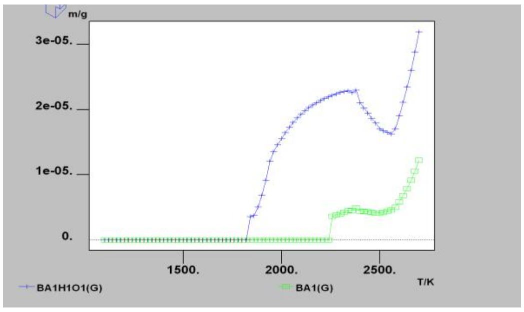
RESEARCH REPORT

VTT-R-01532-12




# Molten corium concrete interactions – Gemini calculations based on the ACE- project


Authors: Suvi Lamminmäki


Confidentiality: Public

| Report's title | |
|---|---|
| Molten corium concrete interactions – Gemini calculations based on the ACE- project | |
| Customer, contact person, address<br>SAFIR2014 Research Program | Order reference<br>24/2011SAF |
| Project name<br>Chemistry of fission products (FISKE) | Project number/Short name<br>73760/<br>FISKE2011/Safir2014 |
| Author(s)<br>Suvi Lamminmäki | Pages<br>21 |
| Keywords<br>MCCI, fission products, | Report identification code<br>VTT-R-01532-12 |

Summary

Seven molten corium concrete interaction experiments were conducted in the Advanced Containment Experiment (ACE) project in the 1990's. The tests were made with different concrete types. Ablation rates for the concretes as well as the release fractions for low-volatile fission products and control materials were measured. Test results were compared to calculations of releases made with computer models. The release fractions of low-volatile fission products were significantly lower than the predictions made with the computer calculations.

The object of this study is to model the ACE- experiments L1 and L6 by using the GEMINI2 software and NUCLEA database (NUCLEA-10_1.GEM). Thermodynamic databases have evolved much since the ACE-experiments were conducted. Under more specific examination are lanthanum, barium, strontium and ruthenium, which the models used in the ACE-experiments had particular problems with. GEMINI2 software can be used to calculate chemical equilibria in different stages of NPP accident.

Gemini- calculations for the both ACE- test cases show that the amounts of gaseous Sr, Ba, La and Ru are very small or non-existent; the amounts of species actually observed in aerosol samples were slightly higher. The calculations made in the ACE- project on the other hand predicted higher amounts of Sr, Ba, La and Ru than were actually measured. The measured liquidus temperatures were lower than those calculated with Gemini- software.

| Confidentiality | Public | |
|---|---|---|
| Espoo 24.2.2012<br>Written by<br><br>Suvi Lamminmäki,<br>Research Trainee | Reviewed by<br><br>Tommi Kekki,<br>Senior Scientist | Accepted by<br><br>Timo Vanttola,<br>Technology Manager |

VTT's contact address
PO Box 1000, 02044 VTT, Finland

Distribution (customer and VTT)
SAFIR2014 Reference group 5
VTT: Timo Vanttola, Eija Karita Puska

## Contents

# 1 Introduction

When assessing the public risk in nuclear power plant accidents, it is important to examine possible melting of the fuel as this could result in large releases of fission products. These releases are partly generated by molten corium and concrete interactions. Seven molten corium concrete interaction experiments were conducted in the Advanced Containment Experiment (ACE) project in the 1990’s. The tests were made with different concrete types. Ablation rates for the concretes as well as the release fractions for low-volatile fission products and control materials were measured. Test results were compared to calculations of releases made with computer models. The release fractions of low-volatile fission products were significantly lower than the predictions made with the computer calculations.

# 2 Goal

The object of this study is to model the ACE- experiments L1 and L6 by using the GEMINI2 software and NUCLEA database (NUCLEA-10_1.GEM). Thermodynamic databases have evolved much since the ACE-experiments were conducted. Under more specific examination are lanthanum, barium, strontium and ruthenium, which the models used in the ACE- experiments had particular problems with. GEMINI2 software can be used to calculate chemical equilibria in different stages of NPP accident.

# 3 Calculated cases

GEMINI2 software was used to calculate chemical equilibria at different temperatures in the ACE- experiment tests L1 and L6. GEMINI2 software uses NUCLEA- database (O-U-Zr-Fe-Cr-Ni-Ag-In-B-C-Ba-La-Ru-Sr-Al-Ca-Mg-Si+Ar-H) for its calculations, equilibria is calculated by minimizing the Gibbs energy of the system. GEMPLOT- software is used for making the graphs of the calculations.

## 3.1 Advanced containment experiment L1

Experiment L1 was made with limestone/common sand concrete. The initial oxidation of Zr was 70 % and the corium mixture was of that used in PWR-plants. The test apparatus had roughly 300 kg of initially powdered corium on top of roughly 190 kg concrete basemat. The interior cross-section of the furnace was 50 cm by 50 cm, the concrete basemat was approximately 30 cm thick and the height above the concrete basemat was roughly 45 cm. Measured solidus temperature was 1393 K and the liquidus temperature was 1568 K. The ablation depth for the basemat was 4 cm. The amount of concrete participating in ablation process was 28 kg. The composition of the corium and the used NUCLEA database forms of the compounds and elements can be seen in the following table 1.

*Table 1. The composition of the corium and the used NUCLEA database forms of the compounds and elements*

| Corium | Mass, kg | w/o | NUCLEA database form |
|---|---|---|---|
| **UO2** | 216 | 72 | TET(OXIDE) |
| **ZrO2** | 42.5 | 14.2 | TET(OXIDE) |
| **Zr** | 13.4 | 4.5 | TET(METAL) |
| **CaO** | 11.4 | 3.8 | FCC_B1 |
| **SiO2** | 12.4 | 4.1 | H_T_QUARTZ |
| **BaO** | 0.8 | 0.26 | TET(OXIDE) |
| **La2O3** | 0.6 | 0.21 | TET(OXIDE) |
| **SrO** | 0.5 | 0.17 | FCC_B1 |
| **CeO2** | 1.3 | 0.42 | not in NUCLEA |
| **MoO2** | 0.5 | 0.17 | not in NUCLEA |
| **SnTe** | 0.003 | 0.001 | not in NUCLEA |
| **ZrTe2** | 0.2 | 0.07 | not in NUCLEA |

The composition and amounts of the concrete and the metal inserts can be seen in table 2.

*Table 2. The composition and amounts of the concrete and the metal inserts in the basemat.*

| Basemat | Mass, kg |
|---|---|
| **Concrete** | 176.2 |
| **Zr metal** | 9.8 |
| **Thermocouples, thermo wells, extension lead wire** | 2.3 |
| **Reinforcing rod** | 2.9 |
| **Aluminium support plate and unistrut frame** | 21.1 |

Table 3 shows the composition of the reinforcing rods.

*Table 3. Composition of the reinforcing rods*

| reinforcing rod | w/o | mass. kg | |
|---|---|---|---|
| **Fe** | 98.83 | 2.86607 | TET(METAL) |
| **Si** | 0.13 | 0.00377 | FCC_A1 |
| **Mn** | 0.38 | 0.01102 | not in NUCLEA |
| **C** | 0.44 | 0.01276 | SER |
| **P** | 0.016 | 0.000464 | not in NUCLEA |
| **S** | 0.033 | 0.000957 | not in NUCLEA |
| **Pb** | 0.002 | 0.000058 | not in NUCLEA |
| **Ni** | 0.04 | 0.00116 | FCC_A1 |
| **Cr** | 0.04 | 0.00116 | TET(METAL) |
| **Mo** | 0.02 | 0.00058 | not in NUCLEA |
| **Cu** | 0.07 | 0.00203 | not in NUCLEA |

The following table 4 shows the composition of the limestone/common sand concrete.

*Table 4. The composition of the limestone/common sand concrete*

| Limestone/common sand concrete | w/o | Mass/kg | NUCLEA database form |
|---|---|---|---|
| **SiO2** | 28.3 | 7.924 | H_T_QUARTZ |
| **MgO** | 9.6 | 2.688 | FCC_B1 |
| **CaO** | 26 | 7.28 | FCC_B1 |
| **Fe2O3** | 1.6 | 0.448 | FCC_B1 |
| **Al2O3** | 3.5 | 0.98 | RHO |
| **Na2O** | 1.1 | 0.308 | not in NUCLEA |
| **K2O** | 0.6 | 0.168 | not in NUCLEA |
| **TiO2** | 0.14 | 0.0392 | not in NUCLEA |
| **BaO** | 0.03 | 0.0084 | FCC_B1 |
| **SrO** | 0.03 | 0.0084 | FCC_B1 |
| **MnO** | 0.05 | 0.014 | not in NUCLEA |
| **ZrO2** | 0.02 | 0.0056 | TET(OXIDE) |
| **V2O5** | 0.01 | 0.0028 | not in NUCLEA |
| **Cr2O3** | 0.009 | 0.00252 | FCC_B1 |
| **NiO** | 0.005 | 0.0014 | not in NUCLEA |
| **CuO** | 0.005 | 0.0014 | not in NUCLEA |
| **ZnO** | 0.007 | 0.00196 | not in NUCLEA |
| **CoO** | 0.003 | 0.00084 | not in NUCLEA |
| **CO2** | 21.4 | 5.992 | G |
| **H2O** | 6.1 | 1.708 | L |

Aerosol releases from test were collected and analyzed. Composition of aerosol from test L1 can be seen in the following table.

*Table 3. Composition of the aerosol released in test L1*

| Species | Mass fraction. wt% |
|---|---|
| **$Al_2O_3$** | 0.578 |
| **BaO** | 0.050 |
| **CaO** | 1.050 |
| **$CeO_2$** | <0.02 |
| **$Cr_2O_3$** | 0.417 |
| **CuO** | 0.358 |
| **$Fe_2O_3$** | 2.443 |
| **$K_2O$** | 2.945 |
| **$La_2O_3$** | <0.006 |
| **MgO** | 2.907 |
| **MnO** | 0.271 |
| **$MoO_3$** | 0.013 |
| **$Na_2O$** | 2.939 |
| **NiO** | 0.132 |
| **$SiO_2$+Si** | 71.226 |
| **$SnO_2$** | 0.584 |
| **SrO** | 0.040 |
| **Te** | 0.704 |
| **$UO_2$** | 1.996 |
| **$WO_3$** | 0.813 |
| **ZnO** | 0.482 |
| **$ZrO_2$** | 0.130 |
| **SiC** | 9.484 |
| **$SO_4^{=}$** | 0.089 |
| **$Cl^-$** | 0.348 |

The total amount of collected aerosol was 1213 g. Maximum melt temperature was 2625 K. Gemini- calculations were performed with these aforementioned ACE- test material composition data. Calculations were made with just the corium and with corium, concrete and inserts. Following figures 1, 2, 3 and 4 show the calculated results for just the corium, plotted with GEMPLOT- software.

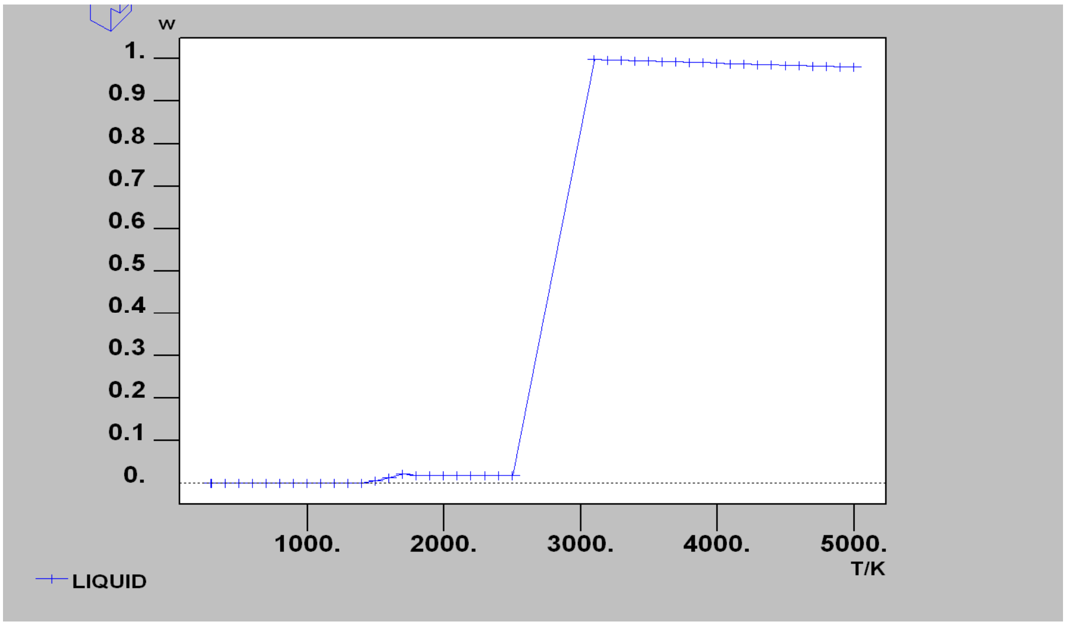



*Figure 1. Amount of corium in liquid form in mass fraction.*

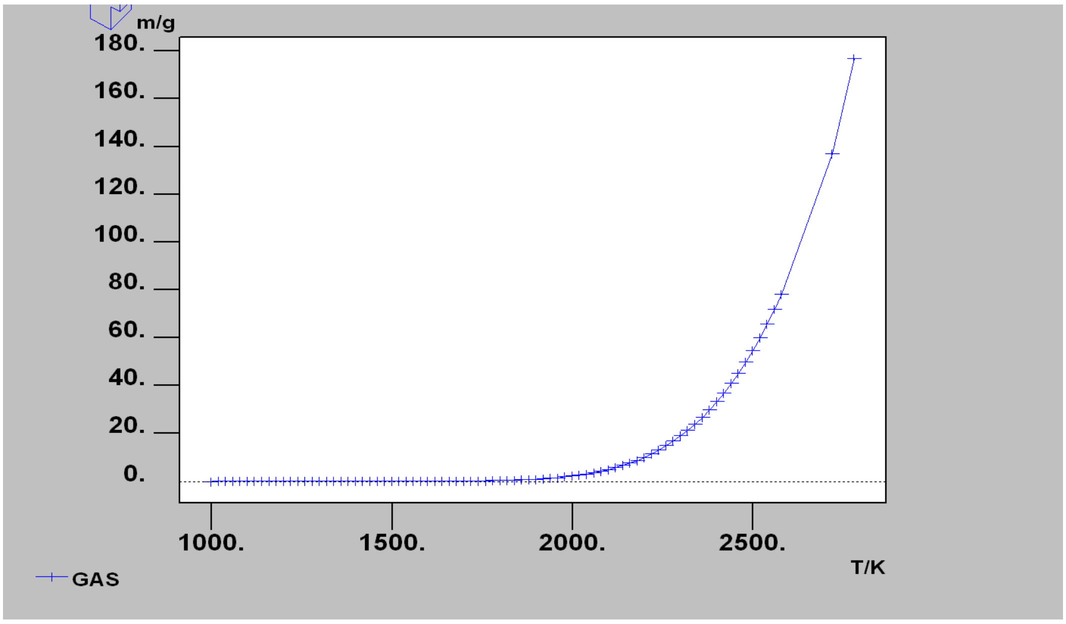



*Figure 2. Amount of corium in gaseous form, in grams.*

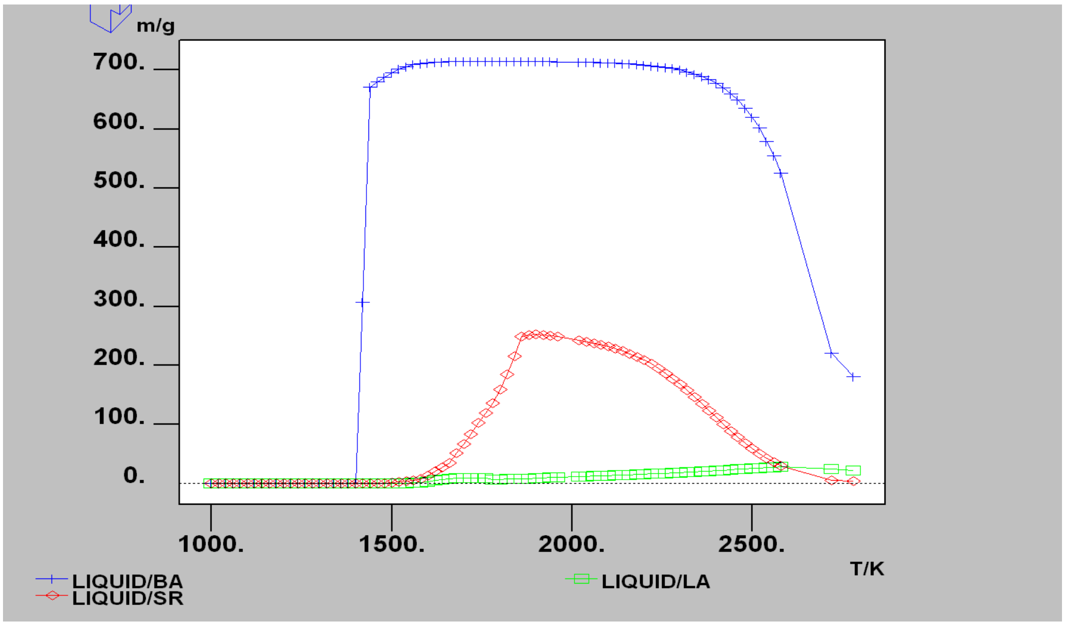



*Figure 3. Amounts of Ba, Sr and La in liquid fraction, in grams.*

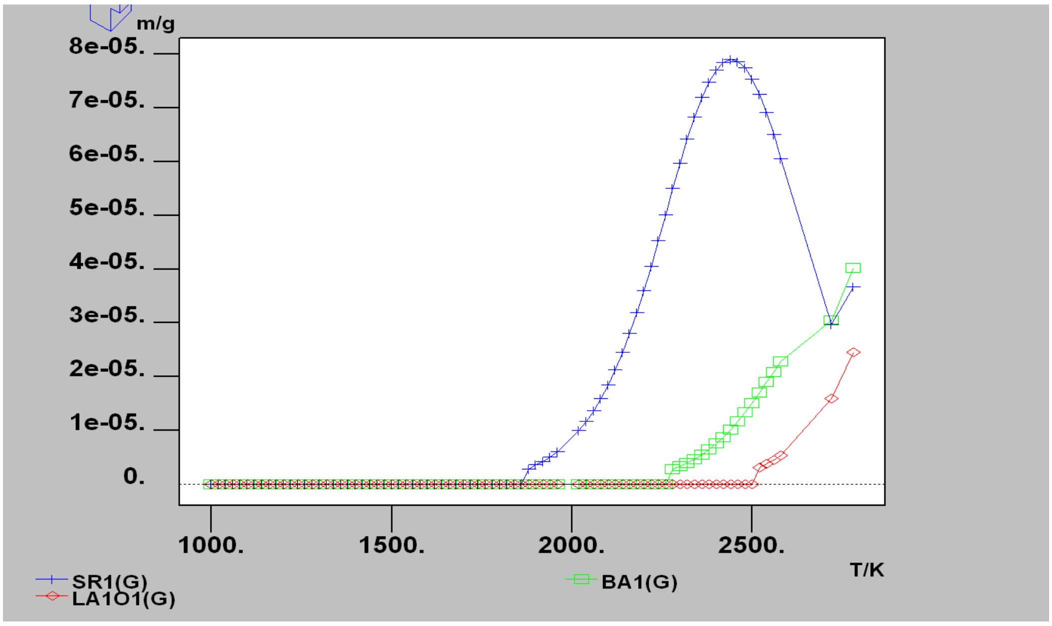



*Figure 4. Amounts of Ba, Sr and La in gas fraction, in grams.*

Following figures 5 - 11, show the calculated results for corium, concrete and inserts, plotted with GEMPLOT- software.

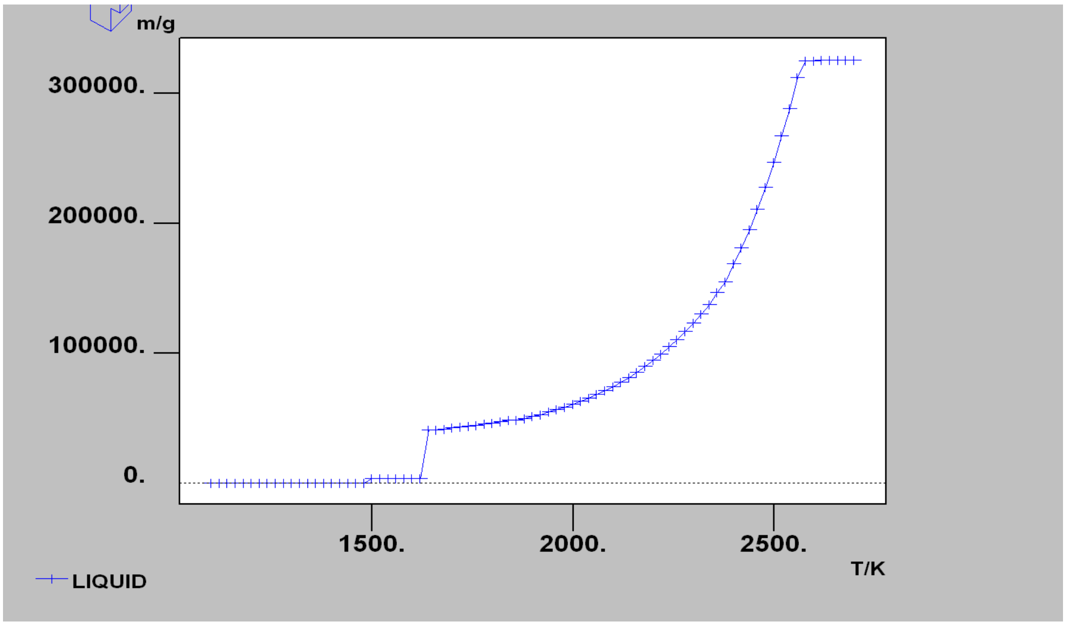



*Figure 5. Amount of corium, concrete and inserts in liquid form in mass fraction.*

Measured solidus temperature was 1393 K and the liquidus temperature was 1568 K. The calculated solidus temperature is approximately 1200 K, but the amount of liquid phase is very small. More significant amounts of liquid phase are reached in temperature of roughly 1450 K. However, the calculated liquidus temperature is higher than that measured in the tests. In contrast to the calculations made with just the corium, it appears that the liquidus temperature is reached earlier with the concrete and the inserts.

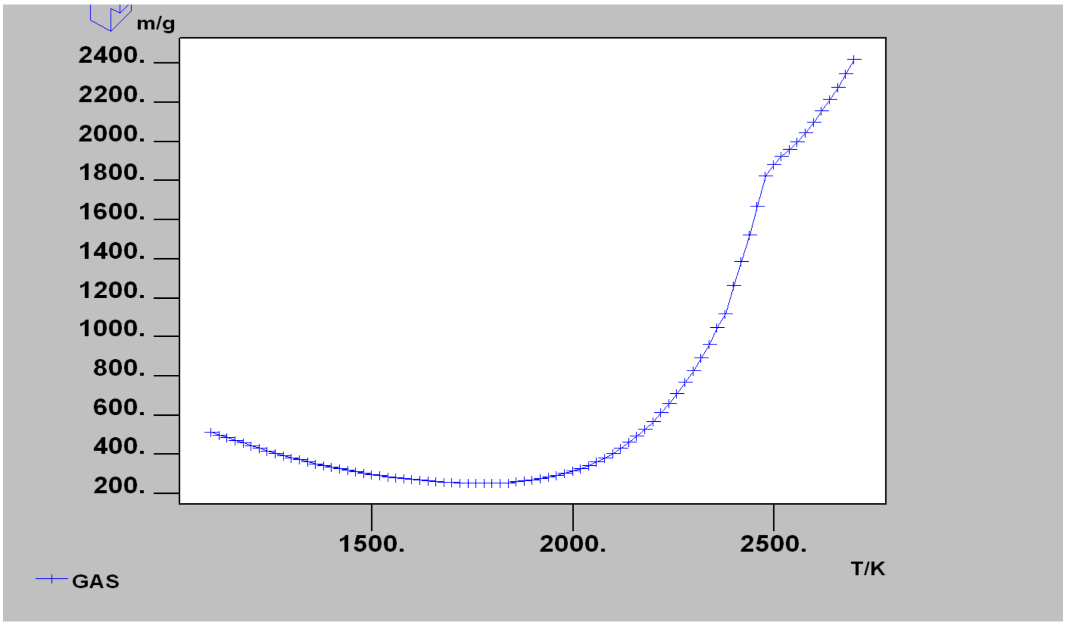



*Figure 6. Amount of corium, concrete and inserts in gaseous form, in grams.*

The total amount of collected aerosol was 1213 g. Maximum melt temperature in the test was 2625 K. The amount of corium, concrete and inserts in gaseous form, by the time the maximum melt temperature is reached, is according to the Gemini- calculation roughly 2000 grams which is higher than the collected aerosol mass. Also the aerosol might contain other than gaseous forms.

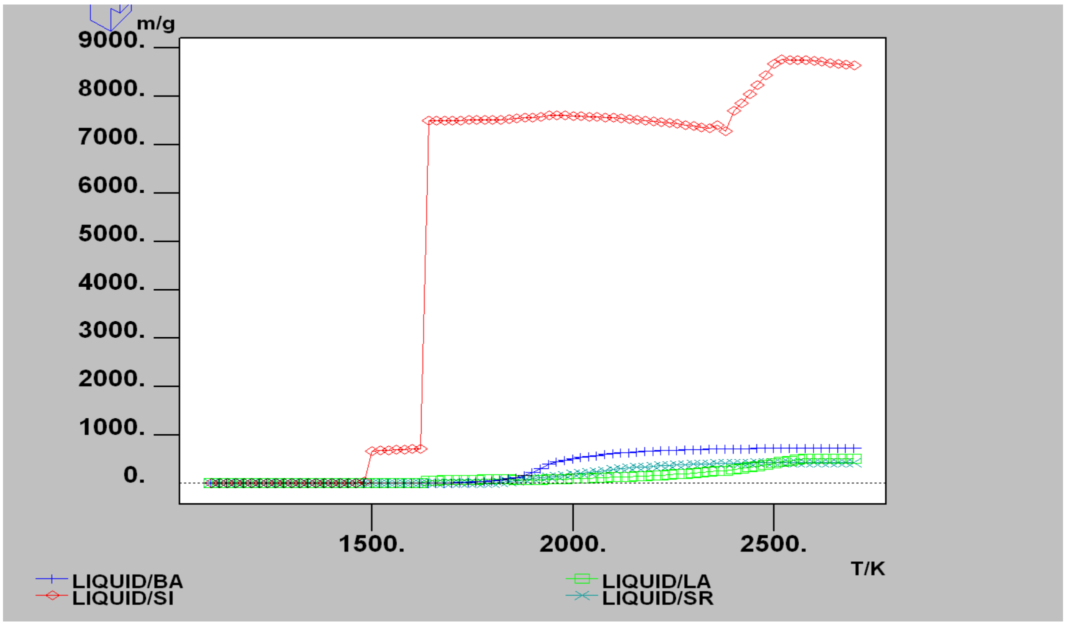



*Figure 7. Amounts of Si, Ba, Sr and La in liquid fraction, in grams.*

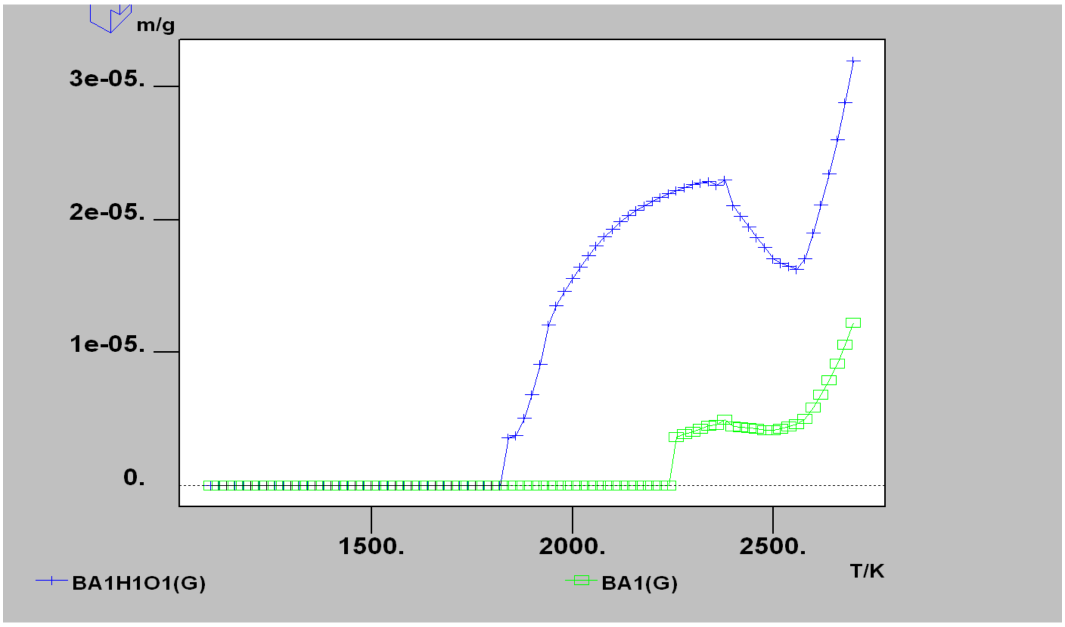



*Figure 8. Amounts of BaHO and Ba in gaseous form, in grams. No other forms of gaseous Ba were formed according to the calculations in this temperature range.*

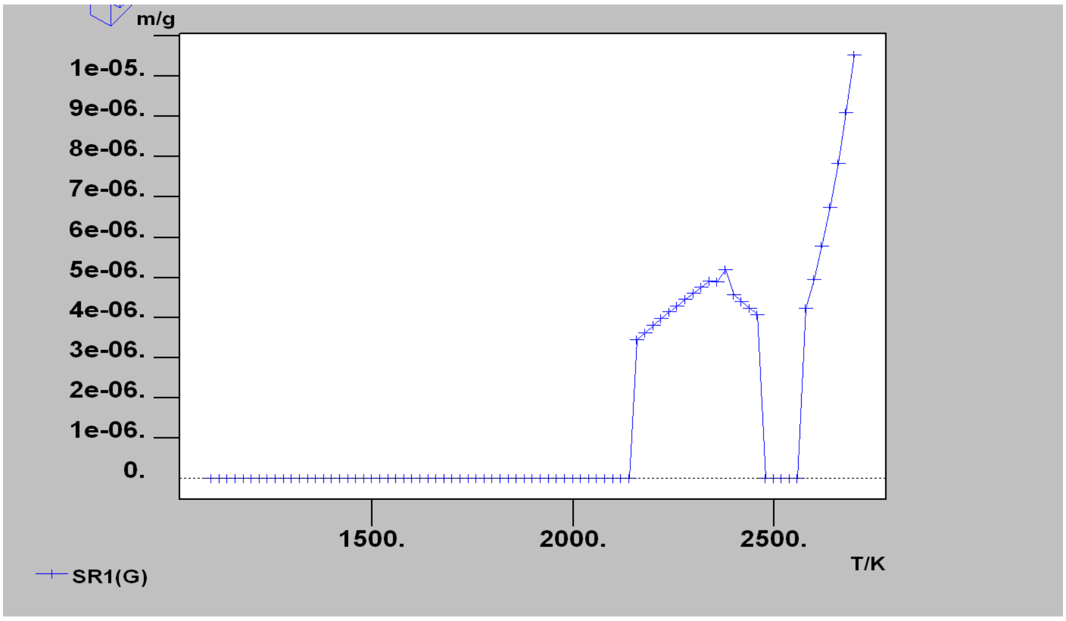



*Figure 9. Amount of Sr in gaseous form, in grams. No other gaseous species of Sr were were formed according to the calculations in this temperature range.*

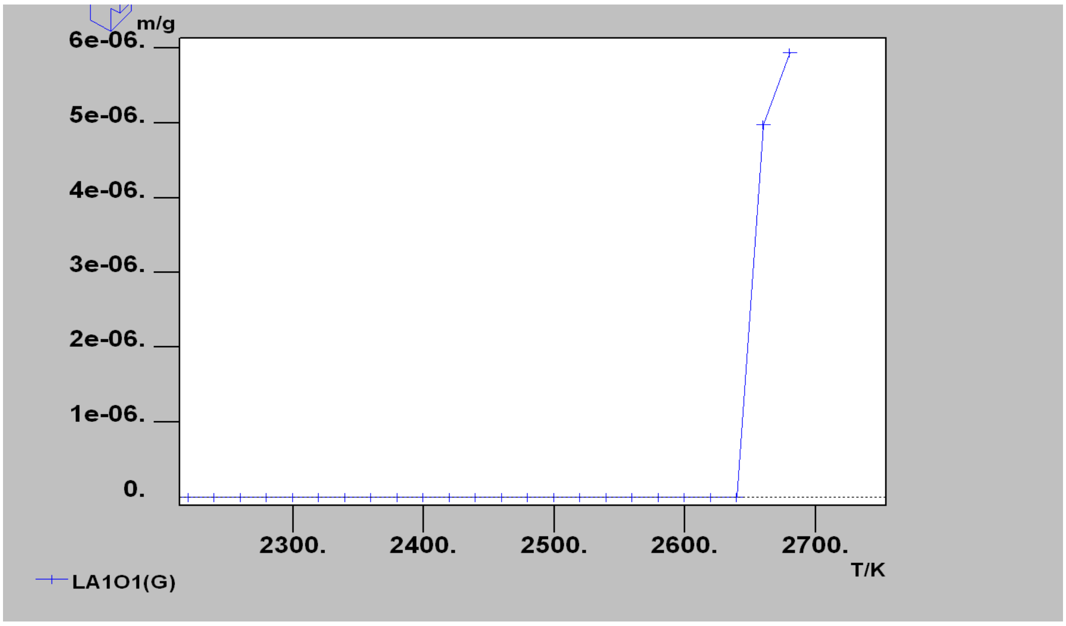



*Figure 10. Amount of gaseous LaO in grams. No other species of gaseous La were calculated.*

According to the Gemini- calculations it seems that only Ba and Sr, of the elements under special observation, have gaseous species in the temperature range of the tests. However, the calculated amounts of gaseous species are significantly lower than the collected aerosol samples indicate.

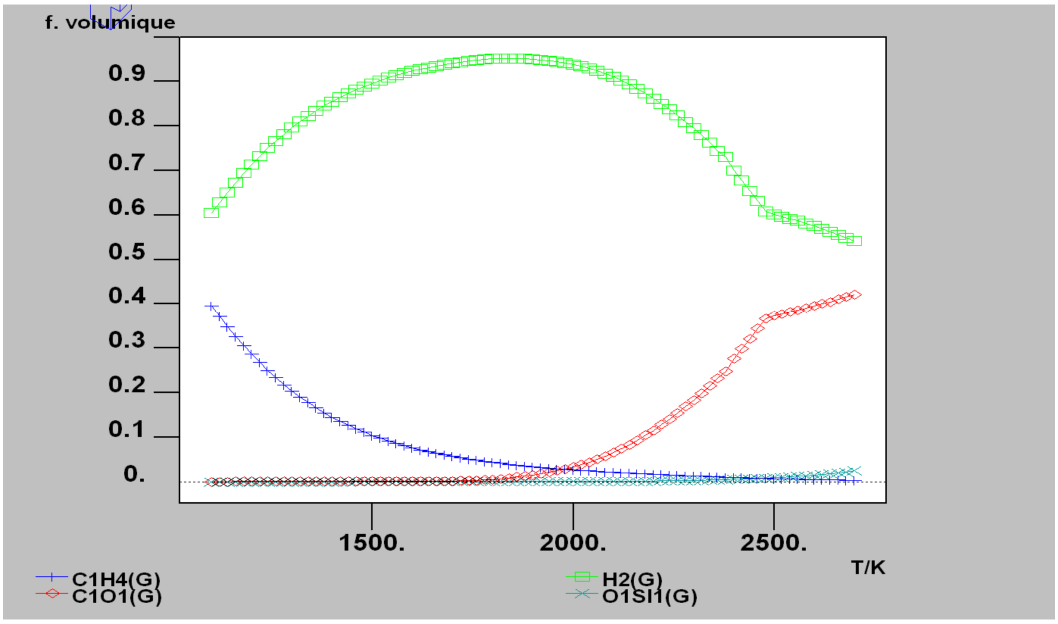



*Figure 11. Main components of the gas fraction in mass fraction.*

## 3.2 Advanced containment experiment L6

Experiment L6 was made with siliceous concrete. The initial oxidation of Zr was 30 % and the corium mixture was of that used in PWR- plants. Again the interior cross-section of the furnace was 50 cm by 50 cm, the concrete basemat was approximately 30 cm thick and the height above the concrete basemat was roughly 45 cm. Measured solidus temperature was 1403 K and the liquidus temperature was 1523 K. The ablation depth for the basemat was 8.8 cm. The amount of concrete participating in ablation process was 72 kg. The composition of the corium and the used NUCLEA database forms of the compounds and elements can be seen in the following table.

*Table 4. The composition of the corium and the used NUCLEA database forms of the compounds and elements*

| Corium | Mass, kg | NUCLEA database form |
|---|---|---|
| UO2 | 219 | TET(OXIDE) |
| ZrO2 | 18.51 | TET(OXIDE) |
| CaO | 7.3 | FCC_B1 |
| SiO2 | 16.89 | H_T_QUARTZ |
| BaO | 0.79 | TET(OXIDE) |
| La2O3 | 0.63 | TET(OXIDE) |
| SrO | 0.53 | FCC_B1 |
| CeO2 | 1.28 | not in NUCLEA |
| MoO2 | 0.94 | not in NUCLEA |

The composition and amounts of the concrete and the metal inserts can be seen in table 7.

*Table 5. Composition and amounts of the concrete and the metal inserts in the basemat.*

| Concerete/metal inserts | Mass, kg | |
|---|---|---|
| Zr | 21.1 | TET(METAL) |
| Zircaloy-4 | 1.8 | |
| Type 304 SS | 9.1 | |
| Ru | 0.38 | TET(METAL) |
| Ag | 1.19 | FCC_A1 |
| In | 0.22 | TET(METAL) |
| ZrTe2 | 0.2 | not in NUCLEA |
| Siliceous concrete | 22.4 | |

Following table shows the composition of Zircaloy-4.

*Table 6. The composition of Zircaloy-4.*

| Zircaloy-4 | Mass, kg | |
|---|---|---|
| Zr | 1.76 | TET(METAL) |
| Sn | 0.03 | not in NUCLEA |
| Fe | 0.004 | TET(METAL) |
| Cr | 0.002 | TET(METAL) |
| O | 0.002 | FCC_C1 |
| C | 0.0004 | SER |
| Si | 0.0002 | FCC_A1 |

The composition of the stainless steel used in the experiment can be seen in table 9.

*Table 7. Composition of type 304 SS.*

| Type 304 SS | Mass, kg | |
|---|---|---|
| Fe | 6.4 | TET(METAL) |
| Cr | 1.7 | TET(METAL) |
| Ni | 7.4 | FCC_A1 |
| Mn | 0.1 | not in NUCLEA |
| Si | 0.05 | FCC_A1 |
| Cu | 0.05 | not in NUCLEA |
| Mo | 0.04 | not in NUCLEA |
| Co | 0.01 | not in NUCLEA |
| C | 0.006 | SER |
| N | 0.006 | not in NUCLEA |
| P | 0.003 | not in NUCLEA |
| S | 0.002 | not in NUCLEA |

Table 10 shows the composition of siliceous concrete.

*Table 8. Composition of siliceous concrete*

| Siliceous concrete | mass % | Mass, kg | |
|---|---|---|---|
| **SiO2** | 69 | 49.68 | H_T_QUARTZ |
| **CaO** | 13.5 | 9.72 | FCC_B1 |
| **Al2O3** | 4 | 2.88 | RHO |
| **K2O** | 1.4 | 1.008 | not in NUCLEA |
| **Fe2O3** | 1 | 0.72 | FCC_B1 |
| **TiO2** | 0.8 | 0.576 | not in NUCLEA |
| **MgO** | 0.7 | 0.504 | FCC_B1 |
| **Na2O** | 0.7 | 0.504 | not in NUCLEA |
| **SO3** | 0.5 | 0.36 | not in NUCLEA |
| **MnO** | 0.03 | 0.0216 | not in NUCLEA |
| **BaO** | 0.02 | 0.0144 | FCC_B1 |
| **SrO** | 0.02 | 0.0144 | FCC_B1 |
| **Cr2O3** | 0.01 | 0.0072 | FCC_B1 |
| **CO2** | 4.2 | 3.024 | G |
| **H2O** | 3.7 | 2.664 | L |

Aerosol releases from test were collected and analyzed. Composition of aerosol from test L6 can be seen in the following table.

*Table 9. Composition of the aerosol released in test L6*

| Species | Mass fraction, wt% |
|---|---|
| **$Al_2O_3$** | 0.09 |
| **BaO** | 0.021 |
| **CaO** | 0.33 |
| **$CeO_2$** | 0.01 |
| **$Cr_2O_3$** | 0.69 |
| **CuO** | 0.13 |
| **$Fe_2O_3$** | 2.10 |
| **$In_2O_3$** | 1.68 |
| **$K_2O$** | 3.46 |
| **$La_2O_3$** | 0.006 |
| **MgO** | 0.84 |
| **MnO** | 0.45 |
| **$MoO_3$** | 0.11 |
| **$Na_2O$** | 1.71 |
| **NiO** | 0.08 |
| **$RuO_2$** | 0.017 |
| **$SiO_2$+Si** | 78.35 |
| **$SnO_2$** | 0.76 |
| **SrO** | 0.018 |
| **Te** | 1.42 |
| **$UO_2$** | 0.64 |
| **$WO_3$** | 0.64 |
| **ZnO** | 0.10 |
| **$ZrO_2$** | 0.07 |

The total amount of aerosol collected was 6546 g. Maximum melt temperature was 2425 K. Gemini- calculations were performed with these aforementioned ACE- test material composition data. Calculations were made again with just the corium and with corium, concrete and inserts. Following figures 12, 13, 14 and 15 show the calculated results for just the corium, plotted with GEMPLOT- software.

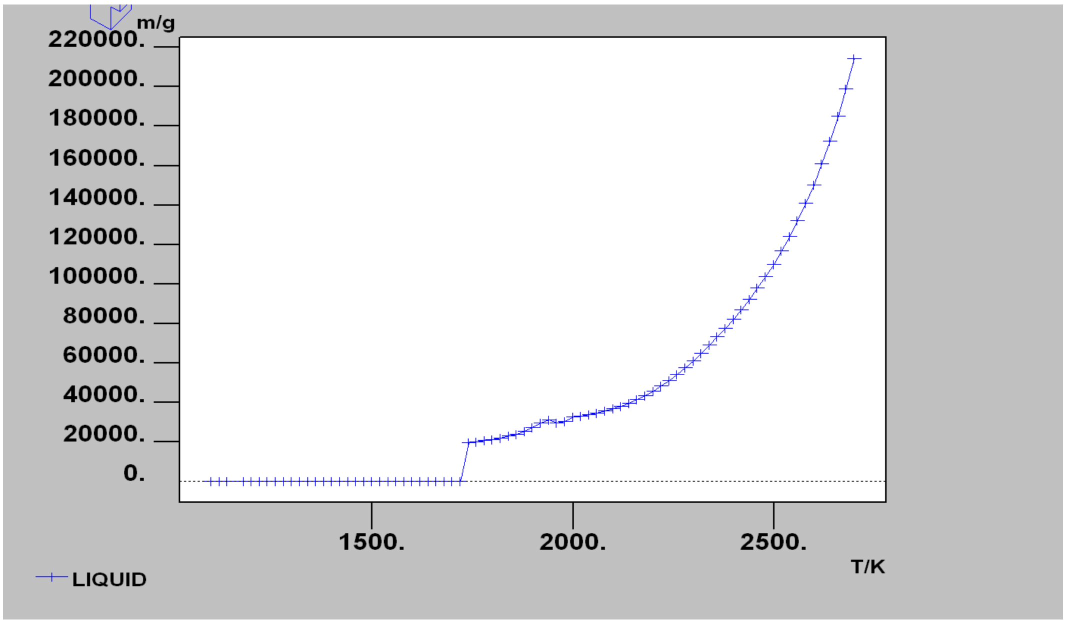



*Figure 12. Amount of corium in liquid form, in mass fraction.*

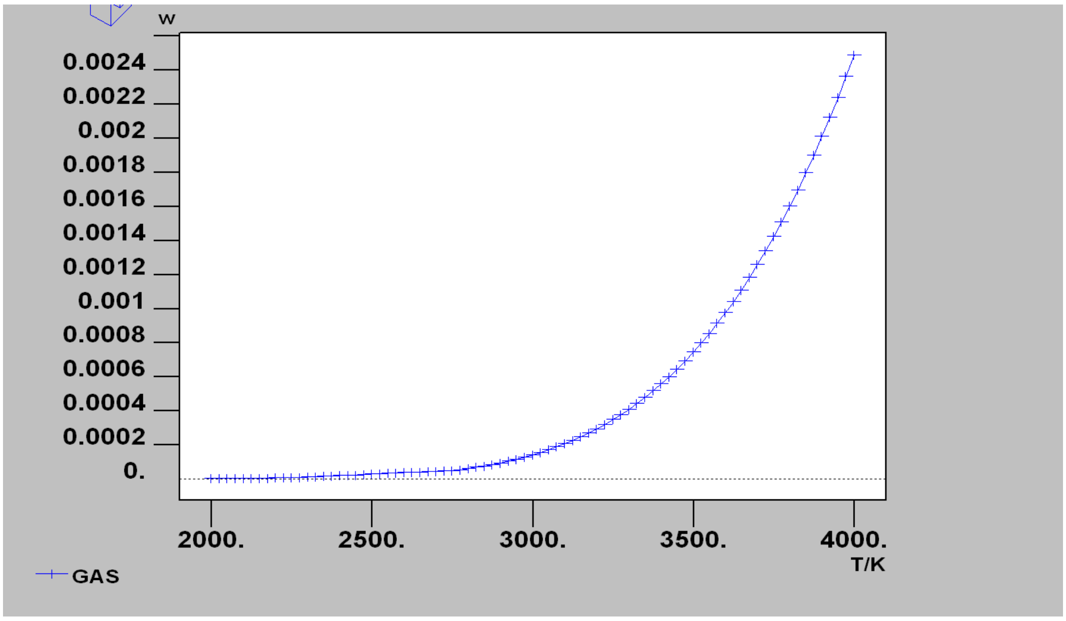



*Figure 13. Amount of corium in gaseous form, in grams.*

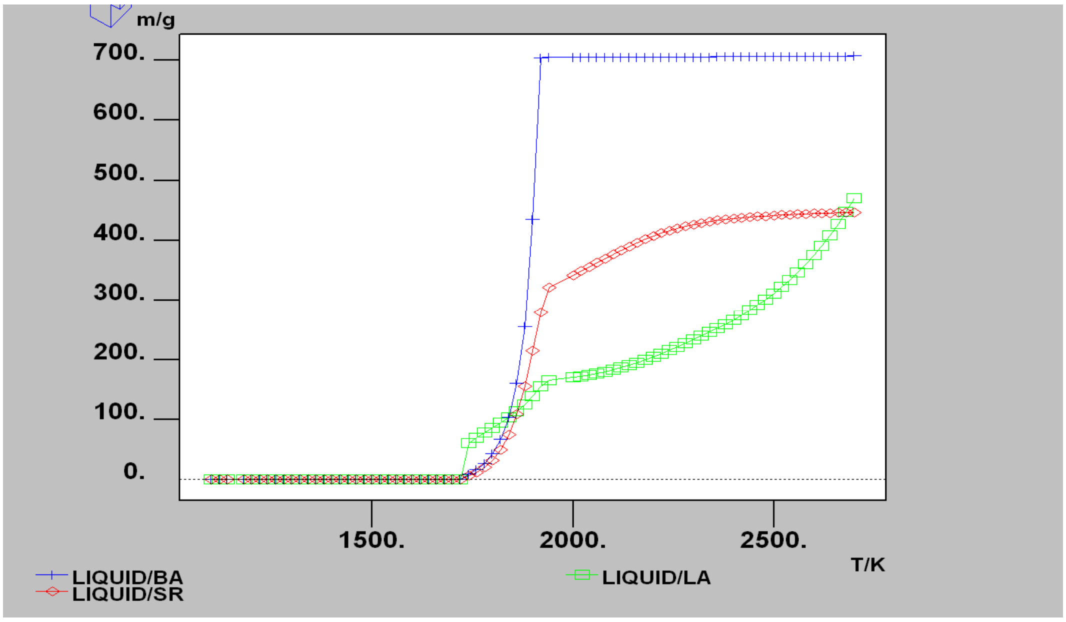



*Figure 14. Amounts of Sr, Ba and La in liquid fraction, in grams.*

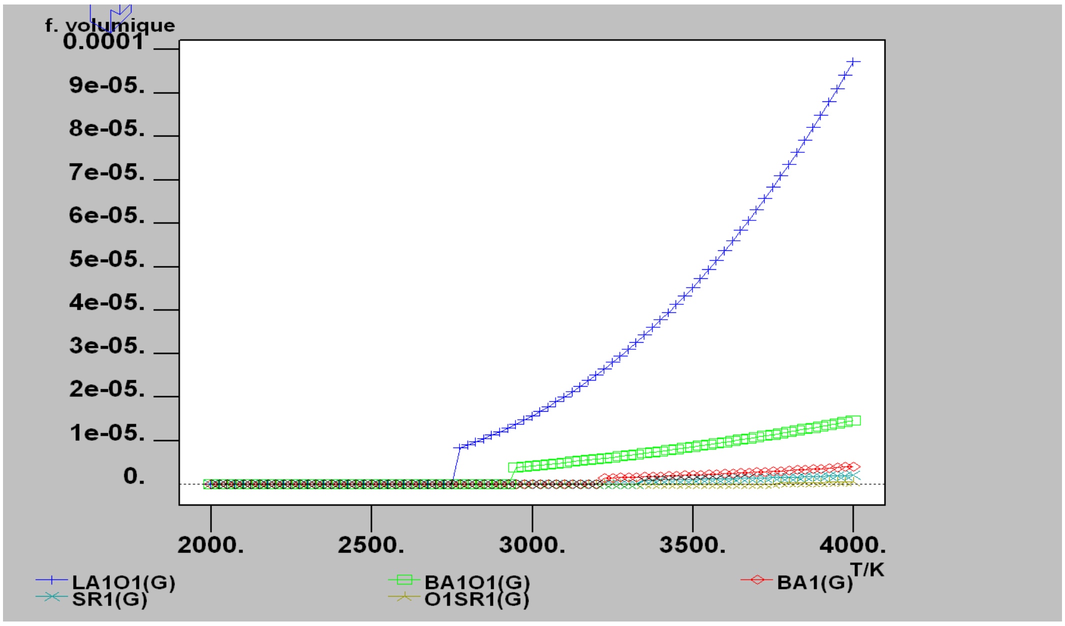



*Figure 15. Amounts of gaseous species of La, Ba and Sr*

Following figures 16 - 21, show the calculated results for corium, concrete and inserts, plotted with GEMPLOT- software.

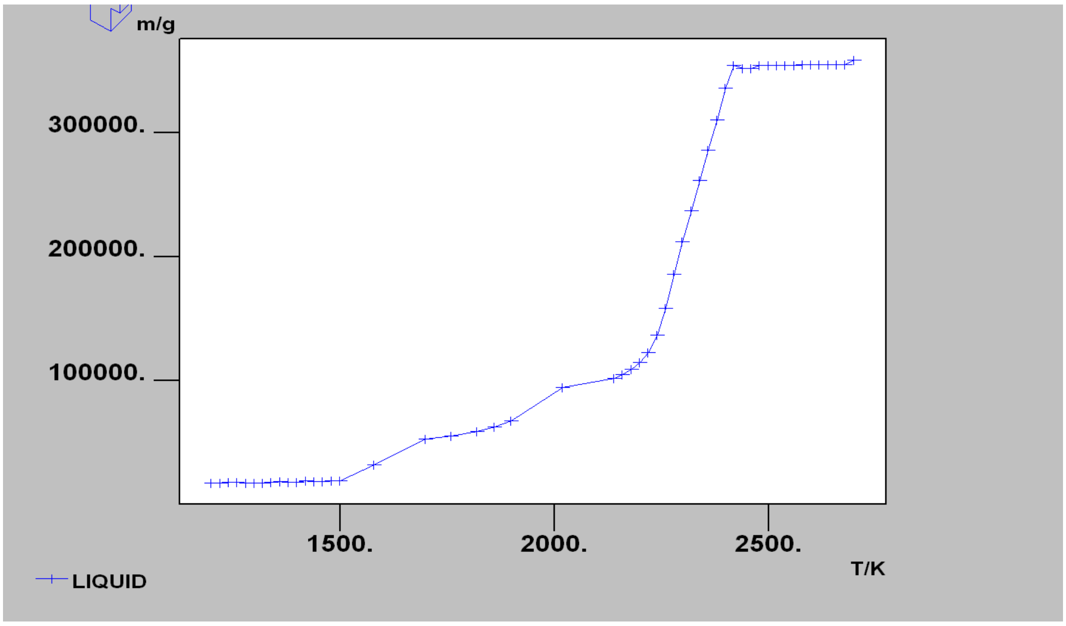



*Figure 16. Amount of corium, concrete and inserts in liquid form in mass fraction.*

Measured solidus temperature was 1403 K and the liquidus temperature was 1523 K. The calculated solidus temperature is again approximately 1200 K, but the amount of liquid phase is also very small. More significant amounts of liquid phase are reached after the temperature of 1500 K. Also in test case L6, the calculated liquidus temperature is higher than that measured in the tests. And in contrast to the calculations made with only the corium the liquidus temperature is reached earlier with the concrete and the inserts.

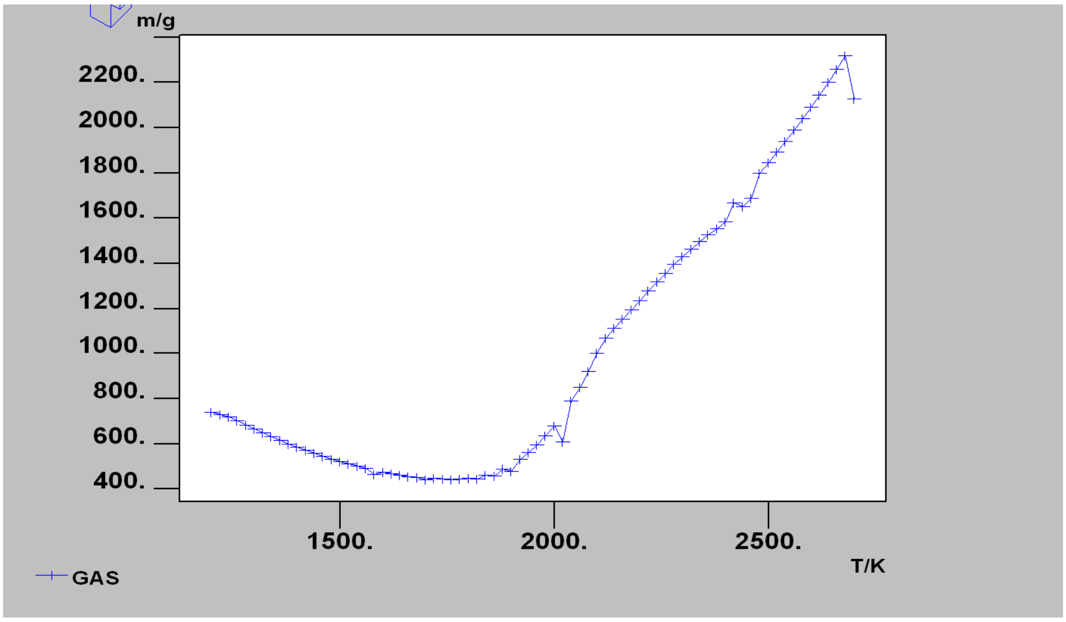



*Figure 17. Amount of corium, concrete and inserts in gaseous form, in grams.*

The total amount of aerosol collected was 6546 g. Maximum melt temperature was 2425 K The amount of corium, concrete and inserts in gaseous form, by the time the maximum melt temperature is reached, is according to the Gemini-calculation roughly 1600 grams. That is significantly lower than the aerosol mass collected in the tests.

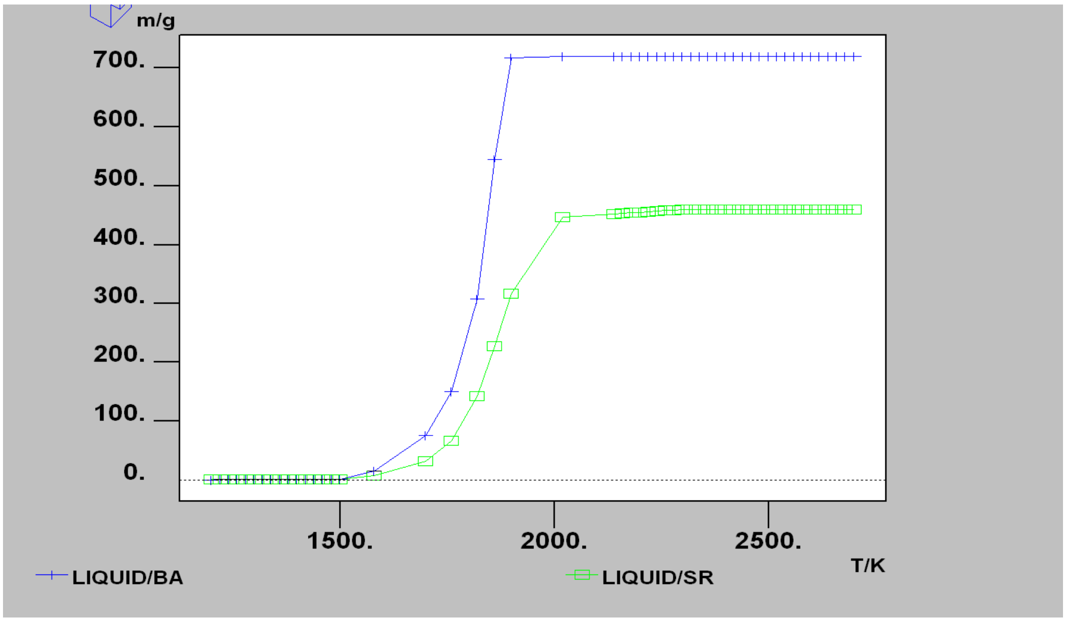



*Figure 18. Amounts of Ba and Sr in liquid fraction, in grams.*

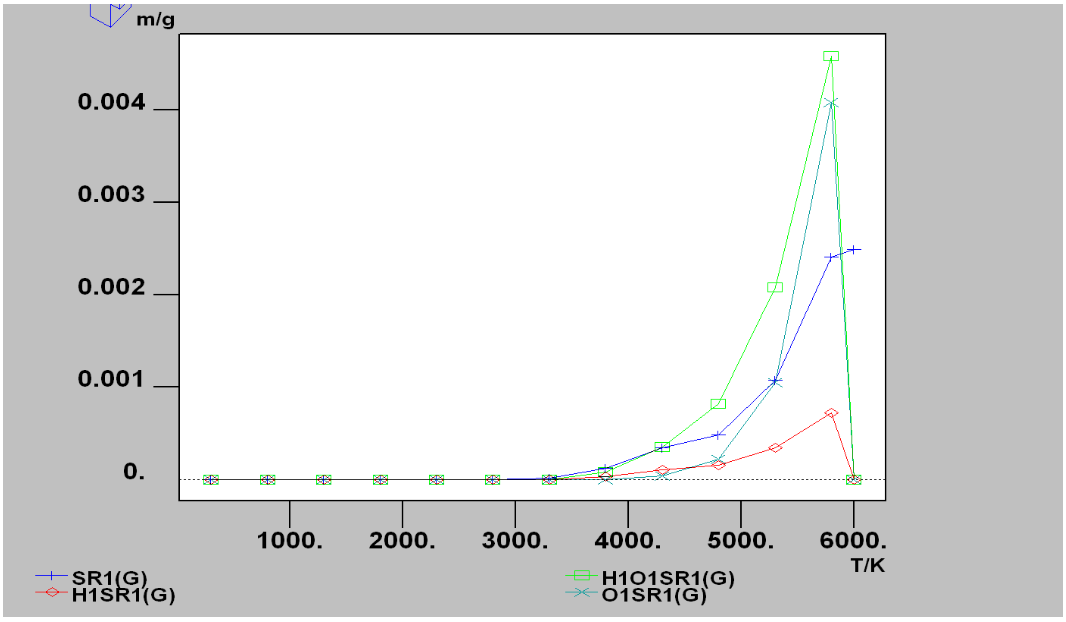



*Figure 19. Amounts of gaseous Sr- species, in grams.*

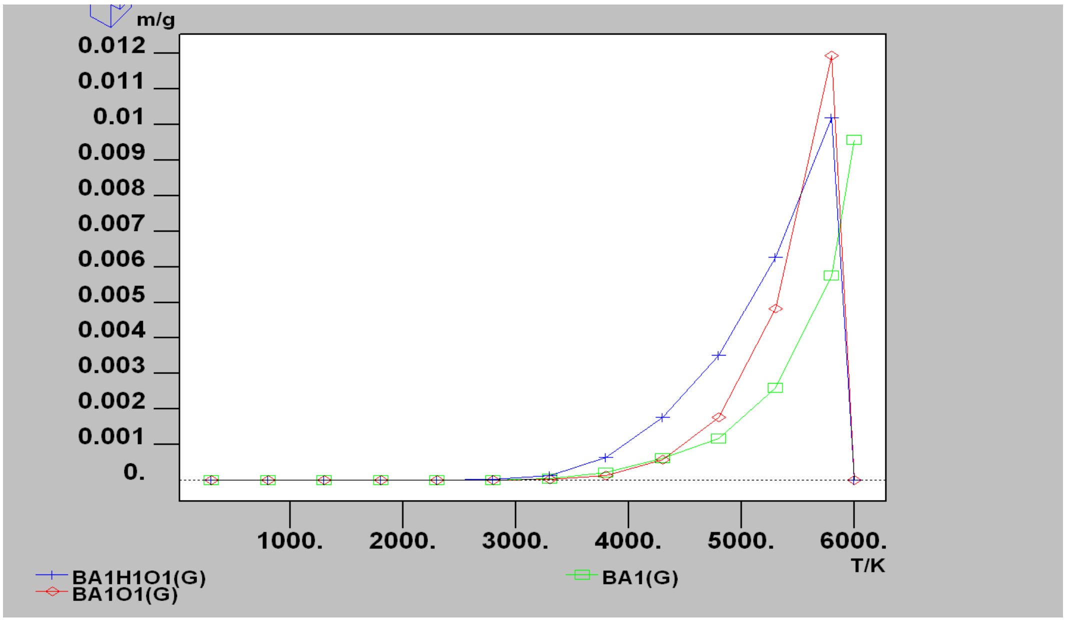



*Figure 20. Amounts of gaseous Ba- species, in grams.*

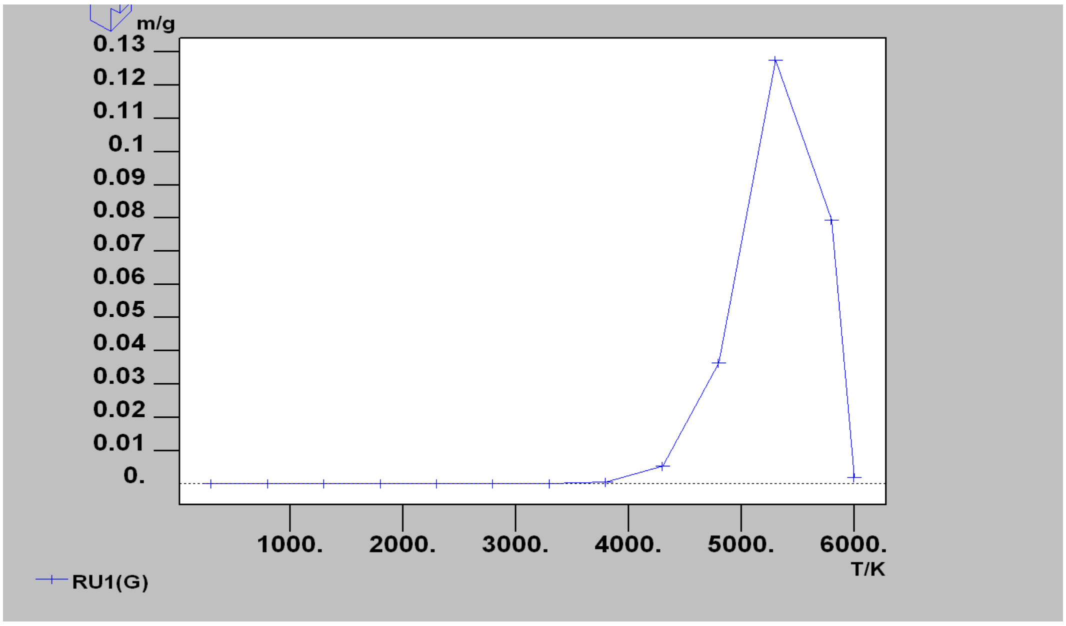



*Figure 21. Amount of gaseous Ru, in grams*

According to the Gemini- calculations none of the elements under special observation, have gaseous species in the temperature range of the test L6. In the collected aerosol samples Sr, Ba, La and Ru were observed in small amounts. The amounts were lower than those observed in test L1.

# 4 Conclusions

Gemini- calculations for the both ACE- test cases show that the amounts of gaseous Sr, Ba, La and Ru are very small or non-existent; the amounts of species actually observed in aerosol samples were slightly higher. The calculations made in the ACE- project on the other hand predicted higher amounts of Sr, Ba, La and Ru than were actually measured. The measured liquidus temperatures were lower than those calculated with Gemini- software.

# References

Wall, I.B., Sehgal, B.R., Molten Corium Concrete Interactions, Advanced Containment Experiments (ACE) Project, Summary Report, (1993).

Advanced Containment Experiments, ACE MCCI Test L1, Test data report, Volume 1, Thermal Hydraulics, (1990).

Advanced Containment Experiments, ACE MCCI Test L1, Test data report, Volume 2, Aerosol analysis, (1990).

Advanced Containment Experiments, ACE MCCI Test L6, Test data report, Volume 2, Aerosol analysis, (1991).

Advanced Containment Experiments, Molten Core-Concrete Interaction: Analysis of Aerosol Samples From Test L6 of The ACE Project, (1991).

Advanced Containment Experiments, ACE MCCI Test L6 Post Test Blind Code Comparison: Thermal Hydraulic Behavior (1991).

Kekki, T., Zilliacus, R., Lindholm, I., Implementation of NUCLEA Database for in and Ex-vessel nuclear Applications, Project report, PRO1/P7018/04, VTT, (2005).