ACID GASES, MERCURY, AND DIOXIN FROM MWCs

ANTHONY LICATA  
Licata Energy & Environmental Consultants, Inc.  
Yonkers, NY

MANYAM BABU  
Dravo Lime Company  
Pittsburgh, PA

LUTZ-PETER NETHE  
Märker Umwelttechnik  
Harburg, Germany

INTRODUCTION

The pursuit to reduce certain emissions at combustion facilities such as solid and hazardous waste-treatment facilities has lead to the development of several new technologies. The desire for improved emission controls is has been expressed in public opinion and ever more stringent regulations, and implemented by the owners and operators of Municipal Waste Combustor (MWC) facilities who want to keep their facilities cost competitive while reducing emissions. The reasons for improving emissions are:

• Higher than desired mercury (Hg) emissions.
• Higher than desired dioxin and furans emissions.
• Pending regulations to reduce acid gas and all other emissions of concern from new and existing facilities.

Environmental control agencies all over the world have sought to reduce emission rates by the implementation of new regulations. Examples of these regulations are Germany’s 17th Federal Regulation on Emission Protection; the Clean Air Act Amendments of 1990; EPA’s New Source Performance Standards (NSPS) and Emission Guidelines; and recent regulatory actions in Minnesota, New Jersey, and Florida to adopt Hg standards. In other cases, public concern and regulatory uncertainty have delayed the implementation and permitting of projects.

The Sorbalit process which is described in this paper economically reduces emissions and has been demonstrated in Europe and the U.S. The process consists of two components:

1) A specially developed agent characterized by a high adsorption material capable of adsorbing toxic elements and acid gases, and

2) Highly efficient air pollution control systems used by MWCs and various other types of combustion sources, which provide through agitation, a vortexing of the adsorbing agent mixture in a collection device, usually a fabric filter or ESP.

The aim of this paper is the presentation of the theoretical design of the Sorbalit® technology. Actual field test results illustrate applications that reduce the concerns related to mercury and dioxin emissions based on practical experience. The adsorbing agent is described in detail and results obtained in various types of air pollution control systems which are applicable to the U.S. are presented. Certain systems such as wet scrubbers that are being employed in Europe will be discussed in another paper.

THE SORBALIT® SYSTEM

Sorbalt is a patented system for controlling emissions of acid gases, mercury, and organics in a single application. The sorbent component of the technology is produced by mixing lime, either calcium hydroxide or calcium oxide with surface-activated substances such as activated carbon or lignite coke, and sulfur-based components in a proprietary process. Sorbalit can be produced with carbon contents ranging from 4 to 65% depending on the technical and economic requirements of each project.

The Sorbalit process produces a homogeneous powder containing calcium, carbon, and sulfur compounds that will not dissociate (demix) when used, either in a slurry or dry form, in air pollution control systems. It is particularly important to avoid flotation or separation of the carbon and sulfur substances that have been added to the lime.
TABLE 1  TYPICAL SORBALIT CHEMICAL AND MATERIAL ANALYSIS

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI @ 1100°C (dry wt %)</td>
<td>27.15</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.06</td>
</tr>
<tr>
<td>CaO</td>
<td>68.57</td>
</tr>
<tr>
<td>MgO</td>
<td>1.38</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.44</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.2</td>
</tr>
<tr>
<td>Total S</td>
<td>0.17</td>
</tr>
<tr>
<td>Total C</td>
<td>4.17</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.49</td>
</tr>
<tr>
<td>BET Surface Area m²/g</td>
<td>34.90</td>
</tr>
<tr>
<td>Moisture %</td>
<td>None</td>
</tr>
<tr>
<td>Bulk Density (Loose) lbs/ft³</td>
<td>26</td>
</tr>
<tr>
<td>Bulk Density (Vibration) lbs/ft³</td>
<td>26</td>
</tr>
<tr>
<td>Angle of Repose °</td>
<td>47.49</td>
</tr>
<tr>
<td>Angle of Slippage °</td>
<td>34</td>
</tr>
</tbody>
</table>

To maintain product uniformity and effective levels of air pollution control, the components must stay in suspension from the manufacturing process through transportation and the air pollution control system. Typical chemical and material analyses of Sorbalit are presented in Table 1.

Theory of Lime Adsorption

This Section discusses the various lime products involved in the process. Calcium oxide (CaO) is called "pebble lime" or "quicklime". Hydrated lime [Ca(OH)₂] is made from CaO by adding 32% by weight of water in a hydrator. Ca(OH)₂ is a powder with a mean particle size of 5 microns and is highly reactive.

CaO is not very reactive with acid gases for scrubbing at the temperatures and conditions that exist in MWC facilities and has to be converted into the hydrate form to be reactive in scrubbing systems. CaO has been demonstrated to remove acid gases in high temperature applications such as furnace injection. CaO converts to Ca(OH)₂ in the slaking process in which four parts of water are added to one part CaO to form Ca(OH)₂ in a slurry that has about 25% solids. This conversion requires two phases that takes place in a slaker. The first phase converts the CaO into Ca(OH)₂. The second phase is to convert the hydrate by mixing 3.96 lbs of free water with one part hydrate (1.32 lbs) that results in a 25% solids slurry (5.28 lbs).²

The reactions of the chemical components (with their molecular weights) of Sorbalit are as follows:

Hydrated Lime

\[
\begin{align*}
\text{CaO} + \text{H₂O} & \rightarrow \text{Ca(OH)₂} + \text{Heat} \\
56 & \quad 18 \quad 74 \\
\text{Ca(OH)₂} + \text{SO₂} & \rightarrow \text{CaSO₃} + \text{H₂O} \\
74 & \quad 64 \quad 120 \quad 18 \\
\end{align*}
\]

Capture Ratio = 74 + 64 = 1.156

Ca(OH)₂ + 2HCl \rightarrow CaCl₂ + 2H₂O
74 \quad 73 \quad 111 \quad 36
Capture Ratio = 74 + 73 = 1.104

1 lb of CaO yields 1.32 lbs of Ca(OH)₂

The stoichiometry of Ca(OH)₂ with acid gases requires:

(I) 1.156 lbs of Ca(OH)₂ to capture 1.0 lb of SO₂
(2) 104 lbs of Ca(OH)₂ to capture 1.0 lb of HCl

The average MWC facility emits the following regulated acid gases: [lbs/ton of municipal solid waste (MSW) burned]

\[
\begin{align*}
\text{SO₂} & = 5.03 \text{ lbs/ton} (212 \text{ ppmdv @ 7% O₂}) \\
\text{HCl} & = 7.03 \text{ lbs/ton} (532 \text{ ppmdv @ 7% O₂})
\end{align*}
\]

Other acid gases such as HF and H₂SO₄ are also emitted in small amounts and collected in the system but are generally not regulated in the U.S.

The characteristic stoichiometric reaction of Ca(OH)₂ per ton of typical MSW is:

\[
\begin{align*}
\text{SO₂} & = 5.03 \text{ lbs SO₂/ton MSW} \\
\times & 1.156 \text{ lbs Ca(OH)₂/lb SO₂} \\
\text{HCl} & = 7.03 \text{ lbs HCl/ton MSW} \\
\times & 1.104 \text{ lbs Ca(OH)₂/lb HCl}
\end{align*}
\]

TOTAL = 5.815 + 7.761 = 13.576 (13.6)

Pebble Lime

\[
\begin{align*}
\text{CaO} + \text{SO₂} & \rightarrow \text{CaSO₃} \quad \text{Capture Ratio} = 56 + 64 = 0.875 \\
56 & \quad 64 \quad 120 \\
\text{CaO} + 2\text{HCl} & \rightarrow \text{CaCl₂} \quad \text{Capture Ratio} = 56 + 73 = 0.767 \\
56 & \quad 73 \quad 111 \\
\end{align*}
\]

The stoichiometry of CaO with acid gases requires:

(3) 0.875 lbs of CaO to capture 1.0 lb of SO₂
(4) 0.767 lbs of CaO to capture 1.0 lb of HCl

The following is the stoichiometric reaction of CaO for MSW: lb CaO/ton MSW

\[
\begin{align*}
\text{SO₂} & = 5.03 \text{ lbs SO₂/ton MSW} \\
\times & 0.875 \text{ lbs CaO/lb SO₂} \\
\text{HCl} & = 7.03 \text{ lbs HCl/ton MWS} \\
\times & 0.767 \text{ lbs CaO/lb HCl}
\end{align*}
\]

TOTAL = 4.401 + 5.392 = 9.793

Since CaO contains about 7% of unreactive material and inerts that are lost in the slaking process, the usage
is adjusted to compensate for impurities. The adjustment is $1.07 \times 9.793 = 10.5$.

Theoretically, a typical MWC would require 13.6 lbs of hydrated lime or 10.5 lbs of pebble lime per ton of MSW burned to capture all of the $SO_2$ and HCl emitted. However, in actual applications this never occurs. Due to the inability to provide absolute contact between the lime and the acid gases, more lime is required in the process to achieve $SO_2$ and HCl emissions of less than 25 ppm. In addition, several unwanted chemical reactions take place that also use some undefined portion of the lime. For example lime will react with carbon dioxide in the flue gas as follows:

$$Ca(OH)_2 + CO_2CaCO_2 + H_2O$$

The ratio of the actual amount of lime used to the theoretical amount required is called the stoichiometric ratio. A typical MWC equipped with a spray dryer and an ESP will require about 35 lbs of pebble lime per ton of MSW while a MWC with a spray dryer baghouse will require about 20 lbs per ton to meet the NSPS standards of 25 ppm of HCl (a 95.3% reduction) and 30 ppm of $SO_2$ (an 85.8% reduction). The stoichiometric ratio for a plant with an ESP would be:

$$35 + 10.5 = 3.33$$

Tables 2 and 3 present typical and actual acid gas emissions using Sorbalit. Typical air pollution system requirements developed by Dravo Lime’s testing program to control acid gas emission to the NSPS requirements are given in Table 4.

### Theory of Carbon Adsorption

The adsorption of mercury and organics such as dioxin into activated carbon and coke is controlled by the properties of both the carbon and the adsorbate, and by the conditions under which they are contacted. This phenomenon is generally believed to result from the diffusion of vapor molecules into the surface of the carbon. These molecules are retained at the surface in the liquid state because of intermolecular or Van der Waals forces. As the temperature falls, or as the partial pressure of the vapor above the carbon rises, the average time that a molecule resides on the surface increases. So does the fraction of the available surface covered by the adsorbate. However, the carbon surface is not uniform and consists of sites whose activities vary. More-active sites will become occupied first and, as the activity of the remaining available sites decreases, the adsorption energy will change.

The physical structure of activated carbon and coke is not known in detail, but it is believed to contain randomly distributed pores in the carbon, between which lies a complex network of irregular interconnected passages. Pores range in diameter down to a few angstroms, and provide a internal surface area from 300 to 1,000 m$^2$/gram of carbon. The volume of pores at each diameter is an important variable that directly affects carbon performance. Dia-

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**Table 2: Sorbalit’s Acid Gas Removal Capabilities**

<table>
<thead>
<tr>
<th>Plant</th>
<th>Emissions ppmv/kg</th>
<th>Gas Temperature °F</th>
<th>Sorbalit Feed Rate lbs/ton of MSW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berlin - Conditioned</td>
<td>2</td>
<td>330</td>
<td>26</td>
</tr>
<tr>
<td>Sorption</td>
<td>(4)</td>
<td>(4)</td>
<td></td>
</tr>
<tr>
<td>Schweinfurt - Spray</td>
<td>2</td>
<td>330</td>
<td>24</td>
</tr>
<tr>
<td>Dry Sorption</td>
<td>(4)</td>
<td>(4)</td>
<td></td>
</tr>
<tr>
<td>Burgau - Dry Sorption</td>
<td>8.3</td>
<td>375</td>
<td>30</td>
</tr>
<tr>
<td>Genebühlach - Dry</td>
<td>34</td>
<td>39</td>
<td>400</td>
</tr>
<tr>
<td>Sorption</td>
<td>(70)</td>
<td>(22)</td>
<td></td>
</tr>
<tr>
<td>Schönbrunn - Conditioned Dry Sorption</td>
<td>10</td>
<td>8</td>
<td>285</td>
</tr>
<tr>
<td>(20)</td>
<td></td>
<td>(7)</td>
<td></td>
</tr>
<tr>
<td>Würzburg - Dry Sorption</td>
<td>2</td>
<td>5</td>
<td>410</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>(5)</td>
<td>50</td>
</tr>
</tbody>
</table>

Note: 1. Fabric filters are used in each plant to control particulates, and flyash recirculation is employed to reduce sorbent usage. 2. Emission data in mg/Nm$^3$ is corrected to 11% O$_2$ and the ppmv is corrected to 7% O$_2$.

**Table 3: Sorbalit’s Typical Acid Gas Removal Capabilities**

<table>
<thead>
<tr>
<th>Item/Control Technology</th>
<th>Dry Sorption</th>
<th>Conditioned Dry Sorption</th>
<th>Spray Dryer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlet Gas Temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>°C</td>
<td>200 - 240</td>
<td>135 - 140</td>
<td>145 - 165</td>
</tr>
<tr>
<td>°F</td>
<td>395 - 465</td>
<td>275 - 285</td>
<td>295 - 330</td>
</tr>
<tr>
<td>Flue Gas Moisture %</td>
<td>7</td>
<td>15</td>
<td>21</td>
</tr>
<tr>
<td>$SO_2$ Emissions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inlet mg/Nm$^3$</td>
<td>650</td>
<td>280</td>
<td>400</td>
</tr>
<tr>
<td>Inlet ppmv</td>
<td>318</td>
<td>137</td>
<td>196</td>
</tr>
<tr>
<td>Outlet mg/Nm$^3$</td>
<td>70</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Outlet ppmv</td>
<td>34</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>% Removal</td>
<td>89.2</td>
<td>92.8</td>
<td>95</td>
</tr>
<tr>
<td>HCl Emissions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inlet mg/Nm$^3$</td>
<td>450</td>
<td>320</td>
<td>420</td>
</tr>
<tr>
<td>Inlet ppmv</td>
<td>390</td>
<td>278</td>
<td>364</td>
</tr>
<tr>
<td>Outlet mg/Nm$^3$</td>
<td>20</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Outlet ppmv</td>
<td>8</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>% Removal</td>
<td>95.5</td>
<td>97.5</td>
<td>98.0</td>
</tr>
<tr>
<td>Sorbalit Feed Rate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kg/ton of MSW</td>
<td>25</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>lbs/ton of MSW</td>
<td>50</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>

Note: 1. Fabric filters are used in each plant to control particulates, and flyash recirculation is employed to reduce sorbent usage. 2. Emission data in mg/Nm$^3$ is corrected to 11% O$_2$ and the ppmv is corrected to 7% O$_2$. 

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TABLE 4 AIR POLLUTION SYSTEM REQUIREMENTS DEVELOPED BY DRAVO LIME’S TESTING PROGRAM

<table>
<thead>
<tr>
<th>Technology</th>
<th>Hydrated Lime</th>
<th>Quick Lime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lbs of Sorbalit per ton of MSW</td>
<td>Stoichiometric Ratio</td>
</tr>
<tr>
<td>Spray dryer/fabric filter</td>
<td>24</td>
<td>1.76</td>
</tr>
<tr>
<td>Spray dryer/ESP</td>
<td>40</td>
<td>2.95</td>
</tr>
<tr>
<td>Dry injection/fabric</td>
<td>50</td>
<td>3.68</td>
</tr>
<tr>
<td>Conditional dry injection/fabric filter</td>
<td>24</td>
<td>1.76</td>
</tr>
</tbody>
</table>

TABLE 5 PROPERTIES OF CARBON PRODUCTS USED IN SORBALIT

<table>
<thead>
<tr>
<th>Material Source</th>
<th>Internal Surface Area (m2/g)</th>
<th>Average Pore Radius (Å)</th>
<th>Average Particle Size (micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous Coal A</td>
<td>950</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>Lignite A</td>
<td>600</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Lignite B</td>
<td>500</td>
<td>25</td>
<td>32</td>
</tr>
<tr>
<td>Lignite D</td>
<td>300</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Bituminous Coal C</td>
<td>800</td>
<td>15</td>
<td>60</td>
</tr>
</tbody>
</table>

FIG. 1 DISTRIBUTION OF PORES IN A GRAIN OF ACTIVATED CARBON

FIG. 2 STRUCTURE OF PORES IN A LIGNITE COKE PARTICLE

grams illustrating the structure of carbon particles and the adsorption of dioxin and mercury are presented in Figures 1 and 2. Physical properties of some carbon products used in Sorbalit are presented in Table 5.

Since adsorption takes place at the carbon-gas interface, the surface area of the carbon is one of the most important factors to consider. The second factor is the pore radius. Laboratory bench scale tests have shown that both increasing the surface area and the addition of sulfur compounds result in higher adsorption rates of elemental Hg. Most of the laboratory work on carbon adsorption has been done on elemental Hg, not with the Hg compounds we normally see in MWC emissions and without humidification.

Field tests at MWCs injection carbon products with a wide range of surface areas have shown that there is not a significant improvement in Hg (total) capture based on the increased carbon surface area. It is important that laboratory programs be developed that simulate field conditions to consider the effects of the surface area of various products. Since high surface area products are more expensive, their performance advantages and cost trade-offs have to be demonstrated.

However, the surface area must be available in the proper range of pore sizes. If too much of the area is available in pores smaller than 5 Å, many molecules will be unable to penetrate the pores and that area of the carbon will essentially be unavailable for adsorption. For most pollution-control applications, the surface areas of pores whose diameters range between 5 and 50 Å yield good efficiency rates because the relative pressure of the vapor is usually too low for the larger pores to become filled.
At high relative pressures, however, the total pore volume becomes important because the macropores also become active.

The adsorption of benzene, for example, has been shown to be affected by pore size distribution. At high benzene concentrations, carbons in which large pores predominate have higher capacities than those in which medium or small pores predominate. But at low concentrations, the large-pore carbon has a lower capacity. The size of the molecules of mercury is approximately 4.5 Å and the dioxin molecule is 10 Å x 3 Å. Both molecules are adsorbed in different parts of the carbon particle. In theory, dioxins are collected in the macropores while the mercury is collected in the micropores. Dioxin, being larger, blocks the passages, preventing mercury from entering the micropores. To increase the mercury capture rate, the amount of carbon used must be significantly increased, the surface area of the carbon must be increased, or sulfur added.

The carbon/mercury balance has been established through Märker’s laboratory experiments. They found that under ideal conditions, three grams of carbon will adsorb one gram of mercury. However, in operating facilities considerably more carbon is required to reduce Hg emissions from 600 µg/Nm³ to 70 µg/Nm³, approximately 300 grams of carbon per gram of Hg are used in MWC applications with a baghouse operating at 135°C.

The actual adsorption capacity of carbon is affected by:

- Gas temperature
- Flue gas moisture
- Inlet concentrations of Hg
- Species of Hg
- Acid content of the flue gas
- Concentration of organics such as dioxin
- Type of carbon used and surface area
- Contact time

The effects of each of these variables has not been quantified. However, through trial and error we have demonstrated the relative effect that flue gas temperature has on Hg adsorption. A temperature correlation curve is presented in Figure 3. Another way of illustrating this impact is by showing the carbon adsorption requirement at different temperatures. The following data has been developed by Märker Umwelttechnik.

<table>
<thead>
<tr>
<th>Carbon/Coke Adsorption</th>
<th>Flue Gas °C</th>
<th>gC/gHg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>135–145</td>
<td>300–400</td>
</tr>
<tr>
<td></td>
<td>145–165</td>
<td>400–500</td>
</tr>
<tr>
<td></td>
<td>165–185</td>
<td>500–600</td>
</tr>
<tr>
<td></td>
<td>185–200</td>
<td>600–800</td>
</tr>
</tbody>
</table>

Theory of Sulfur Adsorption

The addition of sulfur compounds to the process plays a major role in the adsorption of mercury but not in the adsorption of dioxin. Sulfur’s role in the adsorption is two fold, first the sulfur compounds maintain the active state of the carbon. Activity is defined as the amount of open pores in the carbon. Sulfur’s role is to keep these pores open and to allow the mercury to get into the sub-structure pores. The exact process in which the sulfur keeps the pores open has not been defined. One theory is that the sulfur reacts with water which is adsorbed or is on the surface of the carbon particles to form an acid that penetrates the pores. No measurable acids have been observed when applying Sorbalit, most likely because any excess acids would react with the lime.

The second role for sulfur is converting elemental mercury (Hg⁰) to a sulfate. Hg⁰ is more difficult to capture than Hg₂Cl₂, which is the predominate species in MWC emissions⁶ or Hg₂SO₄. Hg⁰ accounts for only 5 to 10% of the total mercury emissions from an MWC. Flue gas constituents such as SO₂ can reduce the dissolved HgCl₂ to Hg⁰ that is driven into the gas stream due to its poor solubility.

\[
\text{SO}_2 + 2 \text{HgCl}_2 + \text{H}_2\text{O} \Rightarrow \text{SO}_3 + \text{Hg}_2\text{Cl}_2 + 2 \text{HCl}
\]

\[
\text{Hg}_2\text{Cl}_2 \Rightarrow \text{HgCl}_2 + \text{Hg} \uparrow
\]

The adsorption capacity of carbon is affected by formation of sulfuric acid on the carbon owing to adsorption of the flue gas constituents SO₂ and H₂O:

\[
\text{SO}_2,\text{gas} \Rightarrow \text{SO}_2,\text{ads}
\]

\[
\text{SO}_2,\text{ads} + \frac{1}{2}\text{O}_2,\text{ads} \Rightarrow \text{SO}_3,\text{ads}
\]

\[
\text{SO}_3,\text{ads} + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{SO}_4,\text{ads}
\]
Elemental mercury then reacts with the sulfuric acid to form mercurous sulfate (Hg$_2$SO$_4$) or in the presence of excess acid mercuric sulfate (HgSO$_4$):

$$2\text{Hg} + 2\text{H}_2\text{SO}_4,\text{ads} \rightarrow \text{Hg}_2\text{SO}_4,\text{ads} + 2\text{H}_2\text{O} + \text{SO}_2$$

or

$$\text{Hg}_2\text{SO}_4,\text{ads} + 2\text{H}_2\text{SO}_4,\text{ads} \rightarrow 2\text{HgSO}_4,\text{ads} + 2\text{H}_2\text{O} + \text{SO}_2$$

Since the lime component of Sorbalit removes the SO$_2$ from the flue gas, some adsorption capacity of the carbon for Hg$^2+$ is diminished. The sulfur component in Sorbalit added during manufacturing, replaces the missing SO$_2$ and enhances the adsorption of Hg$^2+$. Mercuric chloride does not react with the sulfuric acid, but is dissolved in sulfuric acid. No studies concerning the necessary sulfuric acid loading for quantitative precipitation of mercury have been made.

**AREAS OF APPLICATION**

In its simplest form, the air pollution control system consists of a duct or pipe, through which Sorbalit is injected into the flue gas, and a fabric filter or ESP located downstream. This simple solution has an economic advantage because it is easily integrated into existing plants without having to expend significant capital for new equipment.

The following Section deals with the applications for the air pollution control systems employed in various waste treatment plants. Systems which are typically used in the U.S. include dry injection, water conditioning followed by dry injection, and spray dryer technologies. Applications of Sorbalit using these three technologies are illustrated in Drawings 1, 2 and 3. Sorbalit is also employed in several wet scrubbing applications in Europe such as the waste-to-energy plant in Zirndorf, Germany. A description of the wet scrubbing technologies will be presented in another paper.

**Dry Sorption Process**

**Würzburg Waste-to-Energy Plant.** The waste-to-energy plant at Würzburg has two process lines for converting municipal solid waste to energy. Each line has a capacity of 12.5 Mg/h (330 TID). The temperature of the flue gas down stream of the boiler is reduced to 180 to 200°C (356 to 392°F) by means of water cooling.

Before the conversion to the Sorbalit System, hydrated lime was injected into a fluidized bed reactor to control the emission of acid gases. The fluidized bed reactor acted as a preliminary gas reactor before the flue gases were cleaned in a pulse jet fabric filter. In the spring of 1989, tests were conducted to evaluate switching from hydrated lime to Sorbalit with 3% carbon. The Sorbalit usage rate was the same as the hydrated lime feed rate (20–25 kg/t). The dioxin and furan emissions were reduced from 9–10 ngTEQ/Nm$^3$ (NATO toxic equivalents) when hydrated lime was used to 0.02–0.06 ngTEQ/Nm$^3$ when Sorbalit was used, a 99% reduction. All test were conducted using VDI methods. Test data presented in this report has been selected to show the range of emission data from numerous test. Detail test reports can be provided.

Sorbalt also demonstrated a reduction in mercury emissions. As shown in Figure 4, the use of Sorbalit reduces the emission of mercury to a level below the German limit
of 50 μg/Nm³ at 11% O₂. What is remarkable is the fact that this result was achieved without any modification of the equipment configuration. The reduction of Hg is limited by the high flue gas temperature of the facility. Unfortunately, due to a design limitation that may result in potential corrosion, the flue gas temperature cannot be lowered, which would reduce the emission of mercury and lowering their consumption rate of Sorbalit.

**Dry/Wet Conditioned Sorption Process**

**Marion County Waste-to-Energy Plant.** In July of 1992 Sorbalit was tested at Ogden Martin's waste-to-energy facility in Marion County, Oregon. Tests were conducted on Unit #1 which is rated at 10.4 Mg/h (275 T/D) of MSW. The air pollution control system consists of a Research-Cottrell/Teller spray dryer and a fabric filter. During the test program up to .75 Mg/h (20 T/D) of medical waste was also combusted in the units.

Sorbait was injected dry after the spray dryers in the dry venturi feed duct and before the pulse jet fabric filter at a flue gas temperature of 148°C (300°F). All mercury emission tests were performed according to EPA Method 101A. Seven efficiency tests were performed over the four day test program. The inlet concentration averaged 935 μg/dscm³ @12% CO₂ and ranged from 508 to 2,695 μg/dscm³ @12% CO₂. The outlet emissions averaged 131 μg/dscm³ @12% CO₂ and ranged from 10 to 465 μg/dscm³ @12% CO₂. The average Hg removal efficiency for the test program was 87.7%.

**Hazardous Waste Incineration Plant Schöneiche/Berlin.** The incineration plant at Schöneiche near Berlin, in the former GDR, has a hazardous waste capacity of 2.3 Mg/h (60 T/D). Flue gases downstream of the boiler are cooled to a temperature of 140°C (284°F) by water sprays. The gas volume rate during the test was 31,000 Nm³/h (19,657 sf³/m³).

The plant decided to use the carbon enhanced lime technology because it was the only way in which the approved limits for mercury could be achieved without the addition of new control equipment. Before the use of Sorbalit, hydrated lime was employed as the adsorbing agent. Mercury test measurements made in January 1990, on the untreated flue gases before and after the injection of Sorbalit are shown in Figure 5. The measurements showed that reductions in Hg emissions in excess of 88% were achieved in tests conducted by the Berlin Technical Control Association (TÜV) using VDI methods. A complete summary of the most important results of the test program has been prepared by Jungmann of Zurich. These figures represent values well below the maximum emission limit for mercury as stipulated in the German's 17th Federal Pollution Control Directive (17.BimSchV). Since the initial test over 80 measurements for mercury have been made, confirming the initial test results.

These operational tests were conducted with a substantially lower carbon content in the Sorbalit than in the original laboratory experiments. The field tests with a Sorbalit mixture with 3% carbon demonstrated better results than the laboratory tests conducted with hydrated lime and 10% carbon. The laboratory experiments were conducted using elemental Hg which is more difficult to capture than chlorides and sulfates, and the experiments were not conducted using humidified gas. The differences between the operating conditions and the experiments most likely resulted in the improved performance with 3% carbon.

Figure 6 shows the respective levels of the dioxin and furan concentrations in the untreated and in the cleaned flue gases. The dioxin concentration in the Sorbalit treated flue gas was undetectable in some cases. The removal rate fluctuated from 95.6 to 100%.

Concentrations of polychlorinated biphenyls (PCBs) in the untreated and in the cleaned flue gas were also measured. The values are shown in Table 6. The level of PCB content in the untreated flue gas was 130 ng/Nm³. Various types of PCBs were no longer detectable in the cleaned flue gas.

The high rate of removal of the PCBs also leads us to the assumption that additional heavy superchlorinated
compounds, such as hexachlorobenzene and hexachlorocyclohexane, are removed from the flue gases. Separation rates for the polyaromatic hydrocarbons cannot be established until the relevant measurements are available; however, high levels of removal are expected.

It should be emphasized again that these levels for the treated cleaned flue gases were attained without any modifications to the plant or the air pollution control system. The viability of the concept of improving a flue gas cleaning system via the use of modified hydrated lime with carbon is thus confirmed. The air pollution control system at the Schöneiche hazardous waste incineration plant has been using Sorbalit since December 1989. About 50 dioxin measurements have been taken since; never have the limits been exceeded.

**Spray Dryer Systems**

**Hazardous Waste Incineration Plant Schweinfurt.** At the hazardous waste plant at Schweinfurt 2.5 Mg/h (66 T/D) of hazardous waste are converted to energy. The flue gas volume rate is 28,000 Nm$^3$/h (17,755 sft$^3$/m). The original plant consists of a pebble lime slurry preparation plant (slaker) with a spray dryer and a pulse jet fabric filter. In the retrofit, instead of the traditional lime slurry, a Sorbalit with 3% carbon suspension was employed, with no further modifications to the plant being employed. Test results showing the range of emission reductions are presented in Figure 7 for dioxin and in Figure 8 for mercury. Based on these results, the test program was immediately followed by continuous operation.

**Coburg Waste-to-Energy Plant.** The Coburg plant uses Sorbalit made with quick lime rather than hydrated lime. The plant uses a standard slaker to make the slurry for their spray dryer. Results of the performance test will be published after review by the Bavarian EPA has been competed.

**Particulate Collection**

The use of fabric filters is particularly effective. Residual dust levels of $<10$ mg/Nm$^3$ (0.004 gr/sft$^3$) at 11% $O_2$ can be attained and, values of 1 mg/Nm$^3$ (0.0004 gr/sft$^3$)
are quite realistic. This separating capacity is also important regarding the use of Sorbalit, as it means that Sorbalit, to which the separated pollutants are attached, is not emitted, and sorbent usage is reduced.

As a rule of thumb, an ESP requires two to three times the amount of carbon to achieve the same results in Hg reduction as a fabric filter. An economic comparison can be made in a retrofit application on the trade-off of increased operating cost versus the capital cost for installing a fabric filter and associated down time for replacement.

CONCLUSIONS

The objective of the development concept was to modify the lime-based sorbents previously employed at various sources of combustion in a way that makes it suitable as a carrier for absorption materials and to minimize the emissions of toxic substances. This paper has described and presented the operating results from various combustion facilities.

When Sorbalit is employed, the following emission values have been reliably attained:

- <50 g Hg/Nm³ for mercury at 11% O₂ (70 µg/Nm³ at 7% O₂)
- <0.1 ng TEQ/Nm³ for dioxin and furans at 11% O₂
- Reduction to the detectable limit for PCBs
- EPA’s New Source Performance Standards and Emission Guidelines for SO₂ and HCl

Furthermore, the use of this technology in waste combustion processes produces considerable advantages regarding the process engineering and modification to the facilities involved. Sorbalit can be stored and added using standard lime and hydrated lime handling equipment. In retrofit applications where lime or hydrated lime are used, no new equipment may be required. Material handling equipment in most facilities, from the supply silo through conveying and dosing equipment to the mixing lines, filters, and flow controllers, all remain in use.

The gas cleaning process, that is, the injection of Sorbalit into the flue gas flow, followed by vortexing of the flow and subsequent separation on the fabric filter or ESP, can be installed as a “Sorbalit System” downstream of any combustion plant. Many areas of application are envisioned for Sorbalit in the field of flue gas cleaning, some of which have already been put in to practice. Test results for various applications are shown in Table 7.

The Sorbalit system for separating volatile inorganic and organic substances can be integrated into the flue gas cleaning systems of the following processes:

- Solid and hazardous waste incineration plants
- Sewage/sludge incineration plants

Sorbalt is effective in removing mercury over a wide range of operating conditions and applications. Figure 9 presents a graphic summation of test data from European facilities and the Marion County test program. This summary includes dry, dry/wet conditioned and spray dryer equipped plants and clearly shows the effectiveness of the Sorbalit System. The test data indicates that two of the key parameters in deciding the overall removal efficiency of mercury are the inlet concentration and the temperature of the flue gas.

Drawings 4 and 5 show two recent developments in the Sorbalit System that are specific for retrofitting U.S. spray dryer applications. Drawing 4 illustrates the application of...
Sorbait manufactured with quick lime. Drawing 5 shows the application of adding a concentrated form of Sorbalit to an existing facility. This was accomplished by simply adding one storage silo and one mixing tank to the system.

The data in this paper have demonstrated that Sorbalit has the flexibility to be integrated into many existing U.S. applications and systems. Additional information on new systems and wet scrubbers will be published in the near future.

REFERENCES


