Investigation of Heavy Metal Release during Thermal Waste Treatment on a Forward-Acting Grate by Means of Radiotracers

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This paper deals with the determination of location, time and quantity of the release of heavy metals in a pilot-scale grate system by means of short-lived radioactive isotopes during the incineration of municipal waste. The isotopes $^{60}$Zn (half life: 13.8 hours) and $^{65}$Cu (half life: 12.7 hours) were used to represent heavy metals which can be released relatively well and more difficultly, respectively. Due to the implementation of isotopes which emit gamma rays, all measured values could be acquired without direct contact and without the need to take samples. The location of release was determined by means of NaI(Tl)-scintillation detectors positioned alongside the outer walls of the grate. The time and the quantity of the release were measured with a detector located in a special absorption vessel for the purification of a partial flow of the exhaust gases.

1 Introduction and Objective

The possibilities for the optimization of the process control of the so-called classical combustion of residual waste in grate systems have not yet been completely explored [1]. The objectives of the optimization include a further reduction in the amount of flue gas and the pollutant load, an increase in the total efficiency, as well as the improvement of the ash quality. This paper places particular emphasis on the improvement of the ash quality. The goal is to produce an ash which can be implemented in the construction industry through the application of primary measures, in other words, through the process control itself. A prerequisite for this is the maintenance or reduction of the eluate and solid concentration of inorganic salts and heavy metals below the limiting values. The process conditions (in particular temperature, gas atmosphere, residence time) are adjusted so that these pollutants are either evaporated and are, therefore, not present in the ash or are strongly mineral-bound in such a manner that they are no longer available. Results concerning the behavior of heavy metals and salts are already available from experiments done on the laboratory scale [2–4]. These results originate from experiments using small charges (several g to kg) and in batch operation. In order to be able to put this knowledge into practice and for optimization, the next step must be to determine the location and amount of heavy metal evaporation under realistic conditions, in other words, in a continuously-operated pilot plant.

A determination of the heavy metals content is usually carried out through the sampling of the total flue gas flow and the corresponding analysis. A detection directly at the location of evaporation using conventional sampling and analysis is, due to the harsh conditions in the combustion chamber, particularly difficult and cannot be carried out online with respect to the analysis. In addition, a very complex measurement network is necessary for an investigation over the complete firing bed surface.

The radiotracer method provides the possibility to follow the behavior, location and concentration of a certain heavy metal species on-line during the entire combustion process in a technical waste treatment plant. The following quantities can be determined with the help of this method, using the combustion process in a grate system on the pilot-plant scale as example:

- the location of the heavy metal evaporation,
- the time course of the heavy metal evaporation, as well as
- the amount of heavy metal evaporated.

2 Principle of Radiotracer Measurements

The idea behind taking measurements using substances labeled with radioactive isotopes (so-called radiotracers) is the ability to detect them with the help of the emission of ionizing radiation. If gamma-radiation-emitting isotopes are used, it is possible to detect them contact-free without sampling even from outside of opaque apparatuses and vessels. Assuming time-independent boundary conditions during the data acquisition, for instance, through realization of a continuous operational mode, the measured signal is proportional to the tracer concentration. Adverse effects on the process can be avoided in most cases by using short-lived isotopes with a half-life of several hours to several days, such as in nuclear medicine.

In contrast to the investigations presented here, the object of process analyses with the help of radiotracers are usually material transport processes without phase change. In such cases, it is only necessary to guarantee identical transport properties of the original and the labeled material. In most cases this requirement is met for the analysis of gas flow and liquid flow processes by adding a tracer of the same aggregation state. The labeling of liquid flow is also often done by adding well-soluble salts [e.g. 5–10]. The labeling of
solids can often be achieved by absorbing a tracer on the particle surface or by an activation with thermal neutrons in a nuclear reactor [e.g. 11–15]. The need for a chemical identity of the tracer and the original material in contrast to the examples mentioned above exists only in the case of investigation of processes with phase change.

3 Approach and Choice of Tracer

Therefore, the solution to this objective lies in the introduction of the radioactive isotope of a certain heavy metal which occurs in the input waste mass flow of a combustion plant. The isotope must be a short-lived gamma emitter. Radiation detectors located along the sides of the combustion chamber register the time course of the tracer concentration in the waste mass flow at different positions. They make a determination of the location of the marked heavy metal species during the entire residence time in the solid bed possible. The heavy metals evaporated during the combustion process and carried out of the combustion chamber with the flue gas are caught to a certain degree by the absorber. A radiation detector in this absorber registers the temporal concentration course of the heavy metal tracer evaporated. Since the collection of measured values by all detectors is started simultaneously with the introduction of the tracer (DIRAC impulse), concentration changes in the time course of the measured signal at the absorber detector in the range of the combustion chamber can be assigned and the heavy metal evaporation can then be localized in the solid bed. The quantification of the amount of heavy metal evaporated is made possible through a calibration of the absorber detector signal.

The investigations were carried out in a pilot-plant-scale forward-acting grate at the Clausthaler Umweltechnik Institut GmbH (CUTEC) in Clausthal-Zellerfeld. The plant consists of the following components:

– grate,
– combustion chamber,
– heat exchanger,
– flue gas purifier,

as shown in Fig. 1 in a technical flow chart which includes the measurement and testing methods. The plant has a thermal capacity of 0.4 MW making a transfer of the results obtained to the industrial scale possible.

The detection and quantification of the amount of heavy metal evaporated proceeds through gas washing in a special absorber with a liquid absorbt in which the evaporated heavy metals are completely and evenly distributed within a very short time period. In order to limit the expenditure, a partial gas flow of ca. 1 vol.-% of the total gas flow was withdrawn and directed through a special glass gas washer in the bypass, as shown in Fig. 2.

A 0.1 M solution of nitric acid served as washing liquid and lead to a nearly complete absorption of the heavy metals out of the partial flue gas flow. The contents of the absorber were circulated continuously in order to intensify the mass transfer, for a short-term and even distribution of the elutriated heavy metals in particular. A 1.5"-NaI(Tl)-scintillation detector located in the center of the absorber bottom container registered the time course of the relative tracer concentration in the washing liquid, which corresponds to the time course of the heavy metal evaporation in the furnace.

Of the many elements of interest to choose from, copper and zinc were selected for the investigations in the pilot plant. Copper is representative of the nearly nonvolatile elements and zinc of a species which can be easily evaporated under certain conditions [2,16,17].

In the literature, the use of radioactive isotopes of copper and zinc are usually mentioned in connection with the investigation of the ore beneficiation processes [18–21]. For this purpose, samples of the input material of the respective process to be examined were activated in an experimental reactor. The isotopes resulting from the activation with thermal neutrons, 64Cu with a half-life of 12.7 h and 65Zn with a half-life of 244 days, served as radioactive tracers. Other radioactive isotopes can also be formed depending upon the purity of the input material, i.e., 58Mn in the case of activation of copper minerals.
The applications described in [18–21] deal with relatively homogeneous input materials for the ores to be labeled. Since waste, however, is a particularly heterogeneous material, the procedure described in [18–21] is not a suitable solution for the problem presented here. In this case a mixture – also including long-lived isotopes – representative of the elements present in the input material would result and the measuring signal could not be clearly assigned to the heavy metals to be investigated. Therefore, an extremely pure input material of each heavy metal must be used for the activation.

The elements chosen for this investigation, copper and zinc, have radioactive isotopes whose nuclear physical parameters fulfill the above-mentioned requirements of tracer characteristics: $^{64}$Cu and $^{60}$Zn. The isotope $^{64}$Cu arises through the neutron capture by the isotope $^{63}$Cu, has a half-life of 12.7 h, and is detectable without direct contact and sampling-free through the apparatus and container walls due to the gamma radiation from positron annihilation. It can be generated through the activation of highly purified copper in the experimental reactor. The isotope $^{66}$Cu, formed by the activation of the metal in its natural composition from the $^{65}$Cu isotope, has a half-life of only 5 min and is at the time of the tracer injection (after several hours) no longer detectable.

The $^{60}$Zn isotope can also be produced through neutron capture by $^{64}$Zn in the experimental reactor. With a half-life of 13.8 h and an emission of gamma radiation during the isomeric transition to the ground state with an energy of 439 keV, it demonstrates comparable tracer characteristics to $^{64}$Cu. However, the long-lived $^{65}$Zn isotope (244 day half-life) is also formed in the natural mixture of isotopes, which includes the $^{64}$Zn isotope, during the activation of even an ultrapure sample of natural zinc. Therefore, a pure quantity of $^{65}$Zn is necessary for the generation of $^{60}$Zn.

### 4 Activity Estimation and Generation

The activity necessary for the measurement is primarily determined through the concentration measurement of the heavy metal species in the flue gas absorber. The effective activity of the tracer was fixed at 1850 MBq (50 mCi) with respect to the determination of even very low concentration changes in the flue gas. The Monte-Carlo simulation [22] for the estimation of the measuring effect at the absorber detector and the calculation with a method presented in [23] for the measuring effect of the detectors positioned along the grate support the choice of these values.

The formation of the radioactive isotopes $^{64}$Cu and $^{60}$Zn takes place through the reaction of thermal neutrons with the nucleus of the stable starting isotope $^{63}$Cu or $^{64}$Zn. The specific activity of the tracer needed for the solution of the given problem can only be achieved in an experimental reactor with high neutron flux. The irradiation was carried out in the experimental reactor BER II with a potential neutron flux of up to $2 \times 10^{14}$ cm$^{-2}$ s$^{-1}$ at the Hahn-Meitner-Institut in Berlin.

Tab. 1 summarizes the conditions for the neutron activation of the zinc and copper samples.

### Table 1. Conditions for the neutron activation of the zinc and copper sample.

<table>
<thead>
<tr>
<th>Starting isotope</th>
<th>Target isotope</th>
<th>Sample mass in mg</th>
<th>Sample application</th>
<th>Neutron flux in cm$^{-2}$ s$^{-1}$</th>
<th>Irradiation time in h</th>
<th>Activity at the end of irradiation in MBq [24]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{64}$Cu</td>
<td>$^{64}$Cu</td>
<td>40</td>
<td>labeling</td>
<td>$2 \times 10^{14}$</td>
<td>1.5</td>
<td>19 000</td>
</tr>
<tr>
<td>$^{64}$Cu</td>
<td>$^{64}$Cu</td>
<td>0.4</td>
<td>calibration</td>
<td>$2 \times 10^{14}$</td>
<td>1.5</td>
<td>190</td>
</tr>
<tr>
<td>$^{66}$Zn</td>
<td>$^{66}$Zn</td>
<td>75</td>
<td>labeling</td>
<td>$2 \times 10^{14}$</td>
<td>16</td>
<td>7 250</td>
</tr>
<tr>
<td>$^{60}$Zn</td>
<td>$^{60}$Zn</td>
<td>0.75</td>
<td>calibration</td>
<td>$2 \times 10^{14}$</td>
<td>16</td>
<td>72.5</td>
</tr>
</tbody>
</table>

The values listed in the last column of Tab. 1 were calculated with the help of data for the saturation activity given in [24]. The values for the activity at the end of irradiation, which are to a certain degree clearly above the 1850 MBq fixed initial activity, are necessary to compensate for the decay between the end of irradiation and the time at which the isotope is introduced to the system. In spite of similar half-lives, the activity of the copper isotope must be about three times greater than that of the zinc isotope, since the emission probability per nuclear transformation for the effective radiation emitted by the copper isotope due to positron annihilation is only 37%.

Copper granulate with a purity of 99.8% and a grain size between 0.2 and 0.6 mm was used to produce $^{64}$Cu. For the generation of $^{60}$Zn, metal $^{60}$Zn flakes with an average edge length of ca. one millimeter and an enrichment factor of 98.3% were used. As indicated by the sample irradiation, any traces of impurities did not lead to relevant or, from the point of view of radiation protection, risky generation of undesired isotopes.

### 5 Measurements

Eleven slotted collimated, shielded, and water-cooled 1”-NaI(Tl)-scintillation radiation detectors were positioned on the exterior walls of the forward-acting grate in order to determine the location of the heavy metal evaporation. Ten detectors were mounted in pairs on opposite sides at the height of the solid bed next to the forward-acting grate. The sites between two primary air supply zones, and their centers, were chosen as the preferred positions for the detectors (Fig. 1). The first detector was positioned directly behind the tracer input site and served for the quality control of the DIRAC-impulse-shaped tracer addition in particular. The shielding and collimating of the detectors made an oriented acquisition of the radiation from the respective apparatus section of interest possible. This was carried out using multipurpose, modularly set-up cylindrical blocks consisting of ten 1 cm thick metal plates made of a tungsten alloy. The 4 cm high and 1 cm wide collimate slot plates, of which two were positioned per block, were oriented in such a way that the smallest possible area of the forward-acting grate could be registered by the detector. An additional, however, unshielded, 1.5”-NaI(Tl)-scintillation radiation detector was positioned in the hollow in the bottom of the absorber to
wash the partial flue gas flow, which was withdrawn continuously using a lance through a hole drilled in the wall of the post-combustion chamber (Fig. 2).

A model fuel, consisting of 60 ma-% wood, 30 ma-% lava, and 10 ma-% RDF (refuse-derived fuel), was used for the investigations. The pilot plant was operated steady-state with a fuel mass flow of 60 kg/h.

The heavy metals content of the residual waste shows a great range of variation depending upon the type of waste and its composition. This range spans ca. 60 to 2100 mg/kg for copper and 50 to 6500 mg/kg for zinc [i.e. 25,26]. The activated metal samples were pressed into RDF pellets for the examinations described here, so that the average copper content amounted to 800 mg/kg and 1500 mg/kg for zinc.

The addition of the labeled fuel onto the forward-acting grate was carried out using a special input adapter directly on the solid bed at the beginning of the grate. With a continuous fuel mass flow of 60 kg/h and an average fuel residence time of ca. 1 h on the forward-acting grate, a good approximation of a DIRAC-shaped input impulse can be assumed for a short-term addition of 50 g labeled material in the form of RDF pellets.

6 Evaluation and Results

The signals from all of the detectors are conveyed over a special conductor to a PC-supported acquisition system [27]. This system allows for the parallel connection of up to 16 radiation detectors; the minimal adjustable measuring interval applicable for all detectors is 100 milliseconds. The reading of the connected detector counters takes place between two measuring time intervals within a time period of less than one millisecond. The storage capacity of over 65,000 measured values per counter channel allows for an adequate measurement registration duration per experiment. A width of 32 bits for each counter channel prevents a counter overflow. The time courses of the counting rates registered by each detector, proportional to the tracer concentration under steady-state conditions, are represented in real time on the monitor, making a convenient observation of the tracer transport possible.

Measuring intervals with a duration of five seconds were selected for the measurements in the forward-acting grate. The countrate-time courses for the detectors used were presented as results for each experiment. The subsequent processing of the measured values was performed after subtracting the background radiation caused by the natural environment and carrying out a half-life correction for the corresponding nuclide.

From the time course of the measured signal from the detector in the absorber for the washing of the partial flue gas flow, the time point and duration at which the heavy metal tracer evaporation takes place can be seen. Since the measurements for all detectors begin simultaneously, the evaporation location in the furnace can be determined with adequate precision through the countrate-time course along the forward-acting grate.

The amount of heavy metal evaporated per unit time can be determined after appropriate calibration of the test set-up through the measured values collected at the detector in the absorber. The zinc and copper ampoules, referred to in Tab. 1 for the calibration, containing a hundredth of the amount necessary for the labeling served this purpose. Possible mistakes through varying radiation conditions could thereby be prevented. After dissolving the content of an irradiated ampoule for the calibration in a given amount of concentrated nitric acid, a defined volume corresponding to a known copper or zinc content was added at intervals of a few minutes to the uncontaminated liquid in the absorber and the accompanying measured signal registered. The conditions prevailing in the grate system during the experiment were also realized during the calibration procedure.

6.1 Results of the Copper Evaporation Experiment

Fig. 3 shows the results of one of the two experiments carried out in the forward-acting grate combustion plant with activated copper granulate added to the process in the above-described manner in the form of RDF pellets. In both experiments, carried out with stoichiometric (altogether oxidizing) conditions, a copper evaporation of 3 or 5 % could be established. As can be seen in the upper diagram in Fig. 3, the evaporation takes place continuously during the entire tracer residence time on the grate. From the shape of the residence time distribution curves for the different detector positions along the grate, no significant change can be seen at any time that would imply an increased evaporation in a particular zone in the plant. The asymmetric course of the residence time distribution is distinctive, which clearly leads to differences between median and modal values, in other words, between average and most probable residence times. The cause of this residence time behavior, untypical of a forward-acting grate, is most likely the spherical form of the copper granulate used. A portion of the granulate is probably oriented on the moving grate plates in such a way that these particles repeatedly end up under the fixed grate plates, are not forced forward, and are therefore strongly delayed as they pass through the grate system. In spite of these phenomena, a good linear connection between transport path and residence time can be determined by observing the most likely residence time (modal value of the distribution), as shown by the dashed line in Fig. 3.
6.2 Results of the Zinc Evaporation Experiment

Experiments with labeled zinc were carried out under three different operating conditions where the oxygen partial pressure (under-/overstoichiometric) and the combustion temperature were varied. The combustion temperature was influenced through the variation of the moisture content in the input material whereas the oxygen partial pressure was regulated through change of the volumetric flow rate of the primary combustion air supply. As measurements of the oxygen content in the material bed have shown, reducing conditions prevail in the front section of the grate during overstoichiometric as well as understoichiometric operating modes. Reducing conditions and high temperatures are prerequisites for considerable zinc evaporation. The measurements with activated zinc have confirmed this statement. With understoichiometric as well as overstoichiometric conditions, a zinc evaporation could be observed, which takes place within a time period of a few minutes in a narrowly restricted section of the grate in each case, in the section in which the local reducing conditions prevail.

Fig. 4 shows the results of an experiment which was carried out with moist input material under altogether reducing conditions. In the upper diagram in Fig. 4, the rapid evaporation, which is characterized by a steep increase in the zinc concentration in the absorber liquid within a time period of ca. 3 minutes, can be clearly seen. In this time period, more than 80 % of the added tracer amount is evaporated. The evaporation begins ca. 18 minutes after the addition of the labeled RDF pellets to the process. At this time, the main portion of the activated zinc has passed through the detector pair III (Fig. 1) and is then located in the grate section above the second primary air supply zone directly in front of detector pair IV.

In this example, the evaporation can be followed very well using the residence time distribution measured along the forward-acting grate. If a nearly unchanged residence time distribution is registered at the position of the detector pair III, then the expected concentration maximum at the position of the detector pair IV will not be reached. At the end of the grate (detector pair IV), no signal is registered by the detectors.

7 Conclusions

With the investigations described in this paper, it could be shown that the radiotracer method is very suitable to simultaneously quantify and localize the heavy metal evaporation in the process of thermal waste treatment. Using this method, it is possible to follow the actual path of selected heavy metals, which is either not possible with other measuring techniques or only with considerable (sampling and analytical) expenditure.

In addition, mass balances were carried out parallel to the radiotracer investigations. Due to the fluctuations of heavy metals content and specification in the waste, clearer results can be obtained with the help of radiotracer measurement than by means of a classical mass flow analysis [28]. The knowledge gained here contributes significantly toward a better understanding of the impact of an aimed manipulation of process conditions during the combustion and gasification of waste with respect to a controlled evaporation of heavy metals. In addition, the radiotracer method offers solution possibilities for other problems in which the determination of the heavy metal pathways plays a role.
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References