NUCON International, Inc.

P.O. BOX 29151 7000 HUNTLEY ROAD
COLUMBUS, OHIO 43229 U.S.A.

Fixed Bed Adsorption for Mercury Control

By

Joseph C. Enneking
Clinton B Summers

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Joseph C. Enneking, NUCON International Inc., 7000 Huntley Rd., Columbus, OH 43229

Clinton B. Summers, NUCON International Inc., 7000 Huntley Rd., Columbus, OH 43229

Abstract

When it is necessary to remove mercury from effluent streams, the concentrations are normally very low and the species can vary. While wet scrubbing processes can be useful and are sometimes employed to remove other contaminants, adsorption is normally more appropriate for mercury. While many adsorbents are effective in removing the oxidized forms of mercury, impregnated activated carbon is the most effective for elemental mercury.

Physical adsorption of mercury on activated carbon is a reversible process. When the carbon is impregnated with sulfur or a sulfide salt, irreversible chemisorption is operative. The result is that the adsorbent has a very high capacity for removing mercury. The type of activated carbon and the appropriate impregnant has a significant impact on the performance. Process conditions such as temperature, residence times, type of fluid, and mercury concentration impact the performance and life of the adsorbent.

Operating results from a year long test of removal efficiency and adsorption capacity in a column of mercury adsorbent will be presented. Additional studies showing the impact of residence time, bed geometry and adsorbent particle size will be summarized. A variety of laboratory and pilot plant studies have been conducted by different organizations and they will be discussed. Typical applications for this approach to mercury control will be discussed.

Introduction

Mercury is hazardous. The Threshold Limit Values-Time Weighted Average (TLV-TWA), established by AIGCH, is 0.05 mg mercury per cubic meter air.[1] The typical concentration of mercury found in urban air is 0.000007 mg mercury per cubic meter.[2] (In remote and rural areas it is approximately 10% of that level). These levels are considered harmless because they are 10 million times less than the TLV. However, in some industrial environments, concentrations as high as 5 mg per cubic meter of air have been measured. This is 100 times the TLV. In addition, mercury in the atmosphere is eventually deposited to the earth's surface, either through dry or wet deposition (rain or snow). When mercury falls from the air or runs off the ground into the water, certain microorganisms in soils and sediments convert some part of it into methylmercury, a highly toxic form of mercury

The USEPA has taken a number of actions to reduce mercury pollution, including issuing stringent regulations for industries that contribute to U.S. mercury emissions. These regulations eventually will reduce nationwide mercury emissions significantly.

Fixed bed adsorption is the best control technology for many sources of mercury emissions. Mining and other metallurgic activities involving the extraction and processing of virgin and recycled mineral materials result in the release of vapor phase mercury that can be toxic to workers and can exceed emission controls. Mercury mining and small-scale gold and silver mining result in mercury contamination of both water and air. Fluorescent lamps have mercury as a component and their manufacture, use and disposal can result in mercury emissions. Many other products contain mercury such as thermometers, manometers, electrical and electronic switches, and other instruments. Waste incinerators (municipal, medical and hazardous wastes) generally have low volume gas emissions along with stringent effluent mercury standards. Fixed bed adsorption technology easily meets MACT standards.

The technology associated with adsorption is not widely practiced. In order to help people make a preliminary decision about the effectiveness of this approach, a proven approach to experimentation, scale-up, process design parameters, mechanical design and operating characteristics is needed. There has been a wide variety of technical information published on the powder injection methods for coal fired power plants, but there is little available for fixed bed adsorption. The purpose of this paper is to provide that type of information.

Emission Control Methods

The source of mercury may be the feed material itself. This includes coal for power plants and the mixed waste destroyed in hazardous waste combustors. The allowable emissions are ordinarily expressed in concentration or total mass allowed. In either case, selecting or blending the feed materials can provide control over the amount of emissions.

Another effective way of controlling toxic emissions is the use of a liquid phase scrubber. This is a common approach for SOX and NOX control. At coal-fired power plants where these systems are employed along with particulate control, the mercury levels may be reduced to acceptable levels. When this is not effective enough, powdered adsorbent injection can result in a further decrease in mercury emissions. This method is also used in hazardous waste incinerators and is very effective when the oxidized form of the mercury is present. When this approach is not good enough, fixed beds of mercury adsorbent are appropriate because the gas flows are normally low.

With extremely high gas flow rates such as in coal-fired power plants, fixed beds are generally impractical. A better approach for controlling mercury emissions, is to inject powdered adsorbent into the gas stream and remove it in either the electrostatic precipitators or the bag house. Relatively high temperatures (350 °F) and short residence times (seconds) result in relatively poor utilization of the adsorbent. However, this approach has been shown to be technically effective in meeting the proposed standards.

The use of fixed beds of adsorbent to remove small quantities of contaminants from a fluid stream is a standard approach. It finds widespread use in VOC control where the adsorbent is either regenerated in place or discarded after use. In the liquid phase, wastewater from utilities and industrial plants are treated in fixed beds. After the carbon has become saturated, it can be reactivated for reuse.

When mercury adsorbent is used in fixed beds to control mercury emissions from various sources, it is usually contained in vertical cylindrical beds. If conditions are such that the life of the adsorbent will be many years, single beds are usually used. When the mercury concentrations are high and the life is relatively short, dual beds are used, normally in series, so that the lead bed can be used until it is saturated with the mercury. It is then changed out while the other bed operates and the fresh bed is placed in the lag position.

When the fluid is a gas, the residence time to achieve the required outlet concentration is relatively short, on the order of a few seconds. Since the adsorption capacity is quite high, the service life of a charge of adsorbent can be on the order of several years. This results in a relatively trouble free operation since it is completely passive with no rotating or moving equipment. Operation is also simple for liquid phase applications. In this case, though the residence time required is much higher, fractions of an hour instead of fractions of a minute. Therefore the amount of adsorbent is relatively large. The adsorption capacity for mercury in the liquid phase is low and therefore the change out time is considerably shorter than for the gas phase applications.

Since the adsorbent can filter out particles and become plugged up, it is advisable to provide filtration on the inlet stream. Mercury can also attach itself to particles and can be present in adsorbent particles that are liberated from the beds. Therefore, to achieve the relatively low total mercury concentrations required by environmental laws, it is also necessary to install filters downstream of the adsorbent beds.

Adsorbents and Their Performance

While there are multiple adsorptive media used for the removal of mercury available[7], activated carbon is the most commonly used. Depending on the process and the configuration used, the activated carbon is either added to a waste water in powdered form (PAC), or the waste water is passed through a stationary bed of granular or pelleted activated carbon (GAC). One drawback to the use of PAC is the need for additional steps after the adsorption of the mercury (sedimentation or filtration), to complete the mercury removal process.

No matter the form of activated carbon used, the basic process remains the same. Initially, there is physical adsorption of the mercury onto the internal surface area of the carbon. Physical adsorption proceeds well on most activated carbons if mercury is present in an oxidized form and will be related to the surface area and surface chemistry of the activated carbon. This is a reversible process. Simple physical adsorption does not, however, provide adequate removal of elemental mercury in an aqueous waste stream.

For waste streams containing elemental mercury, activated carbons that have been impregnated with compounds that can react with the elemental mercury are much more

efficient. The irreversible chemisorption of elemental mercury by impregnants such as elemental sulfur, metal sulfides, or halide salts (principally KI) dramatically improves the removal of mercury from waste streams. Additionally, impregnated carbons used for the chemisorption of elemental mercury still have sufficient surface area for the physical adsorption of oxidized forms of mercury. In terms of performance, the most important factors will be the surface area of the activated carbon used, the specific impregnant used and the concentration on the carbon surface (usually expressed as a percent, by weight), the concentrations of oxidized and elemental mercury in the waste stream. Additionally, pH, temperature, residence times and other process factors have an effect on the removal of mercury, and should be considered in the selection of adsorbent and process design.

Laboratory Studies and Data

Mercury removal efficiency and adsorption capacity testing, using radioactive mercury, have been performed in the NUCON radioisotope laboratory using ^{159}Hg. The adsorbent was sulfur impregnated pelleted activated carbon made from coal. The tests were performed under the following test conditions.

Table 1 NUCON Laboratory Test Conditions

Gas	Air
Temperature:	30° C
Bed Diameter:	25 mm
Bed Depth:	150 mm
Particle Size:	3 mm pellets
Inlet Concentration:	32 mg Hg./m^3 air
Pressure:	1 atm
Linear Velocity:	3 ft./min.

Tests were conducted using six bed segments, each being 25 mm deep and 25 mm diameter. Samples of gas were taken between each segment so measurements of removal efficiency were made at different residence times. The radioactive isotope content of the samples of gas between the segments was analyzed at periodic intervals. The results of the tests for mercury removal from air are shown in Figure 1.

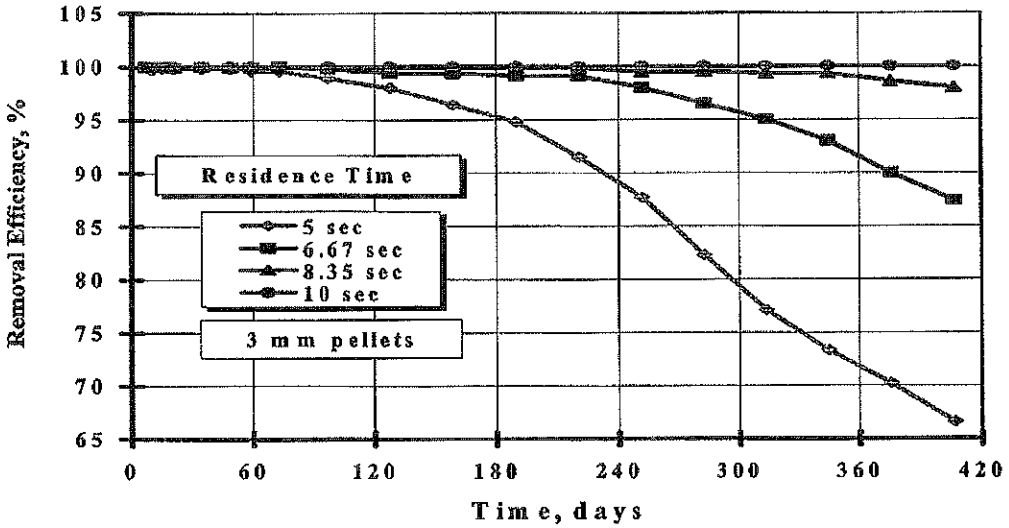

Figure 1 – Mercury Removal Efficiency from Air at Various Residence Times

Even with the very high inlet concentration, the removal efficiency at 10 seconds residence time was 100% after one year of operation.
At the end of the test, the mercury content was measured in each of the bed segments.

Table 2 Adsorption Capacity for Mercury

Bed Segment No.	Amount Adsorbed, g Hg/100 g adsorbent
1	23
2	19
3	15
4	15
5	14
6	0.3

The equilibrium adsorption capacity of 20 g mercury/100 g adsorbent has been repeated in a medium scale pilot plant test used to evaluate the Thor process for destruction of mixed wastes.

The Idaho National Laboratories (INEL) were charged with investigating methods of controlling mercury emissions from the mixed waste incinerators that were being

considered for various DOE installations. After a search of the technical literature, they concluded that a fixed bed of mercury adsorbent would be the best approach. They then assembled laboratory and bench scale adsorption systems to obtain design data for the full-scale units. The results of these tests have been published.[3,4] Operating parameters and test results are shown below:

Table 3 INEL Test Results

Report No.	INEEL/EXT 03-01102	INEEL/EXT 04-01625
Gas	Inert Off Gas	Inert Off Gas
Impurities	NO_2, HCL	
Mercury Conc., mg/cu m	10	16
Temperature, °C	150	107
Residence Time, sec	0.99	0.63
Test Duration, hr	1000	100
Mercury Removal Eff., %	99.9	99.997

The new linear accelerator installed at Oak Ridge national laboratories is designated the "Spallation Neutron Source" (SNS). During operation it emits mercury vapors that are not only toxic but radioactive as well. A system for controlling these mercury emissions had to be installed. To obtain design data for this system laboratory experiments were run to choose the type of carbon and to set operating parameters. This project was performed by ADA Technologies Inc and reported in SNS-108030700-TR0002-R00.[5] As a result of this test program, a 1.5 mm sulfur impregnated activated carbon pelleted product was chosen. The laboratory test results are shown below:

Table 4 SNS Test Results

Gas	Air
Mercury Conc., mg/cu m	0.055
Temperature, °C	38
Residence Time, sec	0.7
Test Duration, hr	60
Mercury Removal Eff., %	99.8

The complete system has been designed and installed at Oak Ridge and is in operation.

The Plasma Enhanced Melter (PEM™), developed by Integrated Environmental Technologies, LLC, is a high temperature technology that addresses dioxin generation and mercury emissions. A bench scale test of the technology was run using medical waste as the feed material. The mercury adsorbent beds achieved a very high removal efficiency under the following conditions.

Table 5 PEM Test Results

Gas Composition:	Syngas
Temperature:	30 °C
Residence time:	20 sec
Inlet mercury concentration:	1300 micro g/dscm
Outlet mercury Concentration:	0.4 micro g/dscm
System Efficiency:	99.99%

Laboratory experiments have been run to show the adsorption capacity of the sulfur impregnated activated carbons for mercury from water.

Design Factors

The design of a mercury adsorbent bed is based on several operating parameters.

The amount of carbon required to attain a given removal efficiency is selected by choosing a residence time. Laboratory test results are an accurate indicator of the performance of a full-scale unit. Therefore, if a 5 second residence time produces a 99.99% removal in the laboratory test, the system can be designed using the same value. The formula is:

$M = 0.583FR$ where

M = mass of carbon in lbs,
F = flow rate in cfm
R = residence time in seconds.

The pressure drop through the activated carbon bed is an important factor in design. For gas phase applications, in order to minimize the cost of energy to operate the fans, the pressure drop through the carbon beds is critical. It varies with velocity through the bed, particle size of the carbon, and the depth of the bed. Pressure drop curves for three typical pellet sizes are shown in figure 2

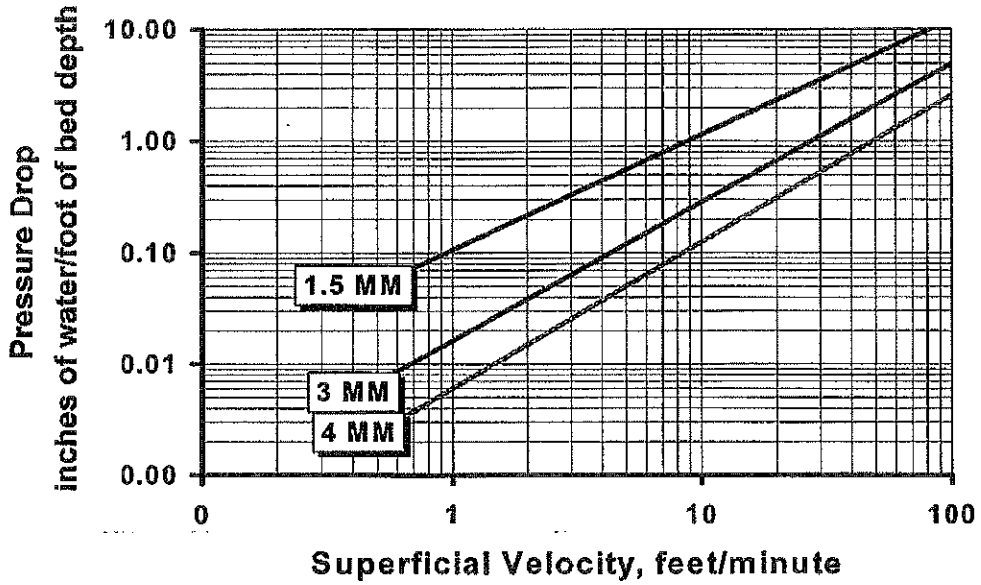

Figure 2 Gas Phase Pressure Drop in a Bed of Pelleted Carbon

For liquid phase, the criterion for selecting the size of the bed is also the residence time. Pressure drop is also an important criterion and a curve for two different pellet sizes in water is shown in Figure 3.

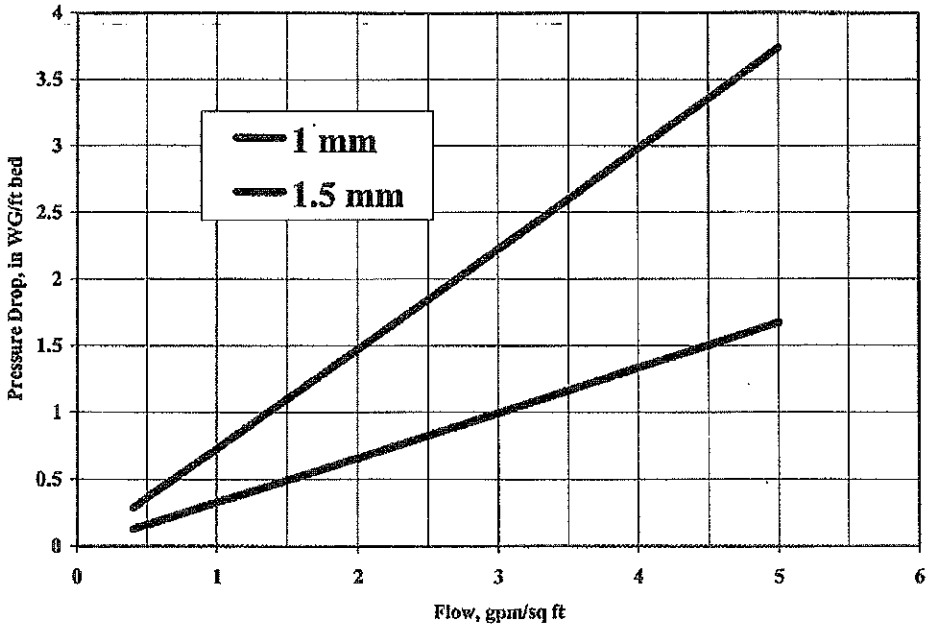

Figure 3 Aqueous Phase Pressure Drop in a Bed of Pelleted Carbon

The flow in most liquid phase systems is upflow. Care must be taken not to exceed the lifting velocity of the carbon. If it exceeds 2 gpm/sq ft, then downflow should be used. The maximum recommended flow rate is 5 gpm/sq ft.

The expected life of the adsorbent is determined by the quantity of mercury in the inlet fluid stream and the dynamic adsorption capacity of the carbon.

L=W/C where

L = life in years
W = mass flow of mercury, lbs/year
C = working capacity, lbs mercury/lb carbon

Since the capacity of the carbon is relatively independent of mercury concentration, the life of the carbon when the concentration is low can be quite long, on the order of many years. Even with high concentrations, the life is long enough that carbon consumption is relatively low and the expense of discarding the spent carbon is minimal.

The selection of the type and orientation of the adsorber will depend on the specifics of the application. When the fluid is a liquid or the pressure of the gas is high, a dished head cylindrical vessel is appropriate. For most liquid phase applications, a vertical orientation is chosen. See Figure 3.

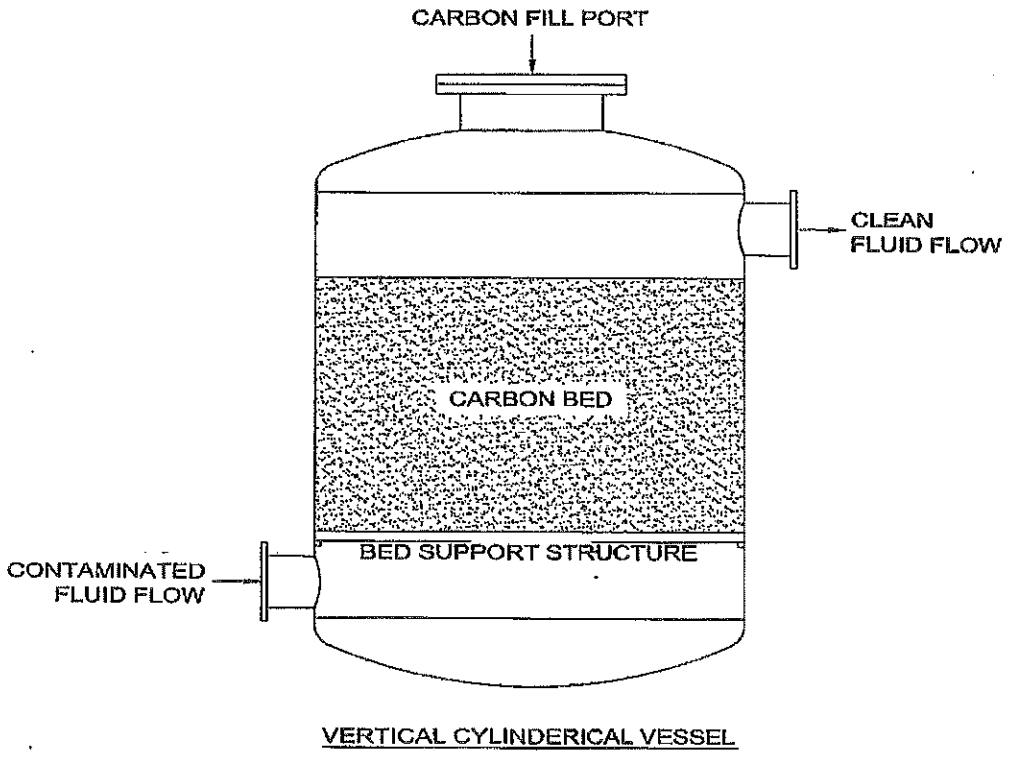

Figure 3 Vertical Cylindrical Vessel

When the gas pressure is high, the cylindrical type is best, but if the flow volume is also high, the cost of installing a very large diameter vertical vessel becomes prohibitive because of the wall thickness and the possible need for field fabrication. In those cases, a horizontal cylindrical vessel can be used. See Fig 4

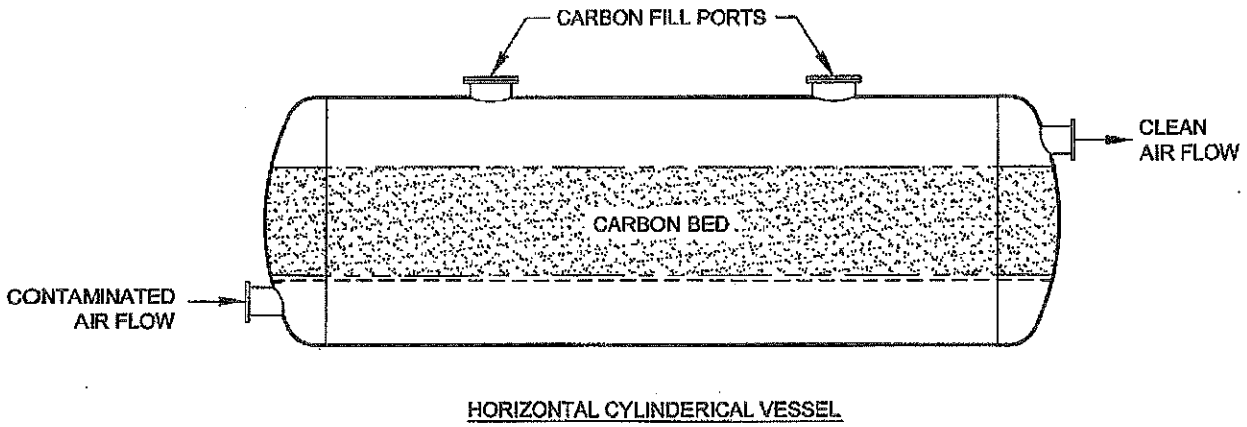

Figure 4 Horizontal Cylindrical Vessel

When an ASME code vessel is required but the amount of carbon is small and the pressure drop is critical, an annular bed adsorber may be the best choice. See Fig 5

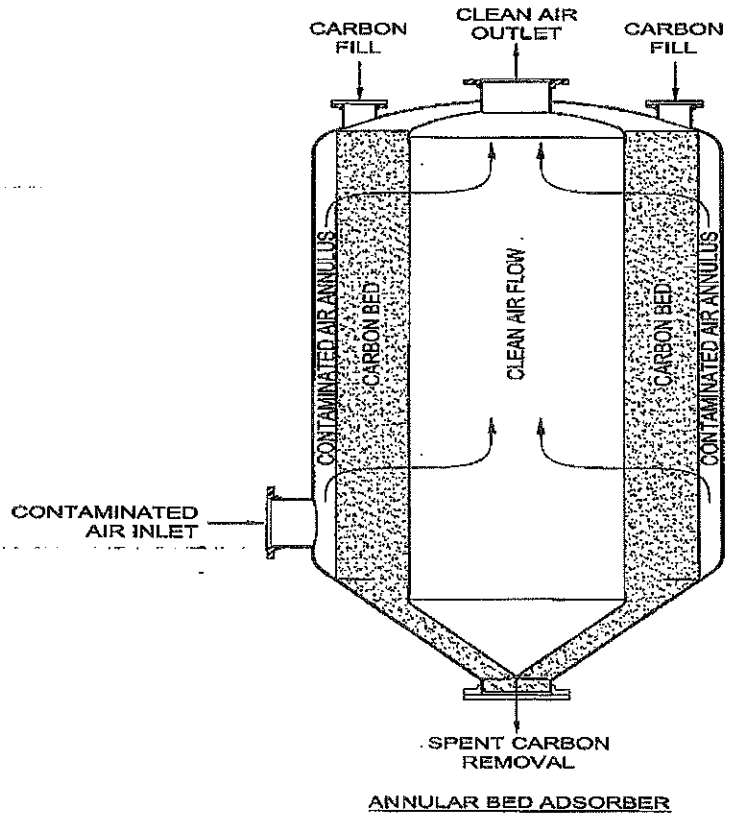

Figure 5 Annular Bed Adsorber

In cases where the air flow is extremely high, the pressure drop through the carbon beds must be kept as low as possible to save energy. In these cases, the bed depth can be thin in a design with multiple vertical beds of carbon in a cube shaped housing. See Fig 6 The air passes into slots on the inlet side of the housing, is diverted through the beds of carbon and exits in adjacent slots. Pressure drops can be as low as 1 inch water column.

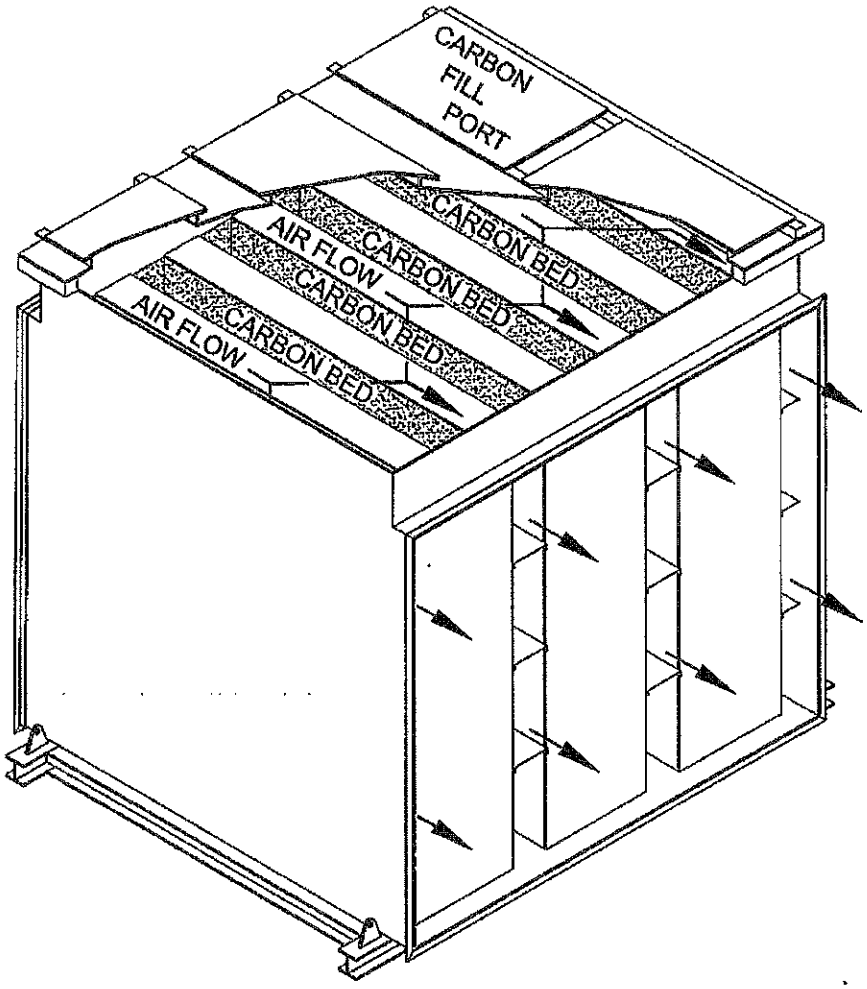

Figure 6 Deep Bed Adsorber

Commercial Experience

A wide variety of fixed bed adsorption systems are in use to control mercury emissions from both gas and liquid phase sources. The following are only examples of the broad application of this technology.

A process has been devised for thermal oxidation of mixed wastes at various DOE sites. The wastes contain mercury and they will employ fixed beds of sulfur-impregnated carbon on the exhaust stream to meet the MACT standards of 8 micro g/cu m. Several laboratory and bench scale tests have been conducted in addition to pilot scale tests. They show that the effluent standards can be met.

Various materials contaminated with mercury have been processed in high temperature retorts to liberate the mercury. They include soil, manufactured parts and even spent mercury adsorbent. Most of the mercury is recovered as a liquid but the effluent from the condensers is passed through a fixed bed of mercury adsorbent. Since there is a large amount of water vapor in the exhaust gas, the temperature must be maintained above 212 °F. At operating temperatures as high as 270 °F, the sulfur-impregnated carbon gives good performance.

Mercury is a component of fluorescent lamps. In the manufacturing process, some of it escapes into occupied areas. Hoods are placed at the leak spots and the air is passed through a fixed bed of mercury adsorbent. The system meets both OSHA and EPA requirements for mercury control.

Used fluorescent lamps are frequently recycled. The mercury is liberated in the process and is captured in a fixed bed of mercury adsorbent. These processes are located in different regions of the country and are relatively small. Each must meet the local EPA regulations for mercury emission and do.

Water scrubbers are sometimes used to quench incinerator exhaust gases or remove other toxic gasses from industrial vents. If the gas stream contains mercury, it can be dissolved in the water and must be removed before the water can be discarded. This situation is also encountered when gas wells contain both mercury and water condensate. Sulfur impregnated activated carbon is effective in removing mercury from water. The scrubber water at a mercury waste recycling plant is treated with sulfur-impregnated carbon and the mercury concentrate is reduced to less than 1 ppb. In another case, the water from a waste incinerator scrubber was treated and had less than 2 ppb mercury concentration.

Water from a mercury cell chlorine/caustic plant exceeded the effluent standards and a sulfur impregnated activated carbon system was added to the chemical treatment process. The process achieved concentration levels of less than 100 ppt. After the plant was closed, it was discovered that mercury contaminated water had leaked into the groundwater at the plant. The same carbon system was employed to pump and treat the groundwater.[6]

Conclusion

The reduction in mercury emissions is an important part of the air and water pollution control efforts. Since it is toxic, it is mandated by EPA regulations. A variety of processes are effective in controlling these emissions. For mercury removal from coal-fired power plants, injection of powdered activated carbon along with scrubbers and particulate removal are effective. This is also the process chosen for most presently

installed waste incinerators. However, for other applications, a fixed bed of mercury adsorbent is the most effective approach.

Many laboratory studies have been conducted to measure the effectiveness of the mercury adsorbent. These studies have contributed data, which has been successfully used in the design of full-scale systems. The design engineer has a wide variety of choices to make depending on the specifics of the application and the emission control requirements.

This technology has been successfully employed in a wide variety of cases where it was necessary to remove mercury from a fluid stream. It will continue to be an important tool in reducing the dangers of mercury in the environment.

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