5-2000

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ACTIVATED CARBON INJECTION FOR MERCURY CONTROL IN COAL-FIRED BOILERS

by

Randy Ray Brintnell

Bachelor of Science, University of North Dakota, 1997

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

Grand Forks, North Dakota
May
2000

This thesis, submitted by Randy Ray Brintnell in partial fulfillment of the requirements for the degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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This thesis meets the standards for appearance, conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

Harvey Knull
Dean of Graduate School

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Title Activated Carbon Injection For Mercury Control in Coal-Fired Boilers

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Signature Randy R.

Date 3-8-2000

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ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. John Erjavec, for his contributions to this project. Without his support and expertise, the completion of this thesis would not have been possible.

I am grateful to the members of my committee, Dr. Rashid Hasan and Dr. Mike Mann, for the time and effort they gave in adding to the quality of this paper. Thanks also goes to Dr. Tom Owens for his help in developing the analytical model. I thank my professors for their respect and friendship. The fellowship that I shared with the members of the chemical engineering faculty made graduate school one of the most positive experiences of my life.

I am very grateful for the financial support provided by the Energy and Environmental Research Center (EERC) throughout my time in school. I would also like to thank Stan Miller for always being available to answer questions and give advice at the EERC.

Special thanks to my friends and family, who always believed in me. My mother has always been a pillar of unwavering support through all of my endeavors. Thanks mom, for always being there.

ABSTRACT

Mercury is a toxic compound causing numerous health problems in humans. One of the ways that mercury is released into the atmosphere is through the burning of coal. The Environmental Protection Agency estimates that the United States consumes 1 billion tons of coal per year and coal-fired utilities emit 73 tons of mercury per year. Though there are currently no regulations on mercury emissions, it will remain an environmental concern.

Activated carbon (AC) injection is a proposed technology for mercury control in coal-fired boilers. We are interested in determining whether the diffusion rate or the absorptive capacity of the sorbent particle limits mercury absorption. A mathematical model was developed to estimate mercury diffusion rates in flue gas. With the model, diffusion rates were studied for mono-sized particles, particle distributions, and temperature variations.

The diffusion rates appear to be the limiting factor except in the cases of small particle diameters (less than two microns at 95% mercury capture) and high temperatures. The results show that carbon requirements increase as the square of the particle diameter. Temperature has very little effect on mercury diffusion to the smaller particles but becomes increasingly important as the size increases. Particle distributions have a great impact on the carbon requirements. The mono-sized particle carbon requirements increased by factors of between 2.8 and 32 depending on the mean particle diameter and the geometric standard deviation.

There is ongoing research to improve sorbent technology. The Energy and Environmental Research Center has developed a promising new sorbent, indole-impregnated activated carbon. To estimate the production cost of the new sorbent, an economic analysis was performed for the production of 500 tons/year.

A high production cost of $7.83/lb. caused the project to be economically unattractive. The raw materials made up 62% of the total product cost. The product cost was fairly insensitive to deviations of all factors except the costs of indole and base carbon. Significant reduction of the production cost must come through the lowering of raw material costs.

CHAPTER I

INTRODUCTION

Mercury has been linked to numerous health problems in humans including kidney damage, neurological damage, and developmental effects. The most common source of mercury introduced to humans is through fish consumption. Methylmercury bio-accumulates in aquatic systems and because fish are unable to secrete the chemical, it is passed on to humans. Although there are currently no regulations on mercury emissions from combustion sources, it will continue to be an environmental concern.

The Environmental Protection Agency (EPA) estimated mercury emissions in the United States to be 158 tons/year.[1] The majority coming from combustion sources including coal-fired boilers, medical waste incinerators (MWI), and municipal waste combustors (MWC). A total of 73 tons/year is emitted through the burning of coal. The current total coal consumption in the U.S. is one billion tons/year, which is expected to be over-shadowed by consumption in China, India, and Indonesia as these countries become more industrialized. The projected worldwide consumption for the year 2020 is 10 billion tons/year and because mercury is thought to be globally distributed, there may be environmental effects in the United States.[2]

Currently coal-fired boilers in the United States have no mercury control system in place. Elemental mercury released in the burning of coal passes through the system and is emitted into the atmosphere. One proposed technology for mercury removal is activated carbon (AC) injection. Fine particles will be injected into the flue gas upstream of the electrostatic precipitator (ESP) or baghouse. The mercury will be absorbed by the sorbent particles and caught in the ESP or baghouse. At the injection rates being considered, the injected carbon is less than 1% of the total particulate matter captured by the removal system. The difficulties associated with this procedure include adequate distribution of sorbent particles in the gas stream, mass transfer of the mercury in a very short residence time, the absorptive capacity of the sorbent, and the long-term stability of the mercury that is bound to the sorbent particle.

The first objective of this study is to provide a model for the diffusion of mercury to a sorbent particle in flue gas. We are interested in providing data that can be used to help determine whether mercury control by AC injection is limited by diffusion or the absorptive capacity. The Energy and Environmental Research Center (EERC) has performed fixed-bed studies to determine mercury capacities (Dunham et el., 1998).[3] The results for an iodine-impregnated activated carbon (IAC) are shown in Table 1.

Table 1. Mercury Capacity of Iodine-AC

	Inlet concentration µg Hg^0/Nm^3	
	60	20
Temperature °F (°C)	µg Hg/g Carbon	
225 (107)	8530	4369
275 (135)	1929	1232
325 (163)	892	506

The capacity appears to be dependent on both the initial mercury concentration and temperature. A comparison will be made between these representative capacities and the results provided by calculations based on diffusion.

A mathematical model was obtained beginning with Fick's law of diffusion and is described in Chapter 3. Carbon-to-mercury weight ratios were then generated using Excel and Mathcad. Chapter 4 discusses mercury diffusion related to mono-sized particles and particles whose sizes follow a log-normal distribution. The effect of temperature on diffusion is also examined.

The second part of the study concerns the production of a new activated carbon developed at the EERC. The proposed plant will produce 500 tons/year of indole-impregnated activated carbon. An economic analysis was prepared for the plant to determine economic feasibility. The economic study includes the purchased equipment cost, total capital investment and total product cost. A description of the process and its equipment is given in Chapter 5, and the economic analysis is discussed in Chapter 6. The conclusions and recommendations are included in Chapter 7.

CHAPTER II

BACKGROUND

Mercury exists in flue gas in elemental (Hg^0) and ionic (Hg^{+2}) forms. Although total mercury concentration in flue gas is relatively constant across the United States, speciation can vary greatly and is very dependent on the type of coal being combusted. Ionic mercury most commonly exists as $HgCl_2$, but also appears to a lesser extent as HgO and HgF_2. Ionic mercury is water-soluble and less volatile making its capture somewhat easier. A study showed that a wet flue gas desulfurization (FDG) scrubber removed all oxidized mercury while allowing the elemental mercury to pass through the system (Chow and Owens, 1994).[4] The mechanisms associated with mercury speciation are not well known, but factors that may contribute are the amount of fly ash, the carbon content of the fly ash, and vapor phase constituents such and HCl and SO_2.[1]

Mercury Control Technologies

Mercury control has been a subject of study for some time. Several methods have been and are now being examined. They include fuel cleaning, activated carbon beds, and activated carbon (AC) injection.

Coal Cleaning

Currently 77 percent of the eastern and midwestern bituminous coals are cleaned in order to meet customer specifications for heating value, ash content and sulfur content.[1] The EPA estimates that conventional coal cleaning reduces mercury levels in coal between 0 and 64% with the average being 21 percent.[1] One advanced coal cleaning study involving conventional cleaning and then selective agglomeration is reported to reduce mercury levels by as much as 82% (Smit, 1996).[1] The feasibility of advanced coal cleaning technologies is still under study.

Carbon Filter Beds

Carbon beds are now being used in power plants in Germany. The original purpose of these beds was to remove residual sulfur dioxide downstream of the flue gas desulfurization system, but they have proven to be efficient in mercury control. A pilot scale MWC study showed mercury removal of 99% (Hartenstein, 1993).[5] If regulations on mercury emissions are imposed, construction specifications for new plants will more than likely include a carbon filter bed. Unfortunately the cost of retrofitting existing plants with a carbon bed may be far too costly.

Activated Carbon (AC) Injection

A less costly alternative in terms of retrofit equipment installation is AC carbon injection. This method requires an injection system to disperse the carbon in the flue gas. The carbon along with bound mercury will be caught in collection system already in place for the removal of fly ash and other suspended particulate matter.

Mercury removal in coal-fired utilities will be challenging due to the low mercury concentration in the flue gas (1 part per billion) and the wide distribution of different species of mercury. The amount of mercury that can be collected depends on the volume of flue gas, its temperature, the amount of fly ash and other constituents in the flue gas. Temperature may have effects on speciation as well as the absorption mechanism once the sorbent has come in contact with the mercury. In most studies conducted to this point, an increase in temperature has corresponded with a decrease in absorption efficiency. The type of coal also has an effect. The EERC found that IAC had 95% mercury capture up to 400°F for one type of coal. The same sorbent used with another type of coal removed 75% of the mercury at 200°F, but dropped to less than 20% at 400°F (Dunham et al., 1998).[3] The same study also showed that some types of activated carbon could change the speciation of the flue gas. For one coal type the IAC appeared to convert all elemental mercury to ionic form. Finally, the constituents in the gas may not only effect speciation but also compete with mercury for bonding sites on the sorbent particle. With all these problems to overcome, a universal mercury control system will be very difficult to develop.

CHAPTER III

DIFFUSION OF MERCURY IN FLUE GAS

The system was modeled as a particle of radius a surrounded by a sphere of flue gas of radius R. A diagram of the proposed system is shown in Figure 1.

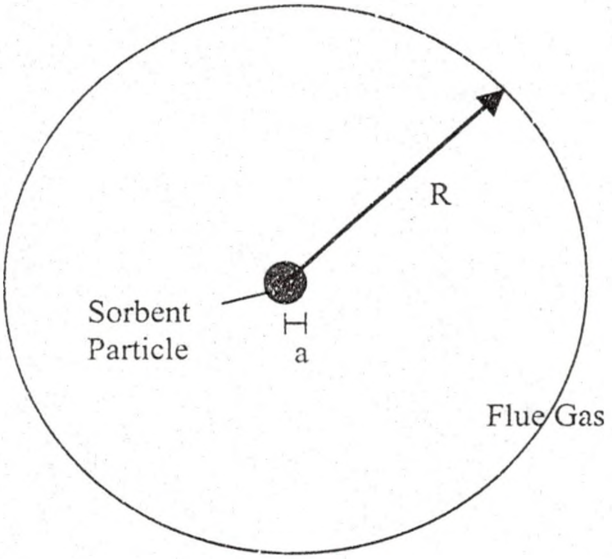

Figure 1. Mercury Removal System

The assumptions are that the particle is a perfect absorber (i.e. all mercury that diffuses to the particle surface will be absorbed). There is no diffusion of mercury into or out of the sphere of radius R. Finally, that there is no particle movement relative to the flue gas. We will examine an analytical and a numerical solution for this problem in the subsequent sections of this chapter.

A 250-megawatt coal-fired utility was modeled in a case study for SO_2 control.[6] The width and height of the flue gas duct were given as 13.25 and 11 (ft) respectively. These dimensions correspond to an effective diameter of 12 (ft). The flue gas velocity was given as 50 (ft/s). Using the density and viscosity of air at 300°F (0.51 lb/ft^3 and 0.023 centipoise), the Reynolds number was calculated as 2 million. To keep particulate matter from settling, gas velocities are generally more than 30 (ft/s). Therefore, all utility gas streams will be highly turbulent. Assuming the particle does not move relative to the flue gas gives the limiting case, and carbon requirements will decrease with increasing turbulence if diffusion to the particle is the limiting factor in mercury capture.

Analytical Solution

Assuming there is no particle movement relative to the flue gas, the concentration of mercury in the gas stream is dependent on the residence time, the diffusivity of mercury in the flue gas and the distance the mercury must diffuse to the sorbent surface. Fick's law in spherical coordinates is given by Equation 1.[7]

$$\frac{\partial C_{Hg}}{\partial t} = D_{Hg}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{Hg}}{\partial r}\right)\right] \qquad (1)$$

The boundary conditions of this system are given in Equations 2 through 4.

$$\frac{\partial C_{Hg}}{\partial r}(R,t)=0 \tag{2}$$

$$C_{Hg}(a,t)=0 \tag{3}$$

$$C_{Hg}(r,0)=C_{Hg0} \tag{4}$$

The first boundary condition (2) states that there will be no diffusion beyond a chosen distance (R) from the center of sorbent particle. The concentration of mercury at the surface of the particle (a) will be assumed to be zero and is represented by the second boundary condition (3). The first two conditions apply to all times greater than zero. The final condition (4) states that at time equal to zero (i.e. at the point of injection) the mercury concentration will be given as the initial concentration in the flue gas at all distances (r) from the sorbent particle.

Equation 1 can be converted to rectangular coordinates by making a simple substitution of $u = C_{Hg}r$ and is given by Equation 5.

$$\frac{\partial u}{\partial t}=D_{Hg}\frac{\partial^2 u}{\partial r^2} \tag{5}$$

The modified boundary conditions are given by Equations 6 through 8.

$$\frac{\partial u}{\partial r}(R,t)=\frac{u}{R} \tag{6}$$

$$u(a,t)=0 \tag{7}$$

$$u(r,0)=C_{Hg0}r \tag{8}$$

Now a Fourier transform can be applied to Equation 5.

$$u=e^{-\lambda^2 D_{Hg}t}\left[A\cos(\lambda r)+B\sin(\lambda r)\right] \tag{9}$$

Applying the first boundary condition (6) to Equation 9 gives Equation 10

$$\lambda\left[B\cos(\lambda R) - A\sin(\lambda R)\right] = \frac{1}{R}\left[A\cos(\lambda R) + B\sin(\lambda R)\right], \tag{10}$$

and Equation 11 satisfies the second condition (7).

$$A\cos(\lambda a) = -B\sin(\lambda a) \tag{11}$$

Combining Equations 10 and 11 gives the defining Equation (12) by which the eigenvalues (λ) of the solution can be found.

$$\tan(\lambda a) = \frac{\sin(\lambda R) - \lambda R\cos(\lambda R)}{\cos(\lambda R) + \lambda R\sin(\lambda R)} \tag{12}$$

Substitution of Equation 11 into 9 gives Equation 13.

$$u = Ae^{-\lambda^2 D_{Hg}t}\left[\cos(\lambda r) - \cot(\lambda a)\sin(\lambda r)\right] \tag{13}$$

The application of the third boundary condition (8) to 13 is displayed in Equation 14.

$$A\left[\cos(\lambda r) - \cot(\lambda a)\sin(\lambda r)\right] = C_{Hg0}r \tag{14}$$

There is a solution for each value of λ obtained from Equation 12 and any linear combination of solutions is also a solution. In order to find all the solutions for the system, both sides of Equation 14 must be multiplied by $\left[\cos(\lambda r) - \cot(\lambda a)\sin(\lambda r)\right]$ and integrated with upper and lower limits of R and a respectively.

$$\sum A_n \int_a^R \left[\cos(\lambda_n r) - \cot(\lambda_n a)\sin(\lambda_n r)\right]^2 dr = C_{Hg0}\int_a^R r\left[\cos(\lambda_n r) - \cot(\lambda_n a)\sin(\lambda_n r)\right]dr \tag{15}$$

The substitution $u = C_{Hg}r$ can again be used with Equation 13 to solve for Equation 16.

$$C_{Hg} = \sum A_n \frac{e^{-\lambda_n^2 D_{Hg}t}\left[\cos(\lambda_n r) - \cot(\lambda_n a)\sin(\lambda_n r)\right]}{r} \tag{16}$$

Finally, Equations 15 and 16 are combined and the solution in standard form with $\xi = r/R$ is presented below.

$$\frac{C_{Hg}}{C_{Hg0}} = \sum \frac{\int_a^R r\left[\cos(\lambda_n r) - \cot(\lambda_n a)\sin(\lambda_n r)\right]dr}{\int_a^R \left[\cos(\lambda_n r) - \cot(\lambda_n a)\sin(\lambda_n r)\right]^2 dr} \frac{e^{-\lambda_n^2 D_{Hg} t}\left[\cos(\lambda_n \xi R) - \cot(\lambda_n a)\sin(\lambda_n \xi R)\right]}{\xi R} \quad (17)$$

In order to work with Equation 17 using Excel, the quotient of integrals has to be simplified. The simplification is shown below.

$$\frac{\int_a^R r\left[\cos(\lambda_n r) - \cot(\lambda_n a)\sin(\lambda_n r)\right]dr}{\int_a^R \left[\cos(\lambda_n r) - \cot(\lambda_n a)\sin(\lambda_n r)\right]^2 dr} =$$

$$2\frac{\left(\alpha\phi - \alpha\phi\theta^2 - \theta\beta + \theta^3\beta + \lambda R\beta\phi - \lambda R\beta\phi\theta^2 + \lambda R\theta\alpha - \lambda R\theta^3\alpha - \lambda a + \lambda a\theta^2\right)}{\left[\lambda\left(\phi\alpha\beta - 2\phi\theta^2\alpha\beta + \lambda R\phi + 2\theta\alpha^2 - 2\theta^3\alpha^2 - \theta + \theta^3 - \lambda a\phi\right)\right]} \quad (18)$$

$$\alpha = \cos(\lambda_n R)$$
$$\beta = \sin(\lambda_n R)$$
$$\theta = \cos(\lambda_n a)$$
$$\phi = \sin(\lambda_n a)$$

Remember that the eiganvalues (λ) are the roots of Equation 12. The first root was found to always equal zero and l'Hôpital's rule shows that Equation 17 approaches zero when λ is zero. The third is large enough that its contribution to the sum in Equation 17 is insignificant. Therefore, the second root of Equation 12 is only one that need be considered. The fractional concentration is plotted as a function of the fractional radius in Figure 2.

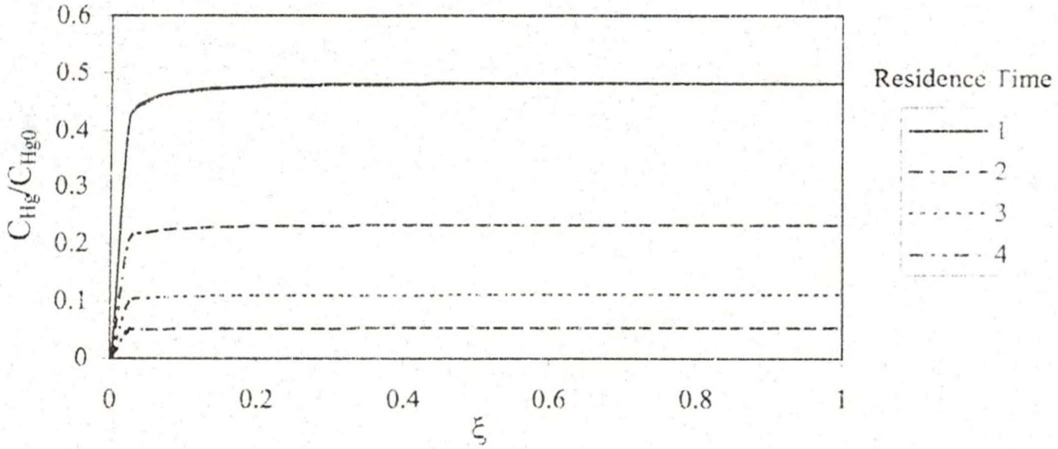

Figure 2. Mercury Concentration Profile

This figure shows the concentration profile of mercury in flue gas at several residence times. The diffusivity of mercury in flue gas is taken as 0.261 (cm^2/s) which is the diffusivity of mercury in air at 140°C.[8] The radius of the particle and radius of the gas sphere in this example are 2 and 600 microns respectively. From the figure, we see that the mercury concentration in 9.05×10^{-10} cubic meters of flue gas is reduced to approximately 5% of the original concentration at a residence time of 4 seconds. Assuming that the original mercury concentration is 10 ($\mu g/m^3$), one 4-micron diameter sorbent particle will remove 9.05×10^{-9} micrograms of mercury.

Numerical Integration

In order to test the validity of the analytical solution, a numerical integration was performed beginning with Equation 5. Equation 5 can be written as the approximation shown in Equation 19.

$$\Delta u \cong D_{Hg}\left[\frac{\Delta^2 u}{(\Delta r)^2}\right](\Delta t) \qquad (19)$$

Applying Simpson's rule to Equation 19 gives Equation 20 and the first boundary condition (6) is represented by Equation 21. The second and third boundary conditions can be directly applied to the numerical integration.

$$u(t_{i+1}, r_j) = u(t_i, r_j) + D_{Hg}\left[\frac{u(t_i, r_{j+1}) - 2u(t_i, r_j) + u(t_i, r_{j-1})}{(\Delta r)^2}\right](\Delta t) \qquad (20)$$

$$u_{J+1} = u_{J-1} + 2\left(\frac{u_J}{R}\right)(\Delta r) \qquad j = J \text{ at } r = R \qquad (21)$$

The curve generation was done using Excel and the comparison between the two methods is shown in Figure 3. Due to the limitations of the numerical integration, the particle radius had to be taken as 8 microns. The gas sphere radius is 1250 microns. The numerical and analytical methods are compared at one and two seconds and as seen in the figure, there is very little difference between the two methods. Therefore, we are confident that Equation 17 accurately represents the proposed system.

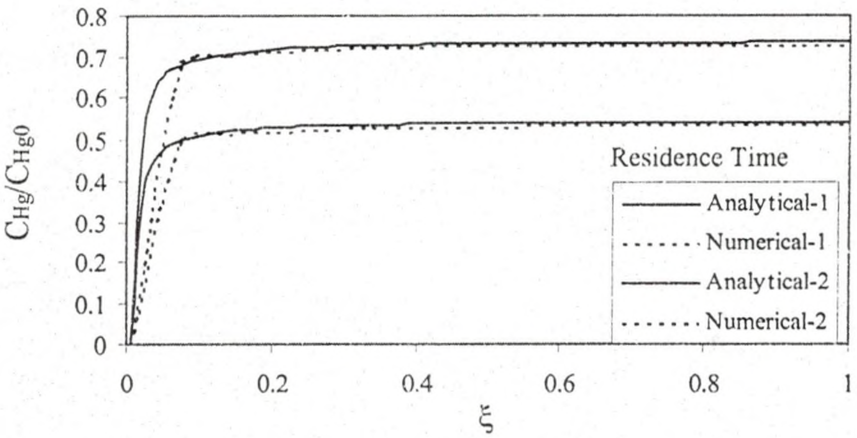

Figure 3. Comparison of Analytical and Numerical Methods

CHAPTER IV

RESULTS AND DISCUSSION

With Equation 17, predictions were generated using Excel and Mathcad. When calculating the weight ratios (kg of carbon used per kg of mercury removed), the initial concentration of mercury in the flue gas was taken as 10 ($\mu g/m^3$) and the density of the carbon sorbent is assumed to be 440 (kg/m^3). The diffusivity remains 0.261 (cm^2/s). This chapter discusses mono-sized particles, particle size distributions and temperature effects on diffusion.

Mono-Sized Particles

As one can imagine there are numerous ways in which the findings can be presented. The number of kilograms of sorbent needed to remove one kilogram of mercury is plotted as a function of residence time in Figure 4. The particle size chosen for this example is four microns in diameter and is based on 95% mercury removal.

In Figure 4, the slope of the curve decreases throughout. The amount of sorbent needed drops off sharply between 1 and 3 seconds, and it seems clear that it would be beneficial to have a residence time of at least 4 seconds. This is the case for all of the particle sizes studied in this paper.

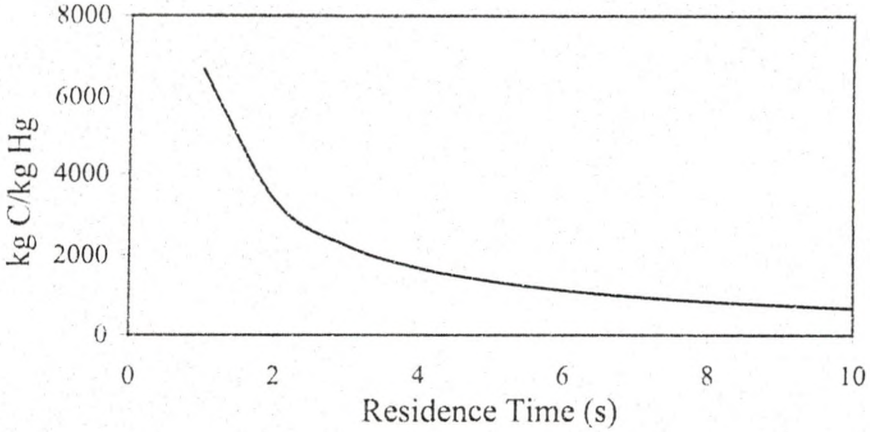

Figure 4. Carbon Requirements for a 4-micron Particle

The carbon-to-mercury weight ratio is plotted against particle diameter in Figure 5. The curves represent 90 and 95% mercury removal at residence times of 4 and 8 seconds.

Each of these curves approximately correspond to the general equation $y = mx^2$, the weight ratio increases as the square of the diameter. This is illustrated by examining the difference between a 4 and 10-micron particle at 4 seconds and 95% removal. The

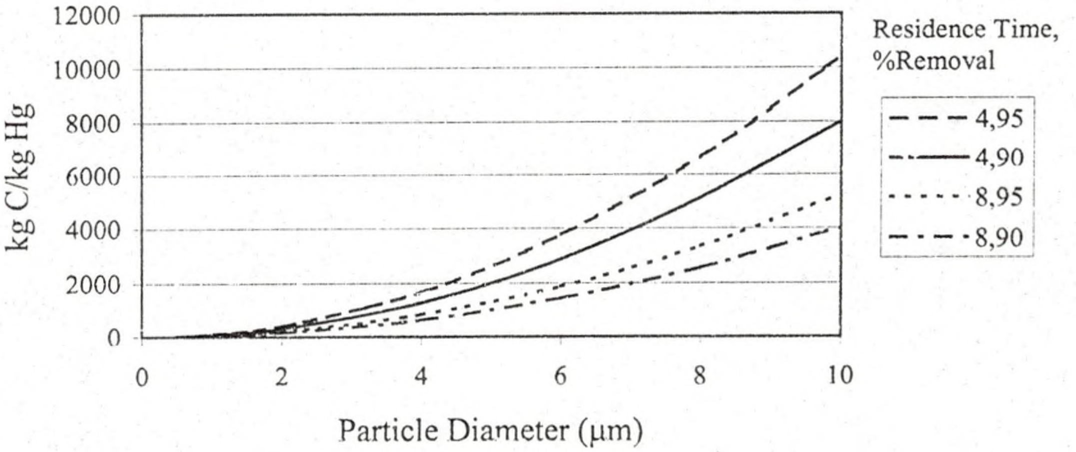

Figure 5. Carbon Requirement as a Function of Particle Diameter

volume of the particle increases 15 times, while the volume of the gas sphere that the sorbent can remove 95% of the mercury in four seconds increases by only 2.5 times. This also means that the sorbent weight and weight of mercury removed increases in the same proportion. Results are shown for residence times of 1 through 5 seconds for 95% mercury removal in Table 2 and required mercury capacitates based on diffusion are given in Table 3.

Table 2. Carbon-to-Mercury Ratios for 95% Mercury Removal

	Diameter (μm)					
	1	2	4	6	8	10
Time (s)	Carbon to mercury weight ratio					
1	420	1676	6683	14990	26573	41436
2	210	839	3347	7511	13330	20790
3	140	559	2233	5015	8899	13884
4	105	421	1675	3764	6680	10423
5	84	336	1341	3013	5348	8344

Table 3. Capacity Requirements for 95% Mercury Removal

	Diameter (μm)					
	1	2	4	6	8	10
Time (s)	μg Hg/ g Carbon					
1	2381	597	150	67	38	24
2	4763	1192	299	133	75	48
3	7138	1787	448	199	112	72
4	9516	2374	597	266	150	96
5	11895	2976	746	332	187	120

The capacity given in Table 1 for an initial concentration of 20 (μg/Nm^3) at 135°C is 1232 μg Hg/ g Carbon. The data in Table 1 is dependent on the inlet mercury concentration. Although the capacities may be somewhat lower for an initial concentration of 10 ($\mu g/m^3$), we will use 1232 as a representative capacity. The results show that particles with diameters of 4-10(μm) are diffusion limited, while the 1 (μm) diameter particles are capacity limited. The 2-micron particle is capacity limited for residence times greater than 2 seconds. Additional weight ratio data and mercury capacities are located in Appendices A and B respectively.

Carbon Particle Distributions

To this point, only mono-sized particles have been examined; however, sorbent particles are actually distributed around a mean diameter. The distribution is generally log-normal and a representation is given in Figure 6. The distribution was generated using Excel based on distribution data for fine particles.[9,10] The mean diameter is 2 microns with a geometric standard deviation of 2.

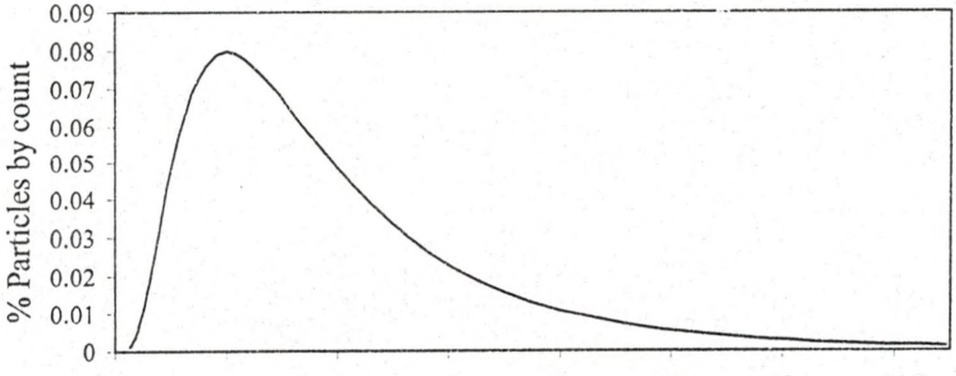

Figure 6. Log-normal Particle Size Distribution

The geometric standard deviation (σ_g) is defined below.[9] The percentages

$$\frac{50\%size}{15.87\%size} \text{ or } \frac{84.13\%size}{50\%size} \tag{22}$$

correspond to the cumulative distribution and the relationship is the slope of the line when the cumulative distribution is plotted on logarithmic probability graph paper as shown in Figure 7.

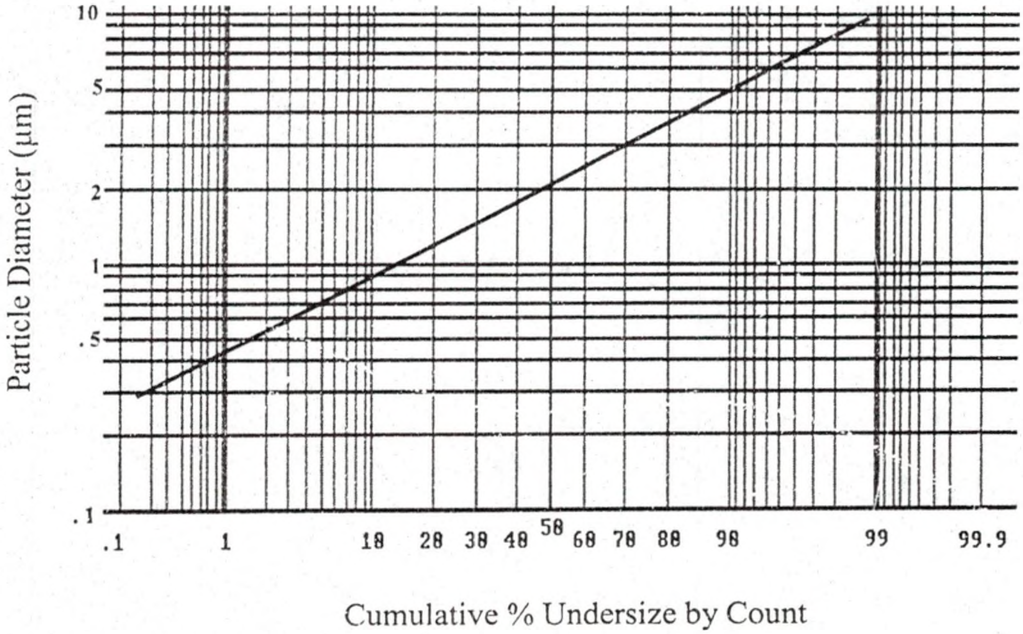

Figure 7. Cumulative Distribution for a 2-micron Particle (σ_g=2)

The area under the curve was divided into 30 parts and a mean diameter was calculated along with a percentage for each division. The carbon-to-mercury weight ratio (90% mercury removal) for the distribution could then be determined and is shown in Table 4. Table 4 also compares the distribution to the mono-sized particle.

Table 4. Carbon-to-Mercury Ratios for Particle Distributions

Diameter (μm)	0.98*		2		4.7**	
σ_g	2.8	1	2	1	1.6	1
Time (s)	Carbon to Mercury Weight Ratio					
1	9873	310	7352	1289	19772	7091
2	4944	155	3682	645	9910	3551
3	3299	103	2457	430	6615	2370
4	2475	78	1843	323	4964	1779
5	1981	62	1475	258	3973	1423
6	1651	52	1230	215	3313	1186
7	1415	44	1054	185	2840	1017
8	1239	39	923	162	2486	890
9	1101	34	820	144	2210	791
10	991	31	738	129	1990	712

*Particle distribution data from "Fine Particles in Gaseous Media"[9]

** Particle distribution data from "Particle Size Analysis in Industrial Hygiene"[10]

The weight ratios for the 4.7 and 2-micron particle distributions are 2.8 and 5.7 times higher than their respective mono-sized particle weight ratios. The 0.98-micron distribution is 32 times higher than its corresponding mono-size ratio. The largest particles in the distribution account for the largest portion of the weight, while contributing little to the overall capture of mercury. In the case of the 2-micron particle distribution, the largest 5.5% of the particles account for 62% of the carbon weight but contribute only 18% to the total amount of mercury captured. For the 0.98-micron particle distribution, the largest particles (6%) contribute 88% to the weight and capture 30% of the total mercury removed. Only the 2-micron particle distribution at residence times greater than 9 seconds is capacity limited.

Temperature

The effect of temperature was also examined in this study. An approximation from *Perry's Chemical Engineers' Handbook* is given in Equation 23.[11]

$$D_1 = D_0\left[\frac{T_1}{T_0}\right]^{3/2} \quad \text{using absolute temperature, °K} \qquad (23)$$

Using 0.261 (cm^2/s) at 140°C as the basis, the diffusivity for 120° and 180°C were calculated as 0.242 and 0.300 (cm^2/s) respectively. Figure 8 shows the effects of temperature (diffusion rate) on the amount of carbon needed for 95% mercury capture.

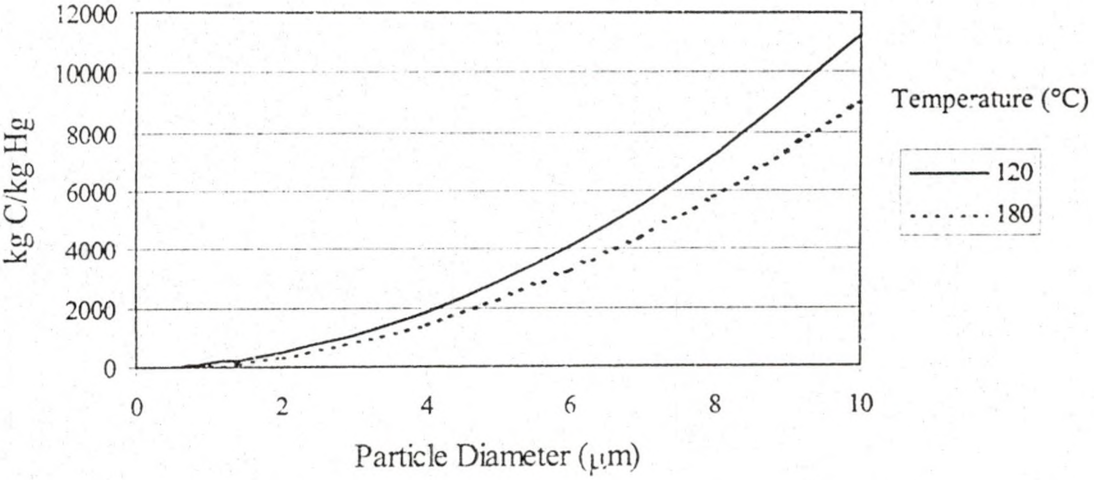

Figure 8. Temperature Effects on Diffusion

This figure shows what one would predict. As the temperature is increased the amount of sorbent needed is reduced. The higher temperature increases the kinetic energy of the flue gas, and the chances of mercury-sorbent interaction increases. Temperature has very little effect on diffusion to small particles. The difference in weight ratios for a 2-micron particle is 88; however, its importance increases with increasing diameter. The difference in ratios for the 6-micron particle is 783.

The capacities of the IAC sorbent in Table 1 drop off sharply with increases in temperature. The required capacities based on diffusion do not change much but they do increase with a rise in temperature. As temperature increases mercury removal will become more capacity limited. Weight ratio data related to temperature can be found in Appendix A.

CHAPTER V

INDOLE-ACTIVATED CARBON PRODUCTION

Indole-activated carbon is a promising new sorbent being developed at the Energy and Environmental Research Center. Although testing is still in its early stages, the EERC believes that it will be a superior sorbent having high absorption capacity and long term stability of bound mercury. Currently this sorbent is being produced in small bench-scale quantities. We want to determine if the sorbent can be produced on a large scale and then determine the economic feasibility (Chapter 7) of the process. This chapter will discuss the design of a plant capable of producing 500 tons of sorbent per year. The plant will operate 24 hours a day, 7 days per week, 50 weeks per year. The remaining two weeks will accommodate maintenance and unscheduled downtime.

Process Description

Indole is heated at its boiling point (253°C) in a reactor for four hours. The indole pitch is then dissolved in methanol (10% solution) and transferred to a stirred tank. A base carbon is then mixed with the indole solution at a carbon to indole ratio of 19:1 by weight. The methanol is boiled off in a dryer and the carbon is transferred to an oven for recarbonization. The heating program for the oven is shown in Table 5.

Table 5. Heating Program for the Process Oven (°C)

25 to 225 at 15°/min
225 to 270 at 1°/min
hold at 270 for 1 hour
cool to room temperature
25 to 750 at 15°/min
hold at 750 for 1 hour

Due to the nature of the heating program, a batch process is preferable to a continuous operation. The estimated time of the heating program is six hours corresponding to four batches per day, each batch containing 714 lb. of carbon. The batch quantities for indole and methanol are 37.6 lb. and 51.2 gallons respectively. All the process equipment was sized using capacity requirements necessary for four batches per day. The process flow diagram is shown in Figure 9.

Process Equipment

The process equipment will be installed vertically when possible to reduce costs associated with product transfer between pieces of equipment. Carbon steel was used for the construction of each piece of equipment except the reactor and oven, which are constructed of stainless steel. Since temperatures in the reactor and oven must be very accurate, electric heating will be used.

The capacity of the reactor (SR) is 30 gallons. The indole pitch will be washed from the reactor with methanol and the 10% indole solution will be achieved in the 200 gallon stirred tank (SRT).

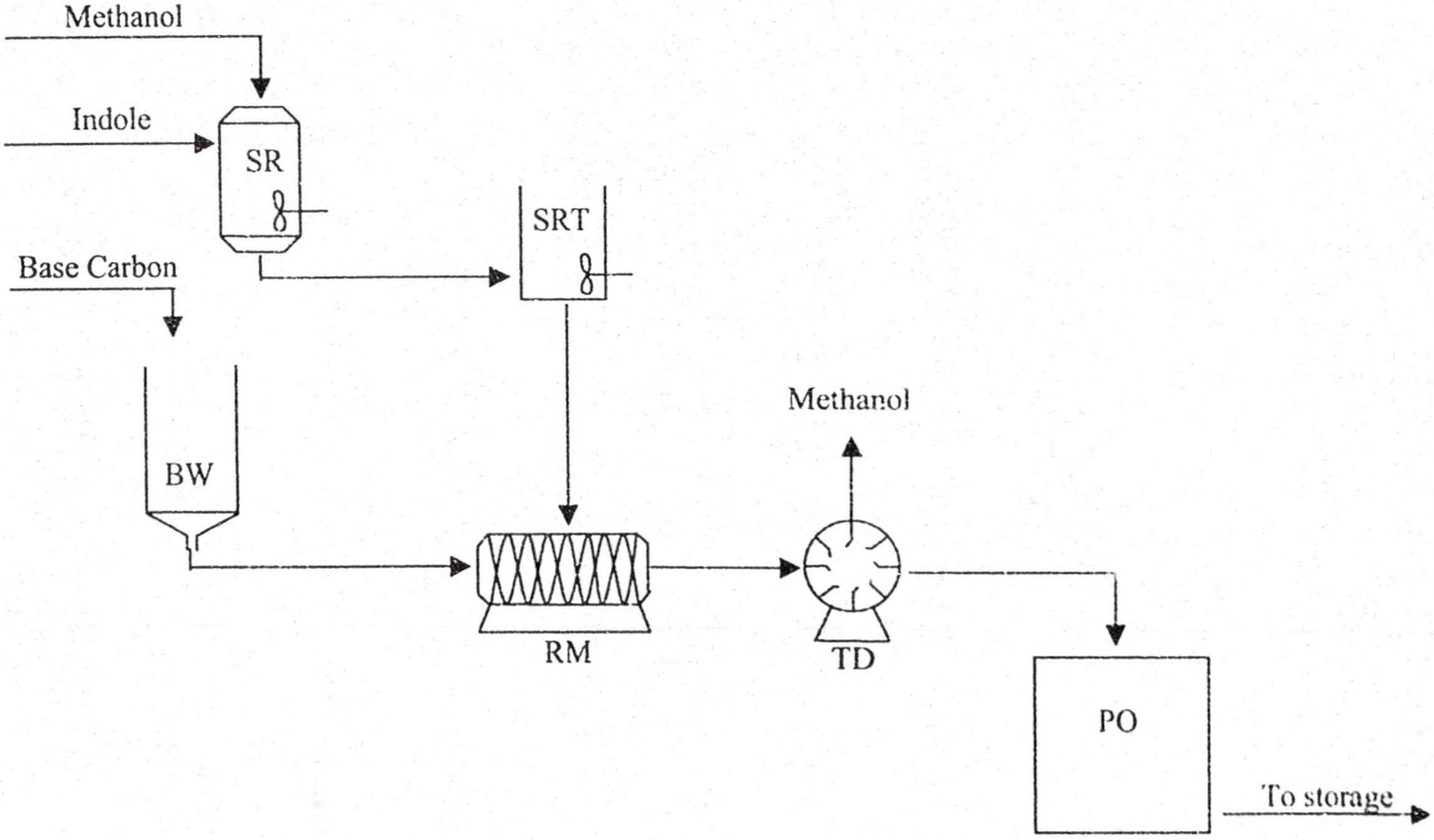

Figure 9. Process Flow Diagram for Indole-Activated Carbon Production

The capacities of the ribbon mixer (RM) and vacuum tumble dryer (TD) are both 40 ft^3. The dryer package includes a jacketed shell, electric water heater, water pump, vacuum pump, condenser, receiver, and piping.

The process oven (PO) will be a cabinet type oven with internal dimensions of 36"x36"x60". The carbon must be placed in 14 covered trays (16"x34"x6") to prevent the product from being blown around within the heating chamber. The oven information was obtained from Gruenberg Oven Company. Although the temperature ramps in the heating cycle are obtainable, the maximum temperature of their oven is 710°C. In Chapter 7, the estimate by Gruenberg was multiplied by 1.5 to accommodate for the needed maximum temperature of 750°C.

A batch weigher (BW) will be used to accurately measure the amount of carbon per batch. The weigher includes conveying equipment to transfer the carbon from storage and then on to the mixer.

There are four pumps in the process. They transfer methanol from storage to the reactor (P-1), from the reactor to the stirred tank (P-2), from the stirred tank to the mixer (P-3), and a recycle pump (P-4) for the methanol evacuated from the dryer.

There will also be two 1000 ft^3 storage silos, one each for the raw carbon (SS-1) and the finished product (SS-2). These silos include loading equipment and are large enough for a 10-day supply. The methanol will be stored in a 3000-gallon tank (ST) accommodating a two-week supply.

CHAPTER VI

ECONOMIC ANALYSIS

An economic analysis was done on the process described in Chapter 6 to determine if the process is economically feasible. The following sections of this chapter discuss the purchased equipment cost (PEC), total capital investment (TCI), total product cost (TPC) and sensitivity analysis. The basis for the analysis is the production of 500 tons of Indole-AC per year.

Purchased Equipment Cost

The purchased equipment cost was calculated at $204,000. Table 6 shows the size and the cost for each piece of equipment. Unless otherwise noted, the prices were obtained from graphical correlations based on capacity needs.[12] Hapman Conveyors estimated the price of the batch weigher. Bulk Equipment Systems Technology, Inc. estimated the price of the storage silos, and the Guenberg Oven Company estimated the price of the process oven. Remember that Gruenberg's estimate was increased by 50% to accommodate our increased temperature needs. The costs estimated by graphical methods were corrected to year 2000 dollars using the Marshall and Swift Equipment Cost Index.[13,14]

Table 6. Purchased Equipment Cost

ID Number	Description	Size	Cost
PO	process oven	45 ft^3	$59,800
TD	vacuum tumble dryer	40 ft^3	$45,400
RM	ribbon mixer	40 ft^3	$16,200
SR	stirred reactor	30 gal	$5,700
BW	batch weigher	N/A	$44,600
SRT	stirred tank	200 gal	$4,900
P-1	pump (methanol storage)	0.25 hp	$1,300
P-2	pump (reactor)	0.25 hp	$1,300
P-3	pump (mixed tank)	0.5 hp	$2,000
P-4	pump (methanol recycle)	0.25 hp	$1,300
SS-1	storage silo (raw carbon)	1000 ft^3	$5,100
SS-2	storage silo (product)	1000 ft^3	$5,100
ST	storage tank (methanol)	3000 gal	$11,300
	Purchased Equipment Cost		$204,000

Total Capital Investment

The total capital investment (TCI) is comprised of the fixed capital investment and the working capital. The TCI for this process is $1,246,000. The working capital includes supplies and products carried in stock, accounts receivable and cash kept on hand for wages and accounts payable. The fixed capital investment is further broken down into direct costs and indirect costs, the components of which can be seen in Table 7. Except for the PEC, the cost of each component was estimated using average percentages for chemical process plants.[12] Since the calculated TCI is completely dependent on the purchased equipment cost, one of the sensitivity analyses was based on changes in the PEC.

Table 7. Total Capital Investment

Total Capital Investment (TCI)			**$1,246,000**
Fixed Capital Investment (FCI)			***$1,059,000***
Direct Costs(DC)			*$703,000*
Purchased Equipment Cost (PEC)*			$204,000
Equipment Installation	40.0%	of PEC	$82,000
Instrumentation and Controls (installed)	18.0%	of PEC	$37,000
Piping (installed)	45.0%	of PEC	$92,000
Electrical (installed)	25.0%	of PEC	$51,000
Buildings	40.0%	of PEC	$82,000
Yard Improvement and Service Facilities	70.0%	of PEC	$143,000
Land	6.0%	of PEC	$12,000
Indirect Costs (IC)			*$356,000*
Engineering and Supervision	17.5%	of DC	$123,000
Construction	18.0%	of DC	$127,000
Contingency	10.0%	of FCI	$106,000
Working Capital (WC)	15.0%	of TCI	***$187,000***

* estimated value, see Table 6

Total Product Cost

The total product cost (TPC) includes manufacturing costs and general expenses. The TPC for the process is $8,243,000 per year. The general expenses are costs associated with administration, distribution and selling, and research and development. The manufacturing cost includes direct production costs (DP), fixed charges (FC), and plant overhead cost (POC). The main component of the DP is the cost of raw materials. The costs of raw materials were obtained from suppliers and are shown in Table 8. There is currently no data available for the amount of methanol that can be recovered in the dryer. Since the methanol cost is very small in comparison to the other raw materials, the methanol quantity is given as if there was no recycle stream.

Table 8. Raw Material Costs

Raw Material	Quantity	Unit Price	Total Cost	Cost/lb. Product	Supplier
Base Carbon	1,000,000 lbs	$1.14	$1,140,000	$1.08	Calgon
Indole	52,580 lbs	$74.10	$3,896,178	$3.70	ABCR
Methanol	71,690 gal	$0.35	$25,092	$0.02	Methanex
	Total Raw Material Cost:		$5,061,270	$4.80	

The life of the plant was assumed to be 20 years. Depreciation was estimated using straight-line depreciation over 20 years for the equipment and 40 years for the buildings. The operating labor was calculated assuming three 8-hour shifts per day with 6 operators per shift paid $15.00 per hour. The remaining components were calculated using industry standard percentages.[12] The averages were used except in the case of the components dependent on the total product cost (utilities, distribution and selling and research and development). These costs were estimated using the low end of industry percentages to avoid inflated costs caused by the unusually high raw material costs. Table 9 shows the individual components that make up the total product cost.

The total product cost is $7.83 per pound. The contribution to the TPC from the raw materials alone is $4.80. The indole is $3.70 or 47% of the TPC and the carbon contributes $1.08 (14%). Any significant reduction in the TPC will depend on a reduction in the raw material costs. The indole and base carbon costs are examined in sensitivity analyses for this reason.

In order to make a 15% rate of return on the investment, the product must be sold for $8.00 per pound. The difference between the selling price and the production cost is only $0.17. The 17-cent difference is constant over a wide range of TPCs and can be attributed to the low total capital investment.

Table 9. Total Product Cost

Total Product Cost (TPC)			**$8,243,000**
Manufacturing Cost (MC)			***$7,600,000***
Direct Production (DP)			*$6,925,000*
Raw Materials*			$5,061,000
Operating Labor (OL)**			$786,000
Supervisory and Clerical Labor (SC)	17.5%	of OL	$138,000
Utilities	9.1%	of TPC	$750,000
Maintenance and Repairs (MR)	6.0%	of FCI	$64,000
Operating Supplies	0.75%	of FCI	$8,000
Laboratory Charges	15.0%	of OL	$118,000
Fixed Charges (FC)			*$83,000*
Depreciation***			$50,000
Local Taxes	2.5%	of FCI	$26,000
Insurance	0.7%	of FCI	$7,000
Plant Overhead Cost (POC)	60.0%	of OL+SC+MR	*$592,000*
General Expenses (GE)			***$643,000***
Administrative Costs	15.0%	of OL+SC+MR	*$148,000*
Distribution and Selling	4.0%	of TPC	*$330,000*
Research and Development	2.0%	of TPC	*$165,000*

*estimated value, see Table 8
**3 shifts, 6 operators per shift, $15.00/hour
***20 year straight-line depreciation on equipment, 40 year straight-line on buildings

Sensitivity Analysis

Sensitivity analyses were done for important parameters in the plant cost. Because the TPC is the greatest portion of the overall cost, most of the focus is there. Analysis was done with the raw materials indole and base carbon along with operating labor and utility costs. The PEC was also examined because of its influence over the total capital investment. In calculating the minimum rate of return, 7-year MACRS depreciation was used for the equipment and 40-year straight-line depreciation for the buildings. The combined local and federal tax rate was assumed to 39%. In all the examples below the selling price represents the amount needed to make a 15% rate of return.

Base Carbon and Indole

The selling price is fairly sensitive to the cost of base carbon as shown in Figure 10. The cost of base carbon was ranged from $0.25 to $2.00 per pound of carbon. At the low end, the price for the product is $7.16 per pound, while at the top it is $8.82. The carbon price was varied while the indole price ($74.10) was held constant.

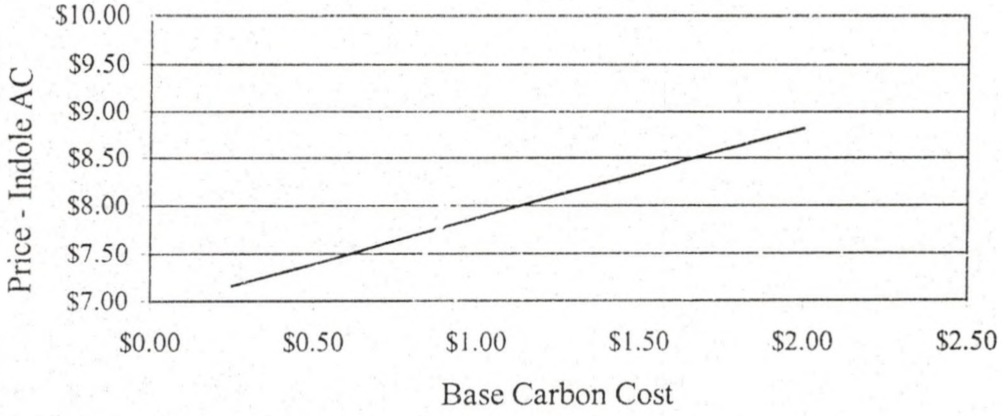

Figure 10. Sensitivity to Base Carbon Cost

The selling price is very sensitive to the cost of the indole. The range is $30 to $100 per pound. The best case reduces the selling price to $5.80 and in the worst case, it is increased to $9.30. Results of the analysis are shown is Figure 11. Here the carbon cost ($1.14) was held constant.

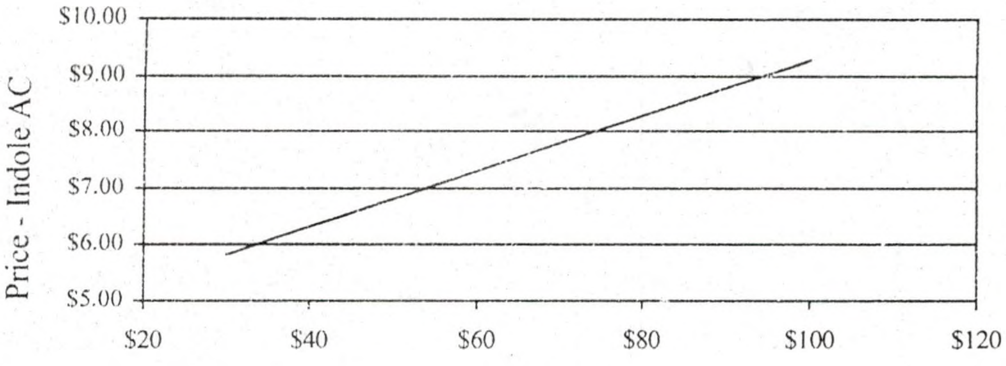

Figure 11. Sensitivity to Indole Cost

Reducing both the carbon and indole cost by half ($0.57 and $37.05 respectively) gives a selling price of $5.71 per pound and reducing both by 25% ($0.86 and $55.58) gave a selling price of $7.16.

Operating Labor, Utilities and PEC

Operating labor, utilities, and the PEC varied linearly with the selling price. Each component was changed while others were held constant, except those that were estimated as direct percentages of the varied parameter. The selling price was insensitive to each of these quantities. A decrease in operating labor of $114,000 (14.5%) or a decrease in utility cost of $250,000 (33%) decreased the selling price by $0.25 per pound of carbon. The PEC had even a smaller effect. Even if the PEC were decreased by 50% ($102,000), the decrease in selling price is only $0.14 per pound.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Mercury absorption through sorbent injection has proven to be diffusion limited in most cases. The assumption that there is no particle movement relative to flue gas may be erroneous due to a highly turbulent gas stream. If the particle does move in the gas stream, the sorbent particle will have access to a larger volume of flue gas and the diffusion predictions given in this paper should be taken as the worst case scenario.

Varying the temperature of the gas stream had a very little effect on the weight ratios of small diameter particles, but as the diameter increases the difference becomes more important. At high temperatures the system is capacity limited, but as absorption and speciation mechanisms become better known, capacities may increase through the use of a more appropriate sorbent.

Small particle diameters (less than 2 microns at 95% removal) were also shown to be capacity limited even at lower temperatures. Particle sizes must be kept as small as possible to reduce carbon-to-mercury weight ratios, but without being so small that there is a great sacrifice in capacity.

There was an enormous difference between mono-sized particles and their respective distributions. The 0.98-micron particle distribution with a geometric standard deviation of 2.8 had a carbon-to-mercury weight ratio 32 times greater than its mono-sized counterpart. Perhaps better quality control methods can be utilized in activated carbon production to reduce the geometric standard deviation for a given particle distribution.

The economic analysis showed a low total capital investment ($1.2 million), but the total product cost ($8.2 million) was very large in comparison. With competitive activated carbons selling for between $0.50 and $4.00 per pound, our carbon selling at $8.00 per pound will attract very little interest. Sixty-two per cent of the TPC is attributed to the raw materials carbon and indole, and any significant decrease in the selling price of the carbon is going to have to come through the lowering of the raw material costs. With the TPC at this level, it is not economically feasible to produce this type of carbon.

Recommendations

If better estimates for diffusion are required, a mathematical model could be developed assuming that the particle moves relative to the flue gas; however, due to the number of factors involved when making this assumption, the solution will prove very difficult to develop. A computer-programmed simulation would have to be written to explore this scenario. Another possible method of studying diffusion is to try sorbent injection at varying flue gas velocities at constant temperature with constituents in the gas stream limited to air and mercury.

Proper understanding of the mechanisms of speciation and absorption is essential and the quest to understand them must continue. If this system is diffusion limited, the gas stream should be kept as hot as possible to increase diffusion rates. Capacity problems will have to be overcome at higher temperatures. There should also be a study involving particle distributions. Since the carbon-to-mercury weight ratio is very dependent on the geometric standard deviation, methods to better control the range of particle sizes in crushing processes should be investigated.

The economic analysis shows the importance of lowering the raw material costs. Currently indole is being produced in bench-scale quantities only. In order to reduce the indole cost, a partnership will need to be developed with a chemical manufacturer or the indole may need to be produced on site. If indole AC is found to be very efficient at mercury capture, perhaps an analysis should be conducted for indole production.

APPENDIX A

CARBON-TO-MERCURY WEIGHT RATIOS

Table 10. Carbon Requirements for 95% Mercury Capture

	Diameter (μm)					
	1	2	4	6	8	10
Time (s)	Carbon to mercury weight ratio					
1	420	1676	6683	14990	26573	41436
2	210	839	3347	7511	13330	20790
3	140	559	2233	5015	8899	13884
4	105	421	1675	3764	6680	10423
5	84	336	1341	3013	5348	8344
6	70	280	1118	2511	4459	6957
7	60	240	958	2153	3824	5966
8	53	210	839	1885	3346	5222
9	47	187	746	1676	2975	4644
10	42	168	671	1509	2679	4181

Table 11. Carbon Requirements for 90% Mercury Capture

	Diameter (μm)					
	1	2	4	6	8	10
Time (s)	Carbon to mercury weight ratio					
1	323	1289	5139	11536	20460	31898
2	161	645	2574	5779	10256	15998
3	108	430	1718	3857	6846	10682
4	81	323	1289	2895	5139	8003
5	65	258	1031	2317	4114	6420
6	54	215	860	1932	3430	5352
7	46	185	737	1656	2941	4591
8	40	162	645	1449	2574	4017
9	36	144	573	1289	2288	3573
10	32	129	516	1160	2060	3216

Table 12. Dependence of Carbon Requirements on Temperature (95% Removal)

	4-second resonance time		8-second resonance time	
	Temperature			
	120°C	180°C	120°C	180°C
Diameter (μm)	Carbon to mercury weight ratio			
0.5	28	23	14	11
1	113	91	57	46
2	453	365	227	183
4	1807	1458	905	730
6	4059	3276	2033	1640
8	7202	5815	3609	2913
10	11236	9071	5632	4546

APPENDIX B

CAPACITY REQUIREMENTS

Table 13. Capacity Requirements for 95% Mercury Capture

	Diameter (µm)					
	1	2	4	6	8	10
Time (s)	µg Hg/ g Carbon					
1	2381	597	150	67	38	24
2	4763	1192	299	133	75	48
3	7138	1787	448	199	112	72
4	9516	2374	597	266	150	96
5	11895	2976	746	332	187	120
6	14269	3571	895	398	224	144
7	16649	4167	1043	464	262	168
8	19024	4760	1192	531	299	191
9	21393	5356	1341	597	336	215
10	23781	5948	1490	663	373	239

Table 14. Capacity Requirements for 90% Mercury Capture

	Diameter (µm)					
	1	2	4	6	8	10
Time (s)	µg Hg/ g Carbon					
1	3097	776	195	87	49	31
2	6194	1550	389	173	98	63
3	9281	2324	582	259	146	94
4	12380	3097	776	345	195	125
5	15470	3873	970	432	243	156
6	18556	4646	1163	518	292	187
7	21656	5418	1356	604	340	218
8	24749	6191	1550	690	389	249
9	27841	6966	1744	776	437	280
10	30930	7737	1937	862	485	311

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