

Hazardous accumulation of radioactive lead on the water wall tubes in coal fired boilers

W.M.M. Huijbregts*, M.P. de Jong*, and C.W.M. Timmermans**

Anti Corrosion Methods and Materials Volume 47, No 5, (2000), pp. 274-279

(Award for excellence paper of the year 2001 of Emerald Literati Club)

Abstract

Dutch power companies recently have become aware of a hazard due to the presence of radioactive ^{210}Pb in their boilers. In an investigation conducted by KEMA in the Netherlands it was discovered that ^{210}Pb isotope accumulates within fire-side deposit layers that form on membrane waterwall tubes.

Because the measured levels of total radioactivity exceeded the governmental regulation limit of 100 Bq/g, refurbishment activities in the boiler, such as renewal of waterwall panels and/or welding repairs because of corrosion damage, are subject to governmental authorization and must be conducted under the supervision of authorised radiation protection officers.

The ^{210}Pb material originates from decay of ^{238}U , which is present in small amounts in coal. During combustion of the coal, heavy metals such as Pb evaporate and are present in the flue gas in the form of Pb, PbCl, PbCl₂, PbS, PbS₂ or PbSO₄, dependent upon the gas environment and temperature. These volatile products subsequently will condense at lower temperatures on the waterwall tubes in the boiler.

Introduction

Corrosion activity in coal fired power boilers and waste incineration plants can be substantial under certain firing conditions. In order to study corrosion and fouling behaviour in boilers corrosion products and deposit layers were examined in detail by microscopic techniques. Figure 1 shows one such corrosion and deposit scale.

The deposit is comprised of the following layers (starting from the outside of the deposits, i.e. from the top of the photograph) : solidified slag particles, then a layer with recrystallized fly ash particles, then a layer of non recrystallized fly ash particles embedded in iron oxide and iron sulfide, then the corrosion scale of the metal (no fly ash particles are present here) and finally the steel itself. The overall thickness of the scale is 425 micron.

* Based at KEMA, Utrechtseweg 310, PO Box 9035, 6800 ET Arnhem

** Based at NRG, Utrechtseweg 310, PO Box 9035, 6800 ET Arnhem



Figure 1. Optical microscopic image of the fire side tube deposit.

The composite deposit and corrosion scale was studied in more detail by means of scanning electron microscopy (SEM). It was observed that lead was present mainly only at a certain depth, that being in the thick recrystallized layer of fly ash. Lead was present on the outside of the deposit layer and, in general, there was a marked border in the deposit layer below which lead was not evident. See Figure 2.

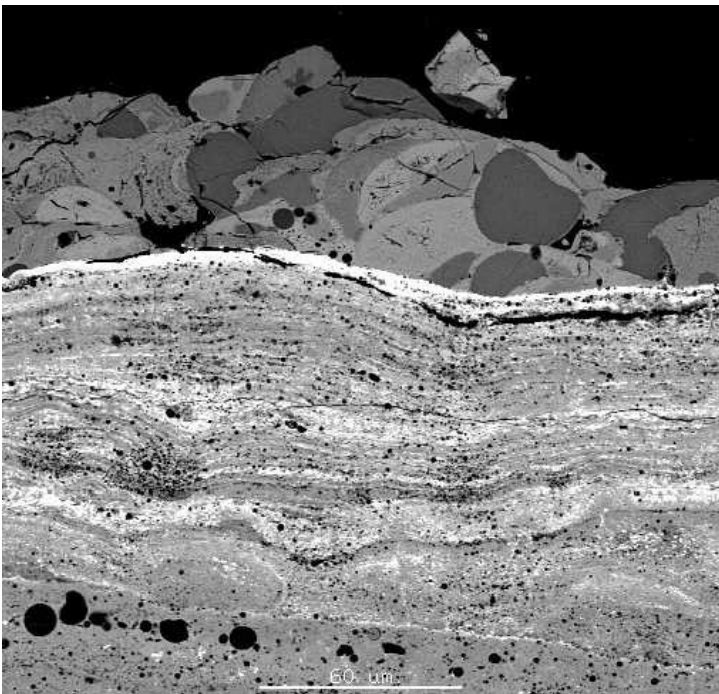


Figure 2 SEM Backscatter electron image. The white particles contain lead.

The pronounced presence of lead on the waterwall tubes, with a clear boundary in the deposit layer warranted more detailed investigation. Under operational conditions there is a heat flux through the

boiler tubes and a steep temperature gradient will be present across the deposit layer. Some lead compounds have low condensation temperatures hence they can condense onto the cool waterwall tubes.

Most types of coal contain trace amounts of radioactive lead isotopes, originating from the decay of natural uranium and thorium. It is readily evident from the half-lives of the lead isotopes that the predominant radionuclide will be ^{210}Pb , which is formed from the uranium-238 decay series. These isotopes are deposited in the scale as well, forming a radioactive layer on the boiler walls.

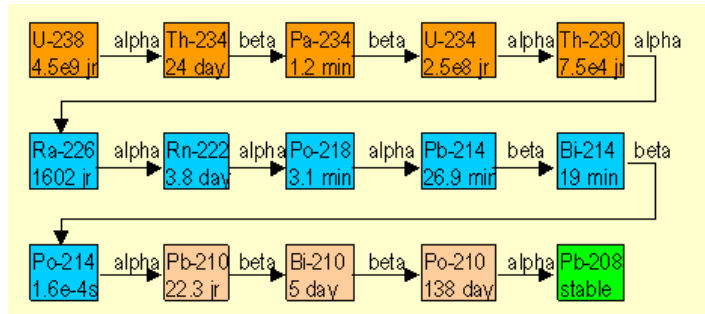


Figure 3. Decay chain of ^{238}U

Field investigations results

Measurements were made in several Dutch coal fired power plants. These revealed that ^{210}Pb concentrations in the deposit layer exceeded the governmental regulation limit of 100 Bq/g. The highest concentrations were found to occur in a relatively narrow region in the first 5 to 10 meters above the burner zone.

Under the current Dutch regulations (after May 2000), a concentration of only 33 Bq/g is allowed without prior authorization, assuming secular equilibrium between ^{210}Pb , ^{210}Bi and ^{210}Po and absence of other radionuclides. Therefore, handling of these scales during boiler inspection and maintenance activities must be formally authorized and supervised, and appropriate measures implemented to protect workers against unintentional exposure (mainly internal) to radiation.

Exposure is only likely to occur when the scales are removed from the walls by force. The deposits are not removable by simple wiping. External radiation is not of concern because the gamma radiation of ^{210}Pb , including the radioactive progeny, is very weak. The main constituent in the external radiation environment is the highly energetic beta radiation of ^{210}Bi , which can also give an excessive dose to the skin if it is placed in direct contact with contaminated walls. However, since internal exposure is the main pathway, radiation protection measures should address primarily the prevention of radioactive dust inhalation and ingestion.

The maintenance outages of three major coal fired power plants in the autumn of 1999 and spring of 2000 were performed under the supervision of radiation protection specialists.

The following precautions were taken:

Since the power plants were unfamiliar with radiation and radioactivity, procedures and instructions for the safe handling of radioactive materials had to be written.

Before the start of the maintenance outages, workers were given oral instruction about the risks of ionizing radiation.

On opening of the boiler, contamination measurements were performed on all accessible parts inside the boiler. The threshold for special precautions was set on two times the background level, upon which further measures were implemented. The special precautions included the setup of a supervised area, access restricted to workers who had received oral and written instructions, dose monitoring of persons, tools and equipment, the use of protective clothing and masks, and the use of point extraction when removing scales for inspection and cutting of the waterwall tubes.

No eating, drinking or smoking was allowed within the controlled area.

During the survey, samples were taken from deposits on the walls for gamma-spectroscopic analysis at the KEMA laboratories in Arnhem.

Thermodynamic calculations

In order to explain the observed radioactive phenomenon, thermodynamic calculations were carried out to detect the thermodynamically stable constituents in the gas phase over a broad temperature range. The software program "HSC" by Outokumpu Corporation was used to make the calculations.

For the thermodynamic calculations, reducing and oxidizing gas compositions were chosen that were typical of Low NO_x coal firing or waste incineration conditions. The chosen gas compositions are listed in table 1. Adding Pb to the modeling gas composition and changing the oxygen (O₂) and chlorine (HCl) content, a more comprehensive understanding was developed about conditions under which lead can condense on the waterwall tubes.

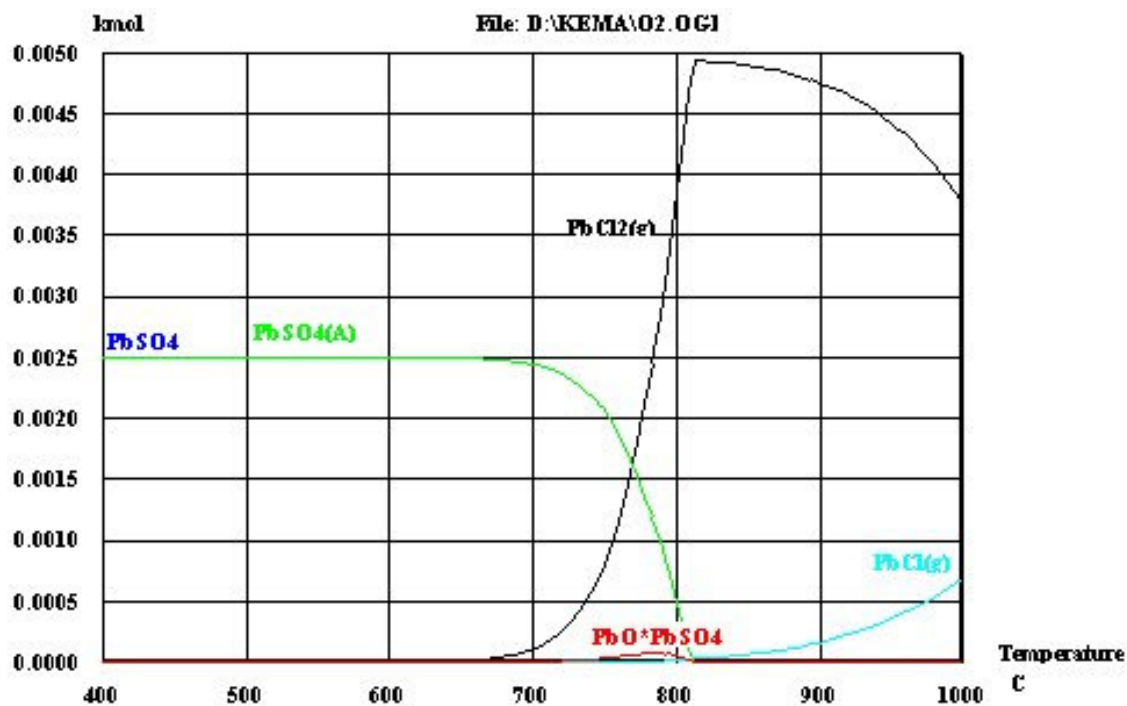
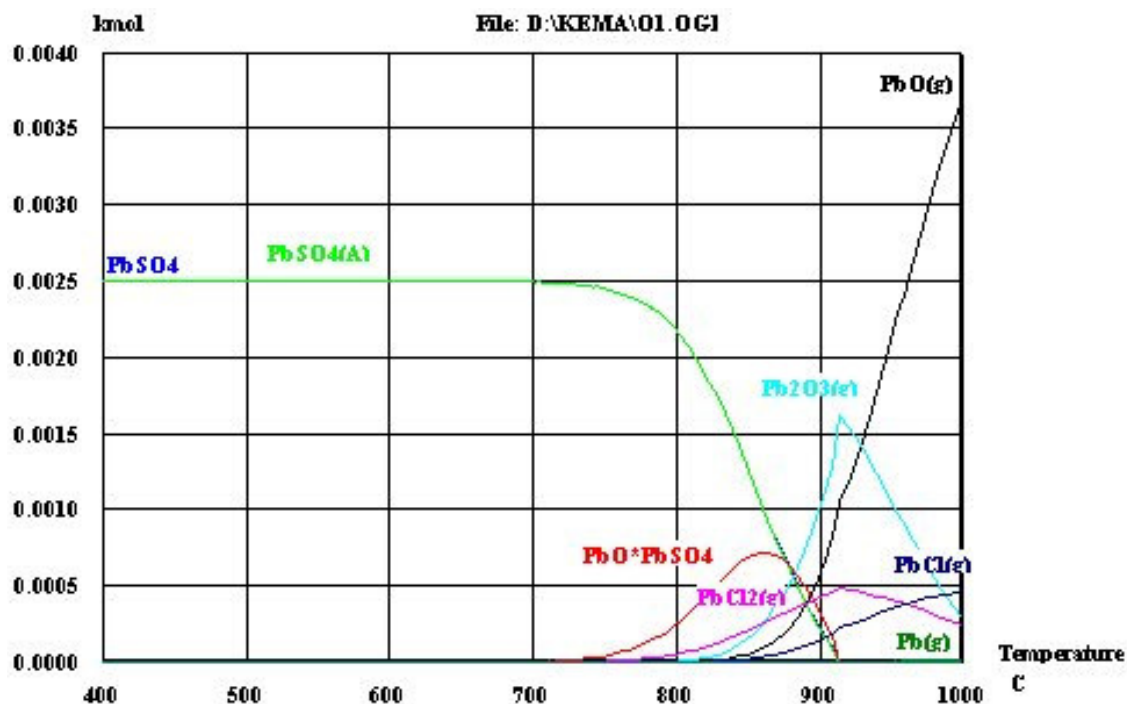
Table 1 - Gas composition used in the thermodynamic calculations. The Pb concentration was 50 vppm for each gas composition

Gas	N ₂	CO ₂	CO	H ₂	H ₂ O	O ₂	H ₂ S	HCl	SO ₂	Cond.temp
	(v%)	(v%)	(v%)	(v%)	(v%)	(v%)	(vppm)	(vppm)	(vppm)	°C
O1	74	12			12	2		50	500	880
O2	74	12			12	2		500	500	770
O3	74	12			12	2		5000	500	660
R1	74	9	3	2	12		500	50		680
R2	74	9	3	2	12		500	500		670
R3	74	9	3	2	12		500	5000		495
R4	74	9	3	2	12		50	500		650
R5	74	9	3	2	12		5000	500		680

The results of the calculations are presented in the Figures 4, 5 and 6.

Under oxidizing combustion conditions, the condensation temperature of lead (lead dewpoint) is more than 660 °C. At low chlorine contents this temperature is even higher, at 880 °C. At these temperatures most of the lead present in the combustion system will condense on the fly ash particles. The condensed product is a mixture of PbSO₄ and PbSO₄(A), the latter being a second crystallographic form of PbSO₄. The solid lead sulphates so formed then will be recovered with the fly ash in the electrostatic dust collection system. Enrichment of the lead on the waterwall tubes is unlikely to occur at metal temperatures greater than 660 °C.

Under reducing conditions the lead dewpoint temperature is much lower, however. This is especially the case when high chlorine concentrations are present in the combustion environment. Under these conditions the lead condensation range is from 680 down to 495 °C. Because of the comparatively high temperature gradient through the deposit scale, the lead can condense even at the outside of the deposit layer, explaining the frequently observed sharp band of lead deposition. However, when the deposit layers are removed regularly by erosion (for example, due to the effects of soot blowers) then lead chlorides can condense directly on the bare metal tube. Other heavy metal chlorides also can be formed in this way, resulting in the particularly heavy corrosion that is frequently observed in waste incineration plants.



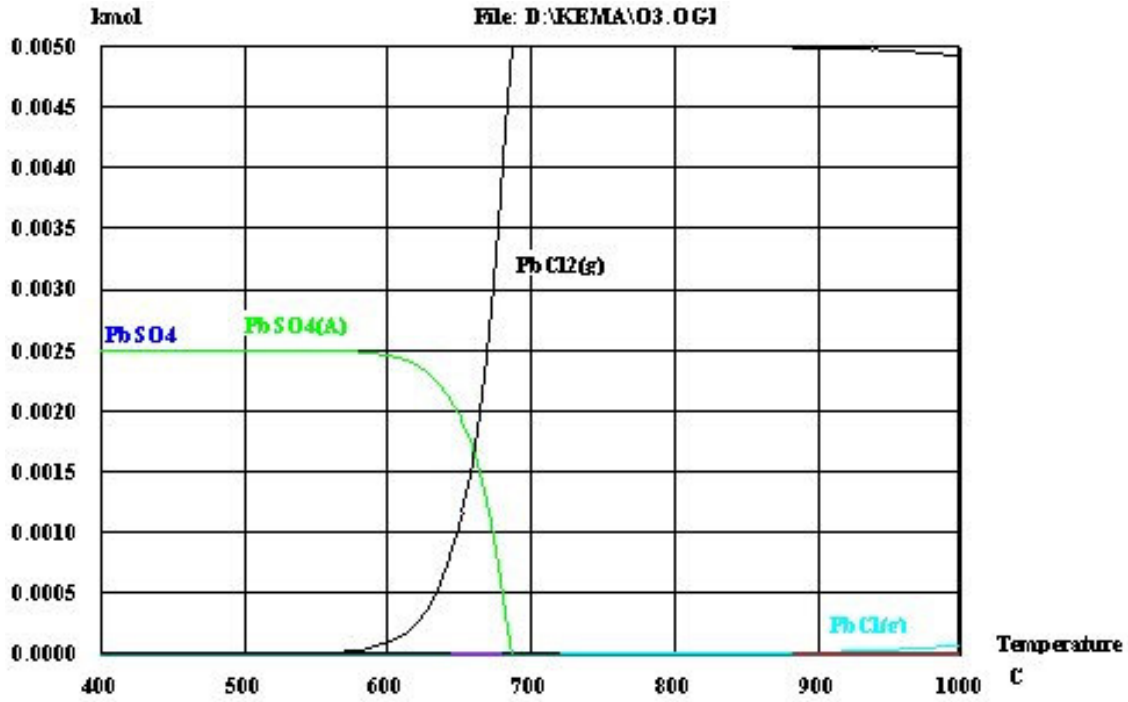
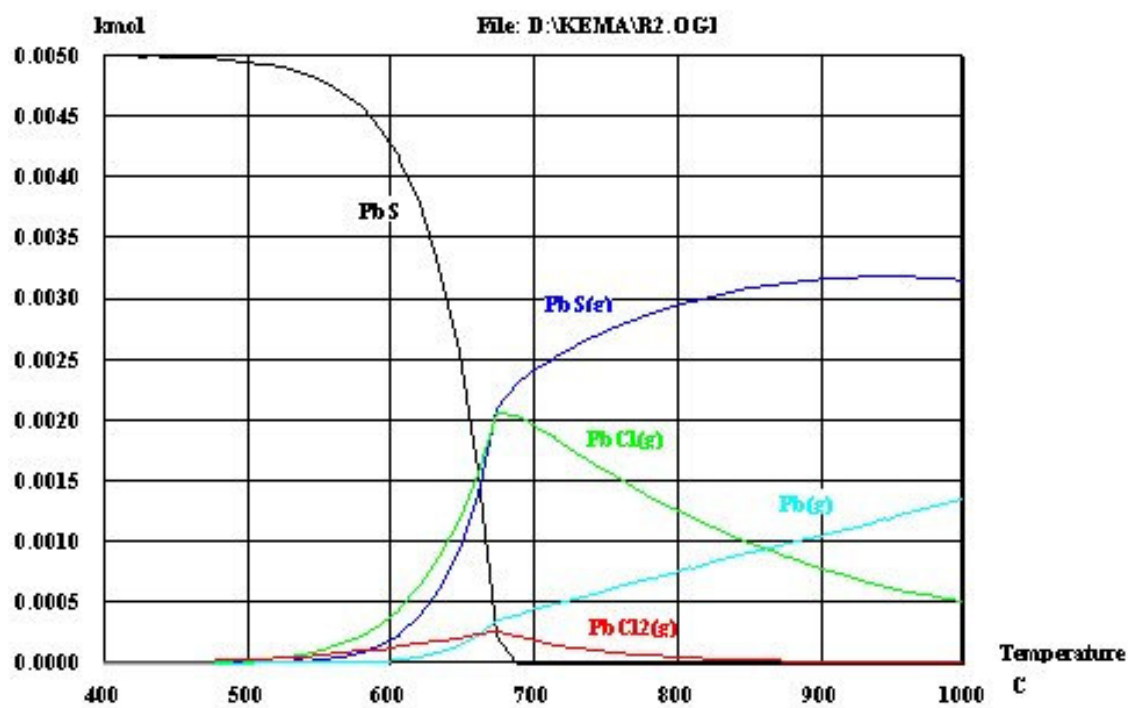
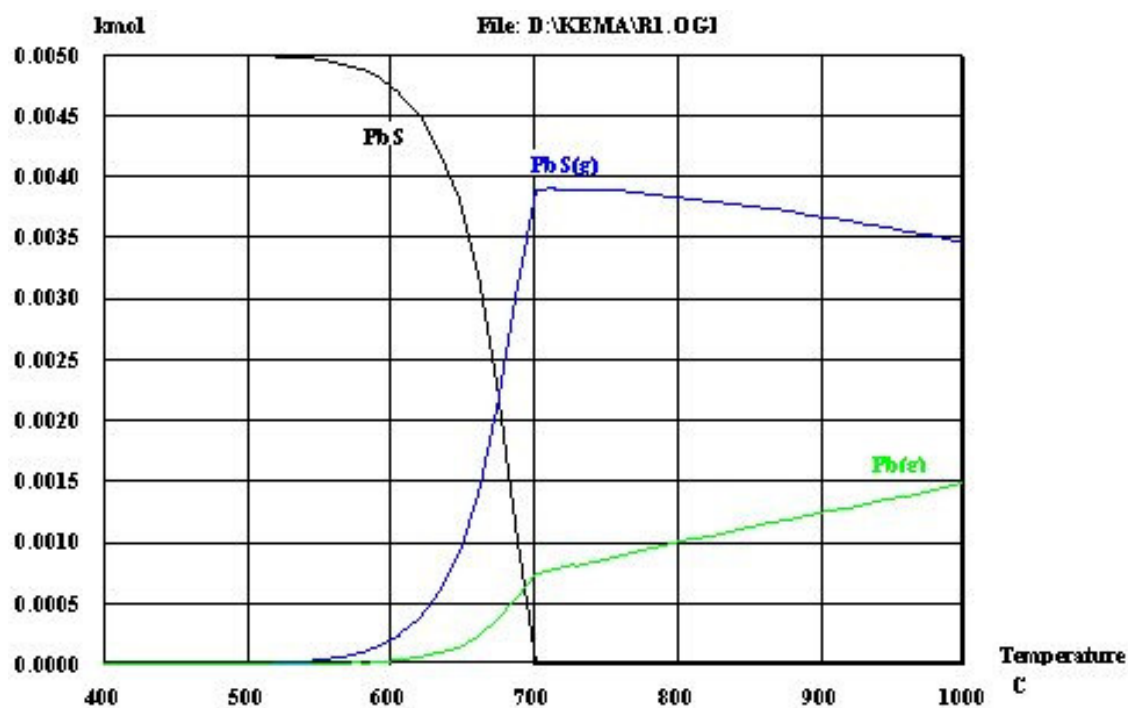


Figure 4 The thermodynamically stable constituents of lead in an oxidizing gas environment O1, O2 and O3. The lead condensation (dewpoint) temperatures are 880, 770 and 660 ° at respectively 50, 500 and 5000 vppm HCl.



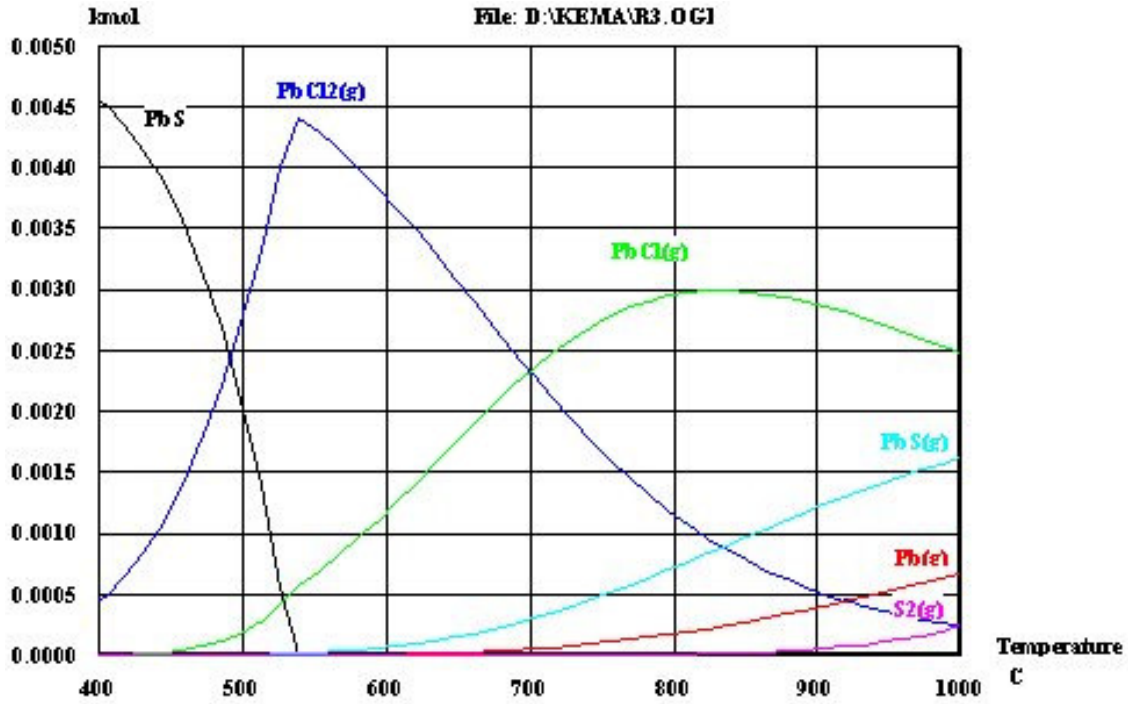
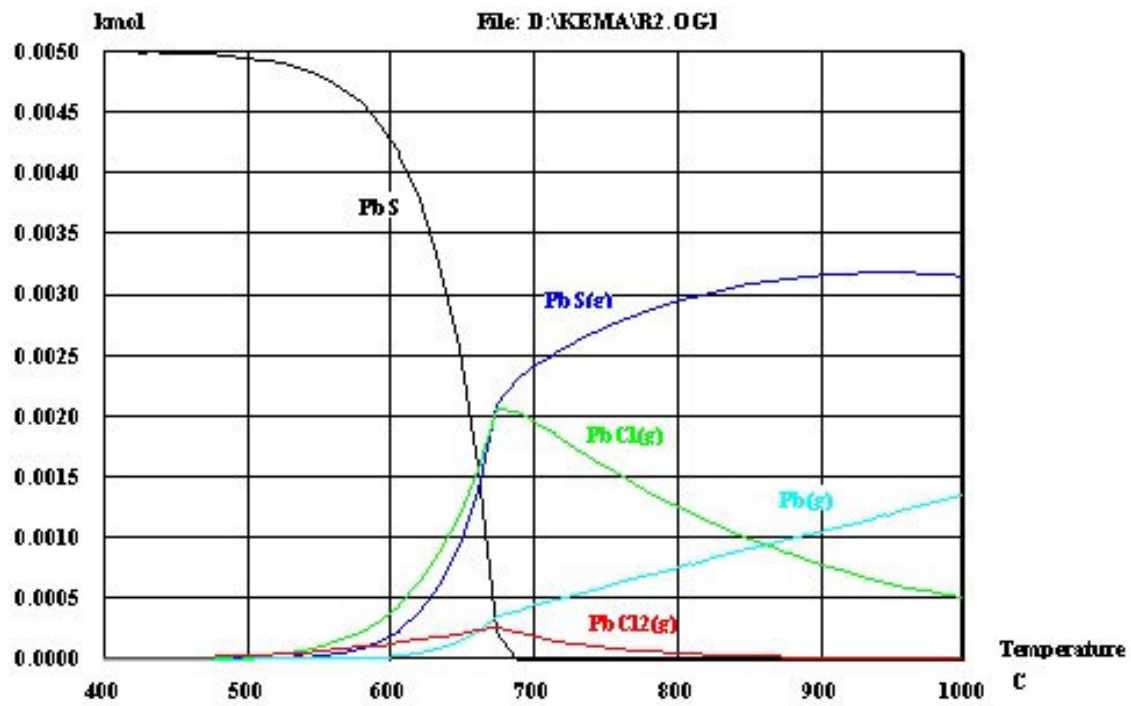
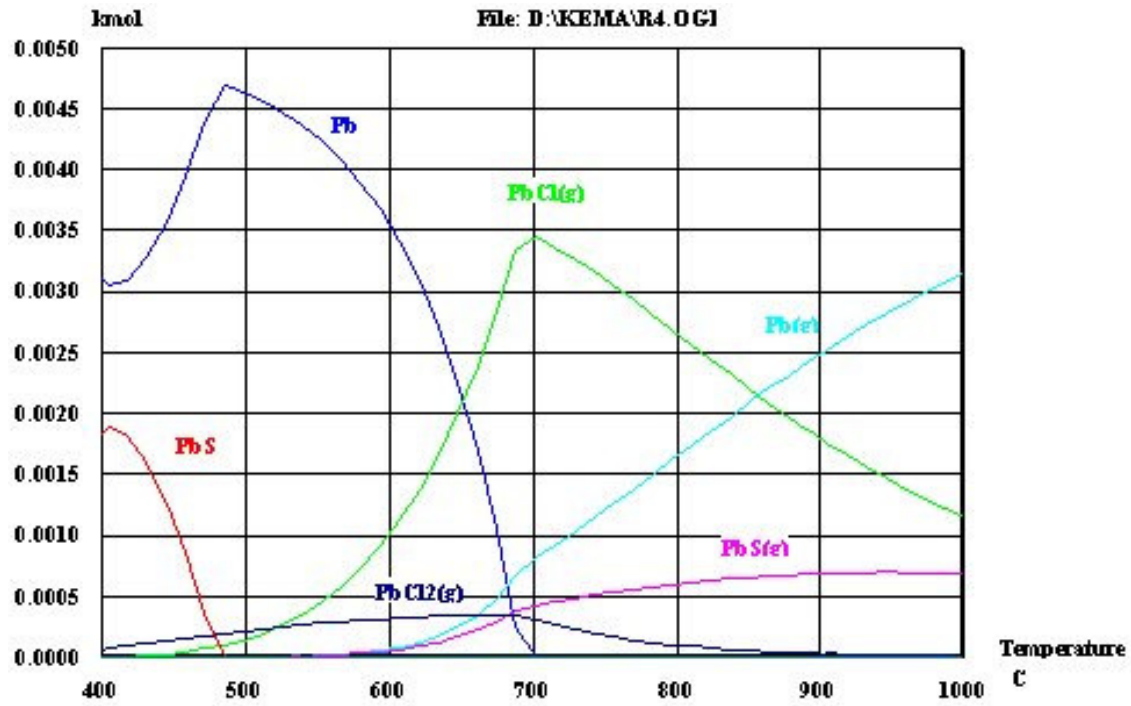


Figure 5 The thermodynamically stable constituents of lead in the reducing gas environments R1, R2 and R3. The lead condensation (dewpoint) temperatures are 680, 670 and 495 °C at 500 vppm H₂S and respectively 50, 500 and 5000 vppm HCl.



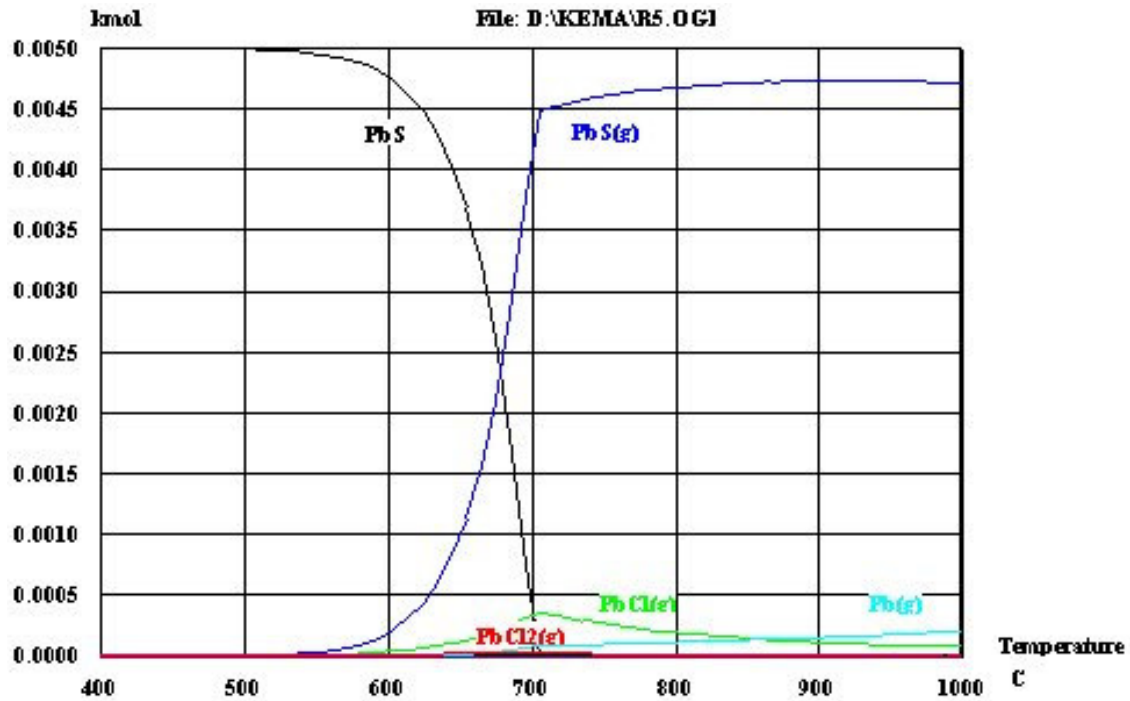


Figure 6 The thermodynamically stable constituents of lead in the reducing gas environment R4, R2 and R5. The lead condensation (dewpoint) temperatures are 650, 670 and 680 °C at 500 vppm HCl and respectively 50, 500 and 5000 vppm H₂S

Measurements of lead deposition on a probe

In order to track the corrosion and fouling layers on the waterwall tubes, a probe was developed that is placed in the waterwall. The probe can be exchanged during full load operation of the boiler (known as the KEMCOP: KEMa COrrOsion Probe). A patent is pending for the system.

In addition to the corrosion scale morphology, the condensation behavior of heavy metals and of the radioactive lead can be investigated. Although only low levels of total activity of the ^{210}Pb isotope are present on the KEMCOP probe it was possible to identify the contamination with a low background n-type HpGe gamma-spectroscopy system and measure it quantitatively.

The cross section of one of the KEMCOP probes after an exposure time of 4 months is shown in Figure 7.

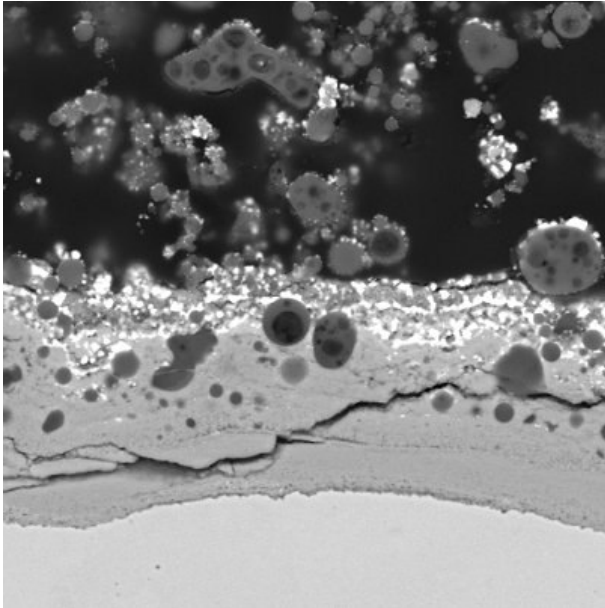


Figure 7 Cross section of one of the deposition probes after an exposure period of 4 months. The element Pb is present on the white areas on the interface between the thick porous deposit of fly ash and the outer oxide layer.

Discussion

Reducing combustion gas environments result in the formation of non-protective oxide layers on carbon steels. In case of more alloyed steels, particularly when chlorine is present in the reducing combustion gas, corrosion also may occur. Condensation of heavy metal chlorides such as PbCl_2 , ZnCl_2 , SnCl_2 can result in the formation of low melting point eutectics that are very corrosive and many corrosion failures in waste incineration plants are known from this cause.

In addition to the problem of boiler membrane wall tube corrosion, the condensation of heavy metals has been found to result in the formation of a radioactive deposition layer, which is due to the co-precipitation of radioactive lead.

The isotope concerned is predominantly ^{210}Pb , which originates from the decay of natural uranium in the coal. The ^{210}Pb -isotope has a relatively long half-life time, so that relatively high activity concentrations can accumulate in wall tube deposits.

The radioactive compounds that accumulate in the deposits constitute a significant occupational health risk for those workers who are involved with inspection, cleaning and repair operations on the boiler wall tubes.

The amount of radioactivity present in several boilers in the Netherlands was measured during boiler outage periods. Measured values were observed that exceeded the governmental regulation limit of

100 Bq/g. These activity concentration values are in the range for which, according to the present Dutch regulations, licensing is required for possession, handling and subsequent disposal of radioactive materials. Therefore, according to the Dutch Nuclear Energy Act the operators of electric power utility boilers are obliged to obtain prior authorization for the implementation, and to conduct statutory supervision of routine wall tube refurbishment activities.

The use of the 'KEMCOP' waterwall probes was found to be a convenient low-cost method by which to obtain invaluable information on the corrosion and fouling (deposit) condition of waterwall tubes (Huijbregts et al., 1998). The technique can provide information about wall tube radioactivity levels enabling preparatory radiological protection measures to be taken to protect workers against the risks of radioactive dust ingestion and consequent internal exposure to radioactive substances.

Conclusions

- The corrosion of the waterwall tubes on coal fired boilers is accompanied by the deposition of heavy metal chlorides and/or sulfides, such as PbCl_2 and PbS .
- A proportion of the condensed total Pb has been found to be the radioactive isotope ^{210}Pb .
- Enrichment due to condensation behavior within wall tube deposits can increase the concentration of radioactive species, and it has been observed that several hundreds of Becquerels per gram of ^{210}Pb can be attained.
- Thermodynamic calculations show that the amount of condensed lead can vary, dependent upon the precise firing conditions within the boiler or incinerator.
- The use of simple low-cost probes in the membrane waterwalls allows the corrosion and build-up of the radioactivity levels within deposits to be tracked easily and conveniently during normal on-load boiler operation.
- The results of this investigation have confirmed that the condensing temperature of lead compounds in oxidizing flue gas environments is relatively high, ca. 880 °C, which normally would be expected to minimize the tendency for lead condensation to take place. However, under reducing combustion conditions, especially in the presence of chloride, the lead condensation temperature decreases drastically to 490 °C and the accumulation of radioactive species within wall tube deposits is highly probable.
- Radioactive concentrations of this degree fall within the scope of statutory regulations for the control and supervision of hazardous nuclear substances, and special precautions are warranted for the protection of personnel engaged in boiler inspection and maintenance activities.

References

1. Huijbregts W.M.M., Rens O., Janssen J., Corrosion in Low NOx boilers. PowerGen Conference, Milan, 1998
2. Website of KEMCOP <http://www.kema.nl>