# ASSESSMENT OF MERCURY EMISSION AT NORCEM'S CEMENT KILN BY USE OF $^{203}$Hg-TRACER

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**Abstract.** In manufacture of cement clinker, mercury (Hg) is introduced in the cement kiln system via the fuels and as constituents in the raw materials, i.e. limestone, iron ore, etc. The permissible emission of Hg to air is very low (0.05 mg/Nm$^3$) due to its toxicity. Thus it is important to know how mercury distributes and behaves in the kiln system. The objective of the study was to measure the distribution of mercury in the kiln system, to measure the hold up time of Hg, to measure the portion of emission through the chimneys, and to see the dependence of the injection sites on these parameters.

The results showed that the amounts of mercury being emitted through the exhaust gases were largely dependent on where it was injected. The residence time of mercury in the system was nevertheless long, after 10 hours it was still increase in the count rate of the mercury absorbed. There was also an immediate increase in the filter dust, but nothing could be measured in the clinker. This is knowledge needed for reduction of mercury emissions.

## Introduction

In manufacture of cement clinker, mercury (Hg) is introduced in the cement kiln system via the fuels (oil, coke, coal, hazardous waste, household waste) and as constituents in the raw materials, i.e. limestone, iron ore, etc. The mercury concentrations are in general low (typically a few ppm), but due to the huge amounts of materials processed the yearly emissions of pollutants can reach considerable values (typically a few kg). However, the permissible emission of Hg to air is very low (0.05 mg/Nm$^3$) due to its toxicity. Thus it is important to

know how mercury distributes and behaves in the kiln system.[1] Because of the high volatility of mercury compounds, Hg was expected to leave the kiln system mainly as part of the exhaust gases, and to a less extent as part of the clinker. In kiln no. 6 at Norcem's Brevik plant there are two points for introduction of fuels, the rotary kiln and the pre-calciner. Moreover, downstream of the pre-calciner the flow is separated in two parallel streams; hence, there are two separate chimneys with filter systems connected to the kiln. The system of kiln, silos, filters and chimneys is presented schematically in Figure 1 where also the points of entrance of raw materials and fuels are indicated. The system is divided into two strings, denoted 1 and 2. They differ most pronounced by the aerofall mill in string 2 which supplies raw materials to both strings.

The high volatility of mercury compounds makes it difficult to obtain well established mass distributions and mass balance of Hg. Therefore it was decided to perform a tracer test using $^{203}$Hg-labelled HgO. (A similar test has been performed for studying sulphur using 35S as tracer, earlier[2]). It is unknown what form mercury is present in, and no initial tests were done to establish the chemical forms of mercury. However, the extremely high temperature and surplus of oxygen in the kiln makes it probable that all mercury present will rapidly be transformed to HgO. Thus, HgO was the preferred compound to inject. The objectives of the test were therefore: To investigate how mercury distributes in the system; find the retention time of mercury in the system; determine how much of the mercury that exits with the clinker and the exhaust gas, respectively; and evaluate to which extent the above mentioned matters are affected by the location of mercury supply.

Before performing the tests permission of emission of the required amount of $^{203}$Hg was granted by the Norwegian Radiation Protection Agency.

Fig 1

## Experimental

Typical mass flow rates in the system named kiln no. 6 are shown in Table 1. These data were used for a conservative estimation of the needed activity, i.e. amounts in the order of GBq per injection. $^{203}$Hg-tracer in the form of HgO (2g per sample) was prepared by irradiating 420 hours in a thermal neutron flux of $1.3 \cdot 10^{13}$ $s^{-1}cm^{-2}$ at Institute for Energy Technology's (IFE) JEEP II nuclear reactor. Four samples were irradiated together; three were used for injections, the last one for determination of activity. After irradiation the samples were allowed to cool for 10 days, but still some activity due to decay of $^{197}$Hg was present. The activity of $^{203}$Hg was determined by ionisation chamber measurement to 7,2GBq after $^{197}$Hg had decayed completely. The amount was lower than estimated, but still considered high enough. Of the three injections performed, one was added to the limestone, one was injected in the precalciner, and the third one was injected directly into the rotary kiln.

On-line NaI(Tl)-detectors were mounted at chimneys in both strings (cfr. Figure 1), i.e. chimney No. 3 in string 1and Aerofall chimney in string 2. The detectors measured $^{203}$Hg-activity extracted from the exhaust gas and accumulated in acidic solutions of $KMnO_4$. This was performed under the supervision of Molab AS according to the European Standard Method EN 13211. The two NaI(Tl)-detectors were calibrated relative to each other to enable comparison. In chimney No. 3, another NaI(Tl)-detector measured the activity directly in the smoke gas. Both detectors in chimney No. 3 were controlled by a system designed and build by IFE. In the Aerofall chimney a Nomad system supplied by Ortec was used. The count rates of the detectors were recorded by PCs as accumulated counts in four pre-defined energy ranges every 120s. Thus, spectra were not recorded, only count rates in preset energy windows. In addition to the on-line measurements, samples of dust collected in filters and samples of clinker were collected. These were measured off-line with γ-spectroscopy at IFE using a lead-shielded

Ge(Li)-detector controlled by an Ortec 92X Spectrum Analyser system controlled by a PC. The solutions with absorbed Hg were calibrated by γ-spectroscopy towards small samples of the dust to enable comparison of the amounts in the different flow paths. For each of the three injections, 46 clinker samples, 46 filter dust samples from string 1 as well as 46 dust samples from string 2 were collected.

During tests all ordinary monitoring of the process went as usual recording flow rates of filter dust (fines), exhaust gases, temperatures at various positions, and moisture contents in exhaust gases.

The tests were performed three consecutive days. In the first test the tracer was added to the milled limestone (called raw meal). In the second test the tracer was injected in the pre-calciner which is common to both strings, and in the third test the tracer was injected in the kiln main burner.

The extracted gas contained different amounts of water vapour which condensed in the bottles. Thus, for one test three bottles for chimney 3 were needed whereas two were sufficient for the Aerofall chimney. This created continuous variation of the geometry of the source seen by the detectors. Before changing the bottle in the Aerofall chimney the accumulated activity in the bottle decreased. The reason is believed to be too much water condensate making the volume too big for the detector’s solid angle.

## Results

**First injection.** The on-line measurements recorded at the chimney sites are shown in Figure 2. In Figure 3 the content of the filter dust is shown. The tracer was injected in the feed in string 1 and it is obvious that the mercury distributes basically in this string.

Fig 2 & 3

**Second injection.** The on-line measurements recorded at the chimney sites are shown in Figure 4. In Figure 5 the content of the filter dust is shown.

Fig 4 & 5

**Third injection.** The on-line measurements recorded at the chimney sites are shown in Figure 6. In Figure 7 the content of the filter dust is shown. To correct the amounts of absorbed mercury in the condensation bottles the measured air flow of the extraction system was used. From Figure 6 it seems that the correction factor of the second period has been measured erroneously.

Fig 6 & 7

**Offline measurements.** There were no traces of radioactivity in any of the clinker samples from any of the tests. Samples were taken out and measured in Marinelli geometry on a lead shielded Ge(Li)-detector. The detection limit for $^{203}$Hg in this geometry was measured to 1Bq based on the background count rate, i.e. background + 3 x standard deviation of the background.

To determine the concentration in the filter dust samples aliquots of 1,5 - 3g was measured. Tests showed that absorption of gamma radiation in the samples was significant for samples larger than 5g.

**Mass balance.** Aliquots of all bottles were measured off-line for determination of their concentration of $^{203}$Hg, and the amount of emitted mercury could be calculated taking account on the emission of gases through the two chimneys. Including the amount of $^{203}$Hg in the filter

dust the total mass balance could be calculated. In Table 2 the mass balance for the three tests are shown.

## Discussion

The results from the first injection, i.e. in the raw meal, show that the response in stack 1 is immediate; there is a sharp peak (nearly 600 cps) in the count rate of the stack detector about two minutes after the injection has taken place. After the initial peak, the stack count rate reaches a lower level (less than 50 cps) and drops slowly. After 10 hours the count rate is still around 10 cps, indicating that there is still more mercury in the system. There are no subsequent peaks in the stack count rate, not even smaller ones, for the rest of the measurement period.

At the peak count rate, the accumulated count rate is about 600 cps, and after 10 hours, the accumulated count rate is about 12 000 cps, see Figure 2. This indicates that only a small fraction, less than 5 %, of the mercury is emitted immediately after injection. Hence, a lot of mercury is absorbed in the system and is only slowly released and emitted to the surroundings via the exhaust gas.

Even after 10 hours, there is a lot of mercury in the system. The gradient of the accumulative count rate curve, as shown in Figure 2, is still rather high, indicating that it may take several more hours before all of the injected mercury has left the system. Extrapolation of the curves in Figure 2 suggests that practically all radioactive mercury will have disappeared from the system about two days after the time of injection. This implies a possible interference with the tests to be executed the following days.

The count rate on string 2 (Aerofall) is much lower than on string 1, see Figure 2. This is as expected, since the mercury tracer was injected only into string 1. However, the fact that some

mercury tracer is detected also on string 2, demonstrates that mercury is absorbed and distributed from one string to another.

The response on string 2 is delayed by approximately 30 minutes compared to string 1. This corresponds to the time it takes for the tracer compound to travel from the injection point via the dust filters and the raw meal dosing silo back into the kiln system (both string 1 and 2), and then finally reach the stack of string 2.

The fact that the response delay on string 2 is as high is half an hour, and not just a few minutes, indicates that hardly any mercury is captured by the raw meal at the top of the tower and redistributed in the calciner. If that was the case, the delay would have been just a few seconds (or minutes). Considering the temperature conditions in the system, this is as expected.

The results of the second injection, i.e. in the pre-calciner, indicate that the count rate at the start of the test is close to zero, meaning that the impact of the tracer injected the day before can be disregarded. The qualitative behaviour of the tracer is very similar to what was the case the day before. There are, however, some quantitative differences:

The response in the chimney is almost immediate, as the day before, but the peak is not as sharp (about 100 cps, compared to 600 cps) and the delay from injection to peak detection is about 3 minutes. The increased delay time can be explained by the injection point being further away from the chimney. The reduced peak height probably is partly due to tracer distribution between both strings (which in theory should roughly halve the emission on string 1), partly to the injection point being further away from the stack (i.e. longer delay time, which increases the possibility for tracer capture by the raw materials).

In accordance with the arguments in the last point above, the accumulative count rate reaches only a level of about 3 000 cps towards the end of the second test day, as compared to about 12 000 the previous day.

This time there is no difference in delay time between string 1 and 2. This is as could be expected, since the tracer was likely to be distributed between the strings after injection in the pre-calciner.

It might seem surprising that the bottle count rate of Aerofall chimney is so much lower than that of chimney No 3, the maximum being about 2 and 10 cps, respectively. However, this is most certainly due to mercury capture in the aerofall mill (raw meal department), which is mainly a temperature phenomenon – the lower the temperature, the more mercury is adsorbed on the raw material particles. During the time of the second test, the exhaust gas temperature of string 2 was on average 126°C, whereas on string 1 it was 183°C. The significant mercury capture in the raw meal on string 2 means that a considerable part of the mercury is transported to the raw meal silo, where it may be stored for several days before it is fed to the kiln. Hence, one might expect a secondary tracer release in the kiln system later.

The bottle count rate on string 2 of the second test is only about twice as high as that of the previous day, see Figures 2 and 4. Considering that in the first test there was no injection into string 2 one might have expected a larger difference. However, the exhaust gas temperature on string 2 was lower during the second test (126 vs. 138°C) – especially right after injection (112 vs. 158°C) – hence the absorption was probably much higher during the second test.

The results of the third injection, i.e. in the kiln, indicate that once more, the count rate at the start of the test is close to zero, meaning that the impact of the tracer injected earlier can be disregarded. The qualitative behaviour of the tracer is similar to what was the case in the preceding tests. However, there are quantitative differences: The bottle count rate on string 2 is much higher than in the previous test. In fact, it is very similar to that on string 1. There was no raw meal production during the third test. This implies that there was no capture of mercury in the aerofall mill during the third test, hence similar emissions on string 1 and 2 had to be

expected. Moreover, this is a very interesting result because it fully demonstrates the role the aerofall mill plays in the external mercury cycle in the system. It is surprising that the chimney detector on string 1 shows an accumulative count rate of about 12 000 cps, i.e. the same level as for the first test, see Figures 2 and 6. One possible explanation is reintroduction of tracer from the two previous tests via the raw meal coming from the raw meal storage silo. This "old" tracer adds to the tracer of the third test and generates higher tracer emissions.

Considering that the exhaust gas temperature and the temperature on string 1 was about the same for all three tests, the fact that the bottle count rate on string 1 is higher the third day than the two previous days supports the suggestion that "old" tracer from raw meal storage silos are being released during the third test.

There is a response delay of about 30 minutes on the bottle count rate of string 2 the third day. The reason is probably that during the first 30 minutes of the test, there were still raw materials being processed in the milling system (the system was being emptied of materials before it was stopped). When the raw meal milling system was stopped completely, the mercury tracer capture also stopped, and there was a sharp increase in the emissions.

## Conclusion

*Distribution of mercury in the system.* A very good mass balance result could not be expected, considering that the purging process is slow and that tracer is to a large extent accumulated in parts of the system and will be released to the surroundings little by little. Hence, to obtain a better mass balance, one would have had to measure for several more days – as well as continuously between the injections. It is likely that part of the tracer accumulated after the first injection is released during the second and third tests, hence explaining the increased recovery as time goes by.

Not considered during the design of the tests was that approximately 10% of the exhaust gas is sucked from string 1 to a coal mill common to both strings. Moreover, on both strings there are cooling towers, electrostatic precipitators and bag filters. Mercury in the gas will be absorbed on particles in the mill system and returned to the kiln through both strings in due time. This circulation will use time and must influenced the residence time of mercury in the system.

During the tests the coal mill was running the first two hours after the first injection whereas it was not running during the first hours of the second injection. During the third injection it was running continuously. This indicates that the corrections or loss of tracer is largest for the first test and least for the third one.

*Residence time.* In Table 3 a list of response times for the various injections and places where the mercury tracer where detected. As is seen, the mercury is moving quite quickly through the system. However, taking into account the circulation of mercury through the aerofall mill and residence time in this circulation, the residence time could not be determined the way the tests were performed.

*Injection site.* It is also seen from Table 3 that the tracer responses measured in the chimneys and in the filter dust samples are differ according to the injection site. While the response in chimney No 3, the chimney close to the kiln, is fast for all sites of injection tested, the time needed for reaching the Aerofall chimney is varying from 1 to 35 minutes. However, here the absorption of mercury in the aerofall mill as well as the temperature of the exhaust gas are very important parameters.

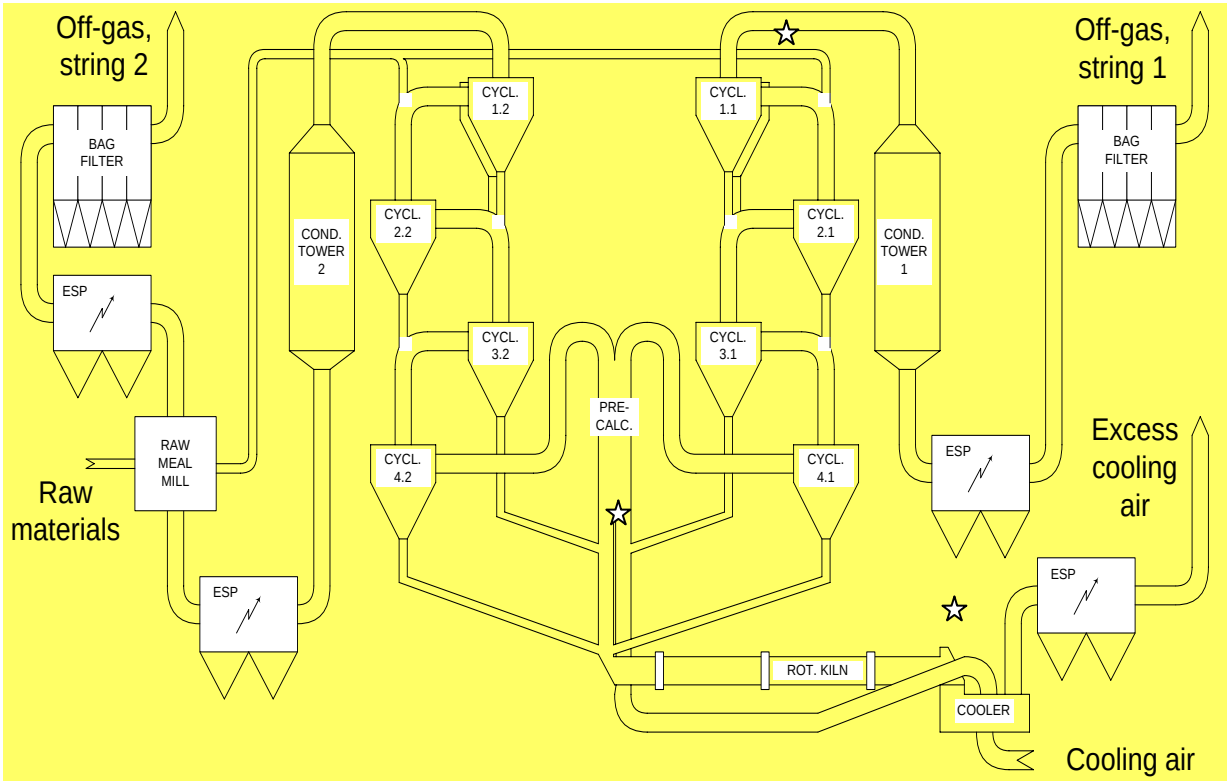


*Figure 1* Processing system comprising rotary kiln, feeding system with silos and exhaust systems with filter units and chimneys. “Off-gas string 1” is called Chimney 3 in the text and “Off-gas string 2” is called Aerofall chimney. The points of injection of tracers are indicated by stars.

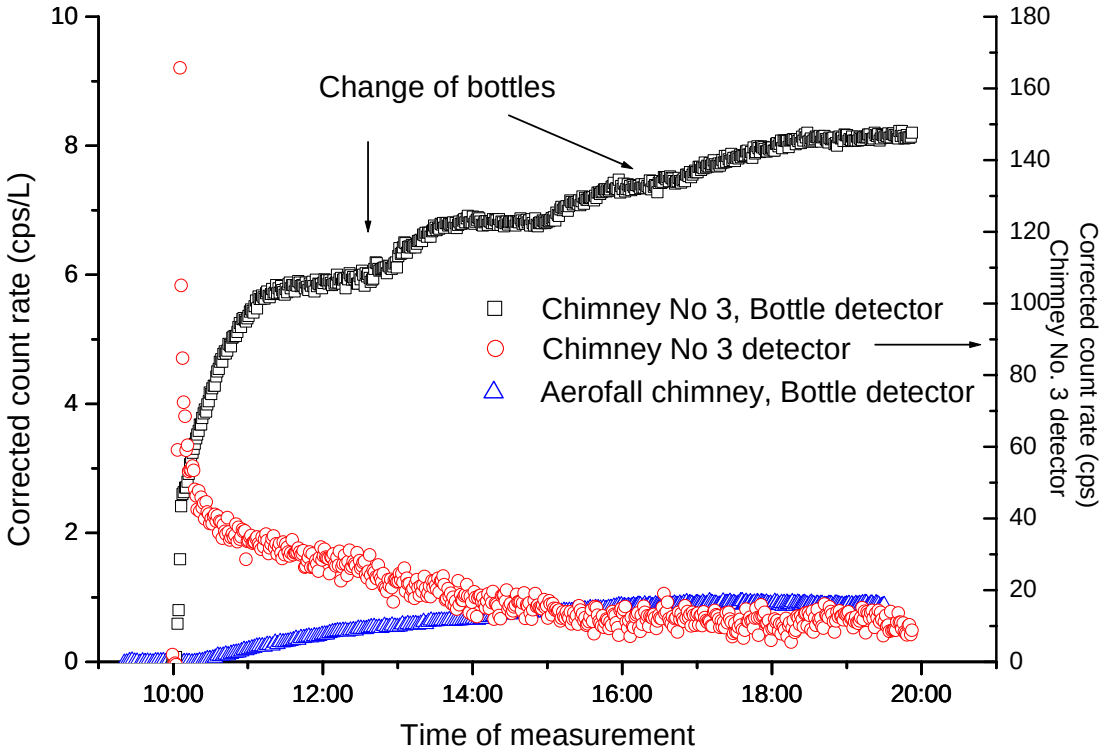


*Figure 2* On-line measurements at both chimney sites, first injection, i.e. injection in the raw meal. Bottle contents show accumulated amounts of $^{203}$Hg.

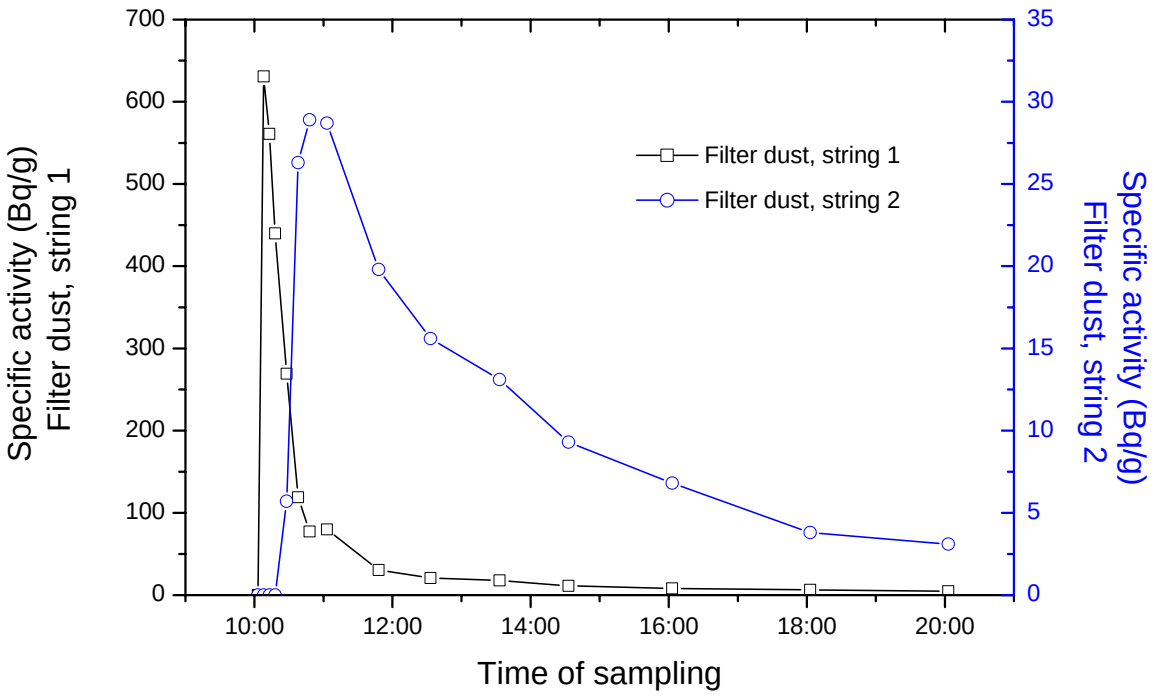


*Figure 3* Off-line measurements of filter dust samples.

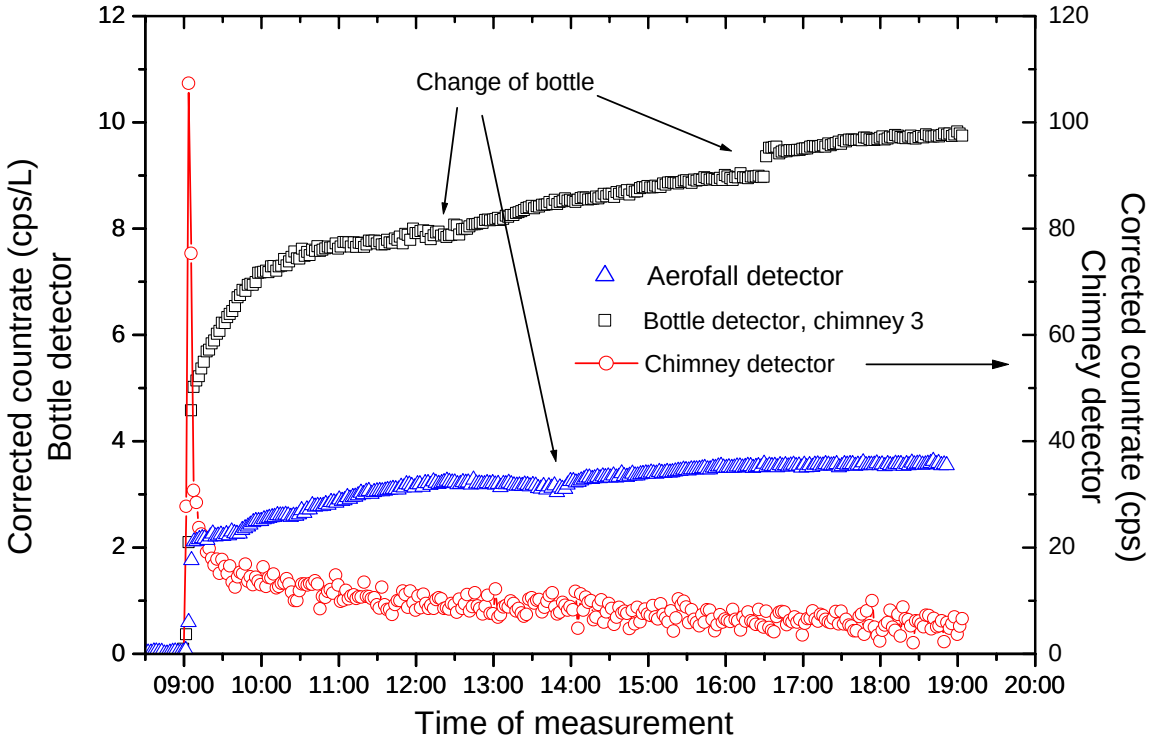


*Figure 4* On-line measurements at both chimney sites, second injection, i.e. injection in the pre-calciner. Bottle contents show accumulated amounts of $^{203}$Hg.

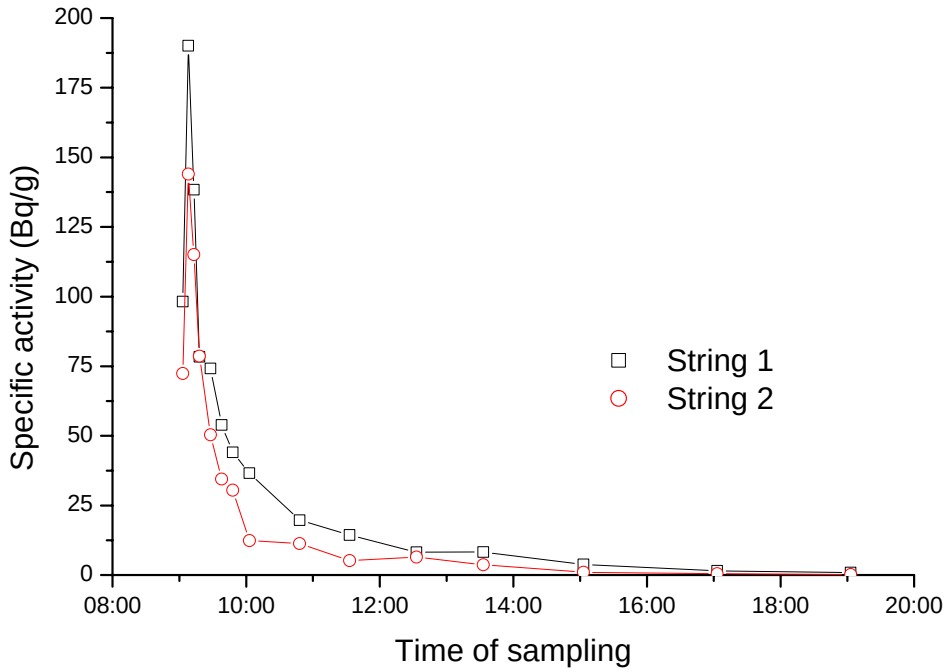


*Figure 5* Off-line measurements of filter dust samples, second injection, i.e. injection in the pre-calciner.

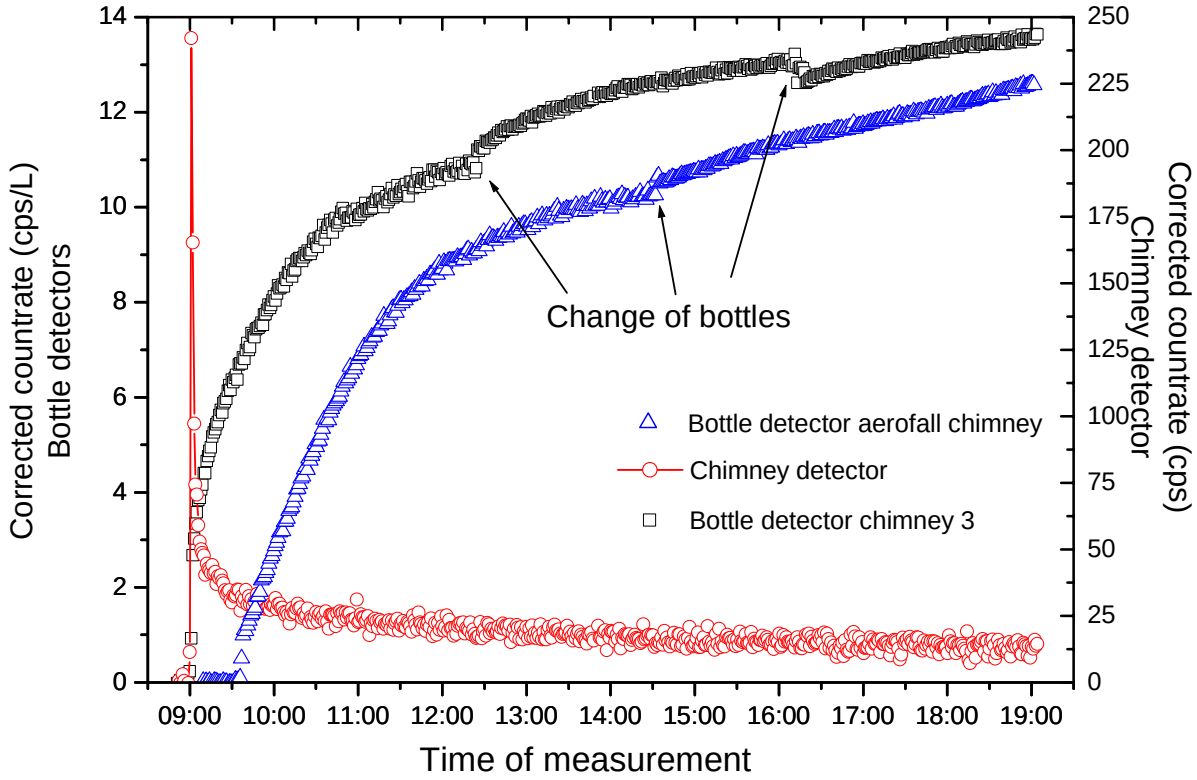


*Figure 6* On-line measurements at both chimney sites, third injection, i.e. injection in the kiln. Bottle contents show accumulated amounts of $^{203}$Hg.

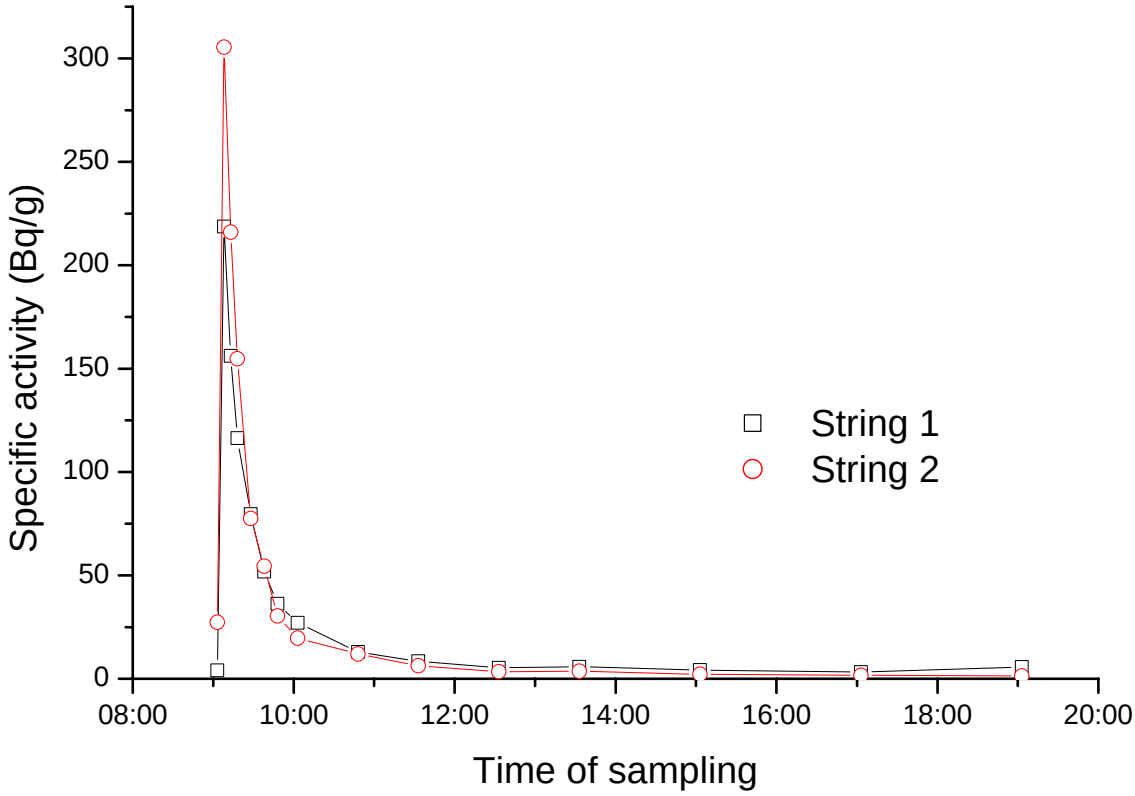


*Figure 7* Off-line measurements of filter dust samples, third injection, i.e. injection in the kiln.

*Table 1* Typical process parameters in production system belonging to rotary kiln No 6.

| Parameter | Rate | Parameter | Rate |
|---|---|---|---|
| Exhaust gas Aerofall chimney | 150 - 180 000 $m^3$/h STP | Clinker production | 125 - 140 tons/h |
| Exhaust gas Chimney No. 3 | 140 - 180 000 $m^3$/h STP | Gas-sampling | 25 L/min STP |

*Table 2* Mass balance measured. Both emission through the exhaust smoke and the amount trapped in the dust are included. The amount recovered is relative to amount injected, i.e. 7,2GBq.

| **Samples, Chimney No 3** | | | | | **Both strings** | |
|---|---|---|---|---|---|---|
| | **Total activity, Chimney (Bq)** | | | **Sum chimney** | **Sum chimneys** | **Recovered** |
| **Injection** | **Part 1** | **Part 2** | **Part 3** | **(Bq)** | **(GBq)** | **(%)** |
| Raw meal | 1,7E+09 | 4,2E+08 | 3,4E+08 | 2,41E+09 | 2,80 | **38,8** |
| Pre-calc. | 2,1E+09 | 3,6E+08 | 1,9E+08 | 2,64E+09 | 3,62 | **50,3** |
| Kiln | 2,4E+09 | 4,4E+08 | 2,6E+08 | 3,13E+09 | 5,93 | **82,3** |
| **Samples, Aerofall chimney** | | | | | | |
| | **Total activity chimney (Bq)** | | | **Sum chimney** | | |
| **Injection** | **Part 1** | | **Part 2** | **(Bq)** | | |
| Raw meal | 2,52E+08 | | 1,34E+08 | 3,86E+08 | | |
| Pre-calc. | 8,79E+08 | | 1,00E+08 | 9,79E+08 | | |
| Kiln | 2,34E+09 | | 4,57E+08 | 2,80E+09 | | |

*Table 3* Response time at detection sites in the chimneys and in the filter dust as a function of injection site.

| **Injection: \Detection site:** | **Raw meal** | **Pre-calciner** | **Kiln** |
|---|---|---|---|
| Chimney No 3 detector | < 1 min | 1 min | < 1 min |
| Aerofall detector | 26 min | 1 min | 35 min |
| Filter dust string 1 | 5 min | 3 min | 3 min |
| Filter dust string 2 | 26 min | 4 min | 4 min |

## References

[1] L. A. Tokheim *"The impact of staged combustion on the operation of a precalciner cement kiln"*, PhD thesis, Telemark University College / Norwegian University of Technology and Science (1999)

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