

# ASSESSMENT OF SULPHUR EMISSION AT NORCEM'S CEMENT KILN BY USE OF $^{35}\text{S}$ -TRACER

D. Ø. Eriksen<sup>1</sup>, L.-A. Tokheim<sup>2</sup>, T. A. Eriksen<sup>2</sup>, V. Martini<sup>1</sup>  
and C. Qvenild<sup>1</sup>

<sup>1</sup>Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway

<sup>2</sup>Norcem AS, P.O. Box 38, N-3991 Brevik, Norway

**Abstract.** Although sulphur is not a major reacting species in making cement clinker, it is introduced as a pollutant in both the energy carrier (oil, coke, coal, household waste) and in the reactants (chalk, silica). Due to the huge amounts processed the total theoretical emission of sulphur, as  $\text{SO}_2$  can be high. However, because of the kiln design and the presence of calcium and alkalis, sulphur is largely converted to sulphates and captured in the clinker product. In kiln no. 6 at Norcem's Brevik plant there are two sites, named primary and secondary, for injection of coal and coke, one in each end of the rotary kiln.

The objective of the study was to measure which portion of the sulphur introduced in the process from the coal and coke that escapes as  $\text{SO}_2$ , and how much sulphur will follow the clinker (solid phase)? Moreover, to see whether there is a difference in  $\text{SO}_2$ -emissions when the coal or coke is introduced in the primary and in the secondary injection site.

$^{35}\text{S}$ -tracer in the form of yellow sulphur,  $\alpha\text{-S}_8$ , absorbed in coke, was prepared by irradiating  $\alpha\text{-S}_8$  in a cold position with thermal neutrons in Institute for Energy Technology's (IFE) JEEP II nuclear reactor. The irradiated sulphur was dissolved in  $\text{CS}_2$  and the solution was subsequently absorbed in finely grained coke.

Two injections were performed, one in the primary (3,8GBq) and one in the secondary site (3GBq).

The results showed clear differences depending on the injection site in the amount of sulphur emitted as  $\text{SO}_2$  and also on how fast the sulphur would exit the kiln as part of the produced clinker.  $^{35}\text{S}$  was detected in the exhaust gas only after the injection at the secondary site, but in minute amounts. Thus, the project was able to recommend that in order to avoid emission of  $\text{SO}_2$  there is an advantage of injecting coal or coke at the primary site. Mass balance calculations gave more than 80% recovery of injected sulphur as  $^{35}\text{S}$ .

## INTRODUCTION

Although sulphur is not a major reacting species in making cement clinker it is introduced as a pollutant in both the energy carrier (oil, coke, coal, house-hold waste) and in the reactants (chalk, silica). Due to the huge amounts processed the total theoretical emission of sulphur, as  $\text{SO}_2$  can be high. However, because of the special design of the kiln system (counter-current flow of gas and solids) and the presence of calcium and alkalis, most of the gaseous sulphur in the kiln or in the precalciner is converted to sulphates, which are eventually captured in the clinker product [1]. The chemical form of the sulphur in the fuels is not known, but is assumed to consist of a variety of compounds. Due to the high temperature in the kiln the chemical form of sulphur was considered of minor importance as all will be oxidised.

In rotary kiln no. 6 at Norcem's Brevik plant there are two sites, named primary and secondary, for injection of coal and coke, one in each end. There are two chimneys connected to this kiln, one Aerofall chimney connected to a filtering device[1], and one traditional chimney named Chimney 3. Figure 1 illustrates the kiln system.

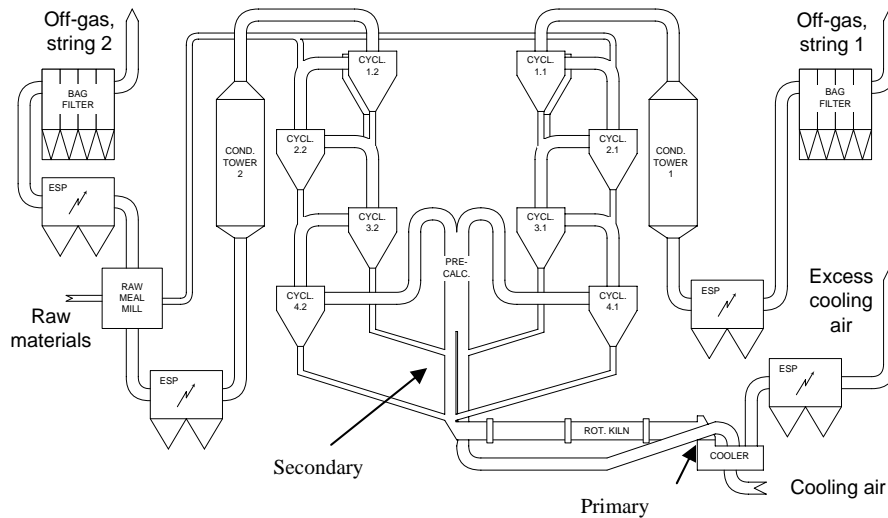


Figure 1. Kiln system at Norcem, Brevik. The figure shows the main units rotary kiln, precalciner, cyclone preheater and cooler, as well as gas conditioning towers and dust cleaning system. The injections sites are also indicated[1].

The objective of the study was twofold: To measure how much of the sulphur introduced in the process from the coal and coke that escapes as  $\text{SO}_2$ , and how much which follows the clinker (solid phase). Secondly, to see whether there is a difference in emission when introducing the coal or coke at the primary or at the secondary injection site.

To commit such a study, it was decided to absorb  $^{35}\text{S}$ -labelled sulphur in coke, inject it into the kiln at the proper positions, to sample the exhaust gases in the two connected chimneys and in the produced clinker powder to measure the residence time, solid-gas distribution and the mass-balance.

It was expected from the standard production analyses that the concentration of  $\text{SO}_2$  in the exhaust gas would be small ( $< 1\%$ ). Thus, the amount of  $^{35}\text{S}$  injected would have to be estimated with the purpose of detecting  $^{35}\text{S}$  in the exhaust gas. In Table 1 typical gas emission rates during production of clinker at Norcem Brevik are given.

In order to perform tests with radioactive tracers outside IFE's laboratory, permission from the Norwegian Radiation Protection Agency (NRPA) was applied for and given.

Table 1. Typical rates of emission and production at Norcem Brevik.

Item	Rate	Item	Rate
Exhaust gas, Aerofall chimney	220 000 m <sup>3</sup> /h STP	Clinker produced	150 tons/h
Exhaust gas, Chimney 3	150 000 m <sup>3</sup> /h STP	Gas sampling	25 L/min STP

## EXPERIMENTAL

### 1. Radioactivity

The necessary amount of <sup>35</sup>S to inject was estimated to 2,5 GBq based on a detection limit of 1 Bq/L, a gas emission of 350 000 m<sup>3</sup>/h STP, gas-sampling of 25 L/min, 1 % sulphur emission and a response peak height of 100 Bq/L.

It was decided to irradiate elemental, yellow sulphur,  $\alpha$ -S<sub>8</sub>, in IFE's research reactor JEEP-II.

#### 1.1. Irradiation

Due to dose exposure of operators it was desirable to reduce the amount of <sup>32</sup>P produced from the <sup>32</sup>S(n,p) <sup>32</sup>P reaction. This reaction has threshold energy of 0,928 MeV[2], which means that epithermal neutrons are needed. Thus, an irradiation position with a very high ratio of thermal- to epithermal neutrons was chosen.

Portions of 50 g of  $\alpha$ -S<sub>8</sub> were exposed to a thermal neutron flux of approximately 5·10<sup>12</sup> cm<sup>-2</sup>s<sup>-1</sup> for 14 days. Also, the low temperature at the irradiation position (< 60 °C) avoided the transfer of rhombic  $\alpha$ -S<sub>8</sub> to monoclinic  $\beta$ -S<sub>8</sub>.

#### 1.2. Production of the labelled <sup>35</sup>S-coke tracer

The irradiated sulphur was poured into a glass jar, CS<sub>2</sub> was added and the sulphur dissolved. Coke as powder was successively added so that the solution was totally absorbed. The CS<sub>2</sub> was then allowed to evaporate by exposure to air. The final radioactive coke was put into a polyethylene flask.

### 2. Injection of tracers

In the first test, Test 1, the secondary injection site was used. The polyethylene flask with the <sup>35</sup>S -impregnated coke was put directly into the hot zone by taping it to a wooden stick.

In the second test, Test 2, the primary site was used. Here the coke was poured into a cold pipe used for blowing coke and air into the kiln. The lid was closed and the coke blown into the hot zone within seconds.

### 3. Sampling

#### 3.1. Gas sampling

Gas was extracted from the chimneys at a rate of 25 L/min by the means of a suction pump. The gas was bubbled through two flasks in series containing 700 mL 0,2M NaOH absorbing the gaseous oxides, i.e. CO<sub>2</sub>, NO<sub>2</sub> and SO<sub>2</sub>. Samples of 20 mL were taken from the first flask according to a predetermined sampling schedule. The second flask was used as an extra gas trap and was not sampled. In the first part samples were taken every second minute. There were two alternating gas absorbing systems in parallel enabling a continuous gas-absorption.

The exhaust gas contained water vapour making the volume in the flasks increase. Thus, all flasks were weighed before and after the test to establish the average water condensation rate, which was shown to be 1,5 mL/min.

As the gas residence time in the kiln was assumed to be quite short, the gas sampling started immediately after the injection.

#### 3.2. Sampling of clinker

Samples of 1 kg of hot freshly produced clinker was put into cans and left for cooling. Sampling continued for 15 hours with the highest sampling rate during the first four hours.

### 4. Measurements of <sup>35</sup>S

All determinations of <sup>35</sup>S were performed at IFE using a Quantulus Low-Level beta-spectrometer made by Wallac Oy, Finland.

#### 4.1. Gas-absorbing solutions

10 mL of the sample solutions was mixed with 10 mL Optiphase Super mix liquid scintillator supplied by Wallac Oy, Finland. Each sample was corrected for quenching by use of the spectral quench parameter[3], SQP, inherent in the Quantulus system. The counting efficiency,  $\epsilon_{SQP}$ , vs. SQP was measured in a separate laboratory experiment. It was found to be a linear function in the actual range. The used relation was:  $\epsilon_{SQP} = -1,7 + 0,003 \cdot SQP$ .

Figure 2 shows two  $\beta$ -spectra containing only background and two containing additional activity of <sup>35</sup>S –spectra. In Figure 3 the net  $\beta$ -spectra of these two samples containing <sup>35</sup>S –spectra is shown. In addition, a spectrum from pure <sup>35</sup>S in CS<sub>2</sub> is shown proving that the extra activity in Figure 2 has the correct origin.

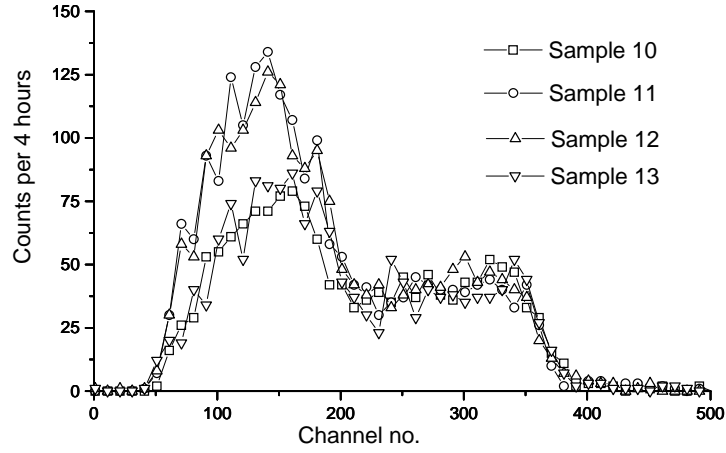


Figure 2.  $\beta$ -spectra of four samples from Test 1, Chimney 3, measured with Quantulus low-level liquid scintillation spectrometer.

The volume in the absorption bottle as a function of sampling time was calculated according to formula (1):

$$V_i(t_i) = V_0 - \sum_{k=1}^i v_k + K \sum_{k=1}^i \Delta t_k = V_0 - i \cdot v_p + K \sum_{k=1}^i \Delta t_k \quad (1)$$

where  $V_0$  is the start volume in the absorption bottle,  $v_k = v_p$  is the sample volume extracted (20mL),  $K$  the condensation rate (1,5mL/min), and  $\Delta t_k$  the time interval between samples  $k-2$  and  $k$ . The content given in Bq in the samples was calculated according to formula (2):

$$D_i(^{35}\text{S}) = R_i(^{35}\text{S})V_i(t_i) / (\varepsilon_{SQP} v_p) \quad (2)$$

where  $D_i$  denotes the disintegration rate (Bq) in sample  $i$ ,  $R_i$  is the measured counting rate (counts per second, cps), and  $\varepsilon_{SQP}$  is counting efficiency (cps/Bq).

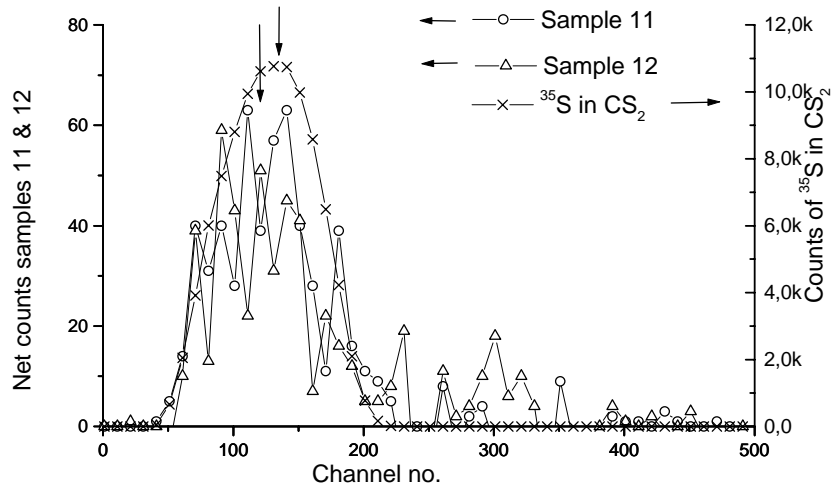


Figure 3. Net  $\beta$ -spectra of two samples from Test 1, Chimney 3, measured with Quantulus low-level liquid scintillation spectrometer. In addition a spectrum from pure  $^{35}\text{S}$  in  $\text{CS}_2$  is shown to prove that the extra activity in Figure 2 is the correct one. The difference in peak positions, indicated by the arrows, is due to different quenching in the different kind of samples.

#### 4.2. $^{35}\text{S}$ in clinker

The clinker samples were inhomogeneous with respect to grain size distributions. All of the 1 kg samples were therefore crushed and run through a divider giving four fractions of 250 g. From one of these fractions 25 g were dissolved in HCl following a procedure used by Norcem for standard clinker analyses[4]. The dissolved sulphur as sulphate was then precipitated as  $\text{BaSO}_4$ . The solution was decanted, the precipitate was washed with 10 mL water and added to 10 mL Instagel liquid scintillator made by Packard Instruments B.V., The Netherlands.

In Figure 4 the production profiles for  $^{35}\text{S}$  in clinker for the two tests are shown.

#### 5. Determination of injected amounts of $^{35}\text{S}$

In addition to the bulk samples (50 g of  $\alpha\text{-S}_8$ ) of sulphur, two packages of 1 g  $\alpha\text{-S}_8$  each were irradiated together with the bulk amounts. These sulphur samples were dissolved in 10 mL  $\text{CS}_2$  and diluted to 50 mL with methanol. Aliquots from such diluted samples were used for standardisation of the injected amounts.

### RESULTS AND DISCUSSION

No  $^{35}\text{S}$  could be detected in the samples from the Aerofall chimney and from the Test 2 (primary injection site). Only two samples in Test 1 showed traces of  $^{35}\text{S}$ . As the absorbing solutions accumulated sulphate from the exhaust gas a steady increase

in  $^{35}\text{S}$ -activity was expected. However, when activity above the background only could be detected in samples 11 and 12, we conclude that we are close to the detection limit and that the dilution due to condensing water vapour and removal of samples brought the activity below detection level. Figure 3 proves that the activity above background comes from  $^{35}\text{S}$ .

In Table 1 the average gas emissions from Chimney 3 and Aerofall chimney are listed. Assuming we are at the detection limit sampling the emissions in Chimney 3, then a gas flow 50 % higher than in the Aerofall chimney would make the  $^{35}\text{S}$ -concentration far below detection limits. The Aerofall chimney has proven to release very little gases like  $\text{SO}_2$ [1].

The radioactive sulphur emitted as sulphate in the clinker is shown in Figure 4 as a function of time after injection. The measured values are normalised according to the production rate of clinker. Thus, the abscissa unit is given as MBq.

As seen from Figure 4, there is an immediate response when injecting at the primary site which is close to the clinker outlet, while the response in Test 1 is slower, but a pronounced peak after approximately 3 hours indicates that sulphur recycles inside the kiln system several times before it leaves the system along with the clinker, mainly as alkali sulphates [1]. In Test 2 this recycle effect is less pronounced.

The background may originate from several sources: traces of  $^{40}\text{K}$  coming from the NaOH-added,  $^{210}\text{Pb}$  in the exhaust gas due to the high temperature in the kiln, and radon and its daughters. The last ones are pollutants in the reacting silicates.

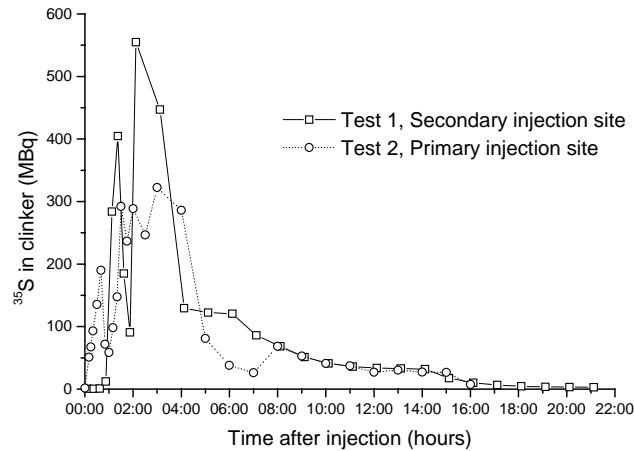


Figure 4. Responses (residence time distributions) of  $^{35}\text{S}$  as sulphate produced in the clinker. The measured values are normalised according to the production rate of clinker. Thus, the abscissa unit is given as MBq.

## CONCLUSION

From the ordinary process analyses it was known that the emission of sulphur was modest, i.e. < 1 % [1]. The tests performed showed that not more than 0,01% of the sulphur added to the process through coal or coke will leave as gas and only through Chimney 3. The Aerofall chimney emits less than Chimney 3, amounts below our detection limits.

A mass balance of recovered  $^{35}\text{S}$  relative to injected showed that 80 - 95 % of injected activity was recovered in the clinker. This is considered very good since some sulphur has been shown to have a very long residence time in the kiln[1].

The residence time distribution of the sulphur showed a difference depending on the injection sites, a result which may be used for reduced emissions of sulphur to the environment.



## REFERENCES

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