

The KNX™ Coal Additive Technology

A Simple Solution for Mercury Emissions Control

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1. Background

KNX™ coal additives and systems, available exclusively from ALSTOM, utilize a proprietary process wherein a bromine-containing chemical is added to the fuel in a coal-fired boiler. The KNX coal additive technology is operated to enhance mercury oxidation, which in turn results in an augmentation of mercury collection in downstream air pollution control equipment.

The technology, invented by Prof. Bernhard Vosteen in Germany, has been commercially applied in some German waste 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 commercialization 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. In many cases, this process significantly facilitates the collection of mercury from coal-fired boilers.

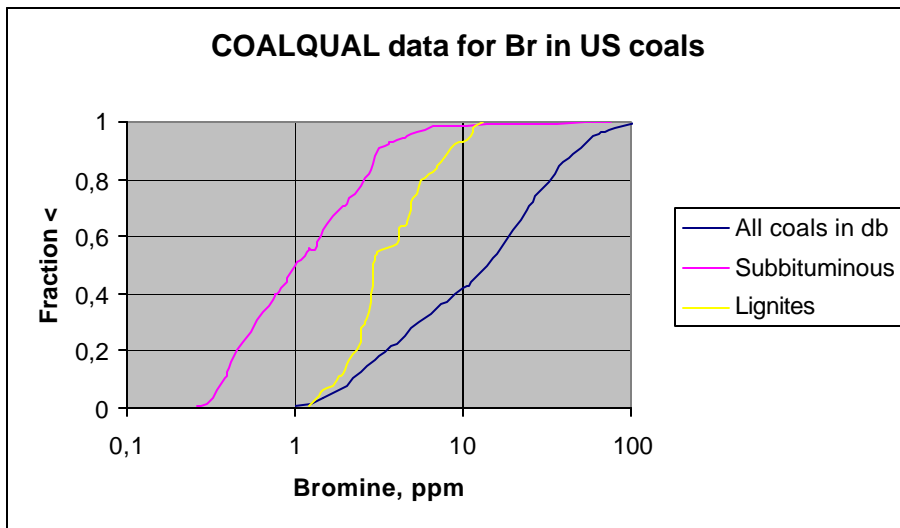
2. Naturally occurring bromine in US coals

Bromine (Br) is a relatively sparsely occurring element, second to chlorine (Cl) among the halogens. The natural mass abundance ratio of Cl/Br is about 600 in the whole universe, whereas in the ocean the ratio is about 250. Based on the chemical similarity of the two elements, one could guess that since the Cl content of US coals range from close to zero to 2000 ppm, the Br content would range from close to zero to merely some tens of ppm.

The US Geological Survey database COALQUAL gives Br data from analyzed coal specimens. The corresponding distribution of Br in the coals in the database is given in Figure No. 1 below.

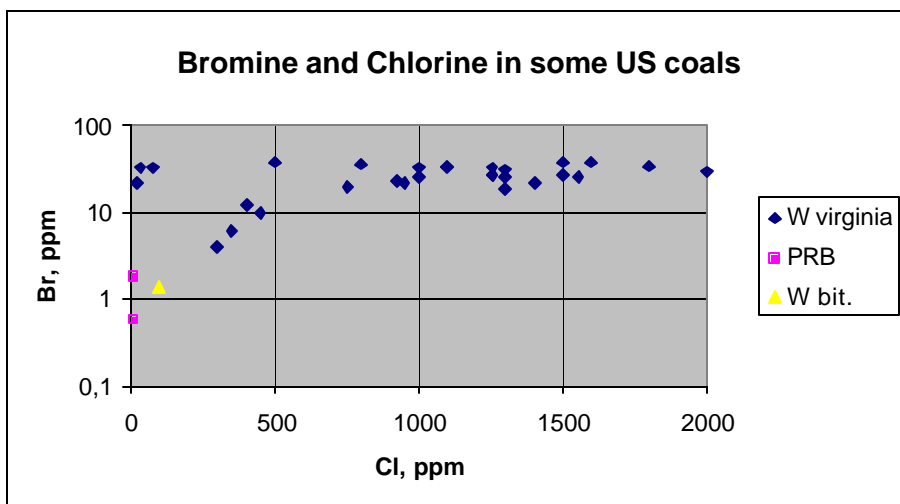
According to this data, US coals have Br contents between 0 and 100 ppm and the mean and median Br concentration of the coals are 20 and 14 ppm respectively. It is moreover noted that the lignite coals (median 3 ppm) and the sub-bituminous (median 1-2 ppm) coals are significantly and systematically deficient in bromine as compared to average US coals, and that the bituminous coals are systematically higher in Br than the lower rank coals.

Fig. 1. Distribution of Br in ppm in the coals listed in the COALQUAL database, <http://energy.er.usgs.gov>



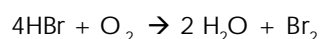
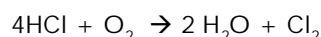
The data in Figure 2 illustrates that there appears to be some correlation between Br and Cl in US coals, at least to the extent that high Br levels are uncommon among the low Cl coals.

Fig. 2. Chlorine and bromine in mainly W. Virginia coals (based on www.wgs.wvnet.edu).

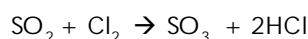


3. Mercury halogenation in flue gases.

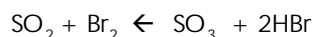
When coal is combusted, its content of mercury is volatilized and, at the combustion temperature, the stable species is metallic mercury. The stable form of the halogens at the high combustion temperature is the formation of acids (HCl, HBr). On cooling of the gases, the diatomic, molecular form of the halogens become stable according to the Deacon type of reactions:



The conversion of bromine starts at a higher temperature than the corresponding conversion of chlorine, so the kinetics of the Deacon are more favorable. Moreover, molecular chlorine (but not molecular bromine) is consumed during boiler passage by SO_2 in the chlorine Griffin reaction:



Molecular bromine, on the other hand, is not consumed by SO_2 within the boiler temperature range:



The net effect of these reactions is that after the combustion zone, there is much more molecular bromine as compared to the corresponding quantities of molecular chlorine:

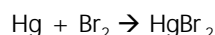
$$\text{Cl}_2 / \text{Cl}_{\text{total}} < < 1$$

$$\text{Br}_2 / \text{Br}_{\text{total}} \rightarrow 1 > > \text{Cl}_2 / \text{HCl}$$

So although for practically all coals, the chlorine in the coal is far higher than the bromine in the coal, the amount of molecular bromine (Br_2) in the flue gas may many times be higher than the amount of molecular chlorine (Cl_2) in the flue gas downstream the combustion zone. It is also observed that in practically all combustion processes almost all the chlorine exists as HCl at the boiler back end.

When the gases have been cooled down below approximately 1300°F and direct halogenation of the metallic mercury is becoming thermodynamically favorable, there will be a very small supply of molecular Cl_2 in the flue gases. Whereas if the bromine content of the coal is high enough, there will be ample supply of Br_2 (typically 1 to 10 ppm in coal) to oxidize the typical amounts of mercury prevailing in coal flue gases:

$$\text{Br}_2 / \text{Hg} > > 1$$



It has been observed that the inherent (in the existing air pollution control equipment) collection of mercury from US power plants burning Eastern bituminous coals is significantly higher than in the plants burning sub-bituminous and lignite coals. In the ICR data collected by the US EPA in 1999, the average mercury collection efficiency for existing plants without any dedicated measures for mercury control 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.

It is generally, but incorrectly, believed that this is due to the effect of the higher chlorine of the bituminous type of coals. An alternative explanation first advanced by Vosteen (B. Vosteen, Air Quality IV, 2003) and supported by the above reasoning, is that the critical species for the halogenation of mercury is not chlorine (at the level of some 1000 ppm in the coal) but rather bromine (at the level of some tens of ppm in the coal) is 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 hot side of the boiler, whereby a predictable halogenation of mercury will be achieved at the cold end of the boiler. This change is an important step to solve the challenging problem of mercury control on most of the coal-fired boilers burning the lower rank coals in the USA. The addition of bromine to PRB and lignite coals renders the problem of mercury control similar to that of boilers that are operated with the high halogen, Eastern bituminous coals.

4. 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 ESP, scrubbers and SCR) and since 2004 to two sewage sludge incinerators. The experience to date with bromine addition has been that there has been reliable mercury oxidation and collection, and no side effects.

The process was recently tested, full-scale, on coal fired utility boilers under US-DOE contract No. DE-FC26-03NT41986 at three different sites burning PRB coals:

- Holcomb Station in Kansas, equipped with spray-drying absorption and bag filter as air pollution control
- Laramie River Station U3 equipped with spray-drying absorption and ESP
- Meramec Station U2 equipped with ESP only

The KNX coal additive technology is operated to promote mercury oxidation. To collect the oxidized mercury, some active collection mechanism is also needed. In the first two cases, this has been accomplished by the addition of modest amounts of pulverized activated carbon (PAC). In the case of the Meramec unit, 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 coal additive in these units was done either by spraying on the coal, on the coal conveyor during silo charging or in the coal feeders upstream of the mills. 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 50 gal drums of bromide compound in solution was sufficient.

The results from the Holcomb unit indicate that the use of the KNX additive increased mercury oxidation at the air pre-heater outlet: from 20 % without addition of the KNX coal additive to more than 80% with only a modest addition of the KNX additive. The fly ash from the Holcomb unit has a very low UBC and very low native mercury collection efficiency. To get high mercury collection efficiency, a small amount of activated carbon injection was necessary. At an addition of 1 lbs/MMacf of ordinary PAC, the mercury collection efficiency was measured between 40 and 60% without the addition of the KNX additive. Under the same conditions, with the addition of the KNX additive, the mercury removal efficiency was measured at 86%. The data indicates that the application of the KNX coal additive

combined with injection of common activated carbon achieved results similar to those obtained when injecting the newly developed impregnated activated carbons.

The results at the Laramie River station were comparable. But, the results were achieved with higher injection rates of PAC, since the ESP is considerably less efficient in the mercury control aspect than the fabric filter.

At the Meramec plant, the UBC in the fly ash is rather high for a PRB firing case with figures varying between 2 and 4%. This carbon material is relatively effective for controlling oxidized mercury. Prior to parametric testing of the Meramec unit, the baseline native mercury removal was measured at around 40%. With the addition of the KNX additive and the natural carbon in the fly ash, the mercury collection efficiency varied with UBC but was typically 80% and was measured in one parametric test as high as 91%.

Further utilization of the KNX technology in different applications is currently being planned in conjunction with different ALSTOM customers. The results of these future uses of the KNX technology are expected to enable ALSTOM to refine and optimize mercury control for a variety of the back-end air pollution control configurations currently being applied for both green field and brown field projects in development.

5. Possible secondary effects of coal Br content adjustment.

The secondary 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 higher native bromine content. Very few, if any negative effects of higher Br as compared to lower Br coals are known.

In examining this matter, 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. Some data regarding the fate of Br and the other halogens in Dutch power plants equipped with SCR, ESP and wet flue gas desulfurization are known:

	F	Cl	Br
Coal (back-calculated), ppm	20	470	10
Flue gas, mg/nm ³	2	47	1

Mass streams in the system:

Collected in flyash, % of total	15	1	13
Gypsum, % of total	35	1	0.2
Sludge, % of total	24	1	0.7
Water discharge, % of total	0.4	88	82
Stack, % of total	25	9	4

Source: R Meij: "Mass Balance Study...", presented at IEA Trace Element Workshop, University of Warwick Sep 6, 1999).

On the cold side of the boiler, one can then say that in the ESP, the Br behaves like F, and in the scrubber it behaves like Cl. Consequently, the ultimate fate of the Br is the discharge thereof from the system, via the WFGD wastewater stream.

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. The very high bromine levels that can occur in chemical waste incinerator boilers are accounted for in the waste incinerator industry by combining the Br and Cl (and F) levels when designing for high temperature corrosion effects. The rationale for doing so is that both Br and Cl exist as the acids HBr and HCl at boiler temperatures. This is supported by the work in the Netherlands (<http://www.ebfrip.org/statements/TNO-AKZO-corrosion-study2002-Final.pdf>)

Halogen-induced high temperature corrosion of super-heaters, is a known and potentially serious issue for fuels having a high Cl/S ratio like in waste-incineration boilers and in bio-fuel boilers, where it is primarily managed through the use of conservative steam temperatures. For coal-fired boilers, page 3-27 of the Combustion-Engineering handbook begins a discussion on the subject of *Chloride As a Factor in Corrosion* by referencing a 1970 ASME study that "the research establishing the mechanism of the liquid-phase-deposit high-temperature corrosion has not shown any significant corrosion at the chloride levels of 0.1 to 0.2 percent (~1,000-2,000 ppm) normally encountered in coal firing" (A.L. Plumley, "Incinerator Corrosion Potential," ASME Incinerator Division Corrosion Symposium, New York: American Society of Mechanical Engineers, 1970.) More recent research has been largely based on results from the UK, as well as on the conclusions in an EPRI report (B Dooley (1993), "Boiler Tube Metallurgical Guide, Vol 1 EPRI Report TR -102433-V1). According to these sources, there appears to be a threshold Cl concentration of 2,000 ppm Cl 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 2,000 ppm Cl. Thus, 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 chloride corrosion mechanism is generally explained as the effect of: (a) alkali halide eutectic melts; or (b) release of the halogen from tube deposits by sulfation attack. The melting point difference between the sodium and potassium bromide and chloride is a mere 46 deg C such that the eutectic temperatures of mixtures with other salts normally will be similar. Sulfation will occur of both bromide and chloride salts. Based on this it can be inferred that the corrosion effect from an increase of Br at the level of some ten ppm will be similar to the effect of an increase in coal Cl by the same amount. Thus, this 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 summarize: The effect of adjusting the Br content of the coal by levels less than 50 ppm is that the corresponding amount will be mainly discharged through the stack in plants having no FGD, and will be discharged with the waste water discharge in the plants with WFGD. As such, no significant effect on boiler corrosion is thus to be expected.

6. Conclusions.

Bromine is active in oxidizing the mercury emitted from the boiler flue gas, and the simple addition to the boiler of small amounts of bromine compounds can provide reliable oxidation of the mercury, which substantially facilitates the problem of mercury collection.

This patented method, invented by Prof. Vosteen of Germany, has been in commercial operation in Germany on chemical waste and sludge incineration and has been successfully demonstrated on a commercial scale on US coal-fired boilers in US-DOE projects with considerable success. This technology is now available in KNX coal additives and systems that are marketed exclusively by ALSTOM in the United States and Canada.

The addition to the boiler of small amounts of bromine compounds for the purpose of improved mercury control has basically the same secondary effect as changing from a coal with low native bromine content to a coal with a higher bromine level. Such changes are not expected to have any significant negative effects on the boiler.

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