Reducing mercury emissions by activated carbon sorbent injection (ACI) has been thoroughly demonstrated as a successful strategy at a growing number of cement plants. Not only is capital cost and process impact low compared to other potential control methods, but ACI is a ‘tunable’ control strategy which can be rapidly adjusted to handle shifts in input mercury concentration from highly variable raw mix components (e.g., limestone) and fuel (e.g., coal, petcoke, tyres). In light of this, understanding what sorbent properties are critical to performance and how new generations of sorbents have combined improvements to fundamental properties with novel chemistry is central to an effective mercury control strategy.

**Mercury diffusion and oxidation/adsorption**
Mercury is removed from the bulk gas following diffusion from the gas stream by oxidation/chemisorption on active sites located on the sorbent surface. Mercury competes for this limited number of active sites with other (more highly-concentrated) constituents of the gas stream such as SO₂, SO₃, and NO₂.

Table 1 uses this understanding of the mercury removal mechanism together with real-world performance data to detail which commonly-discussed sorbent properties are likely to be critical to mercury removal performance:
- particle size and density
- chemisorption active sites
- oxidation efficiency
- competitive acid gas tolerance
- total ash content.

**Particle density and size**
Due to the very limited contact time of the sorbent with the gas stream, intraparticle diffusion of mercury (moving from the particle surface to the interior porosity) is likely not the rate-controlling step in...
removal. Combining this with the mixed finding that some, but not all, empirical data from lab- and full-scale testing shows that sorbents with greater overall porosity demonstrate improved mercury removal performance, indicates that particle density rather than specifically porosity is a contributor to performance.

Assuming minimal diffusion from the sorbent surface to the interior particle porosity in the time allowed with typical sorbent injection applications, particle size and particle density are the primary factors determining the available surface area for diffusion of the mercury from the gas to the particle surface. Effective control of sorbent particle size is more complicated than simply aggressively milling the sorbent during the production process as fine particle sorbents have the potential to re-agglomerate through either contact with moisture or electrostatic attraction. Cabot Norit Activated Carbon’s (Cabot) advanced size control techniques and robust QA/QC processes allow the delivery of fine particle sorbents which maintain their mercury control efficiency throughout storage and final use. Figure 1 compares the mercury removal performance of a Cabot advanced fine particle sorbent versus a standard particle sorbent at Plant A, a full-scale coal-fired site with fuel mercury content ranging between 25-53ppb. Not only is the advanced fine particle sorbent able to obtain >87 per cent removal of input Hg, it also achieves similar removal rates to the standard particle sorbent at half of the required ACI rate.

Chemisorption active sites

Chemisorption active sites are known to derive from the chemistry of the carbon surface itself, with their activity often catalysed by heteroatoms (eg, nitrogen) and metal constituents of the ash of the activated carbon sorbent. These active sites have been demonstrated to exist on activated carbon sorbents derived from a variety of raw material sources (eg, coconut shell, wood, coal). Figure 2 illustrates the fixed-bed (equilibrium) mercury adsorption capacity of sorbents from a variety of raw material sources, including lignite coal-derived Darco® Hg-CC EXTRA and Darco® Hg-LH sorbents produced by Cabot. All tested sorbents were shown to possess a fixed-bed (equilibrium) mercury capacity far above that typically seen with ‘in-flight’ capture in the field (>3000µg/gm vs 20-50µg/gm), indicating that this general family of sorbents is not limited by chemisorption active sites.

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Another observation is that total ash content of the sorbent does not appear to correlate strongly with mercury capacity, and thus is not likely to be a critical factor in determining mercury removal performance.

Oxidation efficiency
Elemental mercury is poorly adsorbed on either cement kiln dust or activated carbon sorbent. Therefore, conversion of mercury to a more adsorbable state through oxidation is typically required depending on the specific gas chemistry of a particular cement facility. Through a similar mechanism, DSI also reduces the available reactive halogens causing the same potential oxidation issue. To remain effective at mercury removal, a sorbent must possess sufficient oxidation capacity, even during very aggressive ‘scrubbing’ conditions. Figure 3 illustrates the performance of Cabot’s ‘DSI tolerant’ advanced activated carbon sorbent under aggressive halogen scrubbing conditions with high rates of calcium-DSI injection at Plant B.

Plant B is a full-scale coal-fired site with a fuel mercury content of 69-109ppb and SO$_2$ content of 5.96-6.81lb/mBtu. Increased DSI rates actually had a positive impact on the sorbent performance. While the DSI “scrubbed” the SO$_2$/SO$_3$/NO$_2$/HCl from the flue gas, the sorbent possesses sufficient oxidation capacity via advanced sorbent surface halogenation techniques to compensate for the effect of the DSI.

Figure 4 further illustrates the performance benefits of the advanced sorbent surface halogenation techniques used for Cabot’s DSI tolerant sorbent. Cabot’s advanced halogenation results in improved halogen distribution across the sorbent surface, increasing oxidation efficiency beyond simply the amount of halogen applied to the sorbent surface. During further testing at Plant B, Cabot’s DSI tolerant sorbent achieved a similar mercury removal at a 44 per cent lower ACI rate versus a competitor halogenated sorbent of similar particle size. Furthermore, the competitor sorbent actually possessed as much as 50 per cent greater weight of halogen applied to its sorbent surface, increasing the risk of corrosion.

Competitive acid gas tolerance
In addition to being derived from the
understanding of the mercury adsorption mechanism, a large body of empirical data illustrates the typical negative impact of \( \text{SO}_2/\text{SO}_3/\text{NO}_2 \) in the flue gas on efficiency of mercury removal by sorbents.

Novel surface chemistry is often required to overcome this negative impact on performance. \( \text{SO}_2/\text{SO}_3/\text{NO}_2 \) can be present in the flue gas through two primary pathways: volatilised from the raw mix/fuel and/or artificially added. Ironically, sodium-based DSI, while injected to reduce \( \text{SO}_2 \), can artificially add \( \text{NO}_2 \) to the flue gas through an unwanted side reaction and thus negatively impact sorbent performance. Once injected into the gas stream, both trona and sodium bicarbonate (SBC) thermally decompose to \( \text{Na}_2\text{CO}_3 \), which at a temperature range of 300-500˚F has the potential to undergo the following series of reactions:

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + \text{SO}_2 &\rightarrow \text{Na}_2\text{SO}_3 + \text{CO}_2 \\
\text{Na}_2\text{SO}_3 + 2\text{NO} + 2\text{O}_2 &\rightarrow 2\text{NaNO}_3 + \text{SO}_3 \\
2\text{NaNO}_3 + \text{SO}_2 &\rightarrow \text{Na}_2\text{SO}_4 + 2\text{NO}_2
\end{align*}
\]

Thus the injection of trona or SBC for \( \text{SO}_2/\text{HCl} \) emissions control has generally been shown to have a significantly negative impact on the efficiency of activated carbon sorbents for mercury emissions control. Figure 5 illustrates the performance of Cabot’s DSI tolerant sorbent at Plant C, a coal-fired site with fuel mercury content in the range of 42-143ppb and gas \( \text{SO}_2 \) in the range of 85-192 ppm. Cabot’s advanced sorbent is not negatively impacted by the progressively increased injection rate of sodium-based DSI.

On the same topic of competitive acid gas tolerance, Plant D is a coal-fired site with relatively high \( \text{SO}_2/\text{SO}_3 \) concentration in the flue gas (7-8ppm \( \text{SO}_3 \)). The presence of these acid gases had caused the plant to struggle with mercury emissions control. Figure 6 compares the performance of a standard fine particle halogenated sorbent to Cabot’s ‘\( \text{SO}_3 \) tolerant’ advanced sorbent. Cabot’s \( \text{SO}_3 \) tolerant sorbent was not only able to achieve >90 per cent mercury removal but similar mercury as compared to the standard sorbent with <54 per cent of the ACI rate.

Each cement facility presents its own unique challenges for mercury emissions control. Understanding the sorbent properties critical to mercury removal is the only way to ensure that a cost-effective mercury control strategy is developed.

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