Identification of release rates as a consequence of thermal impact on RADWASTE – Experimental Studies

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ABSTRACT

Considering the fact that to our experiences fire accidents are of highest significance for the operational safety of a repository for RADWASTE, a broad research project has been carried out in Germany on behalf of BfS (Federal Office for Radiation Protection) to develop a comprehensive approach for the determination of release rates under fire conditions.

Various experiments were performed to target at the adjustment of theoretical models within safety and risk analysis of such installation. The investigations included the study of the release mechanisms caused by combustion of radioactive waste and the heating up of radioactive metallic scrap as well as the research of the behavior of an inactive waste drum in an open fire and the release rates out of waste simulation material. The experiments resulted in the identification of release rates as a consequence of thermal impact on RADWASTE to allow a more realistic look at the nuclide specific risks and their consequences for safety assessments. Finally release fractions are calculated based on the thermal behavior of elements in the case of fire and their release rates.

INTRODUCTION

The aim of this project has been to provide parameter to be used in theoretical models which have been developed within the framework of safety analysis for repositories.

Parameters of interest were heat transfer parameters and nuclide specific temperature depended release rates for various wastes. Having the chance to study the general behaviour of different waste types under real fire conditions was of great interest as well.

The experimental research project consisted of four elements:

1. Investigation of the behaviour of drums in a fire
   (Parameters which are varied are fire load and ventilation rate. The results of this investigation are the validation of computer codes and the derivation of heat transfer parameter Validation of computer codes and the derivation of heat transfer parameter).

2. Analysis of the release mechanism "combustion"
   (In order to gain representative results the release behaviour of the combustion plant of the Jülich research centre in Germany has been studied. The nuclide specific release fractions are derived from activity balances).
3. Investigation of radioactive releases from metallic scrap under thermal exposure
   (The release fraction for metallic scrap has been analysed in technical scale at the Siempelkamp melting plant. The samples are packed in drums, which are heated in an inductive melting oven. The studies were carried out for pure black and white steel as well as for zinc-coated and varnished metals. The respective batches are heated-up to 200 °C, 400 °C, 600 °C and 800 °C. At each temperature step the temperature is hold for one hour and the nuclide specific release rates are measured).
4. Inactive investigations of model samples for several waste characteristics
   (These samples simulate various waste products such as cemented waste, concentrates, mixed waste, metallic waste, resins and combustible waste. All samples are precisely doped with app. 30 different elements. The release rates are element specific measured for distinct temperature steps).

The entire experimental set-up and the applied measurement procedures were described in a poster session on WM 05 on detail already. In our recent contribution we will complete the presentation of this research project with the discussion of the experimental results, e. g. the hitherto existing overestimation of release assumptions in case of fire.

VALIDATION OF FIRE SIMULATING COMPUTER CODES

A sequence of heating-up experiments of typical waste drums in a fire has been performed at the iBMB (Institut für Baustoffe, Massivbau und Brandschutz) of Braunschweig University of Technology, Germany. Under various fire scenarios predictions of the potential consequences of fires could be made for the validation of the available fire models and codes for this application.

The main part of the test facility was a large oven ("OSKAR") with various openings in which 10 different scenarios were carried out. Ten different scenarios were carried out. A typical barrel type waste drum has been installed as a double vessel container. The inner barrel consisted of tinplate and was filled with styrene di-vinyl-benzene copolymer with sulfur acid groups (ion exchanger granulates). The gap between the inner and outer steel barrel has been filled with concrete. Therefore, both - the fire room and the investigated drum - were instrumented with various thermocouples as data collecting devices.

During the experiments gas and surface temperatures, gas composition, velocities and heat flux densities have been measured. Along three lines the temperatures inside the barrel container were measured. The velocity inside the plume, at the door and inside the fan systems was measured by bi-directional probes. To measure the gas concentrations and pressure open pipes are routed to the outside of the fire compartment and connected to the measurement systems.

Fig. 1 pictures the temperature gradient in a typical waste drum caused by a nearby pool fire.

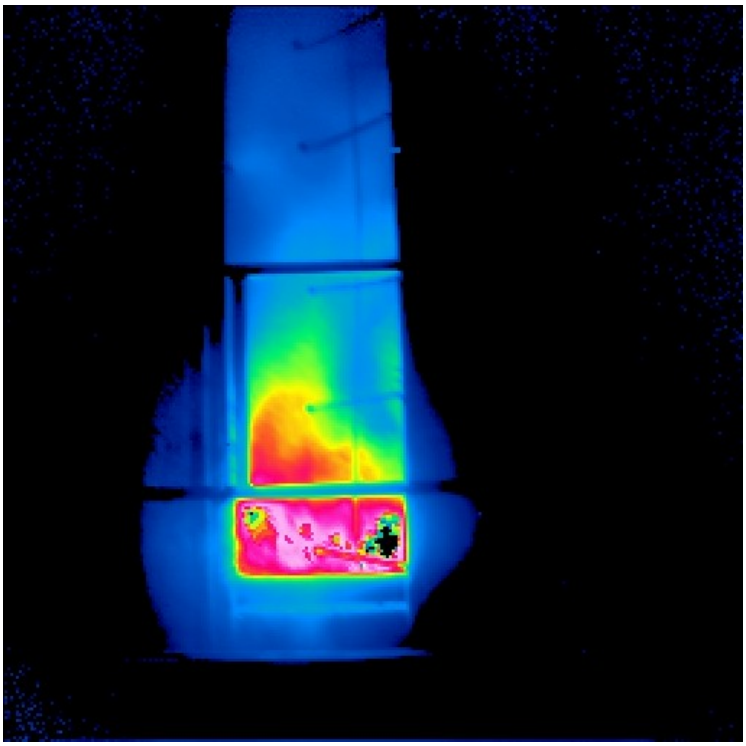

Fig. 1. Temperature gradient during an open pool fire

Result
These experiments described above led to applicative results which allowed the validation of the computer codes CFAST and HEATING (7.1) as well as the derivation of heat transfer parameter.

RELEASE FRACTIONS OF INCINERATED RADIOACTIVE WASTES

The Jülich JÜV-50/2 incinerator at the FZ-Jülich Research Center, Germany, is designed for the incineration of solid and liquid radioactive waste [2]. The incinerator's operational capacity is 50 kg/h based on a heat content of 20.000 KJ/kg of waste. The annual capacity is limited due to the license to 140 Mg/a (120Mg/year of solid waste and 20 Mg/year of liquid waste).

The JÜV 50/2 incinerator is a commercially operated facility. Therefore waste treatment is given by economy and operational logistic as well as by legal requirements such as Federal Immission Control Ordinance or German Radiation Protection Ordinance.

Result
Focus of the examinations of balances of an industrial incineration plant was the analysis of the release mechanism "combustion". In order to gain representative results the release behaviour of the combustion plant of the Jülich research centre has been studied. The investigation of release rates of combusted waste depends on clear balancing of the in- and output amounts of one incineration cycle. Unfortunately the analysis of radioactive releases in the off-gas and ashes appeared to be practicable in only very few cases because of cross contamination effects and

impurities during the campaign-wise operation. As far as balances could be drawn the release rates former meet theoretical assumptions in comparable dimensions.

RELEASES FROM METALLIC SCRAP

The release fraction for metallic scrap has been analyzed in technical scale at the Siempelkamp melting plant ("CARLA"). The samples are packed in drums, which are heated in an inductive melting oven. The studies were carried out for pure black and white steel as well as for zinc-coated and varnished metals. The samples are representative materials from nuclear power plants.

A total of 7 experiments were carried out with several representative sample materials, as given in Table I [3]. Each sample composition was placed in a common 200 l steel drum.

Table I. Sample Compositions

Nr.	Sample material
BV1	Fe- lacquer coated
BV2	Fe- zinc coated; (shear scrap)
BV3	Vanadium Steel; (shear scrap)
BV4	Fe- coated; (shear scrap, compressed)
BV5	Fe- zinc coated; (shear scrap)
BV6	Fe- zinc coated; (shear scrap)
BV7	Fe- zinc coated; (shear scrap)

The experiments were carried out subsequent to a standard melting process to gain from the residual heat. After all measuring equipment was installed the furnace was heated up inductively. Regarding to the filling level and sample material the examined drums were heated up to 800 ° C for one hour and the nuclide specific release rates are measured.

During the entire experiments (heat-up and dwell time) off-gas samples were collected continuously. The off-gas was led through a filter station equipped with changeable glass fiber filters. About 20 filters per experiment were collected. After weighing the filters to achieve balance data concerning the mass release they were analyzed radiological (gamma-spectrometric, detection time 3600 s, nuclide specific).

Result

The results from the investigations of radioactive metallic scrap at the Siempelkamp Company in Krefeld met the theoretical estimations of prior model calculations for assumptions being made for safety assessment analysis for German repository sites.

INACTIVE INVESTIGATIONS OF WASTE SAMPLES

The declared aim of the experimental sequence "Investigation of inactive samples" was to complete the knowledge of the properties of inactive elements which occur in chemical and physical compounds similar to real radioactive waste.

The samples simulated various waste products such as cemented waste, concentrates, mixed waste, metallic waste, resins and combustible waste. All samples were precisely doped with the following different elements:

Li, Na, K, Cs, Be, Mg, Ca, Sr, Ba, Al, Sn, Pb, P, As, Sb, Bi, S, Se, Cu, Zn, Cd, Sc, Y, Ti, Zr, V, Cr, Mo, Mn, Fe, Co, Ni, Ru, Pd, Ce, Sm, Eu, Th

As representatives for the main waste streams the following materials were used as carriers:

1. Cemented waste (diluted or solid inactive elements used to prepare cement sample)
2. Mixed waste (representative mixture from rubber, paper, textile etc. doped with dissolved elements)
3. Metallic waste (steel wool sprayed with element solution)
4. Concentrates (boric oxide doped with dissolved elements and boric oxide mixed with doped and dried cellulose
5. Ion exchange granulates(common ion exchange granulates doped with solution from dissolved elements)

All release investigations with inactive samples were executed at the chemical laboratory of ANALYTIS in Wesseling, Germany. Most of the required instruments were standard equipment of an analytical laboratory.

After preparing the sample and placing it in the gastight reactor both was heated up to distinct temperatures to measure the specific release rates of the doped elements out of each carrier material. To achieve this the temperature was increased and held in the steps 200°C, 400 °C, 600 °C and 800°C for one hour. All released gas was led through acid and alkaline solutions. The washing solutions were changed every new temperature step and transferred to the quantitative analysis unit to determine the amount of released material at a distinct temperature. Analyzing units were ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy), ICP-MS (Inductively Coupled Plasma Mass Spectroscopy) and AAS (Atom Absorption Spectroscopy).

Evaluation of temperature-dependent release rates

The results of the release investigations of the elements and waste samples were performed at 200°C, 400°C, 600°C and 800°C. For mixed wastes the element-specific release rates were calculated as represented in Fig. 2.

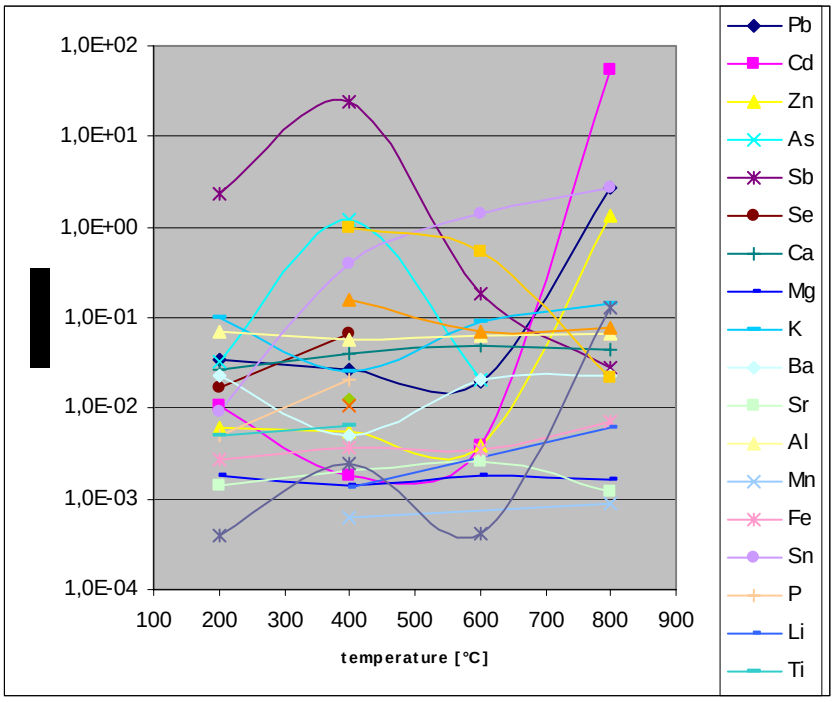

Fig. 2. Element specific release rates for the sample "mixed waste"

Obviously there is no consistent release behaviour for the different elements. Chemical or physical explanations for this are not easy to find due to the very small statistical base the experiments were executed on (number of sequence repeats had to be held low for cost reasons). Therefore the evaluation of the release rates was done element-specifically and not carrier material-specifically.

The theoretical thermodynamic process of vaporization of radioactive material can be modelled by:

$$\dot{m}_D = \sigma_c \; x \; \frac{p_D^0 \; x \; M_D}{R \; x \; T} \qquad \text{(Eq. 1)}$$

With

$\dot{m}_D$ = mass flow of vaporized component as a function of T
σ_c = mass transfer coefficient
p_D^0 = saturation vapor pressure
M_D = molar mass of vaporized substance
R = gas constant
T = temperature in K

As an analogy the saturation vapor pressure p_D^0 will be replaced with the release function f_D^0 as a function of the temperature.

$$\dot{m}_D = \sigma_c \; x \; \frac{f_D^0 \; x \; M_D}{R \; x \; T} \qquad \text{(Eq.2)}$$

The temperature dependence of thermodynamic functions, such as the saturation pressure are often expressed as a function of three parameters:

$$\ln\left(p_D^0\right) = -\frac{A}{T} + B + C \; x \ln\left(T\right) \qquad \text{(Eq.3)}$$

The same assumption builds the base for the release function, too. Parameters A, B and C result from the approximation of the covering data (evaluated element specifically). Table II gives the parameters for each element.

Table II. Element Specific Parameters for the Release Function

Element	Parameter		
	A	B	C
Pb	21145,007	-286,304494	36,7550521
Cd	17394,6906	-246,007126	31,5986024
Cr	detection limit		
Cs	30876,2565	-362,170537	45,8888007
Co	-2361,1734	6,59922516	-3,34270317
Cu	12825,7411	-163,447432	19,4007323
Ni	detection limit		
Zn	9381,4997	-185,255821	23,9608973
As	-18425,216	174,776037	-24,6655839
Sb	-20997,8581	231,745017	-32,3463409
Se	-11462,2658	60,6491929	-8,66894628
Ca	6953,15838	-101,600056	11,5311686
Mg	4757,95195	-67,6754104	6,57388943
Na	detection limit		
K	2305,12191	-39,8465896	3,42199815
Ba	14477,3545	-178,170693	21,3934329
Sr	122,617738	-19,8882562	0,42672849
Be	detection limit		
Al	-859,14248	-2,73582791	-1,63335711
Mn	2248,25804	-77,2364069	8,29824368
Fe	3864,6368	-58,6300844	5,42917289
V	detection limit		
Sn	-13163,4555	79,6070602	-11,1114076
P	-5700,88371	46,4085331	-8,49336901
Ti	detection limit		
Mo	-6882,8713	23,8340087	-4,6111206
S	-15077,3274	126,804563	-17,9958649
Ru	detection limit		
Bi	-2751,70906	-22,7949158	2,04790274
Ce	detection limit		
Sm	detection limit		
Eu	detection limit		
Th	detection limit		
Sc	detection limit		
Y	detection limit		
Pd	detection limit		
Zr	-2188,30164	12,7758337	-4,02940217

With this, the temperature dependent release fraction f_0 is

$$f_0(T) = \exp\left(-\frac{A}{T} + B + C\ x \ln(T)\right) \quad \text{(Eq. 4)}$$

With f_0 is the release rate $\left[\frac{m_{released}}{m_0\ x\ s}\right]$ (Eq. 5)

For the temperature window between 200 °C and 800 °C the measuring results are represented adequately well as the parameters show. For the elements with release rates below their detection limits a quasi-Zero-release is assumed. The beginning claim that remarkable release rates aren't detectable below temperatures lower than 200 °C could not be met. For some elements very obvious overestimations resulted in the temperature window < 200°C by the use of the chosen approximation. In these cases the release fraction was reduced to the 200°C-value as compensation.

CALCULATION OF NUCLIDE SPECIFIC RELEASE FRACTIONS FOR THE DESIGN EVENT

The calculation of release fractions for the design event (fire with 800°C for 1 hour) is carried out in two steps:

I. Temperature fields for the smallest waste container licensed for the German KONRAD Repository (waste container type I) are calculated considering a fire burning for 1 h at 800 °C with a 24 h-cooling down period.
II. The combination of temperature-dependent release rates and time-dependent temperature fields within the container results in time-depenendent release rates, which lead to release fractions by integration.

Evaluation of temperature fields

Transient temperature fields in a waste package were calculated by the use of the finite differences computer code Heating 7.3. Heat transfer parameters used for the calculations were derived from the full scale oven studies [1]. During the fire period the hottest part of the waste package was in the outer shell. After extinguishing the temperature maximum moved into the inner parts of the waste package. In our calculations isothermal volumes in the temperature range from 30°C up to 800°C are considered. Fig. 3 shows the development of isothermal volumes in the range from less than 80°C up to 180°C. (Hotter volumes exist, but they are not mapped in Fig. 3).

The fire starts with temperatures less than 80°C over the whole volume. With the progress of the fire formation of isothermal volumes takes place. Due to the temperature distribution in the waste package the isothermal volumes in the range up to 200°C have their maximum a long time after extinguishing the fire; e. g. for the volume between 80°C and 100°C 15 hours later.

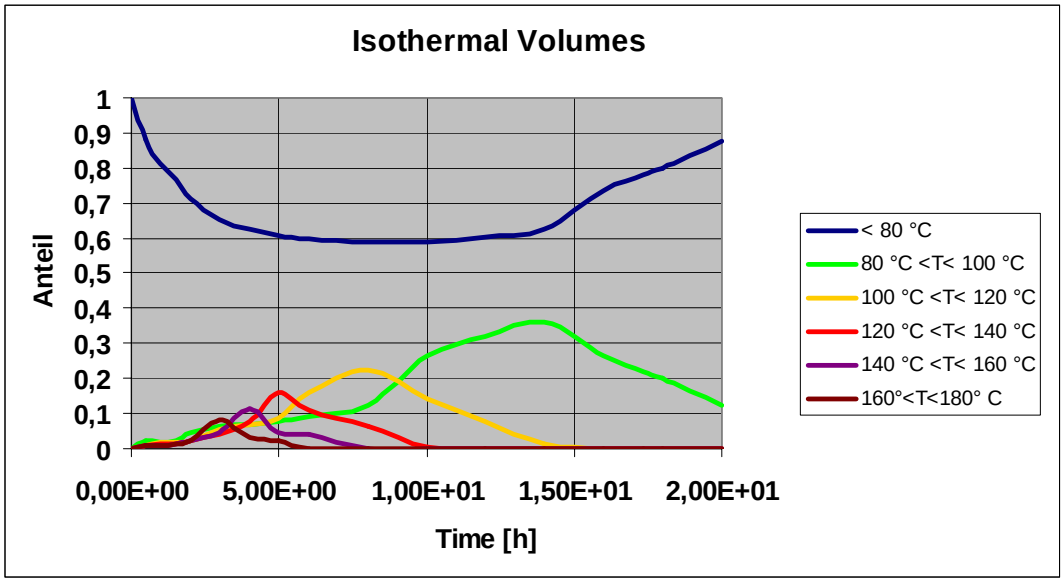

Fig. 3. Evaluation of release fractions

For each temperature range *(T)* a release rate can be calculated. Assuming a homogeneous activity distribution in the waste package the release fraction function F_i of element *i* results from the following relation:

$$F_i = const\ x \sum_{T=100}^{800°C} \int_{t=0}^{24h} V_T(t)\ x\ f_0^D(T)\ x\ dt \qquad \text{(Eq.6)}$$

Results for the elements taken into consideration are summarized in Fig. 4.

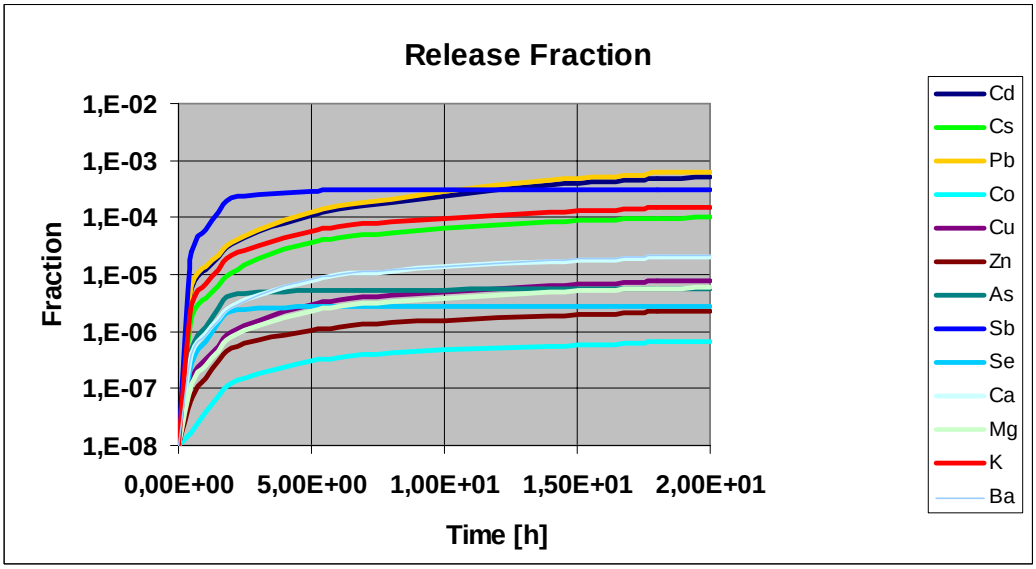

Fig. 4. Release fractions

As can be seen from Fig. 4 there is still a release even 20 hours after extinguishing of the fire. The release stops when there is no volume below 80 °C. (This is an assumption which should be proved in future work). This appears app. after 24. hours.

Results

Release fractions for heavy metals as well as for Cs appear to be the highest. This development meets the calculated pre-estimations in a satisfying way. The investigations resulted for the rest of the elements in clearly lower release rates, which lead to safety reserves in significant dimensions.

CONCLUSIONS

The validation of fire simulating computer codes led allowed the validation of the computer codes CFAST and HEATING as well as the derivation of heat transfer parameter.

The investigation of release fractions of incinerated radioactive wastes approved former theoretical assumptions about the release behavior of incinerated waste in comparable dimensions.

The results from the investigations of radioactive metallic scrap met the theoretical estimations of prior model calculations as well.

The thermodynamical evaluation of the measuring data from the experimental investigations of non-radioactive waste samples showed that there are still reserves concerning the safety assumptions of several elements. The release behavior of the investigated elements in the case of fire – besides heavy metals and CS – was overestimated in safety and risk calculations.

All results of the presented fire experiments could be improved by the extension of the statistical base the results have been calculated on.

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