Possibilities and disadvantages of bromide addition to reduce mercury emissions at coal-fired power stations

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Introduction

The addition of bromide to the fuel is one of the emerging technologies for (additional) capture of mercury from the flue gas of coal-fired power plants. The method was introduced by Dr. Vosteen and is based on the additional oxidation and is based on additional oxidation of elemental mercury by bromine to oxidised mercury, which can be captured in flue gas cleaning devices (ESP, FGD) to a greater extent.

DNV KEMA was hired by VGB Power Tech e.V. to perform a study on the possibilities and disadvantages of bromide addition to reduce mercury emissions from coal-fired power stations, Project No. 357. Based on a large number of experimental studies combined with literature studies, DNV KEMA has gained much experience and knowledge on the behaviour of mercury and other components (like bromide) in coal-fired power plants. DNV KEMA has also performed extensive research on the environmental and occupational health effects of coal-fired power plants, including emissions and by-product quality. Results of these studies are presented in several public papers [10 – 13, 20 – 22 and 24].

The research focused on several aspects of bromide addition for mercury emission reduction. Aspects studied include the principle of the method, experiences, potential additional mercury removal, effects on the environment (possible emission of other components to air and water), effects on by-product quality, costs and cost-effectiveness, corrosion and occupational health. This research was based on current information in literature and knowledge and experience at DNV KEMA based on extensive research at full-scale coal-fired power plants.

Mercury emissions in Europe and worldwide

In [23] an overview is given about the worldwide mercury emissions according to the UNEP-inventory. For the year 2010, the total annual worldwide anthropogenic Hg emissions are estimated at 1,960 tonnes per year. The share of coal burning (all uses) is estimated at 24 %, which is much lower than the figure of 45 % given [14]. According to UNEP, the biggest contribution is made by artisanal and small-scale gold mining, with a share of 37 %. Figure 1 shows the trend in anthropogenic Hg emissions between 1990 and 2005 in different regions. It shows that emissions in Europe have decreased, while other regions, especially Asia, show a large increase.

[15] gives an overview of estimated Hg emissions in Europe in the period 1980 to 2005, revealing that in this period, the total Hg emissions in Europe decreased by more than a factor of 4. The implementation of FGDs in coal-fired power stations contributed significantly to this decrease. The total emissions in Europe (including Russia) from the most important anthropogenic sources are estimated at about 300 tonnes per year.

Figure 1. Trends in estimated annual anthropogenic Hg emissions in different regions [23].
in 2005. The situation has further improved in the years since, due to additional retrofitting of the flue gas cleaning installations in most European countries. For the period 1980 to 2010, the decrease in the EU-27 member states’ emissions amounts to 62 % [8]. The decrease between 1980 and 2010 for the category “public electricity and heat production” was estimated at 59 % by the EEA.

According to the EEA emission inventory, the share of the category “public electricity and heat production” in the total EU-27 Hg emissions amounted to 32 % in 2009. Mercury abatement at coal-fired power plants has increased while meeting the emission values of the LCP Directive 2001/80/EC. The application of best available techniques according to the existing BREF-LCP for coal-fired installations has led to a further increase in the construction and operation of flue gas cleaning technology. Moreover, the co-combustion of biomass, as practiced in many coal-fired power stations, e.g. in the Netherlands, generally leads to a further decrease in Hg emissions. As an example, compared to the year 2000, the emission of mercury by coal-fired power plants in the Netherlands decreased by more than 25 % in 2008 [20]. As a result, the contribution of coal-fired power plants to the total Hg emissions in the Netherlands amounts to about 20 % in recent years [9]. This is lower than this sector’s global share.

**Bromide addition to the fuel for further reduction of Hg emissions**

It is well-known that the presence of chlorine in the fuel has a positive influence on the removal efficiency of mercury in the flue gas cleaning installations of coal-fired power stations [11]. Chlorine leads to the oxidation of elemental mercury (Hg⁰) to oxidised mercury (Hg²⁺), with the formation of HgCl₂(g). This mercury chloride is water soluble and is well captured in the FGD’s wet scrubber. Elemental mercury is not water soluble and will not be captured in the wet FGD. As is the case for chlorine, the presence of bromine in the flue gas also leads to enhanced mercury removal in the flue gas cleaning system of a coal-fired power plant. Dr. Vosseën’s research showed that bromine is, in fact, much more effective in the oxidation of mercury than chlorine [25].

In applying this technique, a calcium bromide solution is added to the coal on the conveyor belt to homogeneously enrich the coal with bromide. The consumption is on the order of 0.1 kilogramme calcium bromide solution (52 %) per tonne of coal. The technique is relatively easy to implement and is suitable for retrofitting.

In recent years, many lab-scale, pilot-scale and full-scale experiments have been conducted using bromide addition to the fuel to reduce mercury emissions. Tests have been executed at waste incineration plants and at coal-fired power plants. [27, 17 and 3 – 5] give results of some full-scale tests at coal-fired power plants in the USA.

In the USA, bromide addition to the fuel has been practiced at many coal-fired power plants in recent years, both in short-term studies as well as over longer periods. On behalf of EPRI, URS Corporation has performed several studies in recent years into the balance of plant effects of bromide addition for mercury control in the USA [3 – 5, 1, 18 and 19].

From the EPRI/URS survey in 2012, [6] conclude that because bromide addition technology has only recently been deployed, the documentation of the technology’s balance-of-plant effects is incomplete. The EPRI/URS survey in 2012 reported Hg concentrations of less than 1 µg/Nm³ at applied Br addition levels of < 40 to 110 mg Br per kg coal for power plants equipped with SCR, ESP and FGD. However, [6] stated that there are some uncertainties regarding these values. It should also be noted that others published higher Hg concentrations at the stack even at high Br addition levels. [16] reported tests with Br addition at levels of 20 to 60 mg Br per kg coal. An Hg concentration lower than 1.5 µg/Nm³ downstream of the FGD could not be achieved because of Hg re-emission from the FGD suspension.

Generally, it is stated in literature that the method of Br addition is relatively simple and inexpensive, although most of the time, no figures are given. DNV KEMA estimated the costs of applying this technique. The yearly costs for Br addition at a level of 25 mg Br per kg fuel is estimated at about EUR 370,000 for a standard 600 MWₑ coal-fired power plant. For Br addition at a level of 50 mg Br per kg fuel the yearly costs are estimated at about EUR 510,000. Calculations show that the cost-effectiveness can be quite unfavourable, especially when the Hg emission levels are already low without Br addition. The cost-effectiveness depends on the extra amount of Hg emission avoided. In Figure 2 this relationship is given for two Br addition levels (25 and 50 mg Br per kg fuel) for a standard 600 MWₑ coal-fired power plant.

**Side effects of bromide addition**

Adding bromide to increase mercury removal from flue gases will have some negative side effects. Literature briefly describes some of these effects. Most of the information in literature refers to the situation in the USA, which is not comparable to the European situation in every respect. To study the possible side effects, DNV KEMA has worked out some theoretical cases based on the behaviour of elements in Dutch coal-fired power stations as measured by DNV KEMA in the past 30 years in extensive mass balance campaigns [13]. The results are based on Br addition to a level of 25 and 50 mg Br per kg coal. In some cases the amount of bromide to be added to realise the desired Hg removal might be higher. In that case the side effects will also be more evident.

Some side effects of the Br addition technology have to be taken into account. The most important side effects as described in the DNV KEMA study concern:— Possible increase in corrosion potential: corrosion effects of bromide addition cannot be entirely excluded; additional (long-term) research is necessary.— Increase of Br emissions to air and water: adding bromide to the fuel might increase the Br emissions to water and air ten-fold or more.— Increase of bromide and mercury concentrations in by-products (ashes and gypsum): this will have negative consequences for the acceptance of the by-products by current customers and may be restricted by environmental regulations; the sale of fly ash for unbound applications and of gypsum as fertilizer might become impossible.— Possible formation of organo-halogens and other secondary products like bro-
mate in water: although no indications based on measurements have been found in the literature, formation of the toxic bromate comes up now and then as a negative secondary effect; also, there is a potential for AOX formation by bromination in the FGD.

Further study of these and other possible side effects of using Br addition to reduce mercury emissions is required.

Several scenario calculations have been performed to estimate the effect of Br addition on Hg and Br concentrations in flue gas and by-products. These calculations were based on the behaviour of elements in Dutch coal-fired power stations as measured by DNV KEMA in the past year on extensive mass balance campaigns. The reference scenario was based on a standard Dutch coal-fired power plant equipped with high-dust SCR, low-temperature ESP and wet FGD and a fuel composition (with relatively low Br concentrations) that can be considered typical for a coal blend as fired in Dutch power stations nowadays. Some results are given in Table 1. The factor increase listed in this table refers to the base case scenario typical for a Dutch coal-fired power plant and some different extra Hg removal scenarios as a result of Br addition.

Discussion and conclusions

Emission inventories indicate a share of less than 15 % for the contribution of Europe including Russia to the total mercury emissions by anthropogenic sources worldwide. About one third of the European emissions originate from public electricity and heat production. As such, the estimated contribution of European power plants to global mercury emissions is less than 5 %. The contribution of EU-27 member states to the global anthropogenic Hg emissions is estimated at about 5 % by UNEP [23]. This results in a share of only about 2 % of the total worldwide anthropogenic Hg emissions for public electricity and heat production in the EU-27 countries. From these figures, it is clear that Hg emission reduction measures at European coal-fired power stations will not be an appropriate (or cost-effective) way to significantly reduce global Hg emissions.

Adding bromide to the fuel will enhance the oxidation of elemental mercury, which promotes the capture of mercury in flue gas cleaning systems, such as FGD and ESP. Several full-scale tests have shown that bromide addition to the fuel results in (further) reduction of mercury emissions at coal-fired power stations.

The results of some full-scale tests show that it is not always possible to decrease the Hg emissions below the level of 1 µg/Nm³ because of mercury re-emission from the FGD. This means that mercury emissions below 1 µg/Nm³ cannot be guaranteed in any case. Specific plant conditions play an important role in the effectiveness of Br addition in reducing the Hg emissions.

Table 1. Calculated effect of Br addition on concentrations in flue gas, effluent and by-products

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Br-addition to the fuel</th>
<th>Increase in concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br emission to the air</td>
<td>25</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>Br emission to water</td>
<td>25</td>
<td>9 (fresh water) / 1.4 (sea water)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>17 (fresh water) / 1.8 (sea water)</td>
</tr>
<tr>
<td>Br in fly ash</td>
<td>25</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>Br in gypsum</td>
<td>25</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>16</td>
</tr>
</tbody>
</table>

In a survey by EPRI/URS, some plants reported a decreased selenium concentration in the fly ash when Br was added to the fuel [6]. This decrease in the fly ash corresponds with increased selenium input in the FGD, possibly leading to an increase in the Se concentration in the emitted waste water. The reason behind the reduced capture of Se in the ash after Br addition is not known; this requires further study.

Generally, it is stated in literature that the method of Br addition is relatively simple and inexpensive although most of the time no figures are given. Indeed, implementation of Br addition to the fuel might be relatively easy to implement. Overall cost-effectiveness, however, might be quite unfavourable in certain circumstances. This depends on the extent of extra mercury-emission reduction that can be achieved. At already low Hg emissions of only a few µg/Nm³, as is the case in many European plants, the cost-effectiveness for removing a small amount of additional Hg will be relatively unfavourable.

The fact that further studies are needed into possible side effects of Br addition for mercury emission reduction is supported by the findings of the 2012 EPRI/URS survey in the USA by [6]. They concluded that, also in the USA, because the bromide addition technology was only recently deployed, the documentation of balance-of-plant effects for this technology is incomplete.

Measurement of mercury at very low levels is not easy. The European standard reference method for mercury (EN 13211) is a wet chemistry method that is considered to have been validated for flue gas emitted from waste incinerators for mercury emissions in the range 1 to 500 µg/m³. However, at a concentration level of 6 µg/Nm³, the repeatability and reproducibility of the method are quoted as 30 % and 62 %, respectively. The relative detection limit is quoted as 2.6 µg/Nm³. This means that at low levels of mercury concentration in the flue gas, the effect of Br addition cannot be assessed with great accuracy with standard measuring methods. By extending the sampling time, a lower detection limit can be reached.

In using Br addition to reduce mercury, the concentration of bromide in the by-products will increase and maybe also the mercury concentration could increase. Increasing the Hg content of the by-products will have negative consequences for customer acceptance and may be restricted by environmental regulations. Furthermore, one of the main objectives of the recently adopted European Industrial Emission Directive (IED) is to prevent “the shifting of pollution from one environmental medium to another”. Therefore, according to the IED, it is undesirable that environmental risks shifts from one emission point to another or to another compartment of the environment.
It depends on various aspects whether or not Br addition might be an effective and useful technique for further reduction of mercury emissions at European coal-fired power stations. The suitability will not be the same for each plant. It depends on the particular plant’s current level of Hg emissions, the achievable Hg emission reduction and the impact of side effects. Especially keeping in mind the differences between the situations in the USA and Europe and the uncertainties surrounding negative side effects, it cannot be stated that Br addition can be considered BAT in Europe. In discussions about the applicability of Br addition, the negative side effects and cost-effectiveness have to be considered against the expected reduction in Hg emissions.

Acknowledgements

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References


