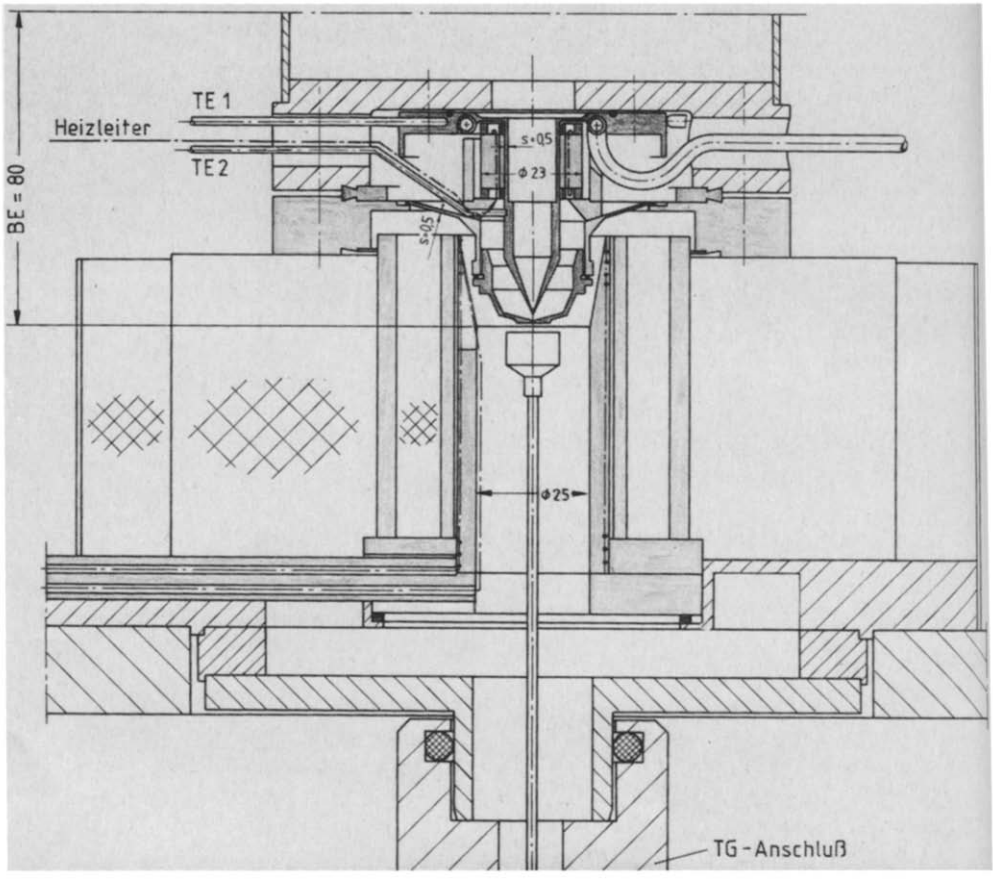


Fig. 4. Schematic design of the new coupling system

Further optimizations of the system are in progress. There are two main efforts.

1. Reducing the intermediate vacuum to about 10^{-2} mb by an oval gear pump.
2. Replacing of the first metallic aperture by a ceramic aperture to avoid chemical interactions.

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