

THE APPLICATION OF ACTIVATED CARBON ENHANCED LIME FOR CONTROLLING ACID GASES, MERCURY, AND DIOXINS FROM MWCs

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INTRODUCTION

Environmental control agencies have sought to reduce Municipal Waste Combustor (MWC) 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 for MWCs.

Sorbalit® is an activated carbon enhanced lime process that reduces MWC emissions and has been successfully 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.

This paper presents 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.

THE SORBALIT SYSTEM

Sorbalit 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 operational requirements of each project.

The Sorbalit process produces a homogeneous formulation containing calcium, carbon, and sulfur compounds that will not dissociate (demix) when used, either in a slurry or dry form. It is particularly important to avoid flotation or separation of the carbon and sulfur substances that have been added to the lime. To maintain product quality and effective levels of air pollution control, the components must stay as a uniform mix from the manufacturing process through transportation and use in the air pollution control system.

Theory of Lime Adsorption

Lime is the largest component of Sorbalit and has the primary role of adsorption of the acid gases present in the flue gas such as SO_2 , HCl, and HF. 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. 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 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 that results in a 25% solids slurry.

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 m²/gram of carbon. The volume of pores at each diameter is an important variable that directly affects carbon performance. Diagrams illustrating the structure of carbon particles and the adsorption of dioxin and mercury are presented in Figures 1 and 2.

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 distribution. 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 mercury (Hg⁰). Most of the laboratory work on carbon adsorption has been done on Hg⁰, not with the Hg compounds we normally see in MWC emissions and without humidification.

Field tests at MWCs injected with 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 Hg⁰ molecule 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 laboratory experiments where 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

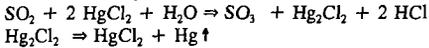
The effects of each of these variables has not been quantified. However, field test programs have demonstrated the relative effect that flue gas temperature has on Hg adsorption as follows:

<u>Carbon/Coke Adsorption</u>	
<u>Flue Gas °C</u>	<u>gC/ gHg</u>
135 - 145	300 - 400
145 - 165	400 - 500
165 - 185	500 - 600
185 - 200	600 - 800

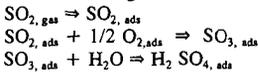
Theory of Sulfur Adsorption

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.

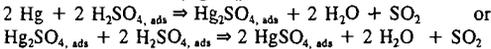
The second role for sulfur is converting Hg^0 to a sulfate. Hg^0 is more difficult to capture than Hg_2Cl_2 , which is the predominant species in MWC emissions or Hg_2SO_4 . Hg^0 accounts for only 5% to 10% of the total mercury emissions from an MWC. Flue gas constituents such as SO_2 can reduce the dissolved $HgCl_2$ to Hg^0 that is driven into the gas stream due to its poor solubility.



The adsorption capacity of carbon is affected by formation of sulfuric acid on the carbon owing to adsorption of the flue gas constituents SO_2 and H_2O :



Hg^0 then reacts with the sulfuric acid to form mercurous sulfate (Hg_2SO_4) or in the presence of excess acid mercuric sulfate ($HgSO_4$):



Since the lime component of Sorbalit removes the SO_2 from the flue gas, some adsorption capacity of the carbon for Hg^0 is diminished. The sulfur component in Sorbalit added during manufacturing, replaces the missing SO_2 and enhances the adsorption of Hg^0 . Mercuric chloride does not react with the sulfuric acid, but is dissolved in sulfuric acid.

Recent tests have demonstrated the significance that sulfur plays in capturing Hg. The test program conducted at the Marion County, OR MWC showed Sorbalit captured more Hg (total and vapor phase) than dry carbon injection. To determine the equivalent performance of carbon and Sorbalit, both were injected at the same carbon feed rate of 5 lbs/hr. Sorbalit captured 87.7% of the total Hg while carbon injection captured 84.2%. More importantly, Sorbalit captured 83.2% of the vapor phase Hg while carbon collected 77.6%.

Hg emissions from coal fired plants are significantly different in two ways from those of MWCs. First, the uncontrolled Hg emissions from U.S. eastern coal ranges from 8 to 30 $\mu g/dscm$ while a typical mass burn MWC would emit 600 $\mu g/dscm$. Secondly, since there is a relatively low chlorine content in coal, the percentage of vapor phase Hg is much higher than in a MWC. As a result, the capture of Hg emissions is more difficult via dry injection. In a test program on a coal fired plant, Sorbalit captured between 44% to 55% of the vapor phase Hg while carbon injection only captured 10% to 15%. These tests were conducted under difficult Hg capture conditions: high temperatures and low moisture.

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 down stream. This simple solution has an economic advantage because it is easily integrated into existing plants without having to expend significant capital for new equipment.

This Section deals with the applications for the air pollution control systems employed in various waste treatment plants. Systems which are typically used in MWCs include dry injection, water conditioning followed by dry injection, and spray dryer technologies. Since spray dryer application will become standard practice in the U.S. we will only present data on this technology. Data on other technologies has been previously published.

MWC Marion County, OR

In July of 1992 Sorbalit was tested at an MWC in Marion County, Oregon. Tests were conducted on Unit #1 which is rated at 10.4 Mt/h (275 T/D) of MSW. The air pollution control system consists of a spray dryer and a fabric filter. During the test program, up to .75 Mt/h (20 T/D) of medical waste was also combusted in the units.

Sorbalit 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). 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 Mt/h (60 T/D). Flue gases down stream 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 scfm). 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 Table 1. The measurements showed that reductions in Hg emissions were in excess of 88%. 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.

The Table 1 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.

Concentrations of polychlorinated biphenyls (PCBs) in the untreated and in the cleaned flue gas were also measured. The values are shown in Table 1. 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.

Hazardous Waste Incineration Plant Schweinfurt

At the hazardous waste plant at Schweinfurt 2.5 Mt/h (66 T/D) of hazardous waste are converted to energy. The flue gas volume rate is 28,000 Nm³/h (17,755 scfm). 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 for dioxin and mercury are presented in Table 1. Based on these results, the test program was immediately followed by continuous operation.

CONCLUSIONS

When an activated carbon enhanced lime product such as Sorbalit is employed, the following emission values have been reliably attained:

- < 50 µg 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 NSPS and Emission Guidelines for SO₂ and HCl

Furthermore, the use of this technology in waste combustion processes obtains a number of advantages in 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 is 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 into practice. Activated carbon enhanced lime technology used for separating volatile inorganic and organic substances can be integrated into the flue gas cleaning systems of the following processes:

- Solid & hazardous waste incineration plants
- Sewage/sludge incineration plants
- Coal fired power plants
- Aluminum smelting plants
- Wood drying plants
- Steel mills
- Glass/ceramic furnaces
- Wood fired boilers

Sorbalit is effective in removing mercury over a wide range of operating conditions and applications. 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.

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.

Table 1

Pollutant		Schöneleche Test			Schweinfurt Test		
		Inlet	Outlet	% Removal	Inlet	Outlet	% Removal
Total PCBs	ng/Nm ³	130	> 1 (nd)	N/A	-	-	-
Dioxins ITEQ	ng/Nm ³	1.74	0.02	98.8	11.59	0.085	99.2
Dioxins ITEQ	ng/Nm ³	0.34	nd	N/A	6.79	0.06	91.1
Hg	μg/Nm ³	250.9	29	88.4	765	47	93.8
Hg	μg/Nm ³	180	2.5	98.6	40	8	80.0

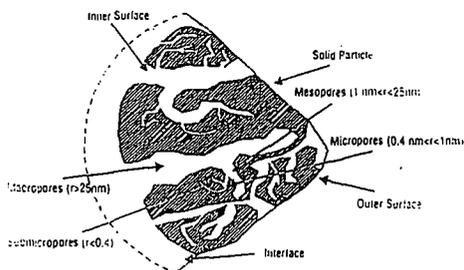


Figure 1: Distribution of pores in a grain of activated carbon

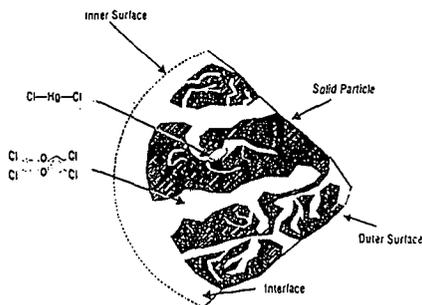


Figure 2: Structure of pores in a light coke particle