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Analysis

Full scale tests show KNXTM is effective for mercury control

A substantial amount of testing, including recent full scale trials on a 600 MW PRB fired unit, has shown that KNXTM technology, in which a bromine-containing chemical, specifically calcium bromide, is added to the fuel, is an effective means of oxidising mercury in coal fired boilers. This greatly increases the Hg capture rate in existing "conventional" air pollution control equipment and promises very low Hg emissions alone or when combined with mercury-specific control technologies such as active carbon injection. The particulars of potential technology layering are very unit specific.

Staff Writer October 1, 2009

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The control of mercury emissions from coal-fired power plants has become an important issue in the US in recent years, and may become so in Europe and elsewhere in the future.

In the USA at the federal level the details of the regulatory regime remain uncertain, with the vacature of the EPA's Clean Air Mercury Rule and the subsequent decision to develop Hg emissions standards under the hazardous air pollutant section of the Clean Air Act calling for maximum achievable control technology (MACT) at all plants. But it is likely that power plants will have to meet more stringent requirements and, in any case, many of the states have or are in the process of developing and implementing their own regulations. For example, the Wisconsin DNR has approved a rule requiring all coal-fired power utilities in that state to reduce their overall mercury emissions by 40%

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by 2010 and 90% by 2015. Reductions may be calculated for each plant singularly or averaged over all plants. The flexibility of this approach allows the utilities to implement high reductions at selected larger plants and lower reductions at other plants with less favourable mercury reduction economics. This requirement goes into effect on 1 January 2010. A mercury control requirement for coal-fired power plants went into effect in Illinois in July 2009 and the state of New Jersey has required mercury control for some time. However, if EPA issues MACT standards these will override the state standards and are likely to remove the flexibility.

In Europe it seems possible that there will be EU-wide regulation of mercury from coal-fired plants at some stage in the future, perhaps as an adaptation of the existing LCPD. The LCPD is expected to be repealed in 2016 and replaced with the Industrial Emissions Directive. This could be the vehicle for mercury control in Europe. Germany already has regulations under BlmSchV

In response to the need for utility-scale mercury control for coal-fired power plants, Alstom has introduced two technologies: MerCureTM, an advanced form of PAC (powdered activated carbon) injection in which deagglomerated sorbent is injected upstream of the air preheater; and KNXTM, a bromine-containing additive (calcium bromide), which is added to the coal prior to combustion to enhance mercury oxidation, which in turn greatly augments mercury collection by downstream “conventional” air pollution control equipment and by mercury-specific collection technologies, eg activated carbon injection.

The KNX technology, invented by Professor Bernhard Vosteen in Germany, has been commercially applied in some German waste incineration plants, as well as in some German sewage sludge incineration plants and is the subject of patents and patent applications in countries throughout the world. Alstom has been granted an exclusive marketing rights license from Vosteen Consulting GmbH for joint exploitation and commercialisation of this technology for fossil fueled boilers, thermal waste treatment units, and other thermal processes in the United States and Canada.

The KNX coal additive can provide reliable and consistent oxidation of mercury in the flue gases, without any known secondary effects, greatly facilitating its collection.

The importance of bromine

When coal is combusted (Figure 2), its mercury content is volatised and, at the combustion temperature, the stable species is metallic mercury (Hg0), while Cl and Br in the coal form HCl and HBr.

On cooling, Cl2 and Br2 form, according to the reactions:

4HCl + O2 ‡ 2H2O + 2Cl2

4HBr + O2 ‡ 2H2O + 2Br2

The conversion to Br2 starts at a higher temperature than the corresponding conversion to Cl2. Also, molecular chlorine is consumed by SO2 at in-boiler temperatures via the reaction:

SO2 + Cl2 + H2O ‡ SO3 + 2HCl

The net result is that downstream of the combustion zone, much more Br2 remains than Cl2, even though, for practically all coals, the total chlorine is far higher than the bromine content.

When the gases have been cooled down below approximately 1400°F and direct halogenation (oxidation) of the metallic mercury is becoming thermodynamically favourable, there will only be a very small supply of molecular Cl2 in the flue gases to oxidise the Hg. Whereas if the bromine content of the coal is high enough, there will be sufficient Br2 to oxidise the typical amounts of mercury prevailing in coal flue gases, to form HgBr2.

These considerations explain why the inherent mercury collection capability of existing air pollution control equipment at US power plants burning Eastern bituminous coals is significantly higher than at plants burning sub-bituminous and lignite coals. In data collected by the US EPA the average mercury collection efficiency for existing plants without any dedicated measures for mercury control but equipped with cold-side ESP's was 16% and 46% for the plants burning PRB and Eastern bituminous coals respectively. And in the plants equipped with spray drying absorption and bag filter the figures were 25% and a surprising 98%, respectively.

An explanation, first advanced by Professor Vosteen, and supported by the above reasoning, is that a critical species for the halogenation of mercury is bromine, even though chlorine may be present at the level of some 1000 ppm in the coal while bromine may be present only at the level of some tens of ppm in the coal (see Figures 3 and 4).

Numerous full-scale tests using calcium bromide (KNX) as a pre-combustion additive to the coal have clearly proven that bromine is indeed the crucial factor.

This notion has the important practical corollary that for coals that show low mercury oxidation, this can be changed by addition of small amounts of bromine compounds to the coal prior to combustion in the boiler, whereby a predictable halogenation of mercury will be achieved at the cold end of the boiler.

It provides a way of addressing the challenging problem of mercury control for coal-fired boilers burning lower rank coals: the addition of bromine to PRB and lignite coals renders the problem of mercury control similar to that of boilers that are operated with Eastern bituminous coals, which have reletaively high halogen levels.

Experience base

The process of bromine addition to improve mercury control has been applied since 2001 to four different chemical waste incinerator plants in Germany (equipped with wet scrubbers, wet ESP and SCR) and since 2004 to four sewage sludge incinerators (equipped with ESP and wet scrubbers). The experience to date with bromine addition has been that there has been reliable mercury oxidation and collection, and no side effects.

In the USA, under US-DOE contract No. DE-FC26-03NT41986, the process has been tested at full scale on coal fired utility boilers at three different sites burning PRB coals:

- Holcomb, with spray-drying absorption and bag filter;

- Laramie River unit 3, with spray-drying absorption and ESP; and

- Meramec unit 2, with ESP only.

As already noted, addition of KNX promotes mercury oxidation. But to collect the oxidised mercury, some active collection mechanism is also needed. In the first two cases, this has been accomplished by the addition of modest amounts of powdered activated carbon, while in the case of Meramec, the UBC (unburnt carbon) content in the ash was sufficient, without the need to inject any additional PAC, to provide high mercury collection efficiency, in one case > 90%.

The addition of KNX in these units was done either by spraying the coal on the coal conveyor during silo charging or applying it in the coal feeders upstream of the mills (see Figure 5).

The KNX additive must be evenly distributed on the coal to provide uniform distribution of the active chemical of the KNX additive throughout the flue gas – the global mixing in a large coal-fired boiler is limited. Because a comparatively small flow of the active chemical of the KNX additive was required – even on a large plant – metered pumping from 55 gal drums of bromide compound in solution was sufficient.

At Holcomb the KNX increased mercury oxidation at the air preheater outlet from 20% (without additive) to more than 80%, using only modest quantities.

The fly ash at Holcomb has a very low level of UBC, providing only limited native mercury collection capability. To get high mercury collection efficiency only a small amount of activated carbon injection was necessary.

With the addition of 1 lb/MMacf of ordinary PAC, the mercury collection efficiency was found to be 40-60% without KNX. When KNX was added, the mercury removal efficiency increased to 86%. The KNX additive combined with injection of common activated carbon therefore achieved results similar to those obtained with the injection of the newly developed bromine impregnated activated carbons.

The results at Laramie were comparable, but required higher PAC injection rates since the ESP was considerably less efficient at collecting mercury than the fabric filter.

At Meramec, the UBC in the fly ash is rather high (for a PRB plant), in the range 2-4%, and as already noted UBC is relatively effective for capturing oxidised mercury.

The baseline native mercury removal at Meramec was measured at around 40%. With KNX but no activated

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carbon, the mercury collection efficiency varied with UBC but was typically 80% and was found in one test to be as high as 91%.

Recent tests

More recently, in December 2007, KNX technology was applied in full-scale tests at a 600 MW PRB fuelled boiler with SCR, ESP and modern limestone forced oxidation WFGD. The mercury emissions at this plant (without controls) were 13 micrograms per m3 of flue gas. The KNX was added to the coal at rates of 4, 12 and 22 ppm bromine. The rate of 22 ppm corresponds to 3.2 gallons per hour, or 42 lb of KNX per hour into the approximately 700 000 lb per hour coal feed to the boiler.

As shown in Figure 6 and Figure 7, coal-pile-to-stack mercury emissions reductions of more than 90% were obtained.

Based on these successful results, further KNX testing was conducted in March 2008. This time, the maximum KNX dosage was increased to 28 ppm (or 4.1 gallons per hour). As seen in Figure 8, coal-pile-to-stack mercury removal increased to 92%. This high removal level was obtained by adding only 44.1 lb per hour of KNX to the coal feed.

KNX will be employed commercially at this unit starting in 2010.

Side effects

The side effects of retrofitting the KNX technology to a system normally operating with a low bromine coal are basically the same as switching to a coal with a somewhat higher native bromine content. Very few, if any negative effects of higher Br as compared to lower Br coals are known.

In considering this, the first obvious question is where does the bromine go in the system? The literature is sparse regarding this matter, since bromine in connection with coal-fired power plants has rarely if ever before been an issue. The following data regarding the fate of Br and the other halogens in Dutch power plants equipped with SCR, ESP and wet flue gas desulphurisation have been published (by R Meij, “Mass balance study…”, presented at IEA Trace Element Workshop, University of Warwick, September 1999):

	F	Cl	Br
Coal (ppm)	20	470	10
Flue gas (mg/m3)	2	47	1
Mass streams in the system (% of total):			
Collected in flyash	15	1	13
Gypsum	35	1	0.2
Sludge	24	1	0.7
Water discharge	0.4	88	82
Stack	25	9	4

On the basis of this mass balance study, in the ESP, the Br appears to behave like F, and in the scrubber it appears to behave like Cl. Consequently, the ultimate fate of the Br is that it is discharged from the system via the WFGD wastewater stream. But it should be mentioned that the actual behaviour of Cl and Br are quite different: molecular bromine is very water soluble, in contrast to molecular chlorine, and while chlorine is entering the WFGD mainly as HCl, bromine is entering it as a mixture of Br2 and HBr, but the absorbed Br2 is immediately reduced back to HBr by the captured SO2.

When it comes to possible effects in the boiler, nothing has been found in the literature pertaining to effects of Br concentration levels that are of relevance in this context. This is supported by research done in the Netherlands (http://www.ebfrip.org/statements/TNO-AKZO-corrosion-study2002-Final.pdf).

Halogen-induced high temperature corrosion of superheaters is a known and potentially serious issue for fuels having a high Cl/S ratio, as in waste-incineration and biofuel boilers, where it is primarily managed through the use of conservative steam temperatures, eg 750°F superheater wall temperature, well below corresponding temperatures in power generation.

For coal-fired boilers, the Combustion-Engineering handbook begins a discussion on the subject of chloride as a factor in corrosion by referencing a 1970 ASME study (by A. L. Plumley) that concludes “the research establishing the mechanism of the liquid-phase-deposit high-temperature corrosion has not shown any significant corrosion at the coal chloride levels of 0.1 to 0.2 percent (~1000-2000 ppm) normally encountered in coal firing.” More recent research has included studies done in the UK as well as a 1993 EPRI report (B Dooley, Boiler tube metallurgical guide, Vol 1, EPRI report TR-102433-V1). According to these sources, there appears to be a threshold Cl concentration of 2000 ppm in the coal, and above that the corrosion rate increases approximately linearly with Cl content. These conclusions are supported by Alstom’s experience over many years in designing coal-fired boilers. The vast majority of US coals have less than 2000 ppm Cl and in most cases, the life of the boiler materials is rarely limited by the halogen (Cl+Br+F) content of the fuel.

The high temperature chlorine corrosion mechanism is generally explained as the effect of: alkali halide eutectic melts; and release of the molecular halogen from tube deposits by local sulphation attack. The gas phase sulphation of native or added bromide salts occurring already during combustion converts most of the halide salts into less critical halide sulphates prior to any contact with the superheater surfaces, ie only a residual amount of halide salts will stick to the superheater surfaces as part of the tube deposits, to be sulphated there locally, setting free molecular halogen. Gas phase sulphation diminishes corrosion risks. The melting point difference between the sodium and potassium bromide and chloride is a mere 46°C such that the eutectic temperatures of mixtures with other salts normally will be similar. Delayed sulphation at tube deposits will occur for both bromide and chloride salts. Based on this it can be inferred that the corrosion effect due to an increase of Br by some 10 ppm will be similar to the effect of an increase in coal Cl by the same amount, ie it is of no importance below a 2000 ppm halogen level, while above that limit an insignificant amount of additional corrosion is to be expected during the life of the boiler.

To summarise: if the Br content of the coal is adjusted by moderate levels of calcium bromide addition for mercury control the unused Br will be mainly discharged through the stack and flyash in plants having no FGD, and will be discharged as bromide with the waste water discharge in plants with WFGD. As such, no significant effect on boiler corrosion is thus to be expected.

Studies by EPRI to examine the balance of plant effects of bromine addition have thus far shown no observed negative impact of bromine on flyash use as a cement replacement. Indeed, tests at Xcel Energy’s Tolk station have demonstrated the ability of of KNX to significantly reduce the amount of activated carbon added for mercury control, thus lowering the carbon content of the flyash and helping to preserve ash sales. These same balance of plant studies have shown the potential increase in concentration of bromine in wet scrubber water and the probable need to control these levels to avoid any potential metal corrosion issues.

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