THERMAL REGENERATION OF ACTIVATED CARBONS

E. Krieger, F. Tepper and A. J. Juhola

MSA Research Corporation
Evans City, Pennsylvania

Introduction

Granular activated carbons are used in tertiary treatment of waste water in several treatment plants, as at Pomona, California, and South Lake Tahoe, California, to name two. Waste water, from the secondary treatment, is passed through carbon beds which then remove the biologically nondegradable impurities and thereby produce water essentially free of organic impurities.

An important phase of the carbon treatment is the regeneration to permit reuse of the carbon over many cycles. The regeneration is accomplished thermally in multiple-hearth furnaces, using flue gas as source of activating gases as well as for heating. Operations of these plants has demonstrated a physical loss of carbon varying from 5% to 10% per regeneration. On each regeneration the carbon also loses some of its adsorptive capacity. Figure 1 presents data, obtained at the Pomona plant, showing these decreases in activity. The iodine number of the virgin carbon is 1090 mg/g and after 10 cycles it has decreased to 608 mg/g. Over the same cycles, the adsorption of water soluble COD impurities decreased from 53% down to about 39% with some leveling off starting at the 5th cycle.

To improve the economics of the carbon treatment, it is necessary to find means for decreasing the physical loss of carbon and loss of adsorptive capacity.

Laboratory Studies to Improve Carbon Regeneration

Mine Safety Appliances Research Corporation has conducted a research program sponsored by the Federal Water Pollution Control Administration to study the regeneration process and determine optimum conditions to reduce carbon losses and adsorptive capacity. The regenerations were done in an indirectly heated rotary tube regenerator shown in Figure 2. Two of the main components are the rotary tube, 3.25 in. inside diameter and 65 in. length, and the three electrically heated furnace sections which can be controlled separately. Each end of the

rotary tube is capped off with a rotary seal, insuring no loss of input and output gases. The gas temperature is measured at five points over the carbon bed. Carbon and gas flows are counter-current.

The regenerating gases are mixtures of N_2, CO_2 and steam, generally made up in proportions not too greatly different from flue gas. The N_2 and CO_2 are metered from compressed gas cylinders. A calibrated boiler is used for steam generation.

The effluent gas stream can be analyzed for CO, CO_2 and H_2 content.

Carbon input rate is generally 450 cc/hr and gas input rate about 10 ft^3/hr (stp).

Carbon residence times are about 1/2 and 1/4 hr.

The recovery of the adsorptive capacity on regeneration is measured by the iodine and molasses numbers and carbon loss by the particle volume decrease. The degree of success is then measured by how closely the iodine and molasses numbers approach the test results of the virgin carbon and by how small the particle volume decrease is.

The carbon used in most of these studies was Filtrasorb 400, once spent at the Pomona, California, plant. Table 1 gives the properties of the spent carbon and also those of the virgin carbon, the latter setting the goals to be attained on the regeneration. For monitoring purposes of the regeneration, the attempt was always made to bring the bulk density down from 0.597 to 0.468 g/cc. This was done by varying the activating gas input rate. By adjustments to other variables, the attempt was then made to also bring the iodine number to 1090 mg/g and molasses number to 250.

TABLE 1 - PROPERTIES OF SPENT AND VIRGIN FILTRASORB 400

Carbon	Bulk density, g/cc	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
spent	0.583	0.500	630	190
virgin	0.468	0.650	1090	250

Step-wise Nature of Carbon Regeneration

The laboratory regeneration studies and also thermodynamic calculations of the Pomona multiple-hearth furnace indicated that the thermal regeneration of wet spent carbon occurs in three naturally occurring steps. These are (1) drying, (2) carbonization of adsorbate, and (3) activation. Figure 3 shows the temperature profile of the gas and carbon in the Pomona furnace. The gas temperatures were measured and the carbon temperatures calculated from the thermodynamic properties of the system. The carbon temperature profile shows that the carbon is dried on traversing the first three hearths; this requires about 22 min. On the 4th hearth, the adsorbate is carbonized or baked. About 70% of the adsorbate is volatilized and the rest breaks down to free carbon lodged in pores. This step requires about 9 min. On hearths 5 and 6, the free carbon residue is oxidized, constituting the activation step. This step requires 15 min.

In the laboratory studies, the regenerations were then conducted in the three steps. Runs were made in which the drying and baking were conducted in the rotary tube with 1/2 hr carbon residence times. In other runs the drying was done separately in an air-convection oven and the baking then done in the rotary tube with 1/2 hr carbon residence time. It was found that the method of drying and baking produced no difference in the quality of the final product. Because of convenience, drying and baking were subsequently carried out separately.

The activating step was found to be more sensitive to the operating conditions. For instance, CO_2 activation produced regenerated carbons of lower iodine number than pure steam activation. Activation at high temperature of 1650° to 1700°F gave better results than activation at 1600°F and lower, although at about 1500°F, activation rate was too slow to be of any importance in the regenerations.

Optimization of gas input, gas composition and temperature, never produced regenerated carbons quite up to the virgin carbon properties. On cyclic studies, in which virgin carbon was successively spent and regenerated, the iodine number moved downward on each regeneration, not unlike the pattern observed at Pomona. These results are shown in Figure 4. After the second cycle, the iodine number of the regenerated carbon was down to 935 mg/g from the original 1090 mg/g. The regenerations had been done under conditions that were considered optimum with respect to gas input and temperature.

The conclusion is that optimization of gas input and temperature does not lead to complete regeneration.

Effect of Metallic Elements on Regeneration

In the cyclic studies, it was observed that the ash content increased with each successive cycle and that, also, it became easier to activate the carbon. Less activating gas input was required to bring the bulk density to the virgin carbon density. Table 2 gives the percentage ash content and decolorizing test results after each regeneration. The ash content increased from 5.7% to 8.6%. The molasses number increased from 250 to the 300 level, which, as will be explained later, is undesirable.

TABLE 2 - ASH CONTENT AND DECOLORIZING TEST RESULTS ON SUCCESSIVE ACTIVATIONS

Cycle No	Bulk density, g/cc	Ash content, %	Iodine number, mg/g	Molasses number
initial	0.469	5.7	1090	250
1	0.468	7.6	1040	310
2	0.469	8.6	935	290

Table 3 shows the drastic decrease in activating gas input rate required to avoid overactivation.

TABLE 3 - ACTIVATING GAS INPUT REQUIRED ON SUCCESSIVE ACTIVATIONS

Cycle No	Gas input, ft^3/hr (stp)		
	N_2	CO_2	H_2O
1	3.6	0.36	1.0
2	1.27	0.17	0.18

The correlation of increased ash content with decrease in iodine number led to an investigation of effects of ash content in the baking and activating steps. Several charges of spent carbon were leached with HCl acid, to remove some of the metallic element content, prior to being regenerated. The ash analysis decreased from about 7.0% to a constant lower limit of 4.7%. Virgin carbon starts with a 5.7% ash analysis. The acid leach also decreased the adsorbate content but no significant difference could be observed in the baked product when

compared to nonacid treated baked product. After activation, however, the acid pretreated carbons consistently had higher iodine numbers. Table 4 shows this comparison. The mean iodine number of the HCl pretreated regenerated carbons is 1034 mg/g compared to 945 mg/g for the nonpretreated.

TABLE 4 - EFFECT OF HCl ACID PRETREATMENT ON IODINE AND MOLASSES NUMBER OF REGENERATED CARBONS

Activation run no	Bulk density, g/cc	Not HCl treated		HCl treated	
		I_2 no, mg/g	Mol no	I_2 no, mg/g	Mol no
(virgin)	(0.468)	(1090)	(250)		
30	0.469	960	290		
32	0.467	950	---		
34	0.478			1020	230
36	0.484			1040	230
39	0.461	930	270		
40	0.468	950	250		
41	0.476	950	260		
47	0.468			1050	230
53	0.472			1020	250
77	0.468	930	250		
79	0.480			1040	230
	means	945	264	1034	234

The mean molasses number of 264 for the nonpretreated is larger than that of the virgin carbon while the mean molasses number of the acid pretreated carbons is smaller. The latter is favorable since activation could be continued to increase the iodine number while raising the molasses number to that of the virgin carbon.

The carbon losses, as measured by particle volume decrease, ranged from 1.6% to 4.0% for the nonpretreated carbons while for the pretreated carbons the range was 2.6% to 5.0%. Some of the advantage of the increased capacity is off-set by increased carbon loss.

The baking and activating conditions were varied for the runs reported in Table 4, but it, nevertheless, became evident that the nonpretreated carbons could be activated to the original bulk density with considerably less activating gas input than the acid pretreated carbons. In Table 5 are operating data on two runs where a valid comparison could be made to show this effect. In the activation Run 79, 30% to 50% more activating gases were required than on Run 30.

TABLE 5 - BAKING AND ACTIVATING CONDITIONS

Run no	Regenerating step	Temperature, °F 1	2	3	Gas input, ft^3/hr (stp) N_2	CO_2	H_2O
29	dry OSF 400 baked	750	1330	1550	7.0	0.90	2.28
30	Run 29 activated	1550	1650	1700	4.0	0.51	1.48
78	dry, HCl treated, baked	800	1350	1550	7.0	0.93	1.96
79	Run 78 activated	1550	1650	1700	6.0	0.80	1.94

TABLE 8 - SURFACE AREA CHANGE AT DIFFERENT PORE DIAMETERS DURING REGENERATION

Carbons compared	Surface area difference, m^2/g >10 Å	>12 Å	>14 Å	>16 Å	>18 Å	>20 Å	>28 Å	>50 Å
F 400 - 79 (HCl)	40	35	30	80	200	150	20	16
F 400 - 67	105	110	105	160	270	215	10	00
F 400 - 68 (CO_2)	160	160	155	165	370	130	20	00
F 400 - 46	130	115	90	155	170	115	-30	-10
F 400 - 36 (HCl)	30	40	40	70	195	150	30	15

Ash Analyses

Since metallic elements in the carbon were now established as contributing to decreased recovery of the iodine number and over recovery of the molasses number, an investigation was made of the ash content of three carbons. The ash analyses for the three carbons are given in Table 6. Run 67 is a nonpretreated regeneration run and Run 79 an acid pretreated run. The virgin carbon is included, to indicate status of the starting material.

Run 67 shows a considerable increase in the oxides, Fe_2O_3, CaO, MgO, K_2O, Na_2O and Cr_2O_3. As is evident from Run 79, these oxides are considerably reduced by the HCl acid leach, hence one or more of these oxides contribute to lowered recovery of the iodine number and over recovery of the molasses number.

TABLE 6 - ASH COMPOSITION OF ACID PRETREATED AND NONPRETREATED REGENERATED CARBONS

	Ash composition, %		
Component	virgin F 400	nonpretreated Run 67	pretreated Run 79
SiO_2	2.36	2.27	2.24
Al_2O_3	2.51	1.94	1.62
Fe_2O_3	0.42	0.80	0.59
CaO	0.17	1.23	0.05
MgO	0.14	0.34	0.09
K_2O	0.06	0.40	0.20
Na_2O	0.04	0.15	0.07
TiO_2	0.03	----	----
Cr_2O_3	0.01	0.12	0.12
Total ash in carbon	5.7	7.2	5.0

Effect of Regeneration on Pore Size Distribution

In pore structure studies performed at Pittsburgh Carbon Company[1,2], it was found that the iodine number was proportional to the surface area of pores larger than 10 Å in diameter and the molasses number was proportional to the surface area of pores larger than 28 Å in diameter. Equations 1 and 2 below show these relationships.

$$I_2 \text{ no} = 17 + 1.07 \times (\text{s a of pores} > 10 \text{ Å}) \quad (1)$$

$$\text{Molasses no} = 129 + (\text{s a of pores} > 28 \text{ Å}) \quad (2)$$

With reference to the iodine and molasses numbers given in Table 4, these equations indicate that acid pretreatment minimizes decrease in surface area of the smaller pores and also prevents increase in surface area of pores larger than 28 Å diameter. Ash build up, as occurs on successive regenerations without acid leach, accelerates these changes.

A further study was conducted to determine the manner in which the surface area changes occurred. Pore size distribution curves were determined for selected carbons, using the water adsorption method[3] and mercury porosimetry. In preparation for the water isotherm determinations (and also porosimetry), the carbons were HCl acid and pure water leached to remove hydrophilic compounds from the carbon surface. The validity of the water adsorption method depends on the water being adsorbed by capillary condensation, with negligible monolayer adsorption. The adsorption method is applicable to maximum pore diameter of 500 to 1000 Å.

Pores in the larger diameter range are measured by mercury porosimetry[4]. These measurements cover the diameter range 30 to 100,000 Å, hence the two methods overlap in the range 30 to 500 Å. For some of the pore size distributions, the agreement in the overlap range is good while for others, some discrepancy exists. The trend is for the mercury porosimeter to measure a larger pore diameter at a given volume. Figure 5 presents two distribution curves, Run 68 showing the best agreement and F 400 the poorest. A possible explanation for the discrepancy is that the carbons are slightly compressed by the mercury at the higher pressures. Maximum pressure at 30 Å is 60,000 lb/in^2.

Figures 6 and 7 present the complete pore size distribution curves of the selected samples. The overlap portion as measured by mercury porosimetry was left out in each case.

Those in Figure 6 show the effects of acid leach, steam activation and CO_2 activation. The virgin F 400 is uppermost in pore volume at the 28 Å diameter, and then Runs 79, 67 and 68 in descending order. The iodine numbers were respectively, 1090, 1040, 940 and 840 mg/g, while the molasses numbers were quite close to each other.

Those in Figure 7 also show effect of acid leach; Run 36 being uppermost was pretreated, while Runs 46 and 67 were not. Runs 46 and 67 are presented together because they have iodine numbers close to each other, i.e. 920 and 940 respectively, but have greatly different molasses numbers, 320 and 260, respectively.

The relationship between the decolorizing tests and pore structure is not always apparent by visual inspection of the pore size distribution curve, but comes more discernable when the cumulative surface areas at different pore sizes are compared. The cumulative surface area can be calculated with the equation

$$\Delta A = \frac{4\ \Delta V}{D}$$

where ΔA is an increment of surface area associated with increment of pore volume ΔV with mean diameter D. By summing up ΔA over the pore volume the surface area of pores larger or smaller than any specified D can then be calculated. This has been done for the carbons of Figure 6 in Figure 8 and for carbons of Figure 7 in Figure 9.

From Figure 8, the surface areas of pores larger than 10 Å in diameter for the carbons F 400, Runs 79, 67 and 68 are 965, 925, 860 and 805 m^2/g, respectively. The surface areas of pores larger than 28 Å are respectively, 120, 100, 110 and 100 m^2/g. Likewise from Figure 9, the surface areas of pores larger than 10 Å in diameter for the carbons Runs 36, 67 and 46 are 915, 860 and 840 m^2/g, respectively. Surface areas of pores larger than 28 Å in diameter are, respectively, 85, 110 and 150 m^2/g. When these surface areas are substituted into equations 1 and 2, the calculated decolorizing numbers agree with test results within $\pm$ 5% in the iodine numbers and within 13% in the molasses numbers. These results are given in Table 7.

TABLE 7 - IODINE AND MOLASSES NUMBERS AS DETERMINED BY TEST AND CALCULATED FROM SURFACE AREA

Carbon	Iodine number, mg/g		Molasses number	
	test	calc	test	calc
Filtrasorb 400	1090	1040	250	250
Run 79 (HCl)	1040	1010	230	230
Run 67	940	940	260	240
Run 68 (CO_2)	840	880	250	230
Run 46	920	920	320	280
Run 36 (HCl)	1040	1000	230	210

Further study of the surface area curves also indicate where the major portion of the adsorption may be occurring. By inspection of the curves in Figure 8, it is observable that most of the change in pore structure occurs in the pores from 14 to 28 Å. Beyond 28 Å, there can be considerable change in pore volume, as is apparent from inspection of curves in Figures 6 and 7. The surface area of these larger pores is, however, too small to be effective. The same is true for Runs 67 and 38, of Figure 9, but Run 46 is an exception. For this carbon considerable change occurs at the 28 Å diameter region.

To show the change in pore structure, the difference in surface area between that of F 400 and each of the other carbons have been calculated for pore diameters from 10 Å to 50 Å. These calculated areas are given in Table 8. Pore structure change for Runs 79, 67 and 68 starts at 14 Å and ends at 28 Å diameter with most occurring at the 19 Å region. For Run 46, the pore structure change varies over the whole range with the largest difference again occurring at the 18 Å diameter. These results indicate a general enlargement of pores larger than 14 Å in diameter. Since the enlargement is greater for the nonpretreated carbons, the results also indicate that the major part of the adsorption occurs in pores of 14 to 28 Å in diameter. From this study it can be concluded, that the metallic oxides catalyze the oxidation of the base carbon structure in this pore diameter range.

Summary

To summarize the results of this experimental program, it was shown that granular carbons spent in tertiary treatment of waste water can be thermally regenerated to properties approaching those of the virgin carbon. Best results are obtained if the spent carbon is HCl leached to remove organometallic compounds of Fe, Ca, Mg, Na and K prior to regeneration, and that the final activation be by steam oxidation. The oxides of these metals catalyze the oxidation of the base carbon structure in the 14 to 28 Å diameter pore size range. The evidence also indicates that these pores are active in the adsorption process.

References

1. A. J. Juhola, W. M. Matz and J. W. Zabor, paper presented at the Am Chem Soc meeting, Div of Sugar Chem, April 1, 1951, "Adsorptive Properties of Activated Carbons."

2. R. J. Grant, "Basic Concept of Adsorption on Activated Carbon", Pittsburgh Activated Carbom Company.

3. E. O. Wiig and A. J. Juhola, JACS 71 2069, 2078 (1949).

4. Measurements made by American Instrument Co, Inc, Silver Springs, Maryland.

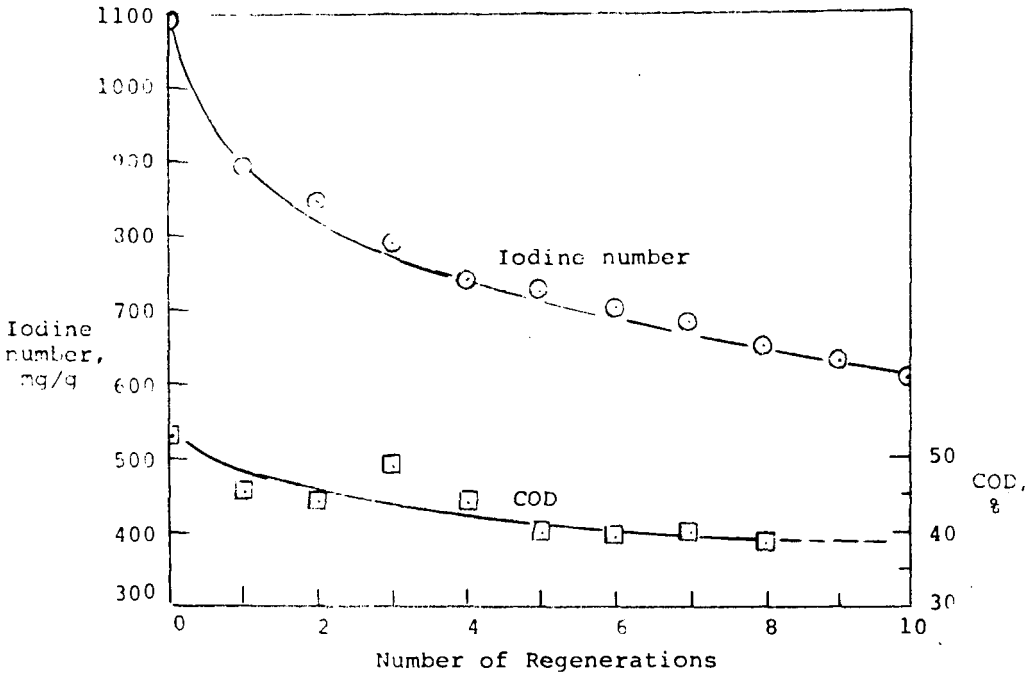

FIGURE 1 - DECREASE IN IODINE NUMBER AND COD ADSORPTIVE CAPACITY WITH SUCCESSIVE REGENERATIONS

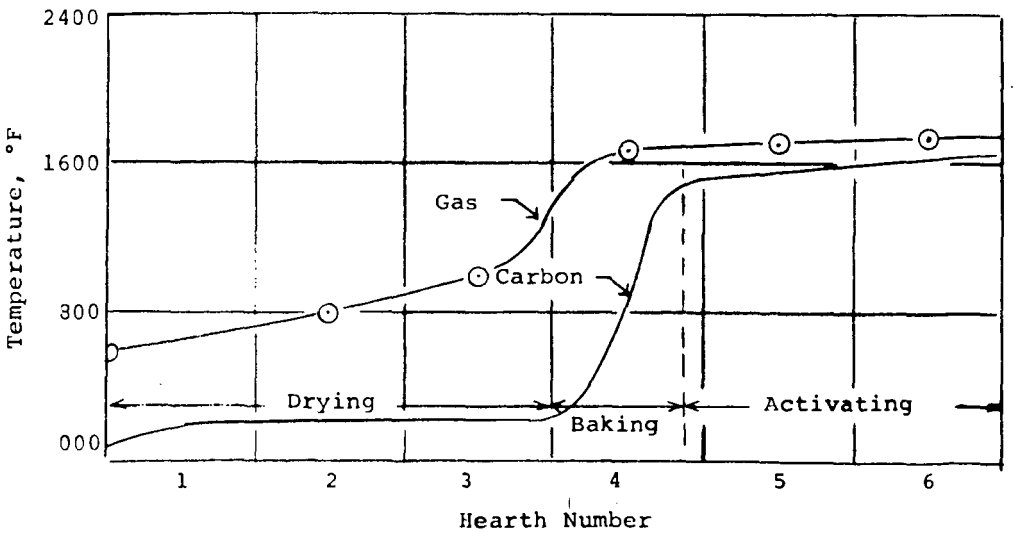

FIGURE 3 - TEMPERATURE PROFILES FOR GAS AND CARBON IN MULTIPLE HEARTH FURNACES, REGENERATION OF WET SPENT CARBON

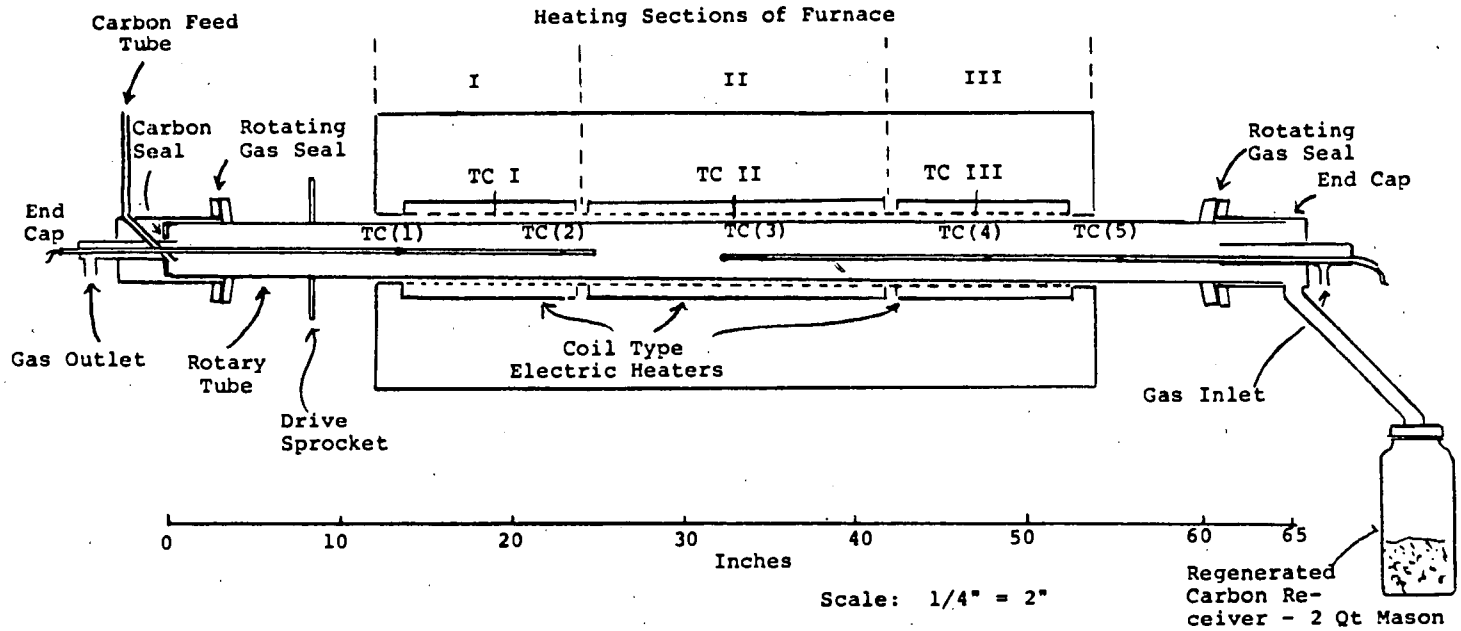

FIGURE 2 - CROSS SECTIONAL VIEW OF ROTATING TUBE, END CAPS AND HEATING FURNACE

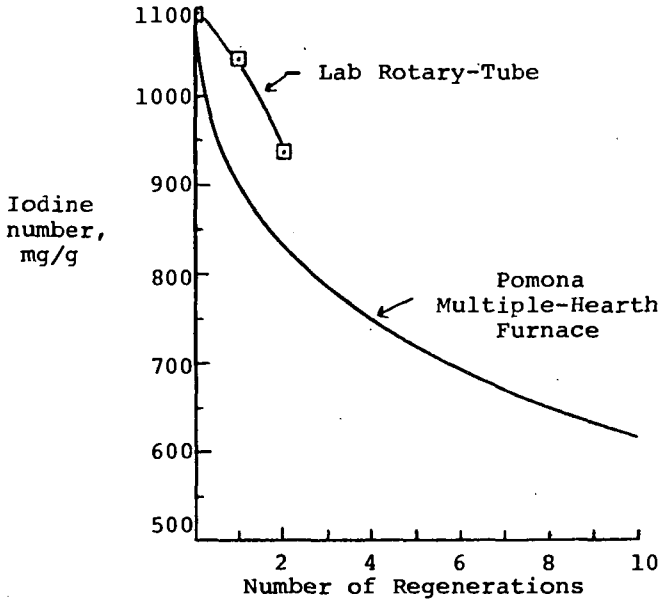

FIGURE 4 - DECREASE OF IODINE NUMBER WITH SUCCESSIVE REGENERATIONS

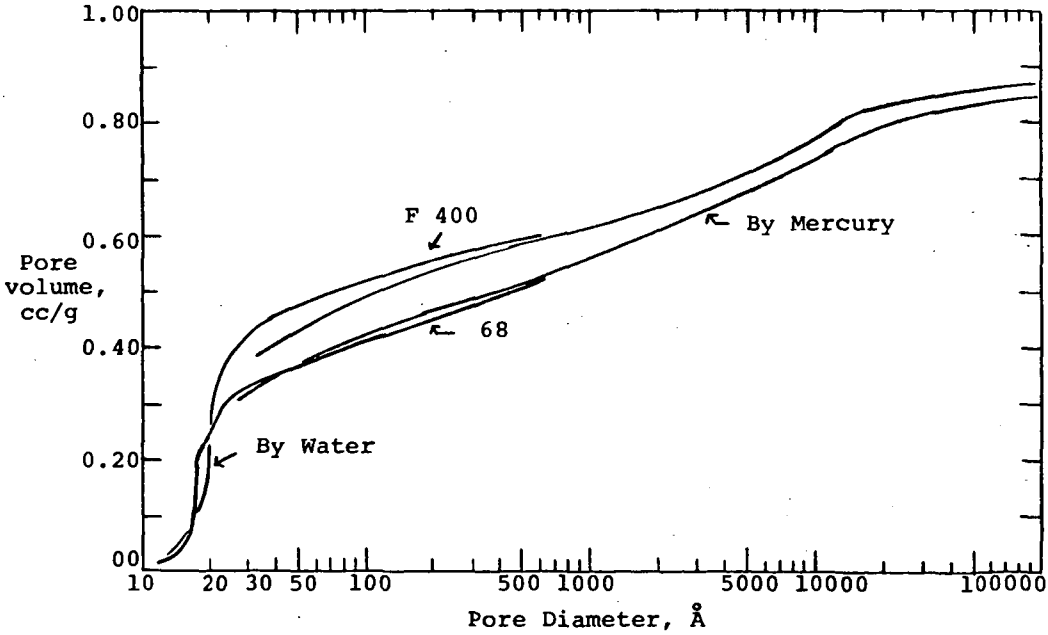

FIGURE 5 - PORE SIZE DISTRIBUTION MEASURED BY WATER ADSORPTION AND BY MERCURY PENETRATION

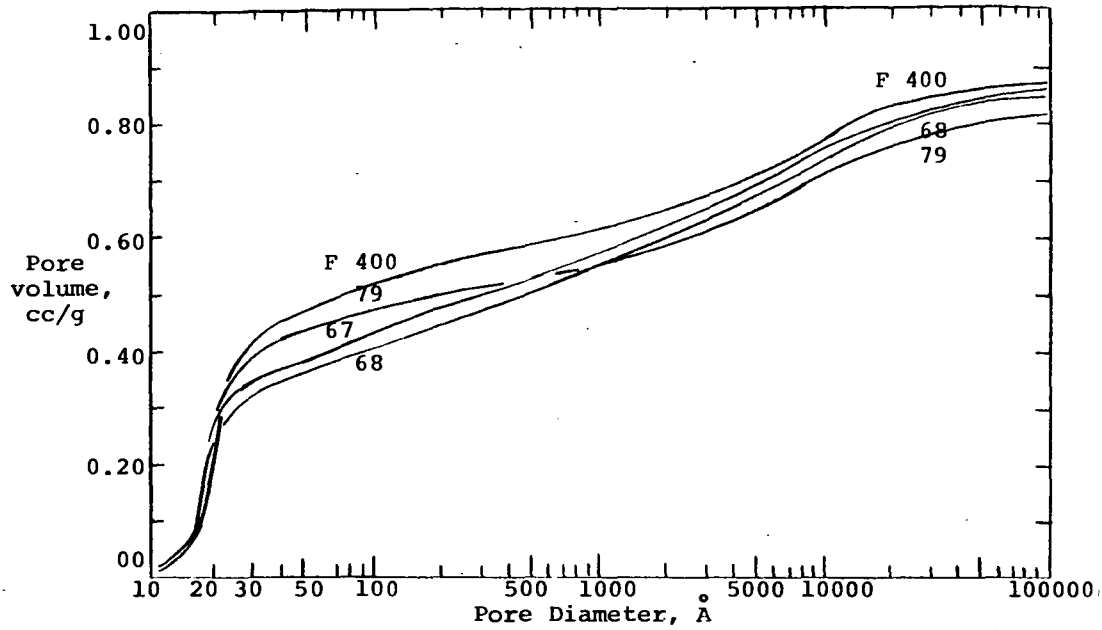

FIGURE 6 - PORE SIZE DISTRIBUTIONS OF REGENERATED CARBONS

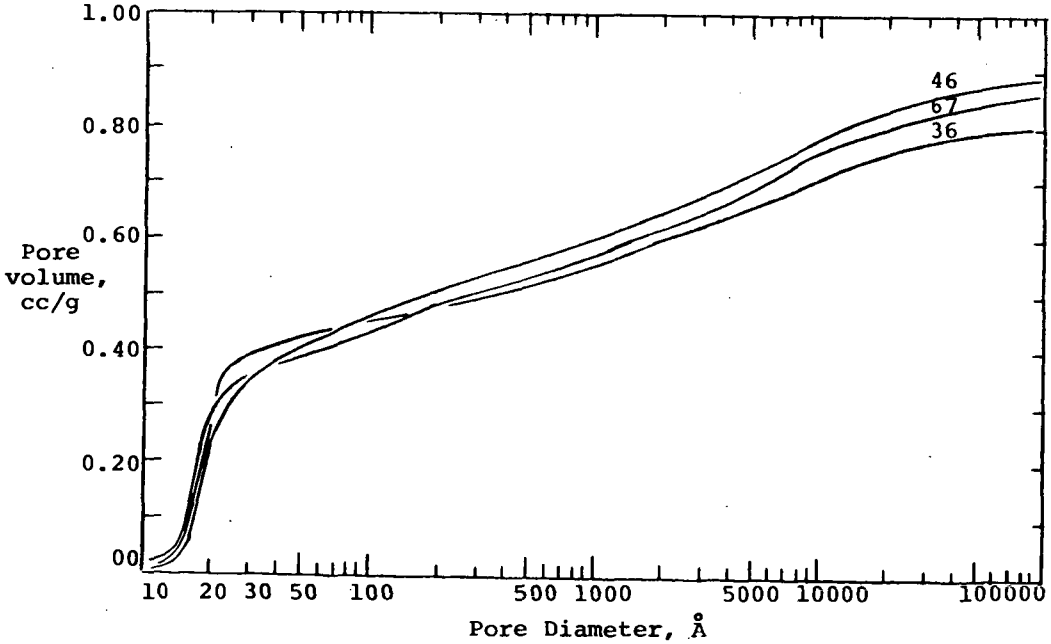

FIGURE 7 - PORE SIZE DISTRIBUTIONS OF REGENERATED CARBONS

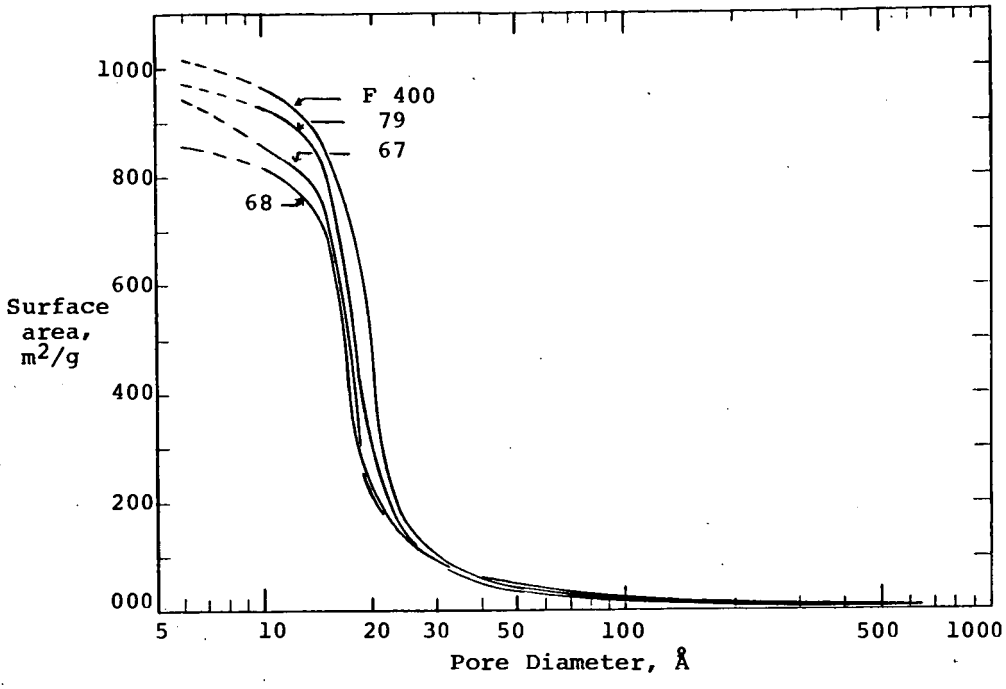

FIGURE 8 - CUMULATIVE SURFACE AREAS OF REGENERATED CARBONS

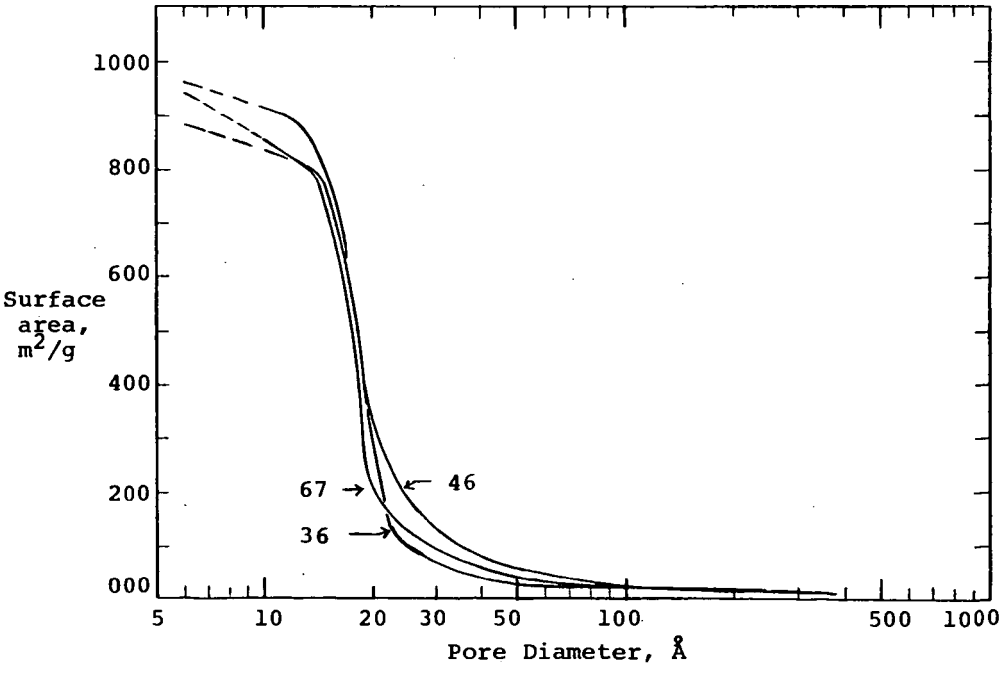

FIGURE 9 - CUMULATIVE SURFACE AREAS OF REGENERATED CARBONS