AQUALINE LS

IODINE RELEASE FROM SODIUM POOL COMBUSTION

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ABSTRACT

Iodine release associated with sodium pool combustion was determined by heating 20 gr sodium containing sodium iodide, which was labelled with ^{131}I and dissolved in the sodium in concentration of 1 ∼ 1,000 ppm, to burn on a nickel crucible in conditioned atmosphere in a closed vessel of 0.4 m^3. Oxygen concentration was changed in 5 ∼ 21 % and humidity in 0 ∼ 89 % by mixing nitrogen gas and air. Combustion products were trapped by a Maypack filter composed of particle filters, copper screens and activated charcoal beds and by a glass beads pack cooled by liquid argon. Iodine collected on these filter elements was determined by radio-gaschromatography.

When the sodium sample burned in the atmosphere of air at room temperature, the release fractions observed were 6 ∼ 33 % for sodium and 1 ∼ 20 % for iodine added in the sodium.

The released iodine was present in aerosol at a ratio of 98 %, and the remainder in the gas form. The release fraction of iodine trended to decrease as oxygen concentration and humidity in the atmosphere increased. No organic iodide was detected in the combustion products.

1. Introduction

Sodium in the primary cooling system of Fast Breeder Reactors contains the radioactive sodium and corrosion products in the course of normal reactor operations and further fission products when any failure of the fuel cladding. In the hazard analysis of the FBRs, therefore, a significant release of energy and radioactivity is postulated to occur from a sodium fire following the sodium leakage from the system boundaries.

Studies of sodium combustion are undertaken at Hitachi Ltd., sponsored by the Power Reactor and Nuclear Fuel Development Corp., to obtain informations characterizing sodium fires and to design engineering safeguards against consequences to the sodium fires. After reviewing reported investigations[1], we directed our effort to the studies of energy release associated with sodium spray combustion and of iodine release associated with sodium pool combustion.

Iodine release associated with sodium combustion has been studied by many investigators[2]~[9] because

of primary importance to the hazard evaluation. These studies reveal that a major part of iodine released from solution in sodium is trapped on particle filters in the chemical forms of sodium iodide and molecular iodine vapor but a minor part remaining as vapor or volatile compounds passes through the filter. Organic iodide was detected in the volatile compounds[9], although it is unstable at elevated temperature by sodium combustion. Thus, attempts were made to confirm the organic formation by a sodium combustion experiment.

2. Experimental

Figure 1 represents an arrangement used in the experiments of iodine release associated with sodium pool combustion. The experimental arrangement consists of a combustion vessel enclosed by a guard vessel, a gas system to control concentrations of oxygen and moisture in the atmosphere, a gas sampling system to collect released iodine in aerosol and gas, and apparatuses to analyze chemical forms of the iodine.

(1) Combustion vessel

The combustion vessel made of type 304 stainless steel is installed vertically in the guard vessel made of carbon steel, and has a volume of 0.4 m^3. On the bottom of the combustion vessel is provided a flange plate, on which a nickel crucible with an electric furnace stands at

a height of 450 mm from the bottom, so that combustion products mix with ambient gas by the aid of natural convection. In addition to manholes, a nozzle is provided on the side of the combustion vessel to lead out leading wires for the furnace and thermocouples for measuring temperatures in the crucible and the upper gas space. Gas sampling is made from a suction tube located at 1,000 mm above the bottom. The guard vessel is kept exhausting to secure safety against leakage of combustion products from the inner vessel.

(2) Gas Controlling System

Gas cylinders are used for supplying nitrogen gas and oxygen gas to the combustion vessel, and for controlling oxygen concentation and humidity in the mixed gas as well as its pressure. Vacuum pumps are provided for evacuation of the combustion vessel and the guard vessesl.

(3) Gas Sampling System

This system branches off from the main sampling tube 4 mm in diameter. One branch is used for sampling iodine with combustion products by a Maypack filter and another branch for counting radioactivity in volatile iodine compounds by the aid of a gaschromatograph.

The Maypack filter is composed of, as shown in Fig. 2, two packs of membrane filter (pore size of 0.3 μ)

for collection of sodium aerosol, one pack of five sheets of copper screen (about 60 mesh), momentarily immersed in hydrogen chloride solution before use, for trapping of molecular iodine vapor and three packs of activated charcoal bed (12 ~ 24 mesh and 10 mm thick), made from coconut shell, for absorption of volatile iodine compounds. This composition is the same one as Kitani, et al.[9] were used. Gas flowing through the Maypack filter vertically fixed, a flow meter and a circulating pump returns to the combustion vessel for long time of sampling.

The sampling system led to the gaschromatograph comprises a filter with use of glass beads 2 ~ 3 mm in diameter, a paper filter 0.5 mm thick, a moisture trap packed with magnesium perchlorate, a iodine sampling tube packed with glass beads of 80 ~ 100 mesh and chilled with liquid argon, flow meter and an exhausting pump. A heater is wound around the tube to release trapped iodine for analysis by the gaschromatograph.

(4) Gas Analyzing Apparatus

A gaschromatograph with an iodine detector of electron capture type is provided in front of a gas trap for γ-ray monitor. The chromatography column (2 mm in diameter and 3m long) is packed with celite (80 ~ 100 mesh) coated with DOP (15 %). The iodine detector has sensitivity to 10^{-12} gr of methyl iodide. The γ-ray

monitor is done by a 2 inches NaI scintillation counter of well type, placed in a lead shield, and by a multi-channel analyzer.

(5) Preparation of Sodium Sample

A solution of radioactive iodine (1 mCi ^{131}I) in the chemical form of sodium iodide, containing sodium carbonate, sodium bicarbonate and sodium sulfite as stabilizers of the iodine, was mixed with the solution containing stable iodine (^{127}I) in the chemical form of sodium iodide. The solution was evaporated to dryness in the nickel crucible with an inner volume of 20 ml. Sodium metal of special grade reagent was placed as much as 5 ～ 20 gr in the crucible and heated in a glove box filled with argon gas at 300 ～ 400 ^{o}C for about 4 hr so as to diasolve the iodine into the sodium. The sodium Released radioactive iodine during this process was below 1 % of the loaded quantity. In some cases, about 0.5 ml kerosene was so injected into the sodium sample that released iodine has a chance to combine with kerosene vapor.

(6) Gas Conditioning and Sodium Burning

The combustion vessel was evacuated below 1 Torr after standing the crucible with the sodium sample on the bottom flange of the vessel. Dry air and nitrogen gas were mixed to make a given value of oxygen concentration by the before-mentioned method. Humidity in the mixed gas was changed by evaporating several gr of water in the combustion vessel. Then, the crucible was heated up by the electric furnace at a rate of 30 ^{o}C/min until ignition of the sodium sample in the crucible. The sodium ignition was observed in the records of temperature in and above the crucible. After the end of sodium combustion, the gas in the vessel was replaced with room air and the air with carbon dioxide gas so as to change deposited sodium on the inner surface of the vessel into sodium carbonate. The vessel inside was washed by steam in nitrogen gas atmosphere, wiped clean with use of gauze by opening the manholes and dried by evacuation for 10 hr.

(7) Gas Sampling

The combustion products in the gas atmosphere was collected by the Maypack filter at 5, 10, 30, 90, 300 and 1,000 min from the beginning of the sodium ignition, by flowing the gas at a rate of 1 l/min through the loop. Sampling time was elongated from 3 ～ 60 min to obtain wanted amounts of the products. The Maypack filter was diassembled to analyze radioactivity of iodine for each filter element and to determine sodium aerosol on the particle filter.

Gas sampling for analyzing volatile iodine was made for a duration of 10 ～ 60 min at a flow rate of 1 l/min, after the sampling by the Maypack filter at the 1,000 min.

The glass beads filter and the paper filter were used to remove sodium aerosol from the gas flow. Since air containing moisture degrades performance of the gaschromatograph, the moisture was trapped by magnesium perchlorate in advance of the iodine sampling in the glass beads, chilled with liquid argon. The substance trapped on the glass beads was carried by 30 ml/min flow of purified nitrogen gas heated at 60 $^\circ$C into the chromatography column also heated at 60 $^\circ$C. The detector of electron capture type was set up at 90 $^\circ$C and 100 μ sec for pulse intervals. The radioactivity was analyzed for the gas flowing out of the detector.

3. Results and Discussion

(1) Release Fractions of Sodium and Iodine

Records of temperature indicated ignition temperature ranging between 370 ~ 480 $^\circ$C and the combustion lasting for 5 ~ 10 min in various cases. Temperatures observed during the combustion were respectively 560 ~ 610 $^\circ$C in the sodium sample, dropping to 100 ~ 200 $^\circ$C at 50 mm and less than 50 $^\circ$C at 150 mm above the sample, and room temperature on the inner wall surface of the vessel. Considerable amounts of combustion products deposited on the inside and outside of the crucible, and particularly on the mouth edge, forming apparently sodium oxide.

Fall out of aerosol was observed on the bottom plate and the lower part of the vessel wall.

A release fraction obtained from loaded and remained amounts of the sodium sample in the crucible trended to increase with decreases in oxygen concentration and humidity in the gas atmosphere. A decrease in oxygen concentration from 21 % to 10 % in dry gas mixture produced increases in the release fraction of sodium from 22 % to 33 % and that of iodine from 3 % to 6 %. In the same way, a decrease in humidity from 89 % to 0 %, (dew point at -60 $^\circ$C) in air produced increases in the release fraction of from 6 % to 22 % and that of iodine 1.5 % to 3 %. These trends are explained by check of oxygen supply to the burning sodium due to film formation of combustion products[7],[8]. White smoke was released in the combustion in the gas mixture of 4.5 % oxygen concentration and 52 % relative humidity, an equivalent condition to the gas atmosphere in the cells for the primary sodium components, generating aerosol at release fraction of 33 % for sodium and 20 % for iodine.

(2) Sodium Trapped on Particle Filter

Sodium aerosol concentrations obtained from amounts of sodium, trapped on the particle filter during the sampling time, are plotted in Fig. 3 as functions of time after the sodium ignition and initial humidity in the gas atmosphere. Hollow circlets denote the aerosol

concentrations obtained from the combustion in dry gas mixtures with 21 % and 10 % oxygen concentration, since no significant difference is observed between both series of results. Solid circlets mark the results obtained in humid air ranging 75 ~ 89 % in relative himidity, appearing to be below the hollow cieclets in the change in the aerosol concentration with the time. The aerosol concentration is depleted linearly with time on log-log scales, being expressed approximately by the minus second power of time, except the initial period when the sodium sample is burning. Scatters of the results in this period is attributable to insufficient mixing of sodium aerosol in the combusion vessel. The depleting trend observed in Fig. 3 is similar to that in other reports[5],[10].

(3) Iodine Trapped by Maypack Filter

Concentration of iodine determined from radioactivity of the Maypack filter elements are represented in Fig. 4 5 and 6 as functions of time after the sodium ignition, initial humidity in the gas atmosphere and iodine concentration in the sodium sample. Marks of circled solid circlet indicate the relation of iodine concentration with time in the case that 1,000 ppm iodine in the sodium sample is released into humid air, and those of solid and hollow circlet the relation in the case that 1 ~ 2 ppm iodine in the sodium sample is released in dry and humid air. Figure 4 reveals that both relations agree with

that of sodium aerosol in the decreasing trend, and that the upper result exceeds than the lower one by a factor of 1,000, equivalent to the iodine concentration in the sodium sample. Figure 5 shows a linear decrease with time in the two kinds of concentration of iodine, which is released from the sodium damples containing different concentrations of iodine and trapped on the five sheets of copper screen. The concentration of iodine trapped on the charcoal beds in Fig. 5 shows also a linear increase with time, similar to that in Fig. 6, in the iodine concentrations, although scatterings are seen in the results in both figures.

Trapping fractions of iodine on each element of the Maypack filter are illustrated in Fig. 7 for the case of the combustion in dry air. The bar graphs show that the most fraction (98 %) of iodine released in the ambient gas is trapped on the first particle filter and the remainder on the second particle filter, the copper screens and the first activated charcoal bed. Radioactive iodine in the third charcoal bed is below the limit of detection. This fact implies that sodium aerosol is accompanied with the released iodine and only a small percent of the iodine is present in the gaseous form.

(4) Volatile Iodine Compounds

The gas containing combustion products of 24 Nl was analyzed by radio-gaschromatography but radioactivity of

^{131}I was undetectable in the separated gas passing through the chromatography column. Data recorded by the detector of electron capture type after separating the room air by the chromatography column indicates, as shown in Fig. 8, peaks of methyl iodide, ethyl iodide, carbon tetrachloride and chloroform under the before-mentioned measuring conditions. The peak value for methyl iodide did not increase from the background value even if in the combustion gas, for examples, changing 66×10^{-12} to 67×10^{-12} gr/l and 17×10^{-12} to 16×10^{-12} gr/l. In addition, the release of methyl iodide was undetectable in combustion of sodium sample after adding 1,000 ppm iodine and 0.5 ml kerosene in the sodium. The depletion of radioactivity between the charcoal beds shows evidence of trapping of gaseous iodine, presumably sodium iodide.

4. Conclusions

(1) Sodium and iodine are released in the ambient gas in association with combustion of sodium containing $1 \sim 1,000$ ppm iodine at fractions of $6 \sim 33$ % for sodium and $1 \sim 20$ % for iodine, depending on oxygen concentration and humidity in the gas. The maximum release fractions of sodium and iodine are obtained in humid air depleted of oxygen.

(2) Released iodine is present at 98 % in aerosol of sodium oxide and the remainder in the copper screens and the activated charcoal beds.

(3) Formation of organic iodide can not be detected in combustion products released from the sodium sample into the gas atmosphere by the radio-gaschromatography and the electron capture detection.

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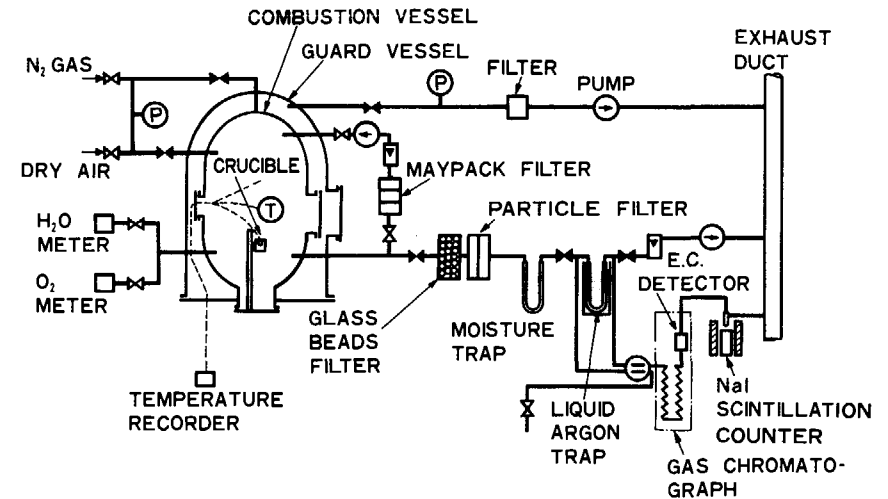
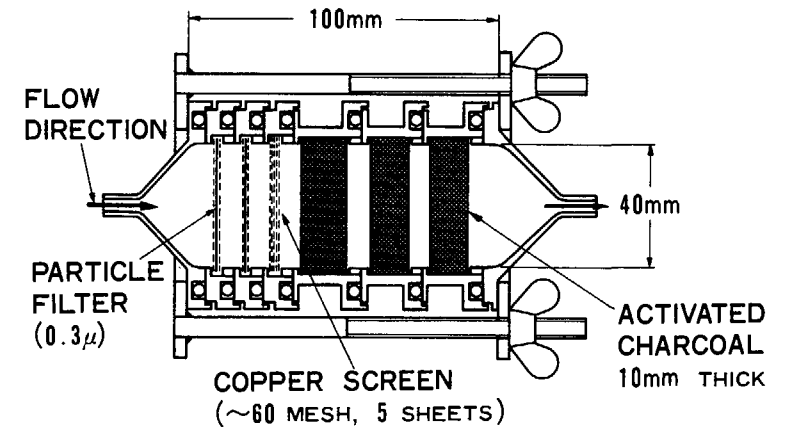aerosols, SM-110/17 (1968)

FIG. 1 IODINE RELEASE TEST ARRANGEMENT
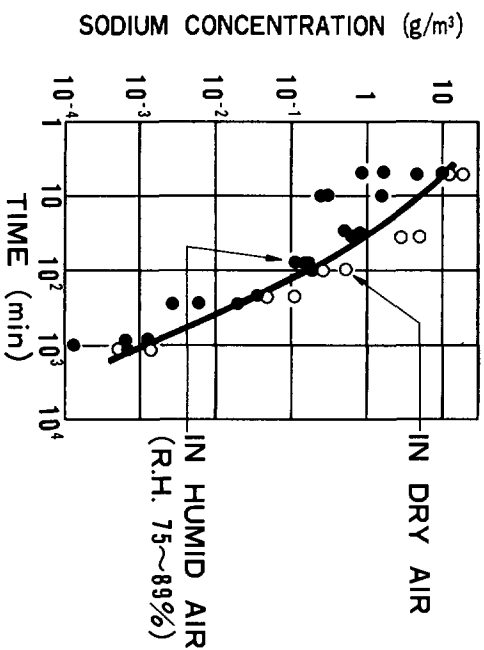

FIG. 2 COMPOSITION OF MAYPACK FILTER

FIG. 3 SODIUM TRAPPED ON PARTICLE FILTER

SODIUM CONCENTRATION (g/m³)
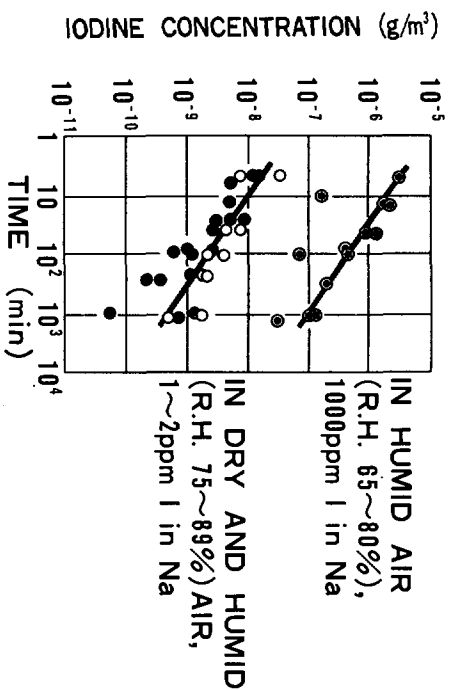
TIME (min)

IN DRY AIR

IN HUMID AIR
(R.H. 75~89%)

FIG. 4 IODINE TRAPPED ON PARTICLE FILTER

IODINE CONCENTRATION (g/m³)

TIME (min)

IN HUMID AIR
(R.H. 65~80%),
1000ppm I in Na

IN DRY AND HUMID
(R.H. 75~89%) AIR,
1~2ppm I in Na

FIG. 5 IODINE TRAPPED ON COPPER SCREEN

IODINE CONCENTRATION (g/m³)

TIME (min)

IN HUMID AIR
(R.H. 65~80%),
1000ppm I in Na

IN DRY AND HUMID
(R.H. 75~89%) AIR,
1~2ppm I in Na
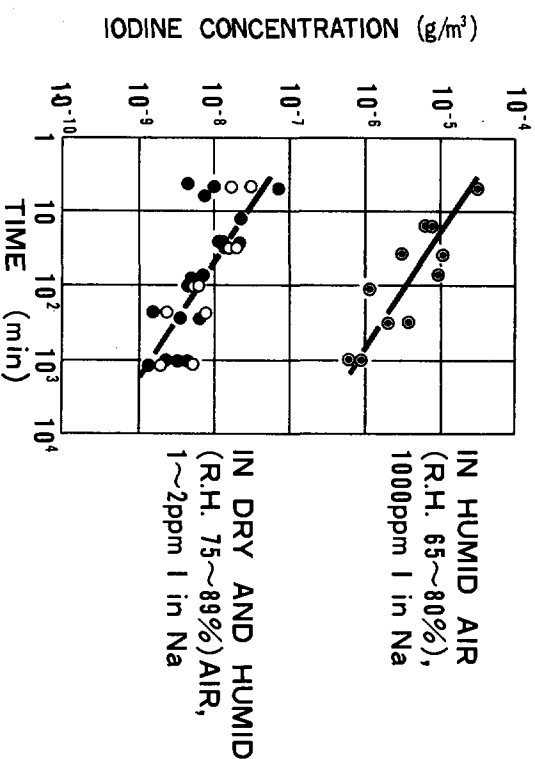
FIG. 6 IODINE TRAPPED ON ACTIVAED CHARCOAL

IODINE CONCENTRATION (g/m³)

TIME (min)

IN HUMID AIR
(R.H. 65~80%),
1000ppm I in Na

IN DRY AND HUMID
(R.H. 75~89%) AIR,
1~2ppm I in Na

FLOW DIRECTION (21% O₂, 0% H₂O)

FILTER ELEMENT

PARTICLE FILTER

PARTICLE FILTER

ACTIVATED CHARCOAL

10^{-3} 10^{-2} 10^{-1} 1 10 10^{2}

TRAPPING FRACTION OF IODINE (%)

FIG. 7 IODINE TRAPPED BY MAYPACK FILTER

OUTPUT OF ELECTRON CAPTURE DETECTOR (—)

5   10   15   20

TIME AFTER HEATING
SAMPLING TUBE (min)

— 150

CH_3I

—100

— 50

C_2H_5I

$CHCl_4$

CCl_4

FIG. 8
RECORD OF VOLATILE
IODINE COMPOUNDS
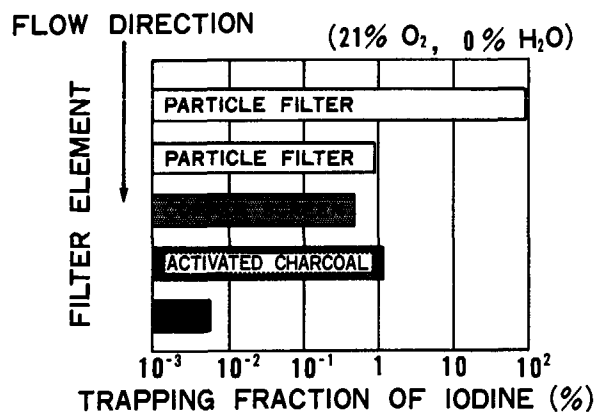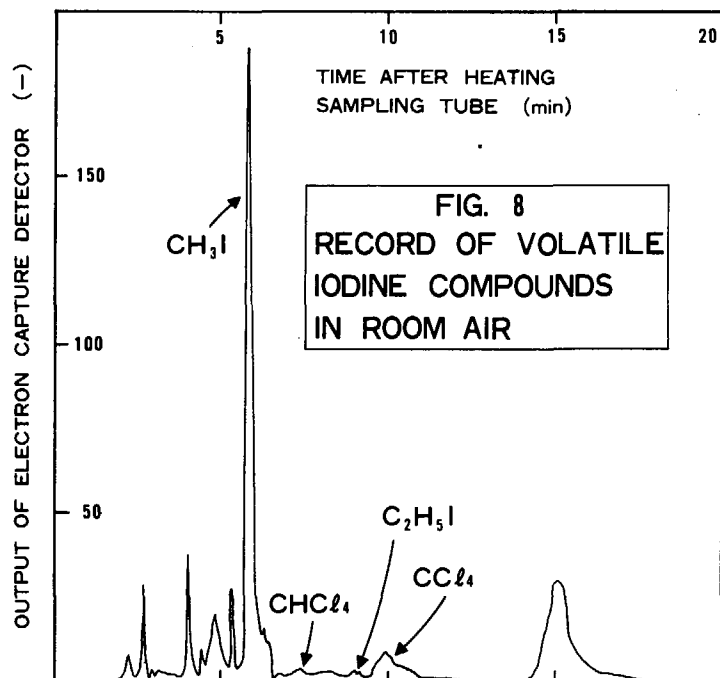### IN ROOM AIR

RELEASE OF FUEL AND FISSION PRODUCTS
FROM HOT SODIUM

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In case of a hypothetical core disruptive accident with tank failure, major quantities of sodium, fuel and fission products will be released from the SNR core catcher into the containment atmosphere due to mechanical, chemical and evaporation processes. Since the core catcher is a long term aerosol source, it is important to study the retention capability of sodium for fuel and fission products, the release rates and the release mechanisms. In the KfK-NALA-program, experiments on this subject were performed with UO_2, Cs, J and Sr in sodium on a small laboratory scale (LS) and on a larger technical scale (TS). In the following, some experimental details and the most important results are described.

In case of the LS experiments, about 100 g of sodium were contaminated with amounts of the order of 1 g of the substance to be investigated and heated up in a small stainless steel vessel (7 cm diameter, 10 cm height) to temperatures between 400 °C and 900 °C. The contamination substances were UO_2 powder (mean particle diameter 20 μm), UO_2 pellets, Cs metallic, NaJ powder and SrO powder. The released aerosols were transported by a variable inert gas stream into cold traps and a filter. After washing and titration, the sodium release rate and the fuel and fission product traces were determined.

The TS experiments were performed in the 4 m³-vessel NABRAUS with mixtures of 2 kg of sodium and 20 g of UO_2 powder (0.2 g of Cs metallic, respectively) in a heating pan (surface area 0.72 m²) at temperatures between 500 °C and 700 °C. The oxygen content of the containment atmosphere could be varied from 0 to 21%. During the experiment, aerosol probes were taken at various sampling ports of the vessel. For a more detailed description of the LS and TS setup, the reader is referred to /‾1_7.