OPTIMIZATION OF THE REGENERATION PROCEDURE FOR GRANULAR ACTIVATED CARBON

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OPTIMIZATION OF THE REGENERATION PROCEDURE
FOR GRANULAR ACTIVATED CARBON

by

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for the

ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

Granular activated carbons, spent in tertiary treatment of waste water, are thermally regenerated in regenerators such as the multiple-hearth furnace. Wet spent carbon is fed to the regenerator and undergoes three naturally occurring steps, namely (1) drying at about 220°F, (2) pyrolysis of the adsorbed pollutants at 500° to 1550°F and (3) activation with flue gas and steam at 1600° to 1700°F. For each adsorption-regeneration cycle, the carbon volume loss varies from 5% to 10% and the activity loss is as high as 13% on the first cycle but at diminishing amounts on subsequent cycles.

Laboratory studies of parameters controlling regeneration show that alkaline and iron oxide ash accumulation in the carbon, during the use cycles, catalyzes the oxidation of pores in the 18Å to 28Å diameter range, the pores most effective in pollutant adsorption. By HCl acid leach, to remove these metallic elements from the spent carbon, the subsequent thermal regeneration proceeds with less destruction of the carbon as measured by the iodine and molasses numbers.

Steam as activating gas is more effective than CO_2 in recovery of the initial properties of the carbon.

Carbon volume decrease during the baking step averages out around 2% and during the activation step at 1.8%. Baking studies indicate that the 2% is not a true carbon loss but rather an apparent volume decrease due to pyrolysis of colloidal pollutants on the carbon particle exterior surfaces. The true loss of carbon during the laboratory regenerations is then about 1.8%. The latter appears to proceed by generation of submicron sized fines from the carbon particle surfaces rather than due to oxidation.

Slow drying of the wet carbon is more effective than fast drying.

Attempted regeneration by leaching with solutions of NaOH, NaOCl, H_2O_2 and CCl_4 were ineffective and/or uneconomical.

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Key Words: Carbon regeneration, chemical regeneration, HCl acid treatment, thermal regeneration, tertiary treatment with carbon.

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SECTION I

CONCLUSIONS

1. Thermal regeneration of wet spent carbon from the tertiary treatment of waste water proceeds by three naturally occurring steps; (1) drying at about 212°F, (2) pyrolysis (baking) of the adsorbate at 500° to 1550°F and (3) activation with steam flue gas mixture at 1650°F to 1700°F. In the Pomona multiple-hearth furnace, Step 1 occurs in 22 min, Step 2 in 9 min and Step 3 in 15 min.

2. Slow drying of the as-received wet spent carbon, as in an air-convection oven at 150°C for 48 hr, produced regenerated carbons of higher iodine number than when drying was done rapidly in 10 to 20 min in the rotary-tube laboratory regenerator. Iodine numbers of the regenerated slow-dried carbons were in the 950 to 970 mg/g range while those of the fast-dried carbons were in the 900 to 935 mg/g range.

3. Low temperature activation at 1600°F produces lower activity regenerated carbons than when the activation is carried out at 1650° to 1700°F. The iodine numbers for the former were in the range 900 to 910 mg/g while for the latter they were 950 mg/g and slightly higher.

4. Thermal regeneration of graded mesh size fractions in the 8 to 60 mesh size range showed no significant difference in rate of regeneration. Spent West Virginia Pulp and Paper Company carbon of 8 to 20 mesh fraction regenerated at essentially the same rate as the 30 to 60 mesh fraction. The finer mesh fractions, however, showed a tendency toward larger carbon losses during the regeneration.

5. The rate of thermal regeneration is more dependent on the pore structure than on particle size. A carbon such as 14 to 30 mesh Darco, with 0.60 cc/g of pores in the 30Å to 1000Å diameter range, regenerates faster and under much milder regeneration conditions than Filtrasorb 400 with 0.20 cc/g of pores in the same diameter range. When granular carbons are sized to smaller particles, pores in the 10,000Å to 100,000Å diameter range are destroyed, but since these pores do not control the regeneration rate, decrease in particle size does not increase the regeneration rate. This generalization applies to processes involving gas diffusion but not to liquid diffusion.

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6. Attempts to regenerate spent carbons by leaching with CCl_4 or with aqueous solutions of NaOH, NaOCl and H_2O_2 were not effective or economical.

7. HCl acid leach of spent carbons had a beneficial effect on the subsequent thermal regeneration. Iodine and molasses numbers of the regenerated products were closer to the initial values than for the nonleached regenerated products.

8. The effectiveness of the HCl acid leach was due to the fact that the acid leached out metallic elements such as Fe, Na, Ca and K which, if left in the carbon, catalyzed the oxidation of the pores in which they happen to be located.

Pore structure studies showed that, in nonleached carbons, enlargement of pores occurred in the 18Å to 28Å diameter range during activation. This fact also implies that pollutant adsorption is predominantly in pores of this size range since the metallic elements that catalyze the pore enlargement are initially a part of the pollutants.

9. Studies to optimize the HCl treatment showed that it could be performed effectively at ambient temperature, at acid to carbon contact time of about 2 to 3 hr, at 0.076 lb acid/lb carbon (38% HCl assay) and 1.4% acid concentration based on weight of HCl. Estimated cost of acid is 0.145¢/lb of regenerated carbon.

10. Steam activation consistently produced regenerated carbons of higher iodine number than CO_2 activation. For HCl acid pretreated carbons, steam activation produced carbons of 1040 mg/g iodine number while with CO_2 activation the iodine number was 960 mg/g. For nonleached carbons, the results were 940 mg/g with steam activation while with CO_2, the iodine number was 880 mg/g.

11. Since the baking is done under conditions that should not cause oxidation of carbon structure, no carbon volume loss should be expected. About a 2% volume decrease consistently appeared. The evidence obtained appears to indicate that this volume decrease is due to pyrolysis of colloidal contaminants on the exterior surface of the carbon particles and not a true loss of the activated carbon.

12. Carbon volume decrease during the activation step averages out around 1.8% and appears to be due to loss of submicron fines broken off the carbon particle exterior surface rather than oxidation by the steam.

13. Cyclic adsorption-regeneration studies, where the spent carbon was not acid leached, showed progressive de-

crease of iodine number over two cycles. On the first cycle
of the study, employing acid leach, the initial iodine num-
ber was attained.

14. In direct-fired furnaces the flue gas usually contains
1 to 2% unreacted oxygen. The laboratory studies showed
that oxygen in these quantities has no effect on the regen-
eration process.

15. A vent gas analysis study was undertaken to determine
whether monitoring the vent gases from the activation step
could be used to control the process. The results produced
too many inconsistencies to recommend the method.

16. Vent gas analyses showed that the H_2O, CO, CO_2 and H_2
react with each other and come to an equilibrium according
to the equation

$$\frac{[CO_2][H_2]}{[H_2O][CO]} = K$$

where the equilibrium constant K varies with temperature.
With excess steam, the utilization of CO_2 is suppressed and
in some cases CO_2 has been produced.

SECTION II

RECOMMENDATIONS

The success of the HCl acid leach pretreatment on the laboratory scale recommends it for application to the large scale regeneration systems. The pretreatment step is economical relative to acid cost, but corrosion is expected to be the difficult problem.

Further studies are recommended on carbon pore structure relative to ease of regeneration. Such a study would lead to a better understanding of the adsorption and regeneration process and form a basis for the selection of carbons best suited for tertiary treatment.

Studies of the effect of particle size on ease of regeneration demonstrated that regeneration of powdered carbons could be done effectively in conventional equipment, with modifications to equipment and procedures of operation. Further study is recommended for this approach.

SECTION III

INTRODUCTION

On the previous program, Contract No. 14-12-107, regeneration equipment was installed and regeneration procedures worked out for study of the regeneration process. Partial answers were found for the regeneration process, but also, new areas of study became apparent which were outside of the scope of the contract.

One of the more important observations made was that the overall regeneration, as practiced in the multiple hearth furnace, consisted of three natural occurring steps; i.e., (1) drying, (2) pyrolysis of adsorbate (baking) and (3) activation. In the activation step, free carbon residue from the baking step is removed by steam oxidation. These three steps were studied, but completely satisfactory answers were not obtained regarding the parameters affecting them.

The present program, Contract No. 14-12-469, was initially contracted for 14 months, but promising areas of further investigation were discovered that were outside the scope of the contract. To investigate these new areas, the contract was extended another 6 months. The continued studies were divided into seven tasks as identified below.

Task 1 - Study of Regeneration Operating Parameters

Task 2 - Adsorption-Regeneration Cycle Studies

Task 3 - Determine Feasibility of Low Grade Carbon as Make Up

Task 4 - Chemical Oxidation and Solvent Extraction

Task 5 - Engineering Studies on Furnaces

Task 6 - Regeneration Control by Effluent Gas Analysis

Task 7 - Regeneration of 25 lb Quantities of Spent Carbon

After considerable study had been made on the hearth furnace operating parameters as part of Task 1 studies, a set of conditions were to be set for the regeneration of one contactor full of carbon at the Pomona, California pilot plant,

a project jointly funded by the County Sanitation Districts
of Los Angeles County and the Federal Water Quality Admin-
istration, U.S. Department of the Interior.

Task 2 had a two-fold purpose. The initial properties of
the spent carbon, as received from the Pomona plant, were
not known exactly, therefore there was some uncertainty in
determining the recovery of the initial properties. This
uncertainty was removed in Task 2 (and also Task 3) studies
since the properties of the starting material were deter-
mined and the same batch of carbon was carried throughout
the cyclic studies. The other purpose was to study the type
and rate of carbon degeneration over a number of cycles of
regeneration.

Task 4 involved study of liquid chemical treatment of the
spent carbon as a primary regenerating process, an alterna-
tive to the thermal regeneration. It also involved study
of chemical pretreatment of spent carbon as an aid to the
thermal regeneration.

Task 4 opened up new areas of investigation in that HCl
leach of the spent carbon prior to thermal regeneration
greatly minimized loss of adsorptive capacity during re-
generation. To investigate the acid leach, and other areas
of promise, the program was extended another six months.

SECTION IV

EQUIPMENT AND PROCEDURES

Rotary-Tube Thermal Regenerating Unit

The thermal regenerations, involving the baking and activating steps, were conducted in a continuous feed, indirectly heated rotary-tube regenerator. If offers the widest range of versatility with respect to operating parameters. Activating gas composition and input rate can be varied to any practical limit. Heat input can be varied independently of the activating gas input rate and the carbon residence time can also be varied independently of the other parameters.

Figure 1 shows the cross sectional view of the rotating tube and sections of the furnace. Thermocouples TC I, TC II, and TC III monitor the three sections of the furnace I, II, and III, which can be temperature controlled independently of each other. Thermocouples TC (1), TC (2), TC (3), TC (4) and TC (5) monitor the gas temperature over the carbon bed.

Other pertinent details of the unit are listed below:

Tube size and material	- 3.25 in. dia by 65 in. length, stainless steel
Flights	- six 1/4 in. deep flights about the full length of tube. This depth flight gives carbon a rolling action rather than a lift and free fall.
Heating	- the heated portion of tube corresponding to furnace length is 42 inches, carbon residence times are reported for the 42 inches rather than the total 65 inches.
Tube inclination	- has been varied from level to 4 inches per 42 inches of tube length.
Carbon residence time	- The carbon residence time can be varied from 10 min to 3.7 hr by varying in-

Carbon feed
tube

Heating sections of furnace

I   II   III

Rotating
gas seal

Carbon
seal

Rotating
gas seal

End cap

TC I   TC II   TC III

End
cap

TC(1)   TC(2)   TC(3)   TC(4)   TC(5)

Gas outlet

Coil type
electric heaters

Rotary
tube

Gas inlet

Drive
sprocket

0   10   20   30   40   50   60   65

Inches

Regenerated
carbon re-
ceiver - 2 qt mason
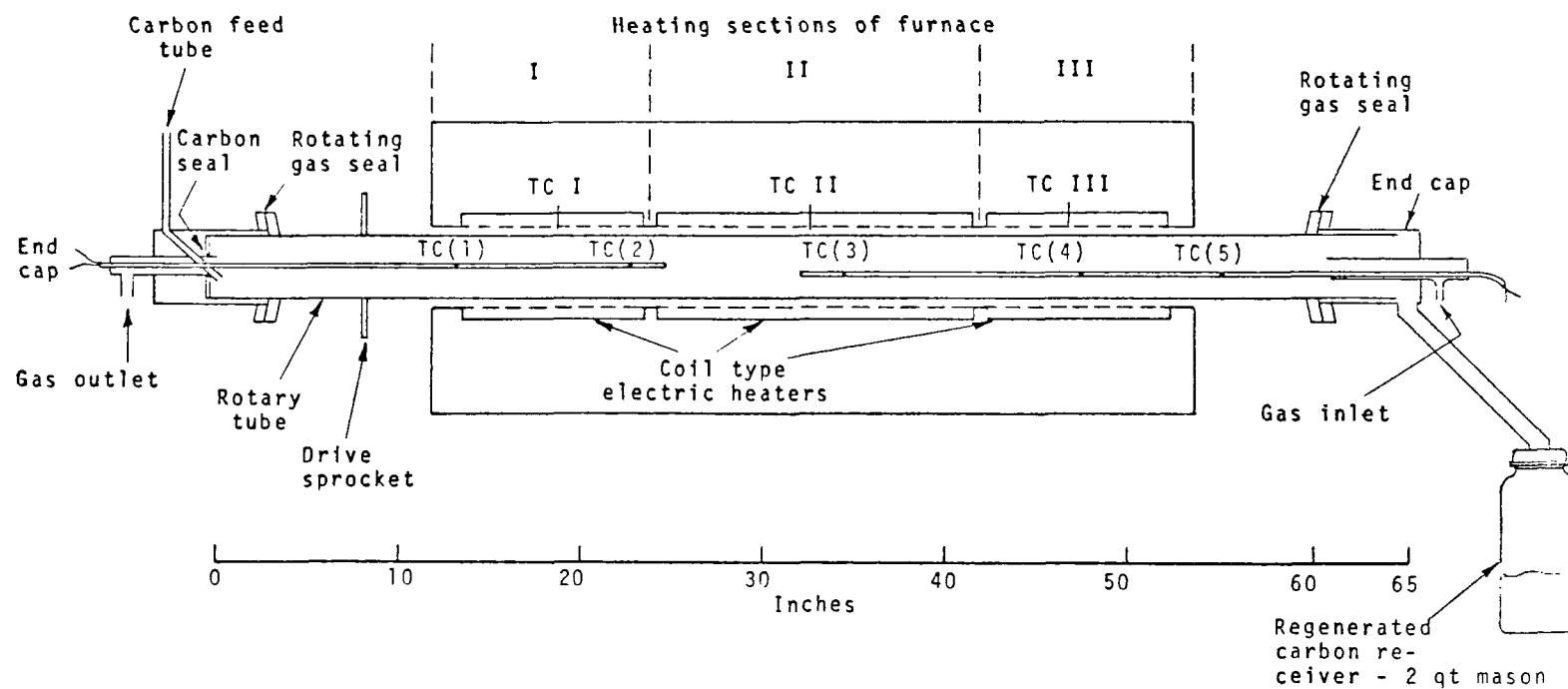
FIGURE 1 - CROSS SECTIONAL VIEW OF ROTATING TUBE, END CAPS AND HEATING FURNACE

	clination and rotation rate. The usual residence time for baking is 30 min and for activating 15 min.
Gas input	- The input gas composition and input rate are varied by metering N_2, CO_2, O_2 from compressed gas cylinders and generating steam by means of a calibrated boiler. To simulate multiple hearth furnace operations, gas mixtures approaching the flue gas mixture are usually used, i.e., 72% N_2, 10% CO_2 and 18% H_2O. Total input can be varied from 4 to 40 ft^3/hr (stp).
Carbon feed rate	- An auger type volumetric feeder is used having a feed rate range between 0.010 and 0.100 ft^3/hr for granular carbons. The usual feed rate is 0.016 ft^3/hr, 453 cm^3/hr.
Vent gas analyses	- About 1.0 ft^3/hr of gas mixture is withdrawn from the main vent gas stream during activation, for CO_2, CO and H_2 analyses. The side-stream is passed in succession through a (1) glass wool filter, (2) water freeze out trap at -80°C and (3) MSA In-Line-Ultra particulate filter, before reaching the gas analyzers. The CO and CO_2 concentrations are analyzed with MSA Lira Model 300 analyzers and the H_2 with an MSA Thermatron.

General Procedure for Thermal Regenerations

Spent carbons, as received from the tertiary treatment pilot plant at Pomoma are first dried for 48 hours in an air-convection oven at 150°C, then sieved to 14 by 40 mesh, and blended as preliminary preparation for the regeneration. The amount of oversize and undersize particles was always small and was discarded. The drying is considered the first

step in the overall regeneration procedure. Generally 2500 cm^3 of the dried spent carbon are measured out for each regeneration run. The second step is baking, wherein the dried spent carbon is passed through the regenerator at a rate to give a 30 min residence time. The gas input during baking has been varied considerably. On some runs a flue gas mixture was used and on others, nitrogen. The latter, of course, is not attainable in a direct-fired hearth furnace, but the runs were made to obtain data on extreme conditions. The gas temperature on most runs was controlled to vary linearly from 800°F at the carbon influent end of the bed to 1550°F at the carbon effluent end. The baking was also tried with wet carbon feed, i.e., 40% by weight of water, to simulate conditions in the Pomona hearth furnace even closer. With wet carbon feed, the baked carbon bulk density was slightly less than with dried carbon feed. However, with wet carbon feed, vent line plugging occurred frequently, hence, dried carbon feed was then standard practice for most of the baking runs.

During baking, the adsorbate is carbonized yielding a volatile portion and a free carbon residue which is then removed by steam oxidation during the activating step. Fifty to seventy percent of the adsorbate is removed as volatiles. For the activating step, the gas temperature profile down the tube is generally 1550°F for section I, 1650°F for section II and 1700°F for section III. The required activating gas input rate is calculated from previous experimental results. For this purpose the bulk density is used as the control test, i.e., gas input is varied to bring the bulk density to that of the virgin carbon.

Further details on the regenerator unit and operating procedures are presented in the final report for Contract 14-12-107[1].

Unit for Leaching Spent Carbons

Task 4 involved leaching experiments with chemical oxidants and solvents to develop a primary regenerative process or, if not successful in this effort, to find an oxidant or solvent that would aid the thermal regeneration process. Chemicals tried in aqueous solution were H_2O_2, NaOH, NaOCl and HCl. In some preliminary experiments, Büchner funnels were used, but their use did not permit sufficient control over temperature and flow rate of solution through the carbon bed. To correct this problem, the unit shown in Figure 2 was constructed.

Glass tube
54 mm OD
47 in. total
length

Solution level at
constant pressure
head

Disk with center
hole to mini-
mize convection
current

Heater
&
insulation

Filtrate
flow

Carbon bed

Screen

12 in. x 18 in.
27 1 cap.
of leach
solution

Pump
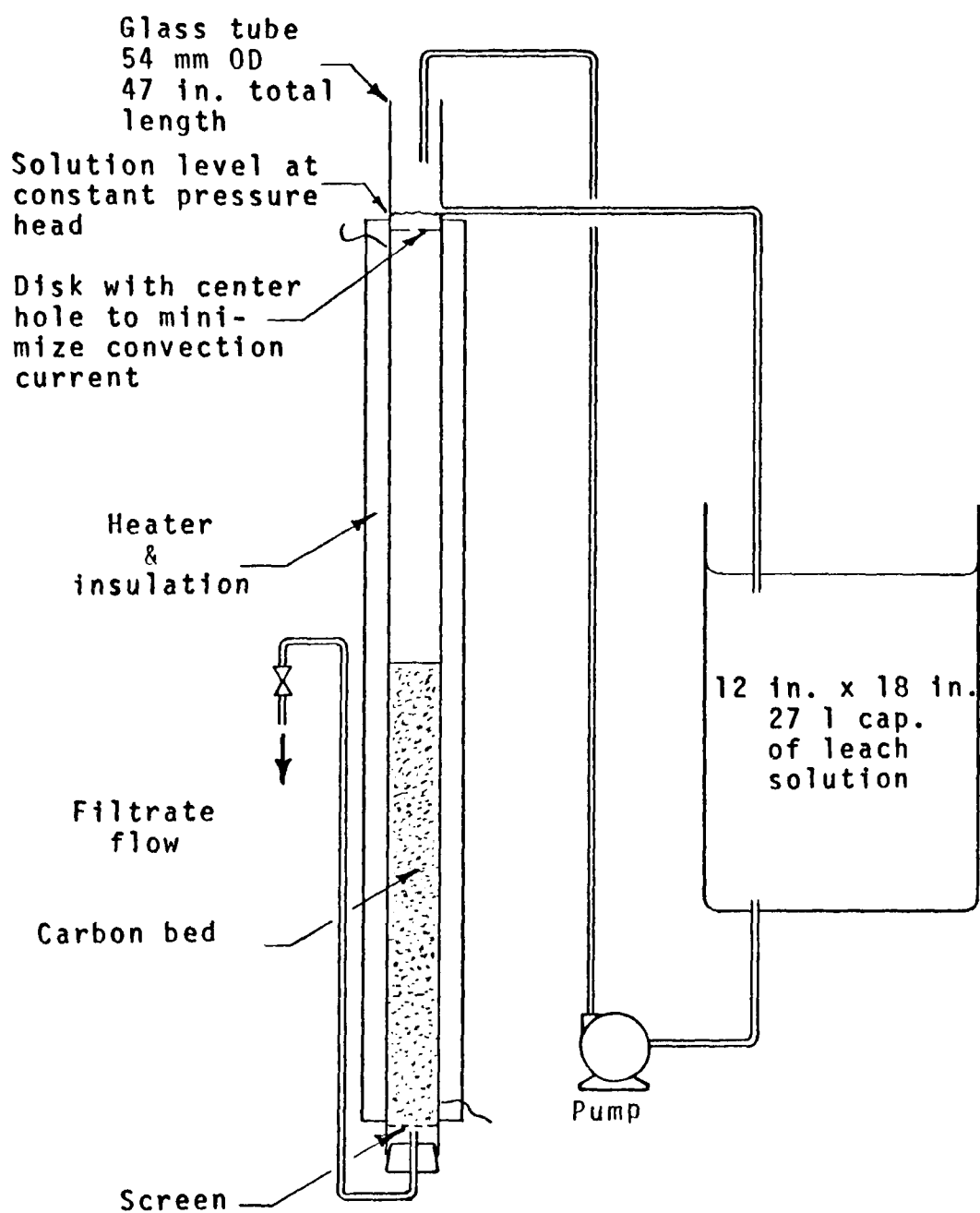
FIGURE 2 - UNIT FOR LEACHING CARBON AT
TEMPERATURES UP TO 100°C

As shown in the figure, the carbon bed is contained in the lower half of the glass tube with a constant head of solution above the bed. The column was heated by resistance wire wrapped around the tube to maintain temperature of solution and carbon bed at temperatures near 95°C. Flow rate was maintained by adjusting the valve attached to the filtrate tube. Flows of 0.5 to 3.0 1/hr were experimented with, but the flow generally was set at 1.0 1/hr.

The progress of the regeneration was monitored by removing the carbon from the column at intervals for drying and weighing. Prior to removing carbon from the column, the carbon bed was leached with pure water to remove the chemicals being used. For HCl acid leaching of larger quantities of spent carbon at ambient temperature, the unit shown in Figure 3 was used.

Carbon Test Procedures

To determine the effectiveness of the regenerating process, various measurements and tests are made on the carbon before and after the three steps of regeneration. These are namely bulk density, particle density by mercury displacement, real density by helium displacement, iodine number and molasses number. The bulk density is based on weight per unit volume of the container occupied by the carbon, the particle density is per unit volume of particles and real density is per unit volume of solids in the carbon particles. Knowledge of the particle and real densities permits calculation of the pore volume of the carbon. The bulk densities are measured during the run for control purpose since they can be determined quickly.

The iodine number is related to the total surface area of the carbon and molasses number to the area of pores larger than 28Å in diameter.

Further details on making these measurements and their significance are given in the final report of Contract 14-12-107[1].

Tables reporting the test results present the bulk density, percent weight decrease, percent bulk and particle volume decreases, pore volume, and iodine and molasses numbers. At the top of each table, property data are given on the spent carbon, representing starting material, and on the virgin carbon, representing the goals to be attained by the regeneration. A comparison of the bulk densities, pore volumes and iodine and molasses numbers of regenerated carbons with those of the virgin carbon, measures the degree of
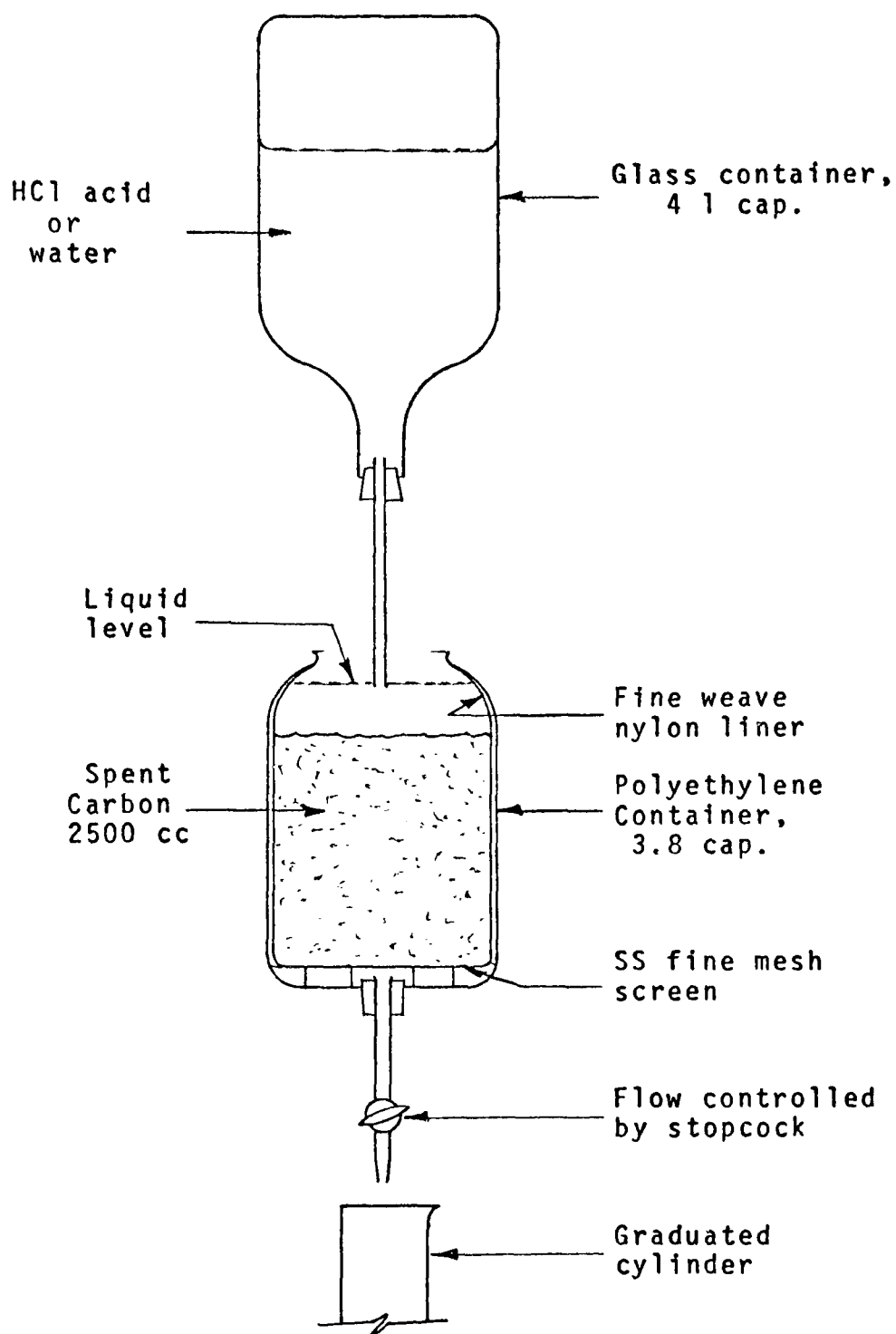
FIGURE 3 - UNIT FOR HC1 LEACHING OF SPENT CARBONS

success of the regeneration. The percent decrease in bulk
and particle volumes measures the carbon loss.

SECTION V

EXPERIMENTAL RESULTS AND DISCUSSIONS

Task 1 - Study of Regeneration Operating Parameters

Effect of Oxygen - In the direct-fired multiple hearth furnace, the carbon comes in contact with flue gas from combustion of natural gas or flue gas mixed with product gases from activation. The flue gas can contain 1% to 2% of oxygen by volume with compositions approximately as given below:

Component	Composition,%	
	With 6% excess air	With 12% excess air
N_2	71.7	71.5
CO_2	9.2	8.7
H_2O	17.9	17.7
O_2	1.0	2.1
	99.8	100.0

The composition of the gas passing over the hearth changes after coming in contact with the carbon. For the Pomona furnace, the calculated composition of gas entering the fourth hearth, where the baking step occurs, is approximately as follows:

Component	ft^3/(hr x lb carbon)	Composition,%[1]
N_2	25.7	46.2
CO_2	3.8	6.8
H_2O	18.2	32.7
CO	3.9	7.0
H_2	4.0	7.2
	55.6	99.9

(1) This is a calculated composition. Due to a gas phase reaction between the CO and H_2O, the volumes

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of CO and H_2O are reduced while CO_2 and H_2 volumes are increased. This reaction is discussed later in the report.

In the Pomona furnace regeneration, steam is added to the flue gas, but if steam were not added the calculated composition of gas entering the fourth hearth would be closer to the percentages given below:

Component	$ft^3/(hr \times lb\ carbon)$	Composition,%
N_2	24.1	67.5
CO_2	2.7	7.6
H_2O	3.8	10.6
CO	2.7	7.6
H_2	2.2	6.2
O_2	0.2	0.6
	35.7	100.1

Two activations were run with flue gas mixture of 1% oxygen. These are Runs 4 and 13, with conditions and results given in Tables I and II.

In regard to the baking step, no attempt was made to exactly duplicate the gas compositions of the hearth furnace. It was rationalized that at the 1550°F maximum temperature, the presence of CO and H_2 would have very little effect. In the baking steps, flue gas mixtures were used with 1% oxygen content. These are Runs 1 and 12 in Tables I and II. A comparison of the results, with and without oxygen, tend to show no significant difference. Run 16 does not fit the pattern of results generally obtained on nonoxygen activations, hence some doubt exists on the validity of the low (920) iodine number.

The possibility exists that the oxygen reacts with the H_2 and CO in gas phase and never reaches the carbon, where it would react exothermally. On subsequent regeneration runs, the addition of oxygen was discontinued.

Baking Wet and Dry OSF 400 - Figure 4 shows the measured gas temperature over each hearth of the Pomona furnace. The carbon temperatures shown here were calculated from the thermodynamic properties of the system. As indicated in the figure,

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TABLE I - REGENERATION CONDITIONS, EFFECT OF OXYGEN

Run no.	Regeneration step	Temperature, °F			Gas input, ft^3/hr (stp)			
		1	2	3	N_2	CO_2	O_2	H_2O
64 (1)	baking	1700	1700	1700	4.8	0.00	0.00	0.00
65 (1)	Run 64 activated	1700	1700	1600	3.6	0.50	0.00	1.90
1	baking	550	1250	1550	6.8	0.90	0.10	1.71
4	Run 1 activated	1550	1650	1720	1.09	0.14	0.015	0.37
7	baking	700	1200	1550	7.9	1.0	0.00	1.27
13	Run 7 activated	1550	1650	1700	2.7	0.34	0.02	0.47
12	baking	750	1250	1500	6.8	0.90	0.05	1.57
16	Run 12 activated	1550	1650	1700	2.7	0.34	0.00	0.56
22	baking	650	1255	1545	7.0	0.90	0.00	2.11
23	Run 22 activated	1545	1650	1700	3.7	0.47	0.00	0.86

(1) Data on runs from contract 14-12-107.

TABLE II - REGENERATION RESULTS, EFFECT OF OXYGEN

Run no.	Bulk density, g/cc	Weight decrease, %	Bulk volume decrease, %	Particle volume decrease, %	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
virgin (1)	0.490	---	---	---	---	990	220
spent (1)	0.570	---	---	---	0.510	650	210
64 (2)	0.522	10.4 ⎤ 17.2	---	1.4 ⎤ 2.2	0.598	---	---
65 (2)	0.486	7.5 ⎦	---	0.8 ⎦	0.625	960	225
1	0.500	12.9 ⎤ 17.4	0.5 ⎤ 1.8	1.8 ⎤ 3.8	0.619	950	210
4	0.480	5.1 ⎦	1.3 ⎦	2.0 ⎦	0.628	950	220
virgin (3)	0.468	---	---	---	0.650	1090	250
spent (3)	0.583	---	---	---	0.500	630	190
7	0.506	13.5 ⎤ 19.5	0.7 ⎤ 1.6	1.4 ⎤ 1.9	0.611	940	211
13	0.476	6.9 ⎦	0.9 ⎦	0.5 ⎦	0.633	950	258
12	0.503	14.2 ⎤ 19.7	0.6 ⎤ 1.5	0.3 ⎤ 1.8	0.615	940	224
16	0.479	6.4 ⎦	0.9 ⎦	1.5 ⎦	0.635	920	253
22	0.510	13.3 ⎤ 19.7	1.0 ⎤ 2.2	0.5 ⎤ 2.2	0.600	950	---
23	0.480	7.2 ⎦	1.2 ⎦	1.7 ⎦	0.630	950	---

(1) Runs 1, 4, 64 and 65 with this once-spent Filtrasorb 400 (OSF 400)
(2) Data from runs on contract 14-12-107
(3) Runs below with this OSF 400

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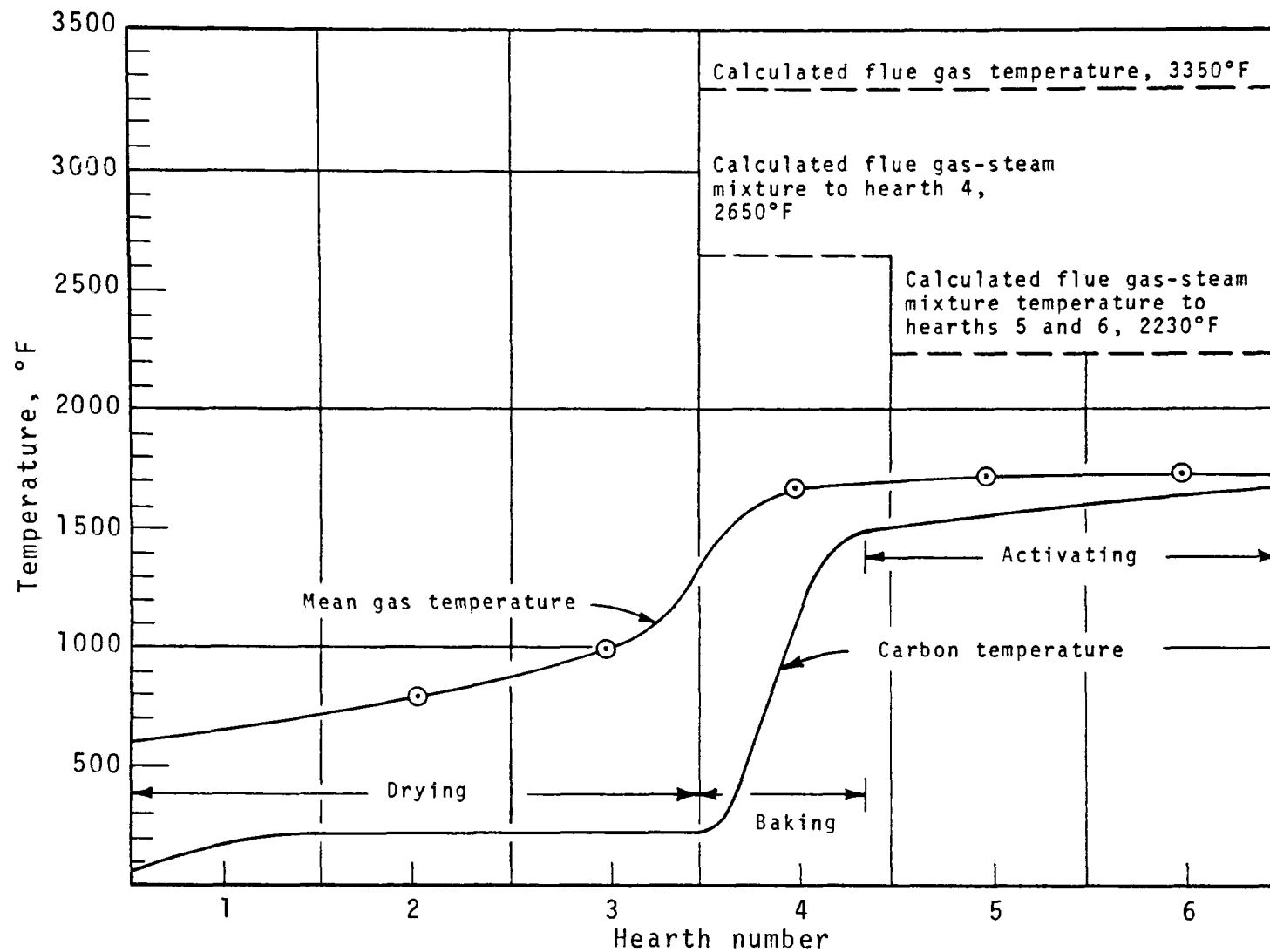
FIGURE 4 – TEMPERATURE PROFILES FOR GAS AND CARBON IN MULTIPLE
HEARTH FURNACE, REGENERATION OF WET SPENT CARBON

wet carbon fed into the furnace dries while traversing the first three hearths and then goes through the baking step on the fourth hearth. Activation occurs over hearths 5 and 6.

To simulate the conditions in the hearth furnace, a number of drying-baking runs were made in the laboratory rotary furnace with rewetted OSF 400. It is necessary to dry the wet spent carbon, as received from Pomona, to permit measurements of its properties. Rewetting consisted of adding water to the carbon just to the point where it was still free flowing. On a dry spent carbon basis this occurred at about 38% water content.

Two regenerations of rewetted carbon were run. The conditions and results are given in Tables III and IV, Runs 2-3 and 8-14. Data on nonwetted carbon runs, Runs 1-4, and 22-23 are also given for comparison. The bulk densities of wet-baked carbons were slightly lower than those of the dry-baked carbons. This would normally be regarded favorably, except on activation the wet-baked carbons had slightly lower iodine numbers, i.e., 900 and 935 mg/g compared to 950 mg/g for the dry-baked carbons. In Task 4, regeneration Runs 9-15, Table XXII, the OSF 400 was wetted with H_2O_2 and in this case also the iodine number was down, i.e., 920 mg/g.

Baking of rewetted carbons caused considerable difficulty by way of vent line plugging. To avoid this problem, subsequent baking runs were made with oven dried OSF 400.

Effect of Temperature - As shown in Figure 4, the gas temperature varies from 600 to 1700°F over hearths 1 to 4 and holds steady at 1700°F over hearths 5 and 6. Various combinations of temperatures on baking and activating were tried. Some were almost duplicates of the hearth furnace conditions, some milder and some more severe. Conditions of regeneration and results which show the effect of temperature are presented in Tables V and VI.

In the regeneration Run 22-23, the baking was carried to the maximum temperature of 1545°F with relatively high input of CO_2 and H_2O. Activation was then conducted at 1545°F to 1700°F. The regenerated carbon iodine number was 950 mg/g. When the baking temperature was increased to 1600°F, as in regeneration Run 48-51, the regenerated carbon iodine number dropped to 910 mg/g. Run 50-52 is in part a repeat of Run 48-51 except that the activating temperature was increased to the 1700°F level. For this run the iodine number dropped to 900 mg/g.

TABLE III - REGENERATION CONDITIONS, WET AND DRY OSF 400

Run no.	Regenerating step and special treatment	Temperature, °F 1	2	3	Gas input, ft^3/hr (stp) N_2	CO_2	O_2	H_2O
1	dried and baked	550	1250	1550	6.8	0.90	0.10	1.71
4	Run 1 activated	1550	1650	1720	1.09	0.14	0.015	0.37
2	dried, rewetted, baked	680	1250	1550	6.8	0.90	0.10	1.71
3	Run 2 activated	1550	1650	1720	1.99	0.26	0.027	0.37
8	rewetted 550 ml H_2O/ 2500 cc and baked	980	1270	1550	7.9	1.00	0.00	1.75
14	Run 8 activated	1550	1650	1700	2.7	0.34	0.00	0.51
22	dried and baked	650	1250	1545	7.0	0.90	0.00	2.11
23	Run 22 activated	1545	1650	1700	3.7	0.47	0.00	0.86

TABLE IV - REGENERATION RESULTS, WET AND DRY OSF 400

Run no.	Bulk density, g/cc	Weight decrease, %	Bulk volume decrease, %	Particle volume decrease, %	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
virgin (1)	0.490	---	---	---	---	990	220
spent (1)	0.570	---	---	---	0.510	650	210
1	0.500	12.9 ⎱ 17.4	0.5 ⎱ 1.8	1.8 ⎱ 3.8	0.619	950	210
4	0.480	5.1 ⎰	1.3 ⎰	2.0 ⎰	0.628	950	220
2	0.500	12.4 ⎱ 18.0	1.7 ⎱ 3.0	2.2 ⎱ 4.1	0.613	923	224
3	0.475	6.4 ⎰	1.3 ⎰	1.9 ⎰	0.631	900	220
virgin (2)	0.468	---	---	---	0.650	1090	250
spent (2)	0.583	---	---	---	0.500	630	190
8	0.507	13.1 ⎱ 18.8	0.5 ⎱ 1.6	0.9 ⎱ 2.8	0.607	940	212
14	0.482	6.5 ⎰	1.1 ⎰	1.9 ⎰	0.629	935	229
22	0.510	13.3 ⎱ 19.7	1.0 ⎱ 2.2	0.5 ⎱ 2.2	0.600	950	---
23	0.480	7.2 ⎰	1.2 ⎰	1.7 ⎰	0.630	950	---

(1) Runs 1, 4, 2 and 3 with this OSF 400
(2) Runs 8, 14, 22 and 23 with this OSF 400

TABLE V - REGENERATION CONDITIONS, EFFECT OF TEMPERATURE

Run no.	Regenerating step	Temperature, °F			Gas input, ft^3/hr (stp)		
		1	2	3	N_2	CO_2	H_2O
22	baking	650	1250	1545	7.0	0.90	2.11
23	Run 22 activated	1545	1650	1700	3.7	0.47	0.86
48	baking	820	1350	1600	7.0	0.93	1.68
51	Run 48 activated	1550	1650	1700	3.33	0.41	0.74
50	baking	800	1350	1600	7.0	0.93	1.71
52	Run 50 activated	1700	1700	1600	3.24	0.44	0.56
10	baking	800	1250	1550	3.7	0.00	0.00
41	Run 10 activated	1560	1650	1700	8.3	1.00	2.62
61	baking	1700	1700	1600	3.7	0.00	0.00
66	Run 61 activated	1700	1700	1600	4.0	0.55	1.49

TABLE VI - REGENERATION RESULTS, EFFECT OF TEMPERATURE

Run no.	Bulk density, g/cc	Weight decrease, %		Bulk volume decrease, %		Particle volume decrease, %		Pore volume, cc/cc	Iodine number, mg/g	Molasses number
virgin	0.468	---		---		---		0.650	1090	250
spent	0.583	---		---		---		0.500	630	190
22	0.510	13.3	19.7	1.0	2.2	0.5	2.2	0.600	950	---
23	0.480	7.2		1.2		1.7		0.630	950	---
48	0.503	15.2	21.4	1.8	2.5	1.9	3.8	0.617	910	260
51	0.471	7.2		0.7		1.9		0.649	910	245
50	0.500	15.8	21.8	1.6	2.8	2.0	4.7	0.623	910	260
52	0.469	7.2		1.2		2.7		0.644	900	250
10	0.53	10.5	20.5	1.0	1.5	0.1	2.3	0.600	980	204
41	0.476	11.1		0.5		2.2		0.636	950	263
61	0.513	13.1	20.1	2.3	3.0	1.9	2.5	0.605	880	220
66	0.477	8.0		0.7		0.6		0.638	940	240

The reason for the difference in the results given above is due to an appreciable amount of low temperature activation during the baking step for Runs 48-51 and 50-52. At temperatures above 1500°F, the rate of activation increases rapidly with temperature. But increasing the temperature at the end of the baking step by 50°F for Runs 48-51 and 50-52 caused a considerable amount of low temperature activation to occur at 1600°F. Low temperature activation appears to be detrimental to the recovery of iodine number, i.e., regeneration of micropores to original state.

To support the above interpretation, regeneration Run 60-61 was run at the 1700°F level but nitrogen sweep gas was used during baking to avoid any activation. In this case the iodine number was 940 mg/g; up considerably from the 900 mg/g as obtained for Run 50, also activated at the 1700°F level.

Regeneration Run 10-41 was performed under a similar temperature schedule as Run 22-23 except that N_2 sweep was used during baking. For this run, the iodine number of the regenerated carbon was 950 mg/g, the same as for Run 22-23. The conclusion is that at temperatures of 1550°F and below, CO_2 and H_2O vapor are relatively inert toward the basic carbon structure.

In regard to the temperature during the activating step, it is desirable to maintain the temperature at or close to the 1700°F level. In those runs where the temperature profile was from 1500° to 1700°F, most of the activation occurs in the third section of the regenerator where the temperature is 1700°F. When the gas reached sections II and III at the lower temperatures, the CO_2 and H_2O contents are partially depleted, hence reaction rates are considerably slower.

Steam and CO_2 Activations - Task 6 results indicated that when CO_2 was utilized to any appreciable extent in the activation step, the iodine number decreased. To verify this trend, regenerations were then conducted in which the activation step was solely with CO_2-N_2 mixture or steam-N_2 mixture. The CO_2-N_2 activation was also carried out on a HCl pretreated carbon.

The conditions of regeneration and results are presented in Tables VII and VIII. Included for comparison are data of Run 61-66, which was activated with a steam-CO_2-N_2 mixture but the CO_2 did not contribute to the activation. Figure 5 presents graphically the results of Table VIII and results obtained in the Task 6 studies. The iodine number of the CO_2-activated, nonleached carbon is 840 mg/g compared to

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TABLE VII - REGENERATION CONDITIONS, STEAM AND CO_2 ACTIVATION

Run no.	Regenerating step	Temperature, °F 1	2	3	Gas input, ft^3/hr (stp) N_2	CO_2	H_2O
62	baking	1700	1700	1600	3.7	0.00	0.00
67	Run 62 activated	1700	1700	1600	4.0	0.00	2.81
64	baking	1700	1700	1600	3.7	0.00	0.00
68	Run 64 activated	1700	1700	1600	2.0	2.91	0.00
61	baking	1700	1700	1600	3.7	0.00	0.00
66	Run 61 activated	1700	1700	1600	4.0	0.55	1.49
--	HC1 leach	---	---	---	---	---	---
95	baking	850	1350	1550	7.0	0.93	1.71
96	Run 95 activated	1550	1650	1700	14.0	4.00	---

TABLE VIII - REGENERATION RESULTS, STEAM AND CO_2 ACTIVATION

Run no.	Bulk density, g/cc	Weight decrease, %	Bulk volume decrease, %	Particle volume decrease, %	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
virgin	0.468	---	---	---	0.650	1090	250
spent	0.583	---	---	---	0.500	630	190
62	0.518	13.3 ⎱ 22.9	2.4 ⎱ 3.7	2.6 ⎱ 3.8	0.603	880	220
67	0.467	11.1 ⎰	1.3 ⎰	1.2 ⎰	0.647	940	260
64	0.516	13.1 ⎱ 21.0	2.2 ⎱ 3.2	2.3 ⎱ 3.7	0.604	900	220
68	0.478	9.1 ⎰	1.0 ⎰	1.4 ⎰	0.645	840	250
61	0.513	13.1 ⎱ 20.1	2.3 ⎱ 3.0	1.9 ⎱ 2.5	0.605	880	220
66	0.477	8.0 ⎰	0.7 ⎰	0.6 ⎰	0.638	940	240
leach	0.555	6.3 ⎱	1.2 ⎱	2.6 ⎱	0.528	---	---
95	0.498	11.7 ⎰ 21.2	1.7 ⎰ 5.0	0.3 ⎰ 4.8	0.624	900	250
96	0.486	4.6 ⎰	2.1 ⎰	1.9 ⎰	0.640	960	240
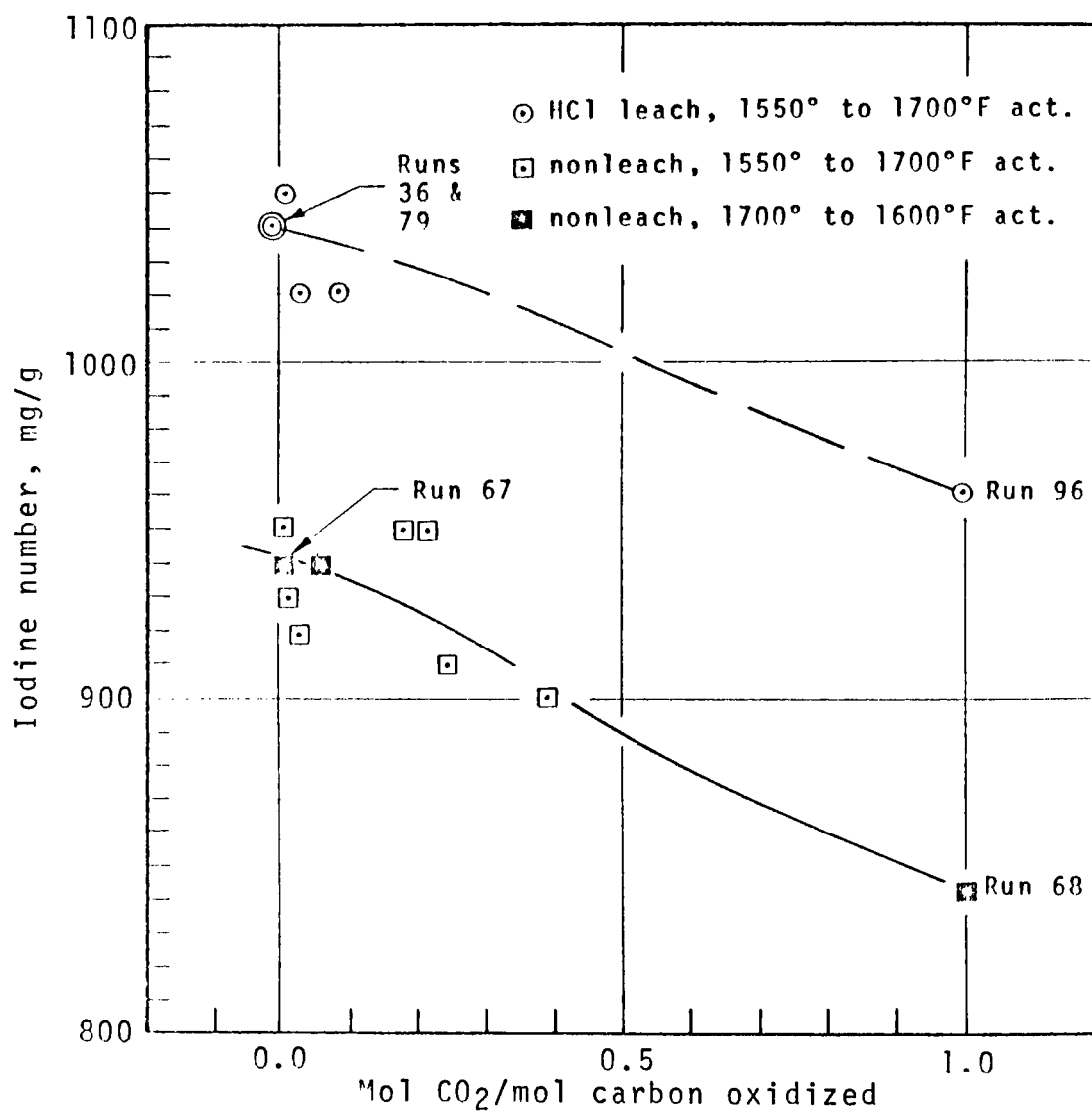
FIGURE 5 - EFFECT OF CO₂ ACTIVATION ON IODINE NUMBER

940 mg/g for the steam activated. For the HCl pretreated carbon, the iodine number of CO_2-activated carbon is 960 mg/g compared to 1040 mg/g for the steam activated. A 100 unit drop in iodine number can be expected when activation is solely by CO_2.

<u>Study of Particle Volume Decrease During Baking</u> - The carbon loss during regeneration is measured by the particle volume decrease. It occurs during both the baking and activating steps. The volume decrease during the activating step is understandable and expected since the activating gases would also be expected to act on the basic carbon structures and, thereby, reduce its volume. The particle volume decrease, however, was unexpected during the baking step when a nitrogen sweep gas is used. A considerable effort was made to determine whether the volume decrease was due to actual loss of basic carbon structure or whether it was due to two other possible effects, i.e., (1) expansion of carbon during adsorption and contraction during removal of adsorbate or (2) decomposition and volatilization of colloidal adsorbate clinging to the exterior surface of the carbon particles. A satisfactory answer to this question was not found, although some of the experimental evidence appeared to favor the colloidal adsorbate hypothesis. Because this question was not resolved, there was uncertainty as to the true carbon loss suffered during the regeneration. Was it about 1.5%, assuming true loss occurring only during the activating step, or was it more like 3.0%, assuming true loss occurring during both steps?

Vent gas analyses have indicated that, at least in part, the particle volume decrease during activation is due to loss of fines of submicron diameter. If fines formation is the mechanism by which particle volume decreases during baking, it would be profitable to determine whether there are conditions by which it could be minimized.

One method that suggested itself was to carry out the baking under extremely mild conditions. This can be done in a fixed-bed oven. The carbon would not be agitated as in a rotary tube to cause possible attrition of weakened particle surface layers. The heatup time for the baking step can be very gradual and over an extended time of at least 50 hr. Evolution of gases would not be rapid enough to carry off any fines. To determine this point, four fixed-bed oven baking runs were made. The baking conditions and test results are given in Tables IX and X. Each spent carbon was HCl acid leached prior to baking according to a standardized procedure given in Task 4.

TABLE IX - BAKING CONDITIONS FINES FORMATION STUDY, OSF 400

Run no.	Treatment	Temperature, °F			Gas input, ft^3/hr (stp)		
		1	2	3	N_2	CO_2	H_2O
---	HCl leach	---	---	---	---		
(1)	Fixed bed	60 → 1550 in 48 hr			1.25		
---	HCl leach	---	---	---	---		
(2)	Fixed bed	60 → 1550 in 48 hr			1.25		
---	HCl leach	---	---	---	---		
(3)	Fixed bed	60 → 1550 in 48 hr			1.25		
80	Rotary tube	850	1350	1550	3.7		
---	HCl leach	---	---	---	---		
(4)	Fixed bed	60 → 1550 in 48 hr			1.25		
92	Rotary tube	850	1350	1550	3.7		
93	Rotary tube	850	1350	1550	3.7		
94	Rotary tube	850	1350	1550	3.7		
97	Rotary tube	850	1350	1550	3.7		

TABLE X - BAKING RESULTS FINES FORMATION STUDY, OSF 400

Run no.	Bulk density, g/cc	Weight decrease, %	Bulk volume decrease, %	Particle volume decrease, %	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
OSF 400	0.583	---	---	---	0.501	630	190
HCl leach (1)	0.555 / 0.506	5.8 / 10.8 } 16.0	0.8 / 2.3 } 3.1	1.6 / 1.2 } 2.8	0.527 / 0.617	--- / ---	--- / ---
HCl leach (2)	0.560 / 0.507	4.8 / 11.1 } 15.4	0.8 / 1.8 } 2.6	1.6 / 0.3 } 1.9	0.520 / 0.614	--- / ---	--- / ---
HCl leach (3) 80	0.562 / 0.511 / 0.510	4.4 / 10.0 / 0.8 } 14.7	0.6 / 1.1 / 0.4 } 2.1	1.0 / 0.2 / 0.4 } 1.6	0.521 / 0.598 / 0.608	600 / 880 / 880	--- / --- / ---
HCl leach (4) 92	0.552 / 0.505 / 0.504	6.1 / 9.9 / 0.4 } 15.8	0.8 / 1.4 / 0.1 } 2.3	1.2 / 0.3 / 0.4 } 1.9	0.519 / 0.622 / 0.618	--- / 930 / 930	--- / --- / 220
93	0.506	0.6	0.8	0.4	0.621	850	240
94	---	0.6		0.7	0.616	920	---
97	0.502	0.1	0.5	1.1	0.617	900	220

In the fixed-bed Run (1), a considerable amount of ash was found on the surface of the baked carbon particles, indicating that oxygen from some source had reached the carbon. This was unexpected since nitrogen was passed through the oven during heat-up and cool-down. On Run (2), the amount of ash formed was considerably less, but still considered too much for the purpose of the run. On Runs (3) and (4), panels of granular carbon, between stainless steel screens, were placed around the OSF 400 carbon beds to shield out external oxygen. Also new stainless steel screens and trays were used to eliminate oxidized surfaces which could release oxygen on contact with hot carbon. On these two runs no ash appeared on the baked carbon surface.

The results of Runs (3) and (4), which are the most valid ones, present conflicting evidence. Particle volume decrease was very small, of the order of 0.3%, while the bulk volume decrease was much larger, i.e., 1.1% and 1.4%. It appears as though the 0.3% decrease in volume of the particles then permitted the particles to fit closer together, hence the larger decrease in bulk volume.

When the fixed-bed runs were then rebaked in the rotary-tube regenerator, again in an inert atmosphere, the bulk volume and particle volume decrease tended to be equal and of the order of 0.4% over repeated baking runs, Runs 80 and 92 to 97. A 0.4% to 0.8% weight loss also occurred on each successive baking run. Vent gas analyses, Table XI, indicate that the weight loss is essentially due to evolved CO and CO_2. However, the amount of oxygen in the N_2 was not sufficient to account for the amount of CO and CO_2 evolved, hence other sources of oxygen pick-up were investigated.

A possible chemisorption could occur when the baked carbon is exposed to air during handling and bulk volume measurements. On each baking run, the chemisorbed oxygen would then be evolved as CO and CO_2. To test this hypothesis, the product of Run 93 was kept under nitrogen and fed to Run 94. In this run, also, there was the usual weight and volume loss, and evolution of CO and CO_2. The conclusion arrived at was that the oxidized surface of the rotary tube yielded oxygen to the carbon. This could mean that on every baking run, whether in inert atmosphere or not, a 0.4% particle volume decrease occurs. This loss is characteristic of the manner in which the unit is operated, i.e., on a long continuous run this loss would not occur after the metal surfaces have become reduced.

The conclusion at this point of the study was that, on <u>HCl leached</u> spent carbons, there is only a negligible loss of carbon volume during baking.

TABLE XI - WEIGHT DECREASE DETERMINED FROM VENT GAS ANALYSES

Run no.	Weight decrease, g/hr	Gas release rate, mol/hr		Weight of gas released, g/hr
		CO	CO_2	
92	1.05	0.035	0.010	1.42
93	1.38	0.035	0.051 [1]	3.32 [1]
94	1.44	0.010	0.025	1.38
97	0.82	0.019	0.009	0.93

(1) This value appears to be in error

The study was continued by considering the carbon losses incurred during the acid leach. Table XII separates out the pertinent data from Table X. For Runs (2), (3) and (4), the particle volume decrease is about 1.3% while the bulk volume decrease is about 0.7%. This is the reverse of the volume decreases occurring during baking. Apparently, the larger particle volume decrease causes a very small change in packing efficiency of the particles.

If a further examination is made of HCl leached-rotary tube baked carbons (see Table XIII), the same pattern is observed on bulk and particle volume decreases as in Table XII. Here, also, the particle volume decrease during baking of previous HCl leached spent carbons is of the order of 0.2%. Acid leach reduced the particle volume by about 2.0%. These baking runs were made in a flue gas atmosphere, and since the particle volume decrease is essentially the same as for the fixed-oven runs, the flue-gas then must also act as an inert gas.

A second conclusion, arrived at from this study, is that colloidal material from the waste water adheres to the exterior surfaces of the carbon particles, thereby enlarging them. The HCl acid leach removed this colloidal material, hence the particle volume decreases during leaching but with little or no particle volume decrease during baking.

When nonleached spent carbon is baked, the colloidal material is subject to heat treatment which will cause it to decompose and volatilize. In reviewing the past runs, evidence has been found which shows that the degree of decomposition and volatilization varies with the conditions of baking. These data are presented in Table XIV.

In the early part of the program, when runs up to and including number 31 were made, Section I of the rotary tube was heated to 750°F. On these runs, the particle volume decrease was on the order of 0.5%. At this temperature, liquid water collected in the carbon influent end of the tube causing operational difficulties. To correct this, the temperature of Section I has since been operated at 800°F and higher. Except for Run 44, the particle volume decrease also rose, now in the 1.4% to 3.3% range. The explanation that appears most reasonable is that when Section I is 750°F, the carbon temperature rise is gradual as it proceeds down the rotary tube into higher temperature sections. Under a gradual temperature rise, the colloidal matter stays fixed to the carbon surface and then decomposes, leaving a deposit of free carbon. The free carbon deposit lessens the volume loss from what would occur if all the colloid had been removed.

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TABLE XII - VOLUME DECREASE DURING HCl LEACH AND FIXED BED BAKING OF OSF 400

Run no.	Volume decrease,%	
	Bulk	Particle
Spent leached	0.8 ⎤	1.6 ⎤
Fixed bed baked, No.(1)	2.3 ⎦ 3.1	1.2 ⎦ 2.8
Spent leached	0.8 ⎤	1.6 ⎤
Fixed bed baked, No.(2)	1.8 ⎦ 2.6	0.3 ⎦ 1.9
Spent leached	0.6 ⎤	1.0 ⎤
Fixed bed baked, No.(3)	1.1 ⎦ 1.7	0.2 ⎦ 1.2
Spent leached	0.8 ⎤	1.2 ⎤
Fixed bed baked, No.(4)	1.4 ⎦ 2.2	0.3 ⎦ 1.5
means, excluding No.(1)	2.2	1.5

TABLE XIII - VOLUME DECREASE DURING HCl LEACH AND ROTARY TUBE BAKING OF OSF 400

Run no.	Volume decrease, %			
	Bulk		Particle	
Spent leached 45	0.0 2.7	2.7		2.8
Spent leached 49	0.4 2.1	2.5	1.9 0.2	2.1
Spent leached 63	0.2 2.4	2.6		2.5
Spent leached 78	0.0 1.9	1.9	1.7 -0.2	1.5
Spent leached 95	1.2 1.7	2.9	2.6 0.3	2.9
means		2.5		2.4

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TABLE XIV - VOLUME DECREASE OF NONLEACHED CARBONS DURING BAKING

Run no.	Section 1 Temperature, °F	Volume decrease, % Bulk	Volume decrease, % Particle
12	750	0.6	0.3
22	650	1.0	0.5
29	750	1.2	0.8
31	750	0.8	0.3
37	850	2.0	1.6
38	850	2.0	1.4
44	810	0.4	0.0
48	820	1.8	1.9
50	800	1.6	2.0
62	1700	2.4	2.6
64	1700	2.2	2.3
71	800	1.8	3.3
72	800	1.6	2.9

When the temperature of Section I is raised to 800°F and higher, the increased temperature causes an increase in expulsion rate of volatiles from within the pores and also in the rate of volatilization of the colloidal matter. The net result is that a greater portion of the colloidal matter is removed with the vent gases, and hence the larger decrease in particle volume.

When these carbons are activated, the prior treatment does not appear to greatly affect the volume decrease. As shown in Table XV, the mean particle volume decrease is about 1.8%. If the particle volume decreases, during HCl leach and baking is accepted as being due primarily to removal of colloidal matter from the exterior surface of the particles, then the true carbon loss is closer to 1.8% rather than the 3.5% to 5.0% as previously reported.

Effect of Particle Size on Ease of Regeneration - A parameter that needed to be investigated was the effect carbon mesh size may have on the ease of regeneration. It is known that powdered carbons regenerate much more rapidly than coarse granular carbons. If the regeneration rate is appreciable within the range of mesh sizes normal in commercial carbons, it is evident that the small particles could be over-activated and thereby suffer excessive particle volume loss while the large particles are still underactivated. A large difference in ease of activation can lead to a new investigation in optimizing mesh size, contacting procedures and regeneration. The ease of regeneration of the open pore structured Darco carbons has demonstrated that wide variations can exist amongst carbons. On the Darco, complete regeneration was always effected by the baking step alone.

This study was conducted primarily with West Virginia Pulp and Paper Company spent carbon since it consisted of coarser mesh sizes than the OSF 400. The original 8 to 30 mesh was sieved and sized to obtain four mesh size fractions, 8 to 12, 20 to 30, 30 to 60 and -60. A powdered -100 mesh OSF 400 and a powdered -100 mesh Nuchar Aqua A were later added to the study. Prior to thermal regeneration, each carbon was HCl acid leached and dried according to procedure given in the Task 4 section of this report.

The conditions of regeneration and results are given in Tables XVI and XVII. The results of the study indicate that the size of the particle does not control the rate of regeneration. In the WVP&P series, no trend is indicated in the iodine number. The iodine number of the OSF 400, Run 85, is in line with those of the baked acid leached granular OSF 400 carbons. However, decrease in particle size appears

TABLE XV - VOLUME DECREASE DURING ACTIVATION

Run no.	Pretreatment	Volume decrease, %	
		Bulk	Particle
29-30	HCl leach	0.4	0.4
31-32	HCl leach	1.4	2.6
37-39	HCl leach	1.4	2.0
38-40	HCl leach	1.3	1.5
48-51	HCl leach	0.7	1.9
50-52	HCl leach	1.2	2.7
	means	1.1	1.8
12-16	none	0.9	1.5
22-23	none	1.2	1.7
29-30	none	0.4	0.4
31-32	none	1.4	2.6
37-39	none	1.4	2.0
38-40	none	1.3	1.5
44-46	none	1.4	2.5
45-47	none	1.1	1.8
49-53	none	0.7	1.7
63-69	none	0.7	1.9
78-79	none	0.9	2.0
	means	1.0	1.8

TABLE XVI - REGENERATION CONDITIONS, EFFECT OF PARTICLE SIZE ON REGENERATION (1)

Run no.	Carbon and mesh size	Regenerating step	Temperature, °F			Gas input, ft^3/hr (stp)		
			1	2	3	N_2	CO_2	H_2O
81	WVP&P, 8 to 12	baking	800	1300	1500	2.0	---	---
88	WVP&P, 8 to 12	Run 81 act.	1555	1650	1700	3.5	0.43	1.13
82	WVP&P, 20 to 30	baking	800	1300	1500	2.0	---	---
89	WVP&P, 20 to 30	Run 82 act.	1555	1650	1700	3.5	0.43	1.14
83	WVP&P, 30 to 60	baking	800	1300	1500	2.0	---	---
90	WVP&P, 30 to 60	Run 83 act.	1550	1650	1700	3.5	0.43	1.25
84	WVP&P, -60	baking	800	1300	1500	0.5	---	---
85	OSF 400, powdered -100	baking	1700	1700	1600	3.0	---	---
87	Nuchar, powdered -100	baking	830	1320	1500	2.0	0.18	0.13

(1) All spent carbons HCl leached prior to regeneration

TABLE XVII - REGENERATION RESULTS - EFFECT OF PARTICLE SIZE ON REGENERATION

Run no.	Carbon	Bulk density, g/cc	Bulk volume decrease, %	Particle volume decrease, %	Weight decrease, %	Iodine number, mg/g	Molasses number
	Spent WVP&P (8 to 30)	0.597	---	---	---	---	180
	OSF 400	0.583	---	---	---	630	190
	Spent Nuchar (-100)	0.304	---	---	---	390	---
	Virgin WVP&P (8 to 30)	0.504	---	---	---	1070	---
	Virgin F 400	0.469	---	---	---	1090	250
	Virgin Nuchar (-100)	0.320	---	---	---	760	290
81	WVP&P	0.538	1.6 ⎤ 2.3	0.4 ⎤ 0.6	7.3 ⎤ 11.7	1000	
88	8 to 12	0.519	0.7 ⎦	0.2 ⎦	4.7 ⎦	1050, 1070	
82	WVP&P	0.532	2.1 ⎤ 3.2	0.6 ⎤ 2.1	8.2 ⎤ 12.5	950	
89	20 to 30	0.519	1.1 ⎦	1.5 ⎦	4.6 ⎦	1010, 1030	
83	WVP&P	0.478	1.8 ⎤ 4.0	0.7 ⎤ 2.0	9.3 ⎤ 14.9	1000	
90	30 to 60	0.457	2.2 ⎦	1.3 ⎦	6.1 ⎦	1060	
84	WVP&P -60	0.630	9.6	---	13.1	1000	230
85	OSF 400 -60	0.694	5.7	---	12.3	870, 860	
87	Nuchar, aqua A -100	0.294	9.0	---	15.1	770	270

to accelerate the carbon loss as measured by bulk volume and particle volume decreases.

A more important factor in rate of regeneration may be the pore size distribution. Granular carbons such as the Darco, of the type used in tertiary treatment, regenerates more readily than WVP&P and Filtrasorb 400, granular or powdered. Pore size distribution curves in Figure 6 of F 400 and the Darco show differences that can explain the greater ease with which the Darco can be regenerated. The Darco has an abundance of pores in the 30Å to 1000Å diameter range which offer passage ways for the gases to diffuse out of or into the small pores. Also a greater portion of the Darco surface area is in larger pores than that of F 400. In F 400, the number of passage ways or pores of 30Å to 1000Å diameter are considerably less, hence gas diffusion out of or into the 20Å pores is then slower. The major portion of the surface area of F 400 is in pores less than 20Å diameter, which can hold the adsorbate molecules more strongly.

The experimental evidence indicates that pores of 1000Å to 100,000Å diameter do not appreciably slow the rate of gas diffusion while pores below 1000Å, particularly in the 30Å region, may be rate controlling. When granular F 400 or Darco are pulverized, some of 1000Å to 100,000Å diameter pore volume becomes interparticulate volume. Hence pulverizing does not appreciably change the gas diffusion rates in the particles. Nuchar Aqua A is expected to have a pore size distribution similar to Darco. Nuchar Aqua A was easily regenerated to the virgin carbon adsorptive capacity at 15% weight decrease and 9.0% vulk volume decrease.

The evidence for the large pores becoming interparticulate volume is the bulk density change that occurred when OSF 400 was sized. In the 14 to 40 mesh granular form, the bulk density is about 0.560 g/cc, but after pulverizing, the bulk density increased to 0.750 g/cc. The bulk density of powdered carbon was based on the minimum volume obtained by tapping a graduated cylinder containing a weighed amount of the carbon until the volume stopped decreasing.

General Conclusions - Aside from the conclusions drawn from the various parameter studies, one important result was not explicitly stated although quite apparent, i.e., that the iodine numbers of the regenerated carbons were all considerably lower than the iodine number of the virgin carbon given at the top of each table. The properties of the virgin carbon were assumed to be initially those of the OSF 400, hence, were the goals to be attained when complete regeneration was accomplished. This assumption was based on the results at-
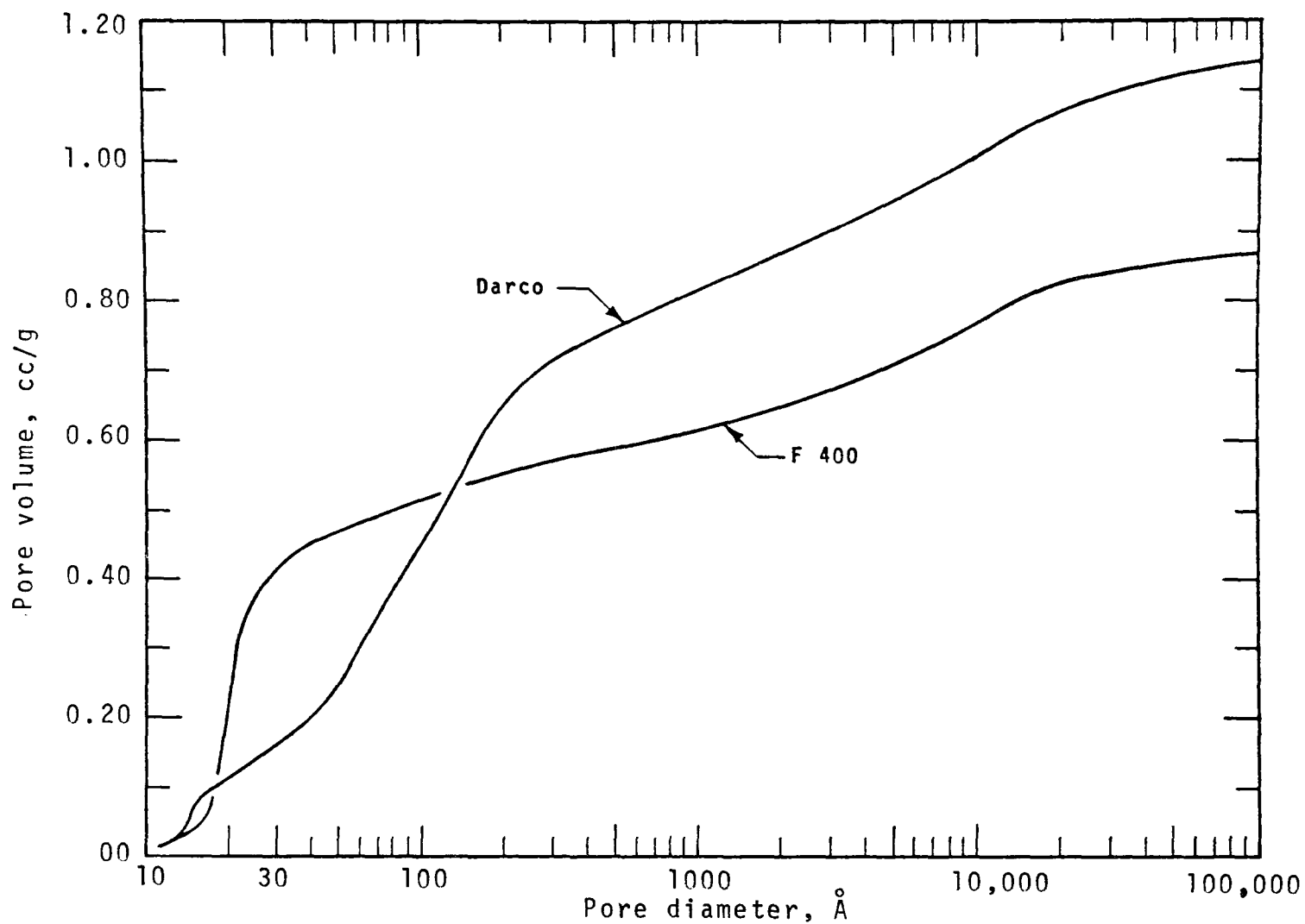
FIGURE 6 - PORE SIZE DISTRIBUTION, DARCO RUN 58 AND FILTRASORB 400

tained on the OSF 400 when regenerated with caustic and then baked in Task 4. The parameter study of Task 1 definitely indicates that manipulations of the temperature, gas composition and gas input rates during thermal regeneration do not create the necessary conditions for a satisfactory regeneration.

Task 2 - Adsorption-Regeneration Cycle Studies

After repeated regenerations, a gradual change in pore structure can be expected to occur which will ultimately cause disintegration of the carbon particles and cause the carbon to lose its adsorptive capacity. Inorganic compounds are also expected to accumulate in the pores and thereby further diminish adsorptive capacity.

To study these possible effects, an adsorption-regeneration cyclic study was carried out with the cooperation of the Pilot Plant Pomona. Starting with 2500 cc bulk volume of Filtrasorb 400, 14 by 40 mesh carbon, the adsorption phase was carried out at the Pomona Plant, with secondary treated waste water, and the regenerating and testing at the MSA Research Corporation laboratory at Evans City, Pennsylvania. Carbon loss occurring on each cycle was made up with virgin Filtrasorb 400.

The fact that the properties of the initial carbon were known at the outset of the cyclic studies avoided one of the problems that had caused considerable uncertainty on all previous regeneration runs.

It had been the original intent to perform ten cycles, but after the third one it was apparent that the carbon was degenerating much faster than had been expected. This trend is shown by the decrease in iodine number and increase in molasses number, as below:

Cycle	Iodine number, mg/g	Molasses number
initial	1090	250
1st	1040	310
2nd	935	290
3rd	940	355

It was also noted that the activating step on the second and third cycles were greatly accelerated. To prevent over activation, it was necessary to greatly reduce the activating gas input rate. Below are input rates which show the large

decrease necessary on the second and third cycles.

Cycle	Activating gas input rate, ft^3/hr (stp)		
	N_2	CO_2	H_2O
1st	3.6	0.36	0.99
2nd	1.27	0.17	0.18
3rd	1.27	0.17	0.12

For each cycle the other activating conditions were essentially the same and, in each case, the final regenerated carbon density was 0.468 g/cc, the bulk density of the virgin carbon.

The overall carbon loss for the first cycle was 5.4%, 2.8% for the second, and 1.2% for the third, as measured by decrease in particle volume. The 5.4% loss is larger than normally experienced while the 2.8% for the second cycle is normal.

In the light of improved results on thermally regenerating HCl leached spent carbon, it became apparent that leaching could have greatly reduced the degeneration rate. The accelerated degeneration rate appears to be associated with the increased ash contents on each successive cycle. Data on ash increase are as follows:

Cycle	Ash,%
virgin	5.7
1st	7.6
2nd	8.6
3rd	9.5

Estimates were made to determine whether the decrease in iodine number was accompanied by a decrease in adsorption of waste water contaminants. The calculations were made using the formula

$$\frac{(Density\ of\ spent\ carbon)-(density\ of\ reg\ carbon)}{(density\ of\ reg\ carbon)} \times 100 = \%\ adsorbate.$$

For the two completed cycles and the adsorption phase of the third, the calculated results are as follows:

Cycle	%, Adsorbate
1st	17.1
2nd	14.1
3rd	15.0

A decrease in adsorptive capacity may be indicated, although the decrease may also be due to fluctuations in adsorbate concentration of the secondary treated waste water.

The regenerations were carried out under conditions that can be attained in a multiple hearth furnace. Further details on the cyclic studies are presented in Tables XVIII and XIX.

Task 3 - Determine Feasibility of Low Grade Carbons as Make Up

The procedure for this task was identical to Task 2 except that a lower grade Filtrasorb 100 was used as make-up carbon. This study was based on the premise that a lower activity carbon would be upgraded during regeneration and, because of the price difference between Filtrasorb 400 and 100, would lead to an economic advantage. The 1969 prices were 28 1/2¢/lb for Filtrasorb 400 and 20 1/2¢/lb for Filtrasorb 100. On the two cycles, the pattern was the same as in Task 3. Any benefit that might have accrued from use of lower grade make-up carbon was obscured by the rapid degeneration. Test results showing the degeneration of the carbon are given below:

Cycle	Iodine number, mg/g	Molasses number
Initial	1090	250
1st	1040	310
2nd	920	310

As in Task 2, the activating gas input had to be decreased considerably on the second cycle to prevent over activating, as indicated below:

Cycle	Activating gas input rate, ft^3/hr (stp)		
	N_2	CO_2	H_2O
1st	2.5	0.32	0.72
2nd	1.27	0.17	0.21

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TABLE XVIII - REGENERATING CONDITIONS, TASKS 2 AND 3

Run no.	Task	Cycle	Regenerating step	Temperature, °F 1	2	3	Gas input, ft^3/hr (stp) N_2	CO_2	H_2O
24	2	1	bake	770	1350	1560	7.0	0.90	1.47
25	2	1	activation	1550	1650	1700	3.6	0.36	0.99
54	2	2	bake	825	1350	1550	7.0	0.93	1.68
56	2	2	activation	1550	1650	1700	1.27	0.17	0.18
26	3	1	bake	760	1340	1560	7.0	0.90	1.57
27	3	1	activation	1550	1660	1700	2.5	0.32	0.72
55	3	2	bake	840	1350	1550	7.0	0.93	1.57
57	3	2	activation	1550	1650	1700	1.27	0.17	0.21
91	2	3	bake	850	1350	1550	7.0	0.90	1.43
98	2	3	activation	1550	1650	1700	1.27	0.17	0.12

TABLE XIX - RESULTS OF REGENERATIONS, TASKS 2 AND 3

Run	Task	Cycle	Regenerating step	Bulk density, g/cc	Weight change, %	Bulk volume change, %	Particle volume change, %	Iodine number, mg/g	Molasses number
virgin	2	1	to Pomona	0.468	---	---	---	1090	250
spent	2	1	adsorption	0.548	+15.3	-3.36	-1.12	---	---
24	2	1	bake	0.493	-11.6 (-4.0)	-2.52 (-7.0)	--- (-5.4)	---	---
25	2	1	activation	0.468	- 5.8	-1.38	---	1040	310
reg	2	2	to Pomona	0.474	---	---	---	---	---
spent	2	2	adsorption	0.541	+13.0	-0.81	+0.84	---	---
54	2	2	bake	0.480	-12.8 (-5.6)	-1.73 (-3.6)	-3.33 (-2.8)	915	270
56	2	2	activation	0.469	- 4.2	-1.12	-0.33	935	290
reg	2	3	to Pomona	0.472	---	---	---	---	---
spent	2	3	adsorption	0.549	+14.6	-0.5	-0.7	---	---
91	2	3	bake	0.482	-15.0 (-5.8)	-1.0 (-2.6)	-0.0 (-1.9)	834	280
98	2	3	activation	0.473	- 3.3	-1.1	-1.2	940	355
virgin	3	1	to Pomona	0.468	---	---	---	1090	250
spent	3	1	adsorption	0.546	+15.4	-0.60	-0.72	---	---
26	3	1	bake	0.484	-12.6 (-4.9)	-1.81 (-3.9)	-0.73 (-2.3)	---	---
27	3	1	activation	0.464	- 5.8	-1.54	-0.86	1040	310
reg	3	2	to Pomona	0.476	---	---	---	---	---
spent	3	2	adsorption	0.538	+11.8	-0.97	-1.98	---	---
55	3	2	bake	0.481	-11.7 (-5.1)	-1.31 (-3.8)	-1.24 (-3.5)	---	---
57	3	2	activation	0.469	- 4.1	-1.51	-0.33	920	310
reg	3	3	to Pomona	0.478	---	---	---	---	---
spent	3	3	adsorption	0.544	+13.2	-0.40	-1.48	---	---

For this task, the conclusions are the same as for Task 2. It is felt that removal of part of the inorganic compounds by HCl leach would have greatly reduced the rate of degradation. The ash content increased in the same manner as in the Task 2 carbons.

Cycle	Ash,%
Initial	5.7
1st	7.9
2nd	8.7

Overall carbon loss on the first cycle was 2.3% and on the second 3.5%.

The estimated adsorbate on the carbon on each cycle was as follows:

Cycle	% Adsorbate
1st	16.7
2nd	13.0
3rd	13.8

Further details on Task 3 studies are also presented in Tables XVIII and XIX.

Task 2A and 2B - Cyclic Adsorption-Regeneration Studies

In view of the improved thermal regeneration of HCl leached carbons, the cyclic studies were resumed during the six months extension period. For these studies, two new 2500 cc batches of virgin Filtrasorb 400 were prepared. Batch 2A was as-received except for sieving out the -40 mesh fraction and batch 2B was leached in succession by HCl acid, pure water, hot caustic solution and pure water. This was done to remove all of the F_2O_3, CaO, MgO, Na_2O and K_2O and part of the SiO_2 and Al_2O_3, see Task 4 on HCl leach. The final ash content was 3.5% compared to 5.7% for the virgin carbon.

These carbons were spent at Pomona as was done in Task 2 and then regenerated at MSA Research laboratories. Prior to the thermal regeneration, each batch of spent carbon was HCl leached.

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The regeneration conditions and results of these two regenerations are presented in Tables XX and XXI.

For both regenerated carbons, the iodine numbers are higher than those of the original by a considerable margin although the final bulk density in each case matched the original. This is the first time this had occurred in the regeneration program.

The molasses numbers did not change significantly which is as desired.

The carbon losses are larger than had been expected. The actual regeneration losses are 4.3% for 2A and 4.4% for 2B as measured by particle volume change. For 2B, the carbon loss during the adsorption phase was 1.3%, by particle volume change, while there was an actual increase of 0.52% in bulk volume. For 2A, the carbon loss during the adsorption phase was very large, being 7.2% by bulk volume change and 8.5% by particle volume change.

The bulk and particle volume changes occurring during each step of the regenerations, for these two carbons, do not fit the general pattern as established in Tables XIII and XV. The bulk volume changes of 2B come closest to fitting the general pattern. In view of the studies made on particle volume decrease during baking in a previous section, most of the apparent baking losses should not be included in the overall regeneration loss. If 2.4% is allowed for the apparent baking loss, the overall adsorption-regeneration cycle loss for 2B is 3.3%. This percentage figure agrees well with the 3.7% overall weight loss.

Ash analyses on 2A and 2B after regeneration were 4.7% and 3.5%.

This was only the first adsorption-regeneration cycle but the results look promising in that original activity is recovered without excess carbon loss.

Task 4 - Chemical Oxidation and Solvent Extraction

H_2O_2 Pretreatment - Two pretreatment experiments were performed with 3% H_2O_2. In Run 9, Tables XXII and XXIII, 2500 cc of dried OSF 400 were wetted with 550 ml of 3% H_2O_2 and then baked in the regenerator. This treatment produced no observable effects on the baked carbon. In Run 11, 2500 cc of dried OSF 400 were leached with 4800 ml of 3% H_2O_2 in Buchner funnels and the leached carbon dried and baked. The leaching reduced the bulk density from 0.583 g/cc to 0.569 g/cc.

TABLE XX - REGENERATION CONDITIONS, TASKS 2A AND 2B, FIRST CYCLE

Run	Regeneration step	Temperature, °F			Gas input, ft^3/hr (stp)		
		1	2	3	N_2	CO_2	H_2O
Spent 2A	dried	---	---	---	---	---	---
HCl leached	---	---	---	---	---	---	---
103	baked	860	1360	1550	7.00	0.90	1.58
104	activated	1550	1650	1700	2.19	0.37	1.12
Spent 2B	dried	---	---	---	---	---	---
HCl leached	---	---	---	---	---	---	---
102	baked	860	1360	1550	7.00	0.90	1.39
105	activated	1550	1650	1700	2.19	0.37	0.81

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TABLE XXI - REGENERATION RESULTS, TASKS 2A AND 2B, FIRST CYCLE

Run	Bulk density, g/cc	Weight change, %	Bulk volume change, %	Particle volume change, %	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
Initial 2A	0.477	---	---	---	0.659	1105	290
Spent 2A	0.540	+5.0	-7.2	-8.5	0.568		
HCl leached	0.527	-3.1	-0.6	-0.5	0.592		
103	0.492	-8.8 ⎱ 11.8	-2.3 ⎱ -11.1	-1.4 ⎱ -12.8	0.631		
104	0.474	-4.8	-1.3	-2.8	0.649	1150	290
Initial 2B	0.473	---	---	---	0.669	1065	285
Spent 2B	0.546	+15.9	+0.5	-1.3	0.551		
HCl leached	0.533	-3.7	-1.4	-0.8	0.574		
102	0.494	-8.6 ⎱ 3.7	-1.3 ⎱ 4.1	-3.0 ⎱ 5.7	0.631		
105	0.475	-5.6	-1.8	-0.7	0.649	1150	300

TABLE XXII - REGENERATION CONDITIONS, CHEMICALLY TREATED OSF 400

Run no.	Regenerating step, special treatment	Temperature, °F 1	2	3	Gas input, ft³/hr (stp) N_2	CO_2	O_2	H_2O
8	baker feed rewetted with 550 ml H_2O per 2500 cc carbon	980	1270	1550	7.9	1.0	0.0	1.60
14	Run 8 activated	1550	1650	1700	2.7	0.34	0.00	0.47
9	baker feed wetted with 550 ml 3% H_2O_2 per 2500 cc carbon	1000	1250	1550	7.9	1.0	0.0	1.32
15	Run 9 activated	1550	1650	1700	2.7	0.34	0.02	0.72
11	baker feed leached with 4800 ml 3% H_2O_2 per 2500 cc carbon	860	1250	1550	7.9	1.0	0.0	1.50
17	Run 11 activated	1700	1700	1600	2.1	0.27	0.00	0.39
18	500 cc carbon leached with caustic, HCl, etc.	---	---	---	---	---	---	---
20	Run 18 baked	485	1230	1550	2.0	0.00	0.00	0.00
21	Run 20, second bake	550	1240	1550	2.0	0.00	0.00	0.00

TABLE XXIII - REGENERATION RESULTS, CHEMICALLY TREATED OSF 400

Run no.	Bulk density, g/cc	Weight decrease, %	Bulk volume decrease, %	Particle volume decrease, %	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
virgin	0.469	---	---	---	0.650	1090	250
spent	0.583	---	---	---	0.500	630	190
8	0.507	13.1 ⎤ 18.8	0.5 ⎤ 1.6	0.9 ⎤ 2.8	0.607	940	212
14	0.482	6.5 ⎦	1.1 ⎦	1.9 ⎦	0.629	935	229
9	0.507	13.5 ⎤ 19.7	0.8 ⎤ 1.9	0.8 ⎤ 1.9	0.611	940	211
15	0.477	7.1 ⎦	1.1 ⎦	1.1 ⎦	0.629	920	237
11	0.504	14.5 ⎤ 19.6	0.9 ⎤ 1.7	0.9 ⎤ 3.1	0.610	960	213
17	0.480	5.9 ⎦	0.8 ⎦	2.2 ⎦	0.629	950	251
18	0.481	18.6 ⎤	2.4 ⎤	6.4 ⎤	0.616	910	---
20	0.467	5.5 ⎬ 21.9	1.8 ⎬ 4.9	--- ⎬ 8.9	---	---	---
21	0.460	0.9 ⎦	0.7 ⎦	2.7 ⎦	0.634	1030	260

On baking, the bulk density reduced to 0.504 g/cc, which is slightly lower than the 0.507 g/cc for untreated baked carbons. The iodine numbers of both carbons after activation were at the same level as for the unpretreated carbons, Run 14 as example, hence no benefit was derived. Additional H_2O_2 treatment would not create more favorable results since the H_2O_2 cost already for the above leaching pretreatment is 7.2¢/lb carbon.

Caustic Leach - Three caustic leach runs were performed to determine the economic feasibility of caustic leaching as an alternate method for spent carbon regeneration.

The first leach run, designated as Run 18, was exploratory to determine the critical parameters. Concentration, flow rate, and temperature were varied. Methanol, caustic-methanol solution,. and periodic pure water and HCl acid leach were also tried. Attempts were made to follow the effectiveness of the treatment by grading the color density of the filtrate, but this method proved to be unreliable since the color kept changing in tone. The only trustworthy method of monitoring was by periodic bulk density determinations.

Table XXIV gives a chronological record of the carbon treatment. The initial volume and weight were 500 cc and 292 g, respectively. About 350 l of the various solutions were passed through the column before the filtrate became essentially colorless. At this point the bulk density was 0.481 g/cc, still above the 0.468 g/cc bulk density of virgin Filtrasorb 400.

The leached carbon was then baked twice in a nitrogen atmosphere to volatilize as much of the adsorbate as possible. The baking treatment brought the density down to 0.460 g/cc and iodine and molasses numbers to high values of 1030 mg/g and 260, respectively. These test results are fairly close to the properties of the virgin carbon received from Pomona on December 9, 1968. On this basis it was assumed that the spent carbon used in most of the regeneration runs of this program had initially the properties of this virgin carbon.

During the leaching, it was noted that if the carbon bed was allowed to boil, even gently, by raising the temperature to 100°C, the filtrate started to carry carbon fines. The movement of the carbon bed may have caused abrasion of the carbon particles. The particle volume decrease during the leach was 6.4%. During baking, it was 2.7%, which is high compared to results on previous OSF 400 baking runs. The higher particle volume decrease here may be another indication of generation of fines during the leaching process.

TABLE XXIV - CAUSTIC SOLUTION AND METHANOL LEACH OF ONCE-SPENT FILTRASORB 400, RUN 18

Volume of leach liq, l	Flow rate, l/hr	Type liquid	Temp, °C	pH of filtrate	Color of filtrate	Bulk den of carbon, g/cc	Bulk volume decrease, %
0	---	---	---	---	---	0.584	---
46	2.5-3.0	5.0% NaOH	50-80		Dark yellow		
9	2.5	1.0% NaOH					
3	2.5	Water					
6	2.5	0.25% NaOH					
6	2.5	0.50% NaOH					
9	2.5	1.0% NaOH					
6	2.5	5.0% NaOH					
3	2.5	0.25% NaOH					
12	4.0	0.10% NaOH					
3	4.0	Water			Light yellow	0.529	0.0

Above leaching done in Buchner funnel
Below leaching continued in heated column, unit shown in Figure

Volume of leach liq, l	Flow rate, l/hr	Type liquid	Temp, °C	pH of filtrate	Color of filtrate	Bulk den of carbon, g/cc	Bulk volume decrease, %
1	1.0	0.10% NaOH	95-100		100 color unit		
4	1.0	0.10% NaOH	"		60		
11	1.0	0.05% NaOH			17		
50	1.0	0.10% NaOH			3		
3	1.0	1.0% NaOH			4		
4	1.0	0.10% NaOH			2.5		
12	1.0	Water		10.7		0.513	1.8
4	1.0	Methanol	60-65	8.8	Light pink		
1	1.0	1.0% NaOH in methanol			Light yellow		
10	1.0	Methanol		10.6	Light pink	0.509	1.8
4	1.0	Water	95-100		Light yellow		
1	1.0	1.3% HCl	80		Green		
12	1.0	Water	95-100	5.3	Colorless	0.492	2.2
1	2.0	0.10% NaOH	95-100		70		
32	2.0	0.10% NaOH			11		
2	2.0	0.10% NaOH			--		
2	2.0	1.3% HCl	80		Colorless		
1	3.0	0.10% NaOH	95-100		30		
3	3.0	0.10% NaOH	"		8		

In the second caustic leach run, Run 19, the caustic concentration was kept very low, at 0.025% and 0.013%. The carbon bed was kept at near 100°C, but actual boiling or movement of the bed was avoided as much as possible. At intervals, the carbon bed was leached with dilute HCl. About 550 l of caustic and HCl solutions were passed through the bed, but filtrate still had low level of color. After 450 l of solution had been passed through the bed, the carbon was taken out, dried and the bulk density measured. No change had occurred in bulk volume (still at 500 cc) but the density was still high, 0.576 g/cc.

Figure 7 shows the decrease in bulk density as function of amount of solution passed through the carbon for each Run 18 and 19. In general, the concentrations of caustic were 5- to 10-fold greater in Run 18 than Run 19. The higher concentration required less solution but reduction in water required was considerably less than 5- to 10-fold.

A third run was made with 25% caustic soda and HCl solution treatments in a batchwise process. Each batch treatment consisted of a routine of caustic soda leach, water leach, HCl leach and water leach; the routine was done twice. In the caustic leach, 235 g (regenerated weight) of spent carbon was placed in a flask with a caustic solution and heated at boiling point temperature for one hour. The caustic solution was filtered from the carbon in a Buchner funnel and the carbon, on the funnel, then leached with six liters of hot pure water, followed by one liter of hot 6% HCl solution and finally with four liters of hot pure water. Each batch treatment required overall 600 g caustic soda, 30 cc concentrated HCl and 24 liters of water.

The results of this run are given in Figure 8, which show the change in bulk density after each batch treatment. At the fifth treatment the effectiveness of the treatment was very small. An extrapolation of the curve indicates that inordinately large quantities of caustic would be required to bring the bulk density down to 0.468 g/cc. At ten-batch treatment, the amount of caustic required would cost 25¢/lb of carbon. If recovery of caustic, for reuse, were possible, the recovery process would have to be better than 98% efficient to avoid excessive material cost.

On the basis of the three caustic soda and HCl leach runs of widely different agent concentrations, the conclusion is that caustic leaching is not competitive with thermal regeneration. Inordinately large amounts of water would have to be used to regenerate the carbon to initial activity. Over 8% of the water purified per pound of carbon would be reused for leach-
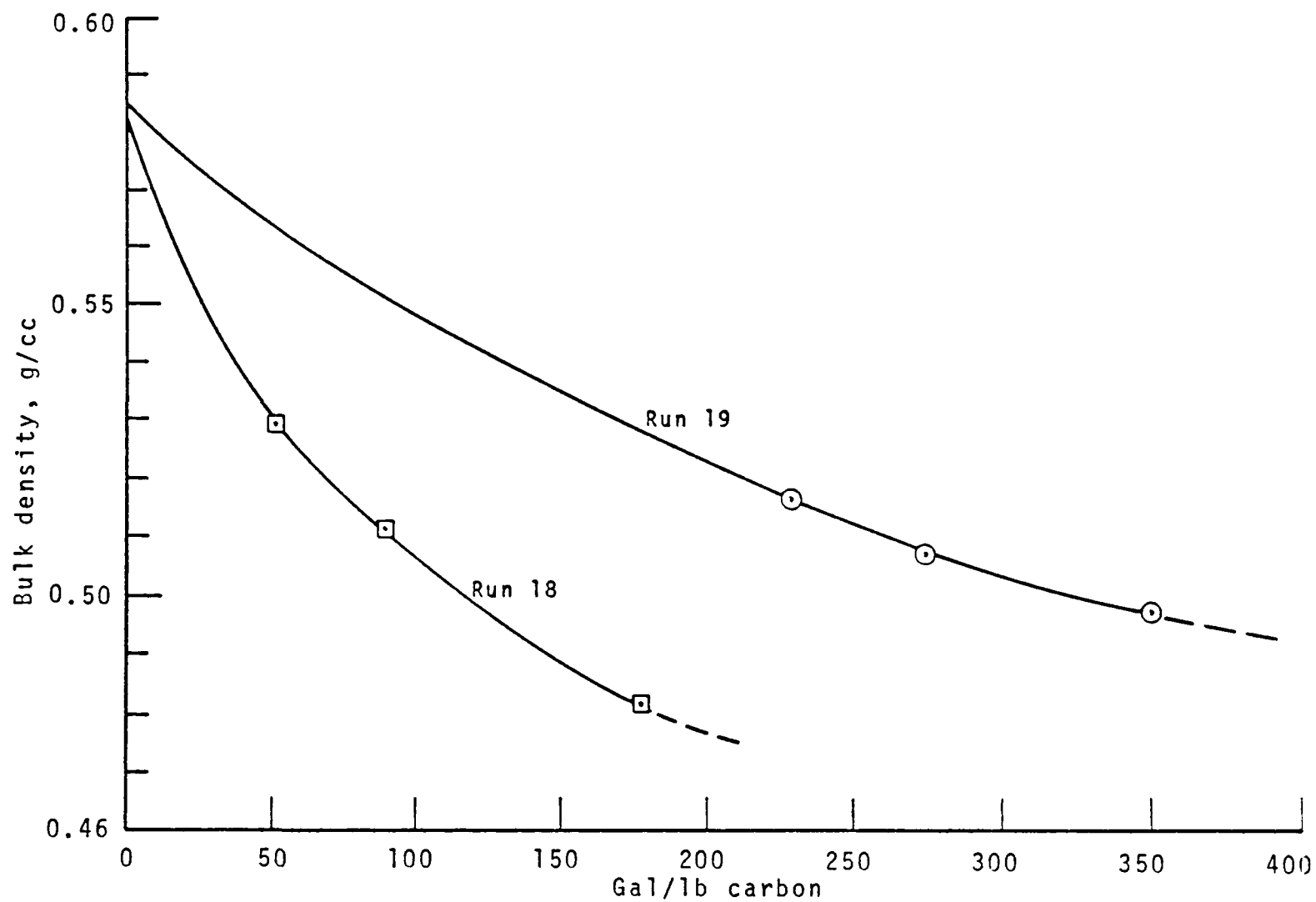
FIGURE 7 - OSF 400 LEACHED WITH LOW CONCENTRATION SOLUTIONS OF CAUSTIC SODA AND HCl,
AND PURE WATER; BULK DENSITY AS FUNCTION OF AMOUNT LIQUID PASSED THROUGH CARBON
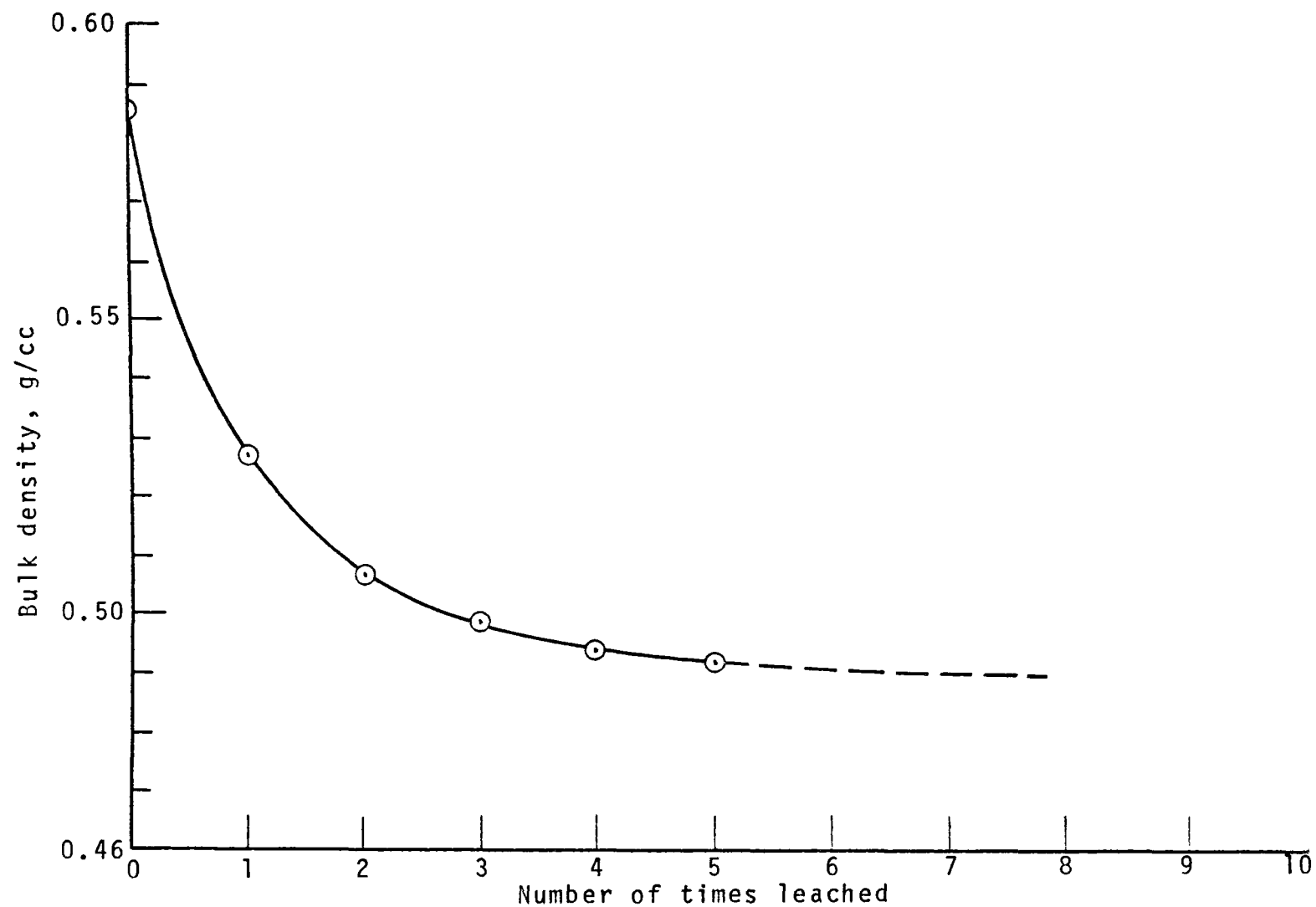
FIGURE 8 - OSF 400 LEACHED WITH HIGH CONCENTRATION CAUSTIC SODA SOLUTION AND HCl
AND PURE WATER IN BATCH TYPE PROCESS; BULK DENSITY AS
FUNCTION OF NUMBER OF BATCH TREATMENTS

ing purposes. The caustic and HCl acid costs would also be excessive. For Run 18, more than 0.84 lb of 76% caustic and 0.15 lb of 37% HCl acid would be required. At 5.35¢/lb for the caustic soda and 1.95¢/lb for the acid, the agent costs would be more than 4.8¢/lb of regenerated carbon. For Run 19, the agent costs would be considerably over 3.3¢/lb of carbon before regeneration could be effected to initial properties.

Of academic interest, it was observed that the leaching efficiency of the caustic solution increases with increased temperature. Periodic HCl acid treatments appear to accelerate the caustic leach.

NaOCl Leach - Two short leaching runs were made with NaOCl solution in the leaching column with 500 cc quantities of OSF 400. The first run was with 35 l of 1.0% NaOCl solution at about 90°C and 1.0 l/hr flow rate. The carbon density decreased from 0.580 to 0.556 g/cc, but bulk volume decreased from 500 to 452 cc. The filtrate was black from finely suspended carbon.

In the second run, 40 l of 0.25% NaOCl solution were run through the column. In this case also, there was considerable disintegration of the carbon. Density decreases from 0.580 to 0.550 g/cc and volume from 500 to 420 cc.

Because of the high carbon losses, NaOCl was judged an unsatisfactory regenerating agent.

CCl_4 Extraction - Fifty cc of OSF 400 were extracted in a 300 ml Soxhlet extractor for 40 turnovers of the CCl_4. The amount of CCl_4 used in the extractor was 210 ml. After the extraction, the treated carbon was air-oven dried at 150°C for several hours and again heated under vacuum at 110°C in preparing samples for CCl_4 adsorptive capacity test. The CCl_4 adsorptive capacity, under static vacuum test, was 36% compared to 38% for the untreated OSF 400. Estimated iodine numbers based on the CCl_4 capacity tests were 550 and 640 mg/g for the treated and untreated carbons, respectively.

No benefit was derived from the CCl_4 extraction.

HCl Leach Pretreatment, Effect on Iodine Number - HCl leach was first conceived as a pretreatment to assist in the removal of adsorbate during the baking step. The rationalization was that organometallic compounds of Fe, Ca and Na adsorbed from waste water would resist volatilization and thereby leave a larger carbon deposit. HCl leached OSF 400 carbon, however, showed no greater adsorbate loss than un-

leached carbons but a large increase in iodine number occurred after the activating step. It is now believed that in the unleached carbon, Fe_2O_3, CaO and Na_2O catalyzed the oxidation of the base carbon structure and thereby lowered the iodine numbers and increased the molasses numbers of the regenerated carbons from what they should have been. HCl leach removed these metals and the thermal regeneration then restored the carbons closer to their initial properties.

Tables XXV and XXVI present regenerating conditions and results of a number of runs made under a variety of conditions but in all the runs HCl acid pretreatment was employed. Regeneration Runs 33-34, 35-36, 45-47, 49-53 and 78-79 were performed under conditions that can be attained in a directly heated multiple hearth furnace. The iodine numbers of these regenerated carbons varied between 1020 and 1050 mg/g compared to 900 to 950 mg/g for thermal regenerated unleached carbon. Since the iodine number of the initial carbon is believed to be 1090 mg/g, there is still room for improvement.

Regeneration Runs 63-69 and 65-70 were performed under conditions that cannot be duplicated in directly heated multiple hearth furnaces because of the inert gas sweep used during baking. The high temperature over the baking step would also be difficult to attain. The inert gas sweep during baking and the higher temperatures are now of academic interest since they produced regenerated carbons of lower iodine numbers.

The HCl leach for these regenerations was done on Buchner funnels with acid solution and leach water heated to near boiling point before being poured over the carbon. About 30 ml of 37% HCl diluted to 500 ml water was used to treat 500 cc of carbon. About 5 l of water was then used to leach out the chloride ion, i.e., until a silver nitrate test was negative. At this point, the pH was still 3.5.

HCl Leach Posttreatment, Effect on Iodine Number - Prior to the HCl pretreatment studies, tests had been carried out to determine the effect HCl leach of regenerated carbons would have on the iodine and molasses numbers. The results showed that the ash content had no effect on molasses number while removal of ash lowered the iodine number in some cases. The results of these tests are summarized in Tables XXVII and XXVIII. This information confirms the fact that the increase in iodine number of regenerated carbons, pretreated with HCl, is due to the effect the pretreatment had on the thermal regeneration rather than being due simply to removal of the ash.

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TABLE XXV - REGENERATION CONDITIONS, HCl LEACH

Run no.	Regenerating step, special treatment	Temperature, °F			Gas input, ft^3/hr (stp)		
		1	2	3	N_2	CO_2	H_2O
---	leach, 150 ml HCl per 2500 cc OSF 400, hot	---	---	---	---	---	---
33	above carbon baked	800	1300	1550	7.0	0.90	1.67
34	Run 33 activated	1550	1650	1700	7.2	0.90	1.84
---	leach, 200 ml HCl per 2500 cc OSF 400, hot	---	---	---	---	---	---
35	above carbon baked	800	1300	1550	7.0	0,90	1.29
36	Run 35 activated	1575	1675	1700	8.3	1.00	2.25
---	leach 100 ml HCL + 50 g NaOH/2500 cc OSF 400	---	---	---	---	---	---
45	above carbon baked	800	1350	1600	7.0	0.90	1.78
47	Run 45 activated	1550	1650	1700	5.8	0.77	1.70
---	leach, 150 ml HCl per 2500 cc OSF 400, hot	---	---	---	---	---	---
49	above carbon baked	810	1350	1600	7.0	0.93	1.71
53	Run 49 activated	1550	1650	1700	3.12	0.41	0.93
---	leach same as for Run 45	---	---	---	---	---	---
63	above carbon baked	1700	1700	1600	3.7	0.00	0.00
69	Run 63 activated	1700	1700	1600	9.2	1.10	2.10
65	OSF 400 baked	1700	1700	1700	3.7	0.00	0.00
---	Run 65 HCl leached	---	---	---	---	---	---
70	above activated	1700	1700	1600	9.2	1.10	2.69
---	leach same as for Run 49	---	---	---	---	---	---
78	above carbon baked	800	1350	1550	7.0	0.93	1.96
79	Run 78 activated	1550	1650	1700	6.0	0.80	1.94

TABLE XXVI - REGENERATION RESULTS, HCl LEACH

Run no.	Bulk density, g/cc	Weight decrease, %	Bulk volume decrease, %	Particle volume decrease, %	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
virgin	0.468	---	---	---	0.650	1090	250
spent	0.583	---	---	---	0.500	630	190
leached	0.557	4.2 ⎤	0.1 ⎤	0.0 ⎤	0.527	660	219
33	0.508	10.2 ⎬ 20.6	1.7 ⎬ 3.7	0.5 ⎬ 1.8	0.604	910	213
34	0.478	7.7 ⎦	1.8 ⎦	1.3 ⎦	0.627	1020	234
leached	0.560	3.8 ⎤	0.0 ⎤	0.1 ⎤	0.524	---	---
35	0.510	10.7 ⎬ 20.2	2.0 ⎬ 3.1	0.5 ⎬ 2.7	0.611	930	210
36	0.484	6.9 ⎦	1.1 ⎦	3.3 ⎦	0.639	1040	215
leached	0.563	3.7 ⎤	0.0 ⎤	0.0 ⎤	---	---	---
45	0.500	13.7 ⎬ 23.4	2.7 ⎬ 3.8	2.8 ⎬ 4.6	0.612	940	240
47	0.468	7.7 ⎦	1.1 ⎦	1.8 ⎦	0.638	1050	230
leached	0.555	5.2 ⎤	0.4 ⎤	0.3 ⎤	0.527	---	---
49	0.495	12.5 ⎬ 21.8	2.1 ⎬ 3.3	1.9 ⎬ 3.9	0.629	970	210
53	0.472	5.6 ⎦	0.7 ⎦	1.7 ⎦	0.645	1020	250
leached	0.544	6.0 ⎤	0.2 ⎤	⎤	---	---	---
63	0.506	9.5 ⎬ 21.6	2.4 ⎬ 3.3	⎬ 4.3	0.614	900	230
69	0.472	7.8 ⎦	0.7 ⎦	1.9 ⎦	0.642	990	210
65	0.517	13.1 ⎤	2.5 ⎤	2.0 ⎤	0.614	820	210
leached	0.507	2.1 ⎬ 21.5	0.0 ⎬ 3.8	1.0 ⎬ 5.0	0.615	---	---
70	0.475	7.7 ⎦	1.3 ⎦	2.1 ⎦	0.642	970	220
leached	0.551	4.6 ⎤	0.0 ⎤	1.7 ⎤	0.519	---	---
78	0.504	10.9 ⎬ 20.0	1.9 ⎬ 2.6	-0.4 ⎬ 3.3	---	1000	230
79	0.480	5.8 ⎦	0.7 ⎦	2.0 ⎦	0.632	1040	230

TABLE XXVII - ASH CONTENT OF REGENERATED CARBONS
BEFORE AND AFTER DILUTE HC1 ACID LEACH

Run no. (regenerated)	Bulk density, g/cc		Ash after regeneration, %	Ash after regeneration & dil HC1 leach, %
	spent	regenerated		
Virgin F 400	---	(0.469)	(5.7)	(5.1)
56 (1)	0.615	0.488	8.4	4.5
63 (1)	0.616	0.445	9.2	4.8
65	0.574	0.486	7.5	5.8
27	0.546	0.464	7.9	5.3
32	0.582	0.467	7.3	4.4

(1) Runs from contract 14-12-107

TABLE XXVIII- DECOLORIZING TEST RESULTS ON HC1
LEACHED AND NONLEACHED CARBONS

Run no.	Iodine number, mg/g		Molasses number	
	no leach	HC1 leach	no leach	HC1 leach
Virgin F 400	1090	1060	240	250
56	880	790	290	280
63	850	840	320	320
65	960	920	220	230
27	1040	1040	310	280
32	950	940	---	270

HCl Leach Pretreatment, Effect of Temperature - The success of the HCl acid pretreatment in improving the thermal regeneration prompted further study to optimize the pretreatment conditions. A rapid preliminary study was made, according to the procedure used previously to determine whether an effective leaching could be performed at ambient temperature. The leaching was done by passing 500 ml HCl solution through 500 ml of OSF 400 in a Buchner funnel. The acid filtrate was recycled twice and discarded. Pure water was then passed through the bed until the filtrate was essentially neutral and free of chloride ion. About 2 liters of water was used in each case to leach out the acid.

The results of this study are presented graphically in Figure 9. Leaching was done at near boiling point and at ambient temperature. A good measure of contact time is not obtainable with this procedure, hence, the data obtained is not suitable for scale-up purposes. Ash analysis, by ignition was made on the original OSF 400 and each leached batch. In order to put the ash analyses on a comparable basis, the measured ash content was multiplied by the ratio, 0.468/density of spent carbon. This gives the would-be ash analysis after regeneration to 0.468 g/cc bulk density.

The curves in Figure 9 show that there is not a significant difference between cold and hot leach and that in the acid to carbon contact time employed, the ash content cannot readily be reduced below 4.5%. Since it is considerably better to operate at ambient temperature, because of reduced corrosion and avoidance of heating costs in large scale operations, the hot leach studies were discontinued.

HCl Leach Pretreatment, Effect of Concentration - With knowledge obtained from the preliminary studies, another test procedure was devised so that reliable information could be obtained on contact time versus amount of acid needed. Five glass tubes were set up to permit five simultaneous leaching experiments. Tube dimensions were: I.D. = 4.8 cm, length = 63 cm. Five hundred cc of OSF 400 was placed in each tube, giving carbon bed depth of 34 to 36 cm. The carbon in each case was then submerged in water so that the water level came to the top of the carbon bed. (This would simulate the condition of a contactor at Pomona, after a backwash, in case the acid leaching could be done in the contactors.) Five hundred ml acid were then added to each of four tubes and pure water into the fifth. Acid concentrations used were: 5, 10, 20 and 30 ml concentrated HCl diluted to 500 ml. Flow through each bed was controlled by means of a stopcock at lower end of tube and, for this set of experiments, flow was set at 100 ml/hr. This gives a contact time of about
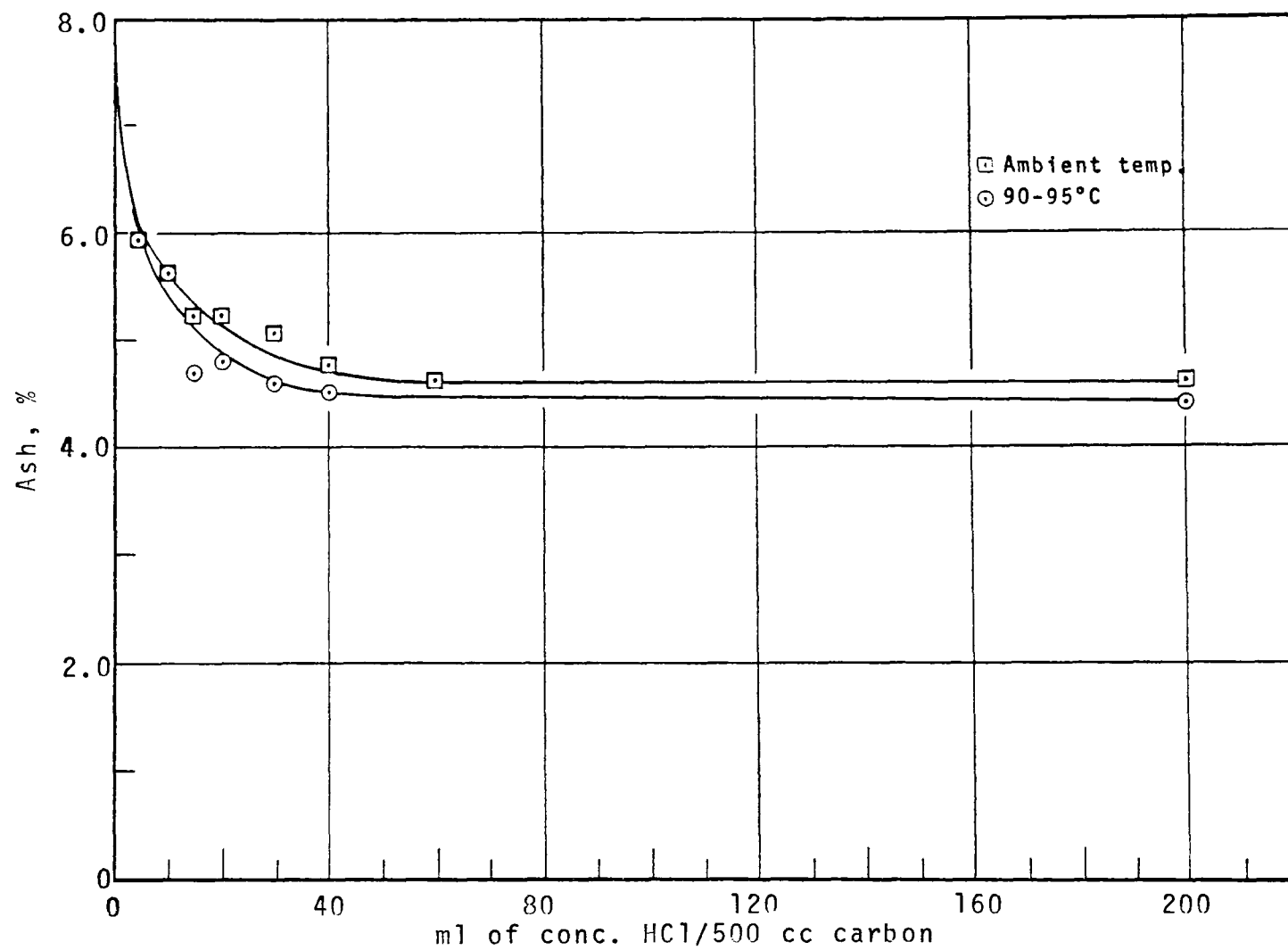
FIGURE 9 - ASH CONTENT OF HCl LEACHED OSF 400

2 hr. After the acid level reached the top of each carbon bed, water was added to the tube and flow continued at previous rate. The pH, measured on each 50 ml of filtrate, are plotted in Figure 10 as function of the filtrate volume. Elemental analyses were also made on the filtrate of the 20 ml acid experiments. Qualitative chloride tests were made on each filtrate with silver nitrate.

After the acid leach was completed, carbon samples were taken from the top, midsection and bottom for ash analyses. The results of the ash analyses are given in Table XXIX. Also, in calculating these results, the measured ash content was multiplied by the ratio, 0.468/bulk density of spent carbon, to put the results on a comparable basis.

On analyzing the data obtained thus far, several trends were noted. A part of metallic ions comes off very easily. Pure water passed through the bed, reduced the ash content from 8.2 to 6.8%. The pH rose from about 5.0 to 6.0 at the same time.

When 5 ml of acid were added, the ash content reduced to 5.1% at the top part of the bed but was still 6.2% at the bottom. In this experiment, also the pH rose from 5.0 to 6.0 indicating that no free acid penetrated the bed. The filtrate contained Ca and Na ions, but no other metal ions, in concentrations given in Table XXX. These facts signify that the 5 ml of acid was completely consumed within the bed. For the 500 cc carbon (235 g regenerated weight), 5 ml of acid is definitely too small to give uniform removal of the metallic elements.

When 10 ml or more of acid was added, the ash content dropped to the 4.8% level with variation between 4.5 to 5.4%. This variation appears to be experimental error since no logical trend is indicated. The pH of the filtrates passed through a minimum, below 1.0, indicating penetration of acid.

Elemental analyses were made on the filtrate of Experiment 1 (20 ml acid) at several filtrate volumes. The results of the analyses are given in Table XXXI. The R_2O_3 is mainly

TABLE XXXI - ANALYSIS OF FILTRATE FROM EXPERIMENT 1

Filtrate volume, ml	Element content of filtrate, mg/ml		
	Na	Ca	R_2O_3
700	0.055	1.98	3.78
800	0.045	1.77	2.18
1000	0.020	trace	0.46
2000	-----	----	---- 0.11 mg/ml total solids
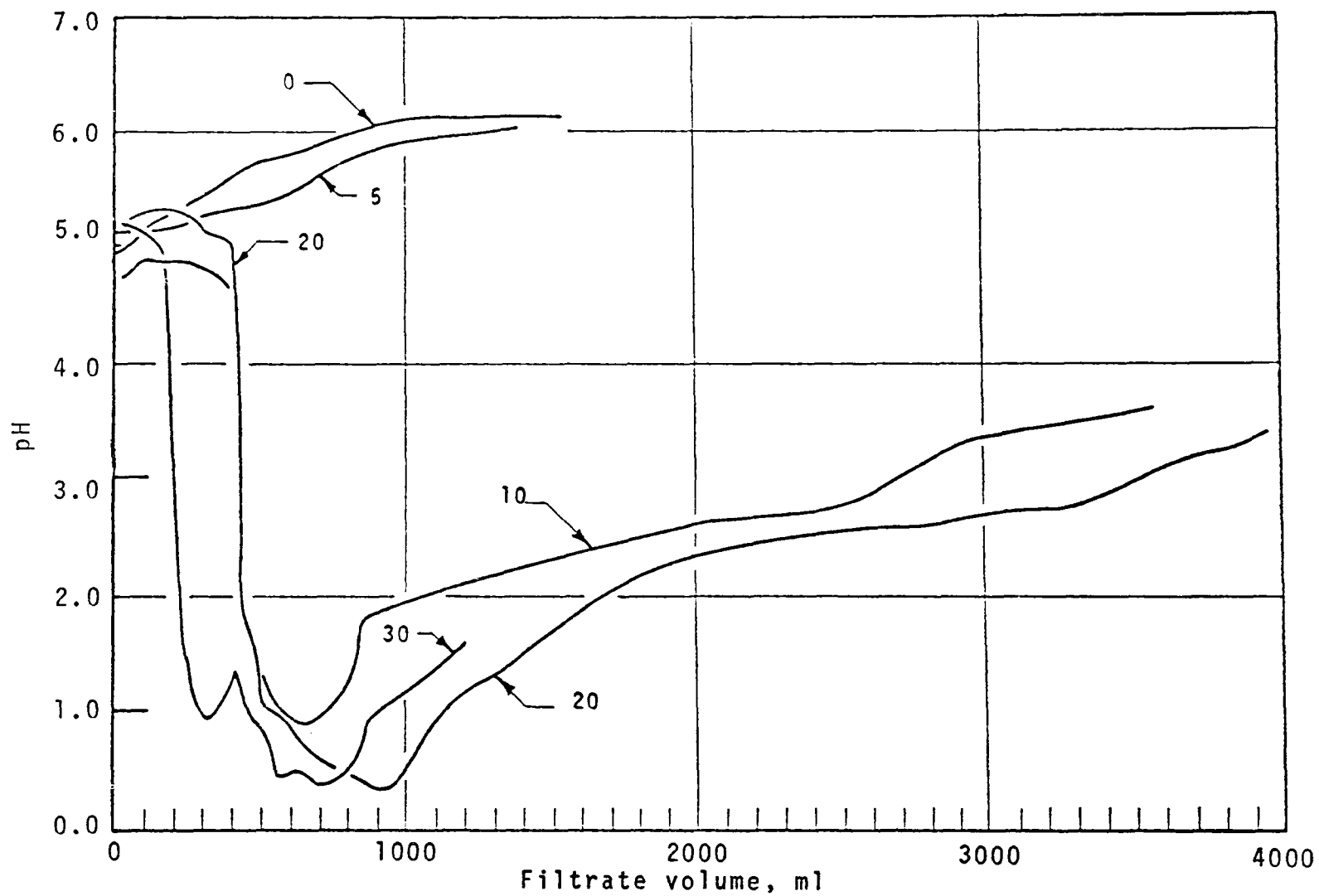
FIGURE 10 - pH OF FILTRATE FROM HCl LEACH OF OSF 400 WHEN ACID TO CARBON CONTACT TIME IS 2 HR

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TABLE XXIX - ASH CONTENT OF HCl LEACHED OSF 400

Experiment no.	Acid used, ml	Ash content, %		
		top	middle	bottom
5	0	6.8	---	6.8
3	5	5.1	4.9	6.2
2	10	4.6	4.7	5.4
1	20	4.7	5.1	4.9
4	30	4.8	4.5	5.0

Initial ash content of unleached OSF 400 = 8.2%
Ash content of virgin F 400   = 5.7%

TABLE XXX - ANALYSIS OF FILTRATE FROM EXPERIMENT 3

Filtrate volume, ml	Element content of filtrate, mg/ml			
	Na	Ca	Cl	Residue on evap. to dryness
500	0.070	0.225	---	2.14
1000	0.010	0.170	0.36	1.32

Fe with smaller amounts of Cr, Mn and Al. If the mean
atomic weight of R is assumed to be 56 g/mol, that of iron,
then the metallic elemental composition of leached ash is
approximately 1% Na, 49% Ca and 50% R. It comes out that
one percent of ash reduction is chemically equivalent to
2.6 g HCl. Pure water reduces the ash content from 8.2% to
6.8%, while 10 ml of acid reduces it down to about 4.8%
hence, the water aids the acid considerably. If it is as-
sumed the acid contributes to the ash reduction from 6.8 to
4.8%, i.e., 2.0%, then the amount of HCl required is 5.2 g.
Ten ml of concentrated HCl contains 4.5 g HCl, hence over
10 ml are required for the reaction.

HCl Leach Pretreatment, Effect of Contact Time - A series of
leaching experiments were conducted at nominal contact times
of 1, 2 and 4 hr. Since the contact time varies with void
volume in the carbon bed and the void volume in turn depends
on the manner the carbon was loaded into the contactor, the
actual contact time can vary for a given carbon loading.
Void volume can vary from about 40% to 55%, hence a contact
time of 2 hr calculated for 40% void could in reality be
2.9 hr for an expanded bed of 55% void. To avoid this error,
the contact times are reported in terms of liquid flow rate
per unit weight of carbon, thus:

ml liquid/ (g carbon x hr)	gal. liquid/ (lb carbon x hr)	Contact time range, hr
0.850	0.102	1 to 1.4
0.426	0.051	2 to 2.7
0.213	0.025	4 to 5.5

Progress of the leaching experiments was measured by deter-
mining pH of the filtrate and chloride ion concentration with
silver nitrate. When chloride ion concentration became very
low, the water leach phase of the treatment was then stopped
and carbon then dried and analyzed.

Figures 11 and 12 show the effluent pH curves at the various
contact times for 5 and 20 ml acid dosages. Figure 11 shows
that at the 5 ml acid dosage, the chloride ion does not pen-
etrate to any extent as a free acid even at the shortest
contact time. Most of the acid is converted to salts. At
the 10, 20 and 30 ml acid dosages, free acid penetrated the
carbon bed, indicating that more than the stoichiometric
amount of acid was added. Curves of Figure 12 also show no
definite trends regarding contact time, which indicates that
the chemical reaction and acid diffusion are relatively fast.
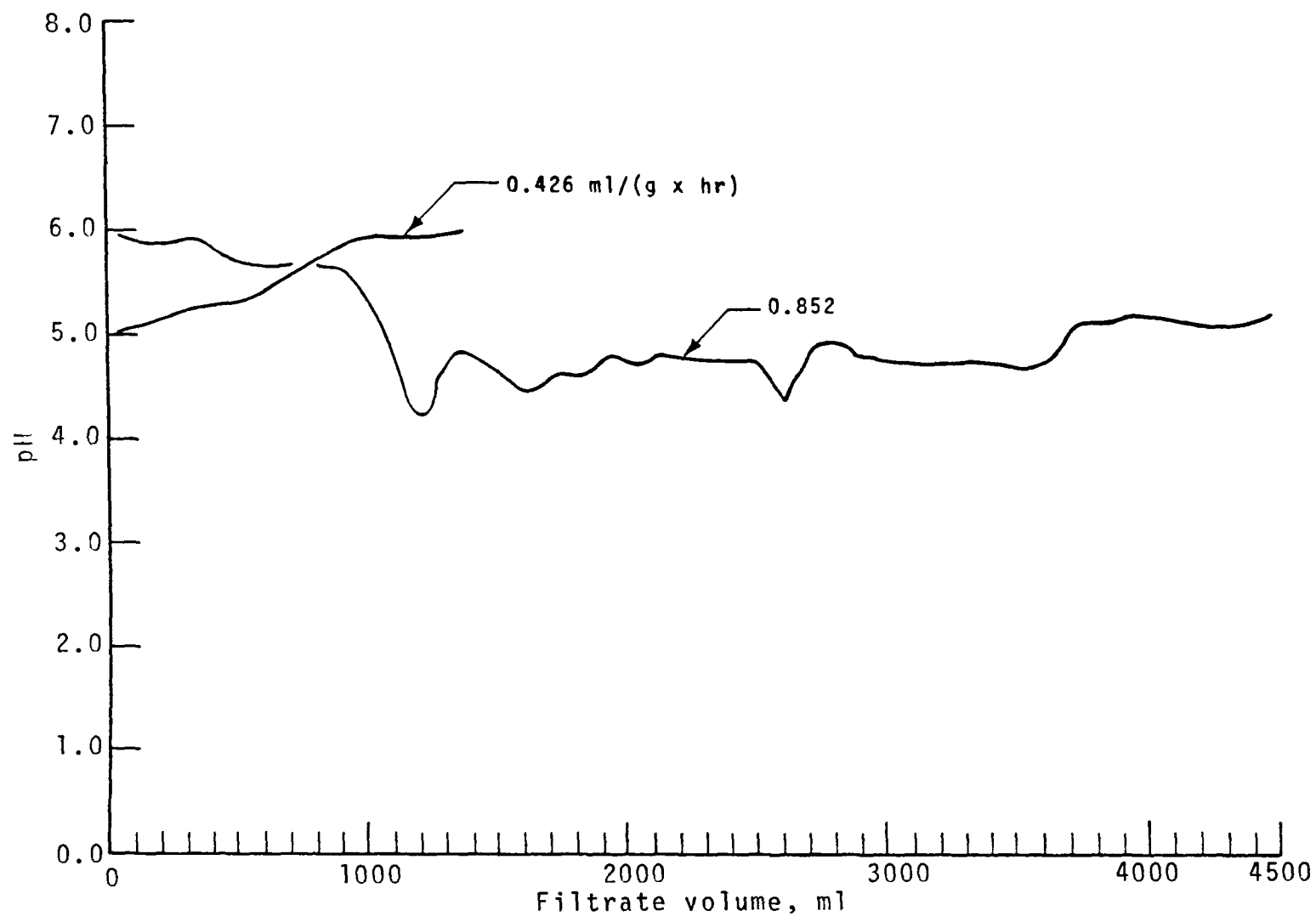
FIGURE 11 - pH OF FILTRATE FROM HCl LEACH WHEN 5 ml OF ACID
IS ADDED TO 500 cc OSF 400
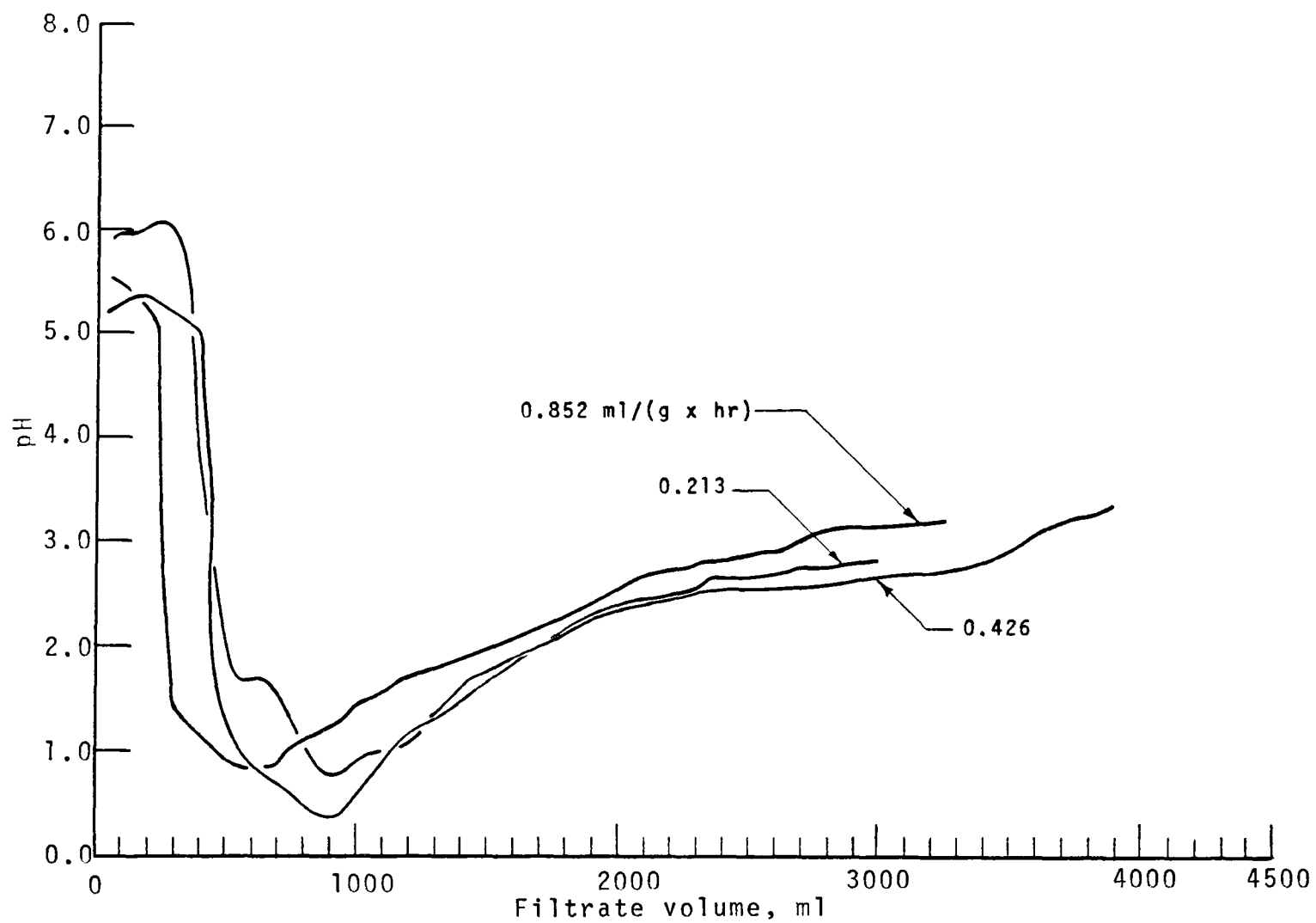
FIGURE 12 - pH OF FILTRATE FROM HCl LEACH WHEN 20 ml OF ACID
IS ADDED TO 500 cc OSF 400

On the 0.426 experiment of Figure 12, the carbon was analyzed for chlorine after the acid treatment. The amount of chlorine found was 0.2% as compared to 0.04% of the virgin Filtrasorb 400. Although the filtrate was free of chloride ion, according to the silver nitrate test, some chloride still remained in the carbon. At present, it is not known whether the chloride will be liberated from the carbon during regeneration. Ash analyses of the HCl treated carbons have shown only traces of chloride.

Table XXXII presents ash analysis data on the leached carbons sampled from three positions in the carbon bed. Figure 13 gives the ash analyses for the lower end of the carbon bed. The results indicate that the 10 ml dosage is not sufficient to bring the ash content down to the 4.8% level, for the 235 g carbon being leached. The optimum amount of acid may be 14 to 15 ml for a 0.426 ml/(g x hr) flow rate, as indicated by the broken line curve.

HCl Leach Pretreatment, Effect on Ash Content - There is a logical reason why the acid leach reduces the ash content to a lower limit of about 4.8% regardless of amount of acid used and contact time. Pittsburgh Carbon Company has found that HCl leach reduces the ash content of Filtrasorb 400 type carbon by about 1.0%, i.e., for initial ash content of 5.7% the ash content after leach is about 4.7%.

The elemental analysis of ash from Filtrasorb 400 type carbon, as determined by Pittsburgh Carbon Company, is approximately as follows:

Component	%	
SiO_2	41.4	
Al_2O_3	44.0	85.4
Fe_2O_3	7.4	
CaO	2.9	
MgO	2.4	14.6
K_2O	1.0	
Na_2O	0.7	
	99.8	

In the analysis the two relatively insoluble components, SiO_2 and Al_2O_3, constitute 85.4% of the ash. The others are quite soluble in HCl. By taking the ratio of 85.4/99.8 times 5.7% we get 4.9% as the nonsoluble portion of the ash on the carbon. This means that the acid leach has removed all the inorganic compounds retained by the carbon plus 15% of the ash initially on the carbon and leaving essentially an $SiO_2-Al_2O_3$

TABLE XXXII - ASH ANALYSES OF HCl LEACHED CARBONS

Experiment no.	Acid, ml	Flow rate, ml/hr	ml/(g x hr)	Ash content, % top	center	bottom
as received	---	---	---	8.2	8.2	8.2
5	0	100	0.425	6.8	---	6.8
---	5	50	0.213	---	---	---
3	5	100	0.425	5.0	4.9	6.2
6	5	200	0.850	4.9	---	6.4
8	10	50	0.213	4.7	---	5.2
2	10	100	0.425	4.7	4.7	5.4
10	10	200	0.850	4.7	---	5.5
11	20	50	0.213	4.8	4.9	4.6
1	20	100	0.425	4.7	5.1	4.8
13	20	200	0.850	4.7	5.0	5.0
7	30	50	0.213	5.0	---	4.6
4	30	100	0.425	4.9	---	4.8
12	30	200	0.850	4.8	---	4.7
9(Run 79)	0	100	0.425	---	---	4.6
14(F-400)	15	200	0.850	5.0	4.9	4.9
15(F-400)	30	100	0.425	---	---	4.5
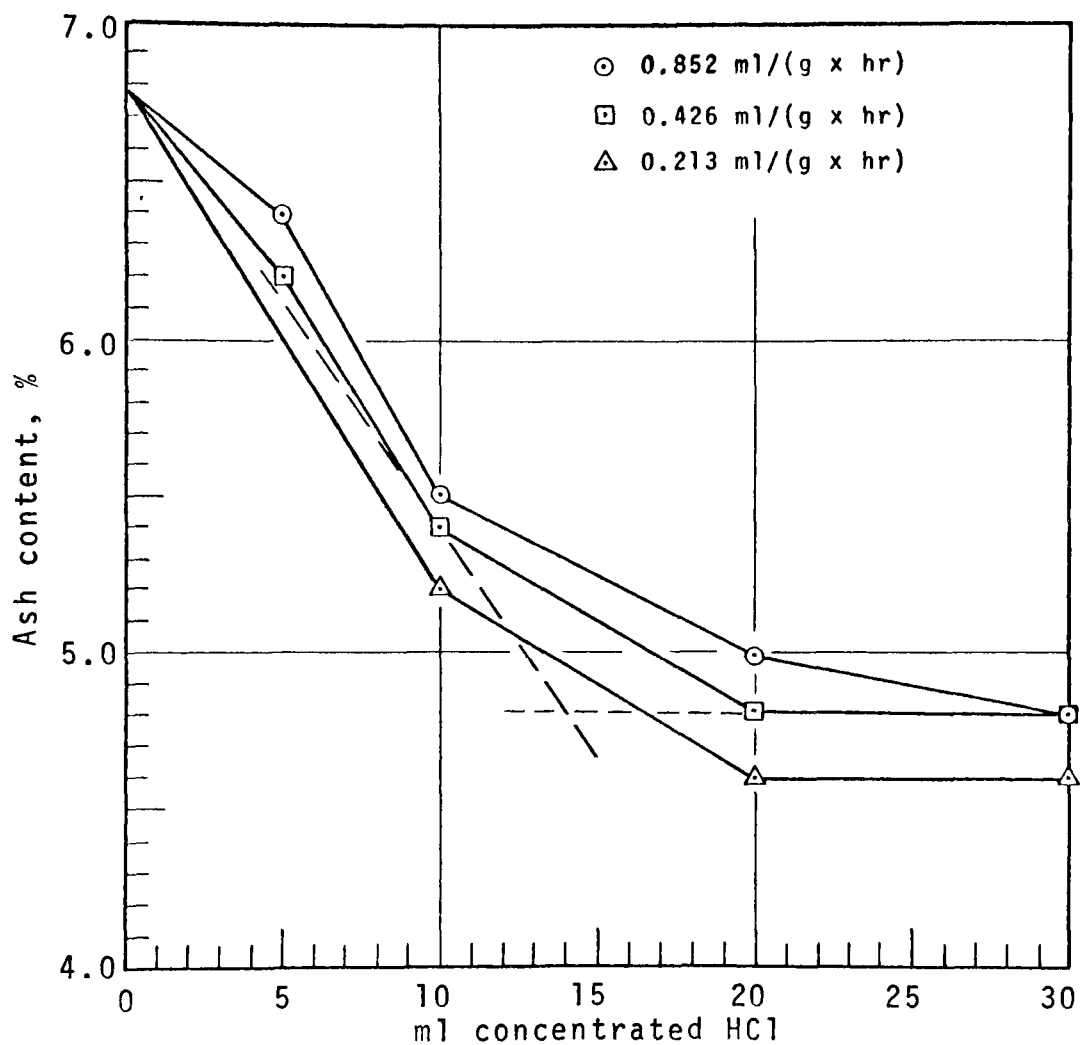
FIGURE 13 - ASH CONTENT OF CARBON AT LOWER END OF BED
WHEN BED IS TREATED WITH DIFFERENT QUANTITIES OF ACID

residue. To remove these compounds requires a caustic leach in addition to the HCl leach. This investigation was started in Task 2B but since this study progressed only through the first cycle, no definite conclusion could be drawn.

A more complete study was made by determining the ash content for Run 67, a nonpretreated regeneration run, and Run 79, an acid pretreated run. The analyses are given in Table XXXIII with those of a virgin Filtrasorb 400. Run 67 shows a considerable increase in the oxides, Fe_2O_3, CaO, MgO, H_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 the lowered recovery of iodine number and over recovery of the molasses number.

HCl Leach Pretreatment, Effect on Pore Structure - In pore structure studies performed at Pittsburgh Carbon Company[2,3] it was found that the iodine number was proportional to the surface area of pores larger than 10Å in diameter and the molasses number was porportional to the surface area of pores larger than 28Å in diameter. Equations 1 and 2 below show these relationships.

$$I_2 \text{ No.} = 17 + 1.07 \text{ x (s.a. of pores } > 10\text{Å)} \tag{1}$$

$$\text{Molasses No.} = 129 + (\text{s.a. of pores } > 28\text{Å)} \tag{2}$$

With reference to the iodine and molasses numbers given in previous experimental results, these equations indicate that acid pretreatment minimizes the decrease in surface area of the smaller pores and also prevents increase in surface area of pores larger than 28Å 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[4] 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 500Å to 1000Å.

Pores in the larger diameter range are measured by mercury porosimetry[5]. These measurements cover the diameter range 30Å to 100,000Å, hence the two methods overlap in the range

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

Component	Ash composition, %		
	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

30Å to 500Å. 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 14 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 30Å is 60,000 lb/in^2.

Figures 15 and 16 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 15 show the effects of acid leach, steam activation and CO_2 activation. The virgin F 400 is uppermost in pore volume at the 28Å 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 16 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 readily 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

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

where $\triangle A$ is an increment of surface area associated with increment of pore volume $\triangle V$ with mean diameter D. By summing up $\triangle A$ 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 15 in Figure 17 and for carbons of Figure 16 in Figure 18.

From Figure 17, the surface areas of pores larger than 10Å 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 28Å are respectively 120, 100, 110 and 100 m^2/g. Likewise from Figure 18, the surface areas of pores larger than 10Å in diameter for the carbons Runs 36, 67

80
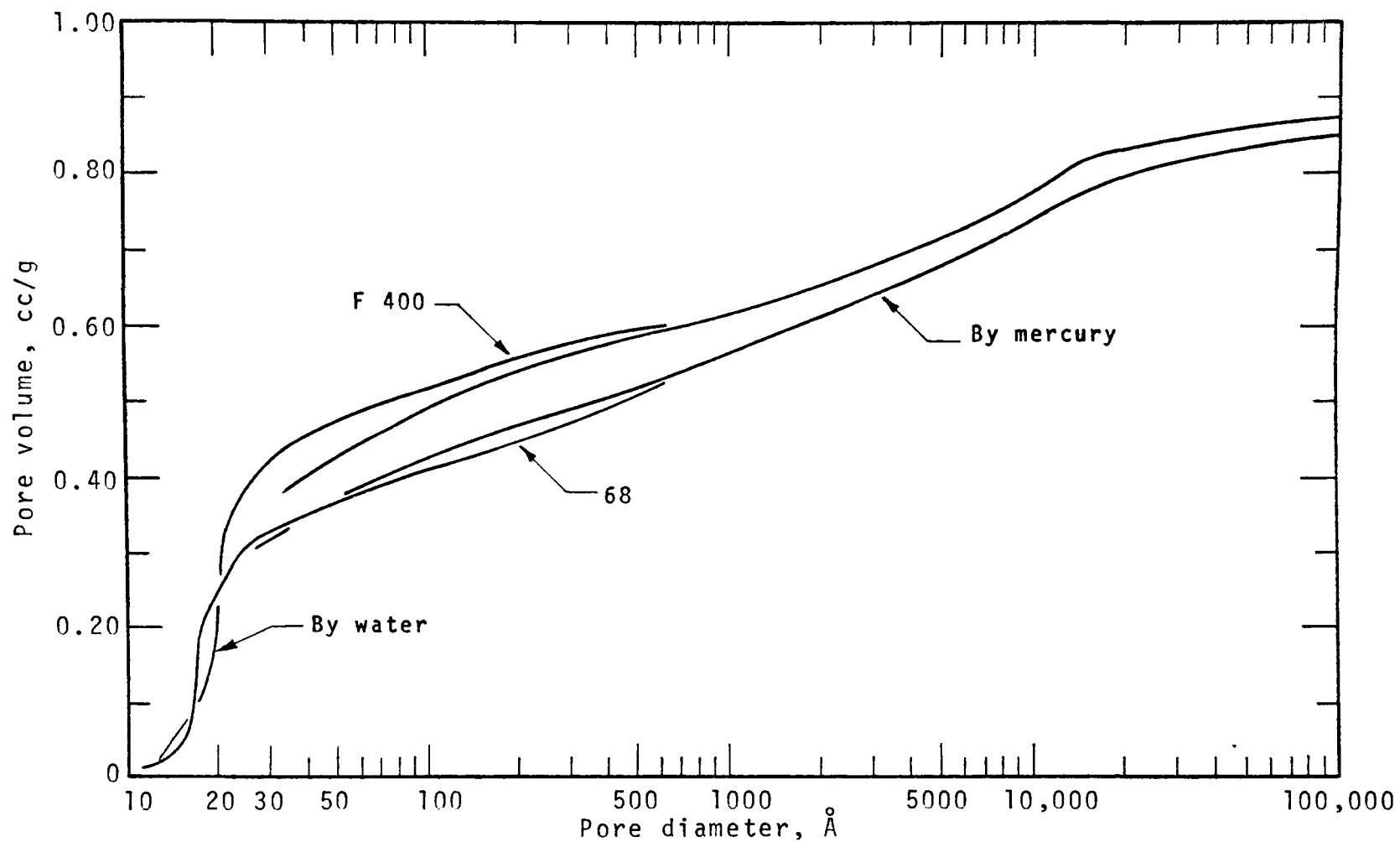
FIGURE 14 - PORE SIZE DISTRIBUTION MEASURED BY WATER ADSORPTION
AND BY MERCURY PENETRATION

81
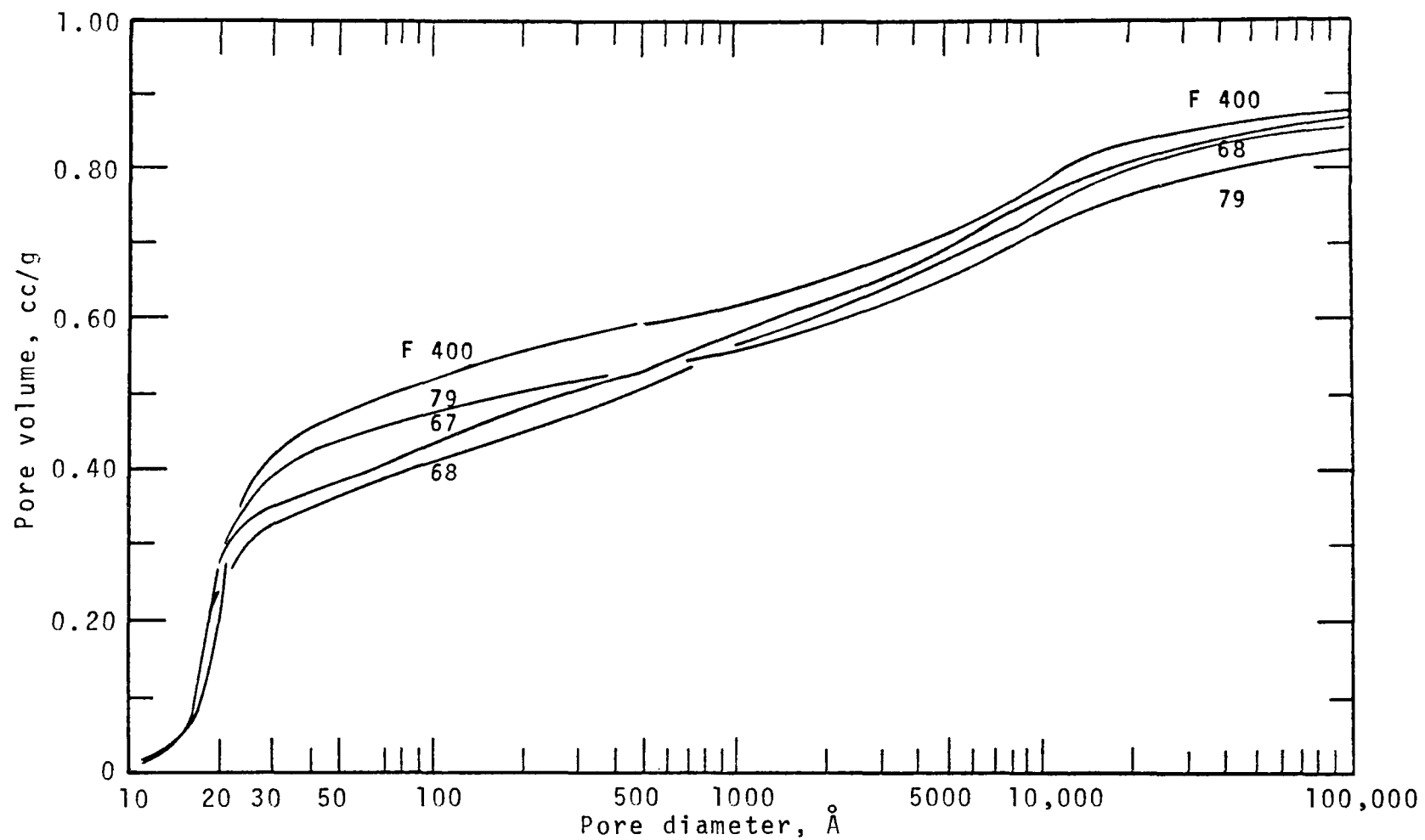
FIGURE 15 - PORE SIZE DISTRIBUTIONS OF REGENERATED CARBONS
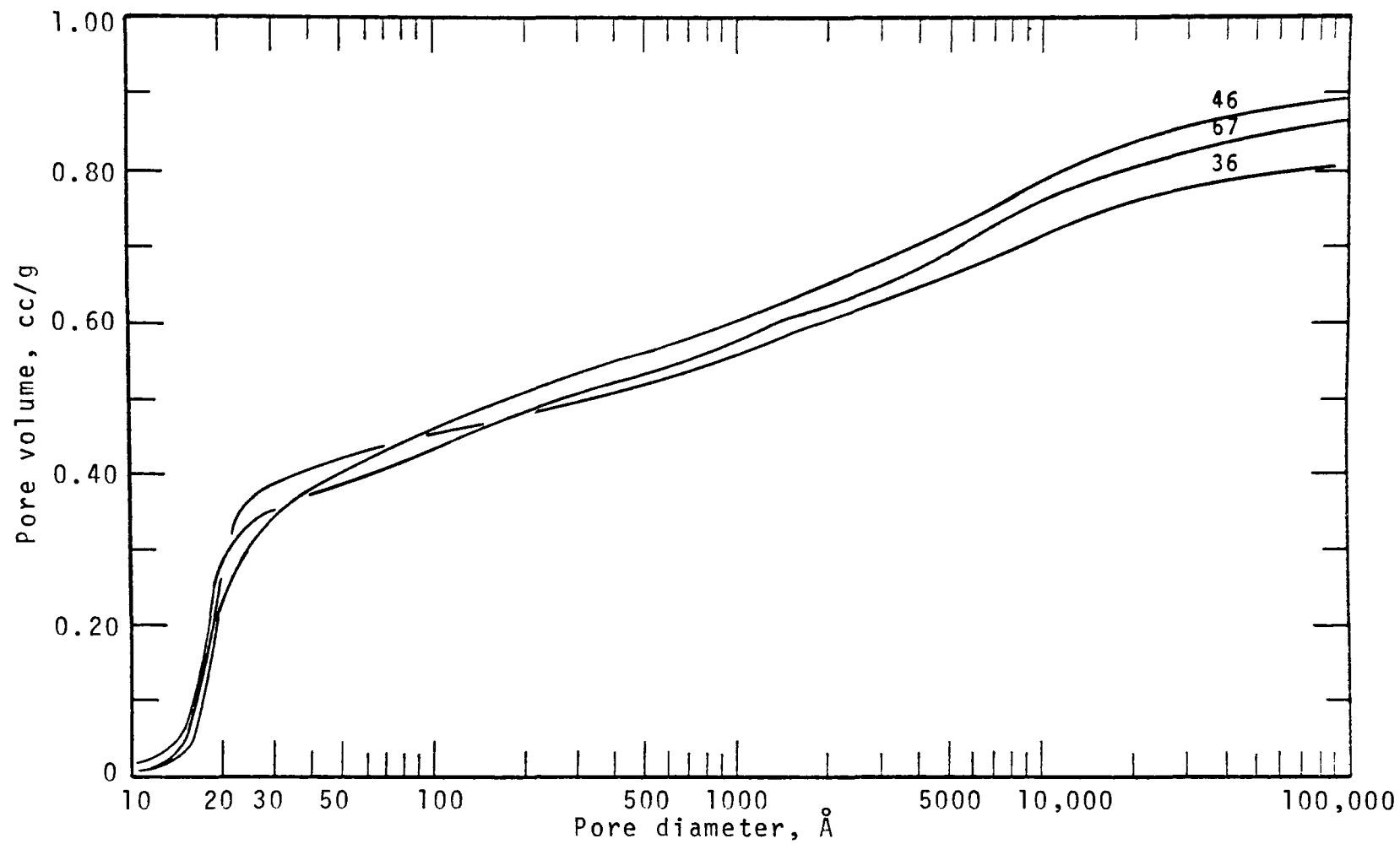
FIGURE 16 - PORE SIZE DISTRIBUTIONS OF REGENERATED CARBONS
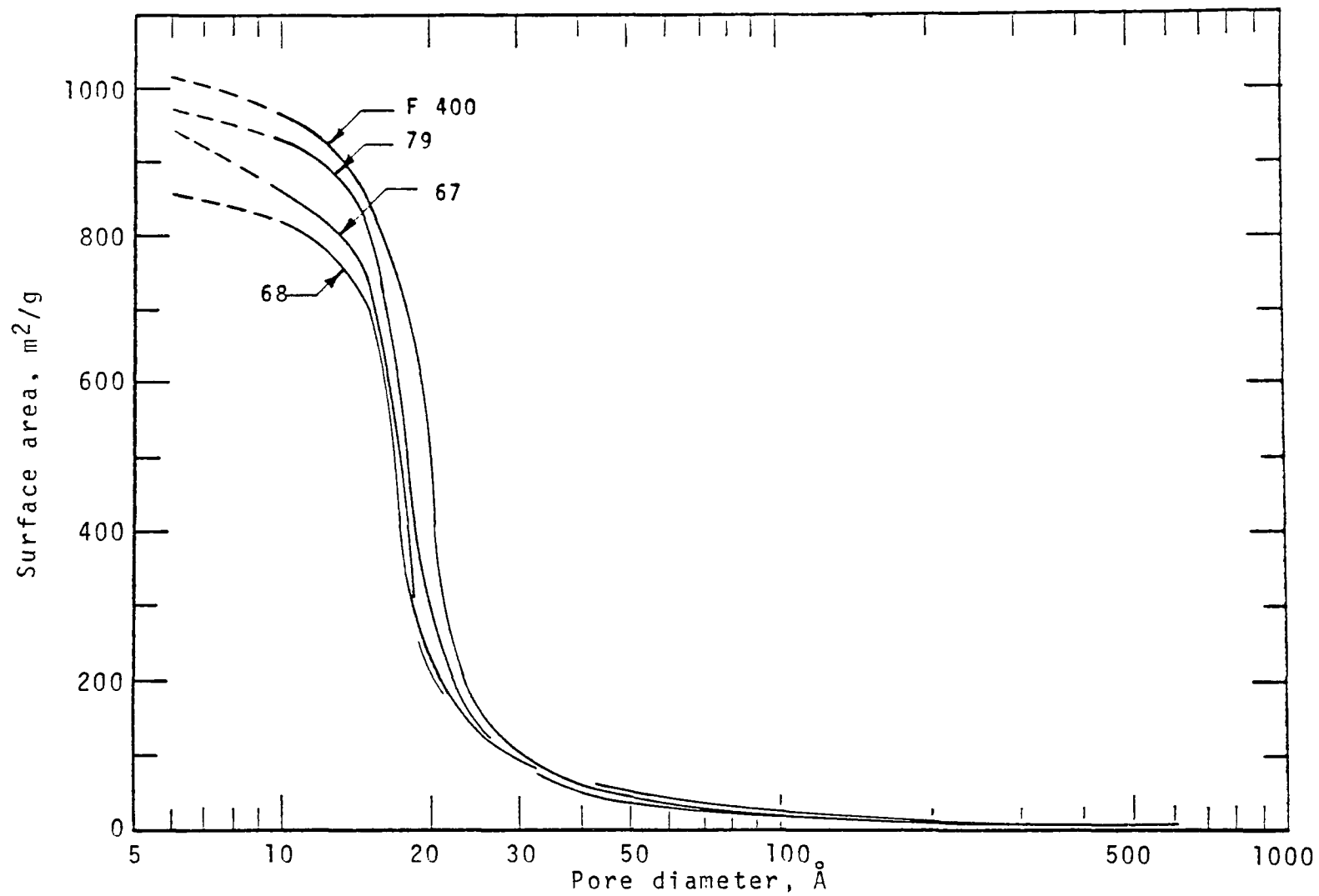
FIGURE 17 - CUMULATIVE SURFACE AREAS OF REGENERATED CARBONS
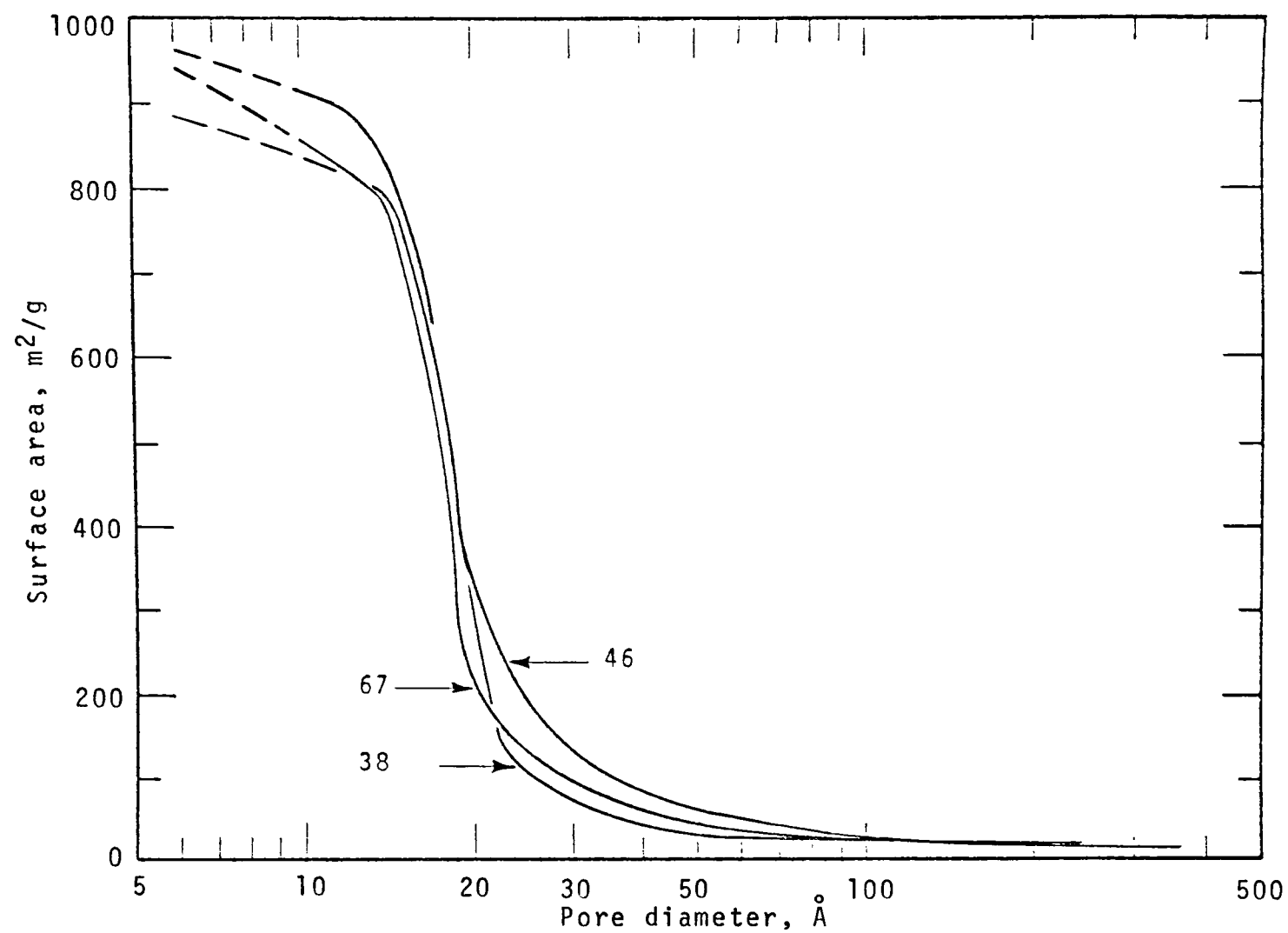
FIGURE 18 - CUMULATIVE SURFACE AREAS OF REGENERATED CARBONS

and 46 are 915, 860 and 840 m^2/g, respectively. Surface areas of pores larger than 28Å 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 ± 5% in the iodine numbers and within 13% in the molasses numbers. These results are given in Table XXXIV.

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

	Iodine number, mg/g		Molasses number	
Carbon	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
(Run 58 [Darco]	580	620	370	420)

Further study of the surface area curves also indicates where the major portion of the adsorption may be occurring. By inspection of the curves in Figure 17, it is observable that most of the change in pore structure occurs in the pores from 14Å to 28Å. Beyond 28Å, there can be considerable change in pore volumes, as is apparent from inspection of curves in Figures 15 and 16. 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 18, but Run 46 is an exception. For this carbon considerable change occurs at the 28Å 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 has been calculated at pore diameters from 10Å to 50Å. These calcualted areas are given in Table XXXV. For Runs 79, 67, 68 and 36, the surface area changes, as already noted, occur mostly in the 14Å to 28Å diameter range. The results indicate a shift in the pore sizes. Pore volume in the 20Å to 28Å range decreases while the volume in the 14Å to 20Å increases. It appears as though the pores that were originally 18Å to 22Å diameter have decreased to 14Å to 18Å diameter. The net effect, however, is that the cumulative surface area of pores larger than 10Å diameter decrease on regeneration. Further study is desirable to clarify the exact changes that do really occur.

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

	Surface area difference, m^2/g							
	10Å	12Å	14Å	16Å	18Å	20Å	28Å	50Å
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	79	195	150	30	15

The results definitely do show that HCl pretreatment minimizes pore structure changes. The results also suggest that the regeneration action takes place mostly in pores of 18Å to 28Å diameter. These pores must then also be the most active in the adsorption process.

HCl Leach Pretreatment, Standardized Procedure - Based on the parameter studies, a standardized procedure was adopted for treatment of carbons as for Task 2A, 2B and 7. The procedure was as follows carried out in the unit shown in Figure 3.

Carbon Bed - 2500 cc of dried spent carbon are placed in the contactor.

Wetting of Carbon Bed - Pure water is run upflow until water level is at top of carbon bed.

HCl Acid - 75 ml of 37.9% HCl acid is diluted to 2500 ml and passed downflow through carbon bed at 500 ml/hr flow rate.

Water Leach - After HCl solution has passed through carbon bed, 16 l of pure water are passed downflow through carbon bed at 500 ml/hr flow rate.

Drying of Carbon - Treated carbon is removed from contactor and dried in air convection oven at 150°C for about 48 hr. The carbon is ready for thermal regeneration.

Based on the preceding laboratory data, the scaled-up conditions for acid leaching of carbon bed of size in the Pomona contactor are given below.

Tamperature	- Ambient
Carbon volume	- 269 ft^3 (6 ft dia by 9.5 ft depth)
Carbon weight	- 6650 lb
HCl acid per unit carbon	- 0.076 lb acid/lb carbon (37.9% assay)
Total HCl acid	- 505 lb (0.076 x 6650)
Flow rate per unit carbon weight	- 0.426 lb/(lb x hr) - 0.051 gal/(lb x hr)
Flow rate of acid solution and water	- 340 gal/hr (0.051 x 6650)
Leach acid solution volume	- 1700 gal (340 x [500 x 100])
Leach water volume	- 10,200 gal
pH of filtrate at end of leaching operation	- 3.0 to 3.5
Chloride ion concentration in filtrate at end of leaching operation	- nil
Ash content of leached spent carbon	- 4.1% based on spent carbon density of 0.548 g/cc - 4.8% based on reg. carbon density of 0.468 g/cc
Overall leaching time	- 35 hr
Acid-carbon contact time	- 2 to 3 hr

To perform the acid leach, the contactor is given its final back-wash. Then the water level in the bed is lowered so that it is level with the carbon surface. Acid solution is then pumped through the bed at rate and quantity stated above, followed by the water leach. From this point on the carbon is handled in the usual manner.

At the 0.076 lb acid/lb carbon rate, the acid cost is about 0.145¢/lb of regenerated carbon when 37.9% assay technical grade acid sells for 1.95¢/lb.

Task 5 - Engineering Studies on Furnaces

The anticipated need for engineering studies was based on the premise that the regeneration is controlled by the parameters; temperature, gas composition, gas input rate and carbon residence time as investigated in Task 1. At the time the program was outlined, difficulties were expected in attaining the precise conditions in a direct-fired multiple hearth furnace and that indirect-heated rotary furnaces may have to be used to carry out the regeneration in whole or in part. As the program progressed, it was found out that the main obstacle in the way of satisfactory regenerations was the metallic elements. When these elements were leached out with HCl, it became apparent that the multiple hearth furnace could perform an adequate regeneration and the need for engineering studies of various other furnaces was no longer necessary.

Task 6 - Regeneration Control by Effluent Gas Analysis

The analysis of effluent gas from the activating step appeared to offer an instant monitoring method for the activation. When the baking and activating are run in succession as in the multiple hearth furnace, it is essential that the activating effluent gas in withdrawn from the regenerator before any appreciable mixing has occurred with the gas released from the baking step. In the pomona furnace the point of withdrawal would be at the fourth hearth.

In order for the effluent gas analysis to be meaningful, an analysis of the input gas composition and also a good control of the input rate are essential.

Vent gas analyses were conducted on 25 activation runs. However, an answer as to the possibility of this method for monitoring purposes cannot be given, as yet, because of a number of unexplained deviations that have appeared in the results. These deviations, however, appear to be giving information about the activating process.

The concept of vent gas analysis for activation monitoring was based on the premise that the carbon entering the activating step is essentially free of combined oxygen, sulfur and hydrogen, or at least present in quantities too small to invalidate the results for monitoring purposes. It was also assumed that the gas entering the activating step is essentially N_2, CO_2, H_2O and an insignificant amount of O_2. The activating reactions should then be basically:

$$CO_2 + C \longrightarrow 2CO \tag{1}$$

$$H_2O + C \longrightarrow CO + H_2 \tag{2}$$
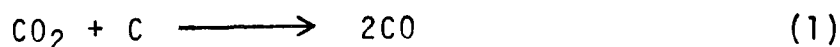
The input flow rates of N_2, CO_2 and H_2O are known and of these the N_2 flow rate remains unchanged on passage through the regenerator. Since either reaction seldom goes to completion, the vent gas is usually a mixture of N_2, CO_2, H_2O, CO and H_2. A partial stream of the vent gas was passed through a cold trap at -80°C to remove the water, hence the percentage compositions of CO_2, CO and H_2 in N_2 were analyzed. Since N_2 makes up the balance of the gas and its flow rate is known, it is then possible to calculate the flow rate of each component.

The gas utilization is then a simple subtraction of gas output rate from the gas input rate, thus:

<u>CO_2 utilization</u>

$$(CO_2 \ ft^3/hr \ input) - (CO_2 \ ft^3/hr \ output) =$$
$$(CO_2 \ ft^3/hr \ utilization) \tag{3}$$

<u>H_2O utilization</u>
Is equal to $H_2 \ ft^3/hr$ output \hfill (4)

<u>H_2O unreacted</u>

$$(H_2O \ vapor \ ft^3/hr \ input) - (H_2 \ ft^3/hr \ output) =$$
$$(H_2O \ ft^3/hr \ unreacted) \tag{5}$$

The CO_2 utilization can also be calculated from the CO and H_2 output rates, thus

$$\frac{(CO \ ft^3/hr \ output) - (H_2 \ ft^3/hr \ utilization)}{2} =$$
$$(CO_2 \ ft^3/hr \ utilization) \tag{6}$$

All gas measurements were converted to standard temperature and pressure (stp).

<u>Input and Output Gas Results</u> - For the record, the input and output gas compositions are summarized in Appendix A. In most activations, the input CO_2 and N_2 ratio was that of the flue gas mixture. The H_2O vapor concentration was varied considerably relative to the N_2-CO_2 mixture. In Run 67, no CO_2 was added, only N_2 and H_2O vapors. In Run 68, no H_2O vapor was added, only N_2 and CO_2. However, for this run the CO_2 concentrations were above the analyzer capacity and, therefore, no analyses are recorded for this run.

Gas Phase Equilibria - According to thermodynamics, a gas mixture consisting of H_2O, CO and CO_2 and H_2 can be expected to react at the activating temperatures according to the equation,

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \qquad (7)$$
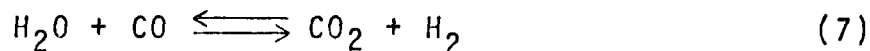
and come to an equilibrium, which varies with temperature. The equilibrium equation and values of the equilibrium constant K are given below for several temperatures of interest.

$$\frac{(CO_2)\ (H_2)}{(H_2O)\ (CO)} = K \qquad (8)$$

The quantity in each bracket is the mole percent of the gas.

Temperature °F	K
1400	1.36
1500	1.04
1600	0.86
1700	0.73
1800	0.63

If, after reaching equilibrium at the elevated temperature, the gas mixture is cooled rapidly, it can retain the elevated temperature equilibrium composition. That this happens to some degree during the activation runs is indicated by the K values given in the last column of Table XXXVII. They vary from 0.61 to 1.42, suggesting approach to equilibria at temperatures from 1400°F to 1800°F. Since the temperature of zone one in the regenerator was either near 1550° or 1700°F., it had been expected that K for the 1550°F runs would stabilize near 1.0 and for the 1700°F runs near 0.7. However, the temperature of zone one had no bearing on the K value. At present no explanation can be offered for the observed variation in values of K.

CO_2 Utilization - The CO_2 utilizations as calculated from the CO_2 input and output rates, Equation 3, were for most activation runs less than when calculated from the CO and H_2 output rates according to Equation 6. The CO_2 utilizations and the differences are reported in Table XXXVI.

In the attempt to determine the significance of the difference in CO_2 utilization, it was found that a low order of correlation exists between this difference and the percentage particle volume decrease. The percentage figures for the particle volume decreases are given in the last column of Table XXXVI

TABLE XXXVI - CO_2 UTILIZATION

Run	CO_2 utilization, ft^3/hr (stp) Direct	$CO-H_2$ anal	Difference CO_2 utilization, ft^3/hr	Particle volume decrease, %
32	0.22	0.23	-0.01	2.6
34 (HCl)	0.00	0.02	-0.02	1.3
36 (HCl)	-0.13	-0.02	-0.11	3.3
39	-0.07	0.02	-0.09	2.0
40	0.14	0.16	0.02	1.5
41	-0.12	-0.01	-0.11	2.2
47 (HCl)	-0.07	0.01	-0.08	1.8
51	0.15	0.18	-0.03	1.9
52	0.20	0.30	-0.10	2.7
53 (HCl)	-0.02	0.06	-0.08	1.7
66	0.11	0.07	+0.04	0.6
67 (HCl)	-0.53	-0.52	-0.01	1.2
69 (HCl)	-0.09	0.02	-0.11	1.9
70	-0.10	-0.05	-0.05	2.1
76 (WVP&P)	0.08	0.11	-0.03	1.6
77	0.07	0.03	+0.04	0.5
79 (HCl)	-0.08	-0.03	-0.05	2.0
88 (HCl)	-0.01	0.03	-0.04	0.2
89 (HCl)	-0.01	0.00	-0.01	1.5
90 (HCl)	-0.11	-0.04	-0.07	1.3
98 Task 2	0.00	+0.10	-0.10	1.2
104 Task 2A (HCl)	-0.14	-0.03	-0.11	2.8
105 Task 2B (HCl)	-0.06	+0.07	-0.13	0.7
106 (WVP&P) (HCl)	-0.03	+0.01	-0.04	1.7
108 (WVP&P (HCl)	-0.15	-0.05	-0.10	2.1

TABLE XXXVII - RESULTS OF GAS ANALYSIS DURING ACTIVATION

Run no.	Gas utilization, %			Rate carbon oxidation, g/hr			Weight decrease, g/hr [1]	K
	CO_2	H_2O	CO_2+H_2O	By gas anal	By weighing	Difference		
32	47.0	74.8	65.9	16.8	21.5	4.7	5.6	0.86
34 (HCl)	2.5	40.0	28.3	11.4	17.0	5.6	3.7	0.67
36 (HCl)	-2.0	42.7	28.8	15.3	16.5	1.0	7.4	0.93
39	2.0	63.0	43.6	20.8	21.6	0.8	3.3	1.32
40	25.0	74.0	54.0	13.0	16.3	3.3	3.2	1.36
41	0.0	59.0	41.6	23.3	26.3	3.0	5.1	1.14
47 (HCl)	1.3	43.5	31.3	11.4	15.4	4.0	3.5	0.85
51	43.9	73.0	62.6	10.9	14.5	3.6	3.8	0.78
52	68.2	82.5	76.2	11.7	16.3	4.6	4.7	0.87
53 (HCl)	14.6	65.5	50.0	10.1	11.4	1.3	3.2	1.12
66	12.7	69.8	54.4	16.8	20.0	3.2	1.3	0.86
67	---	73.0	54.0	23.2	27.7	4.5	4.6	1.42
69 (HCl)	2.0	46.0	31.4	15.9	17.6	1.7	4.0	0.95
70 (HCl)	-4.1	35.2	23.0	13.6	17.0	3.4	4.2	0.85
76	26.8	61.6	49.5	9.1	13.0	3.9	3.4	0.79
77	3.5	42.9	31.9	17.0	24.5	7.5	0.6	0.61
79 (HCl)	-6.0	43.3	28.8	12.3	13.5	1.2	4.9	0.86
88 (HCl)	7.0	57.5	43.6	7.7	12.8	4.9	0.4	0.60
89 (HCl)	1.0	47.4	34.7	8.2	11.8	3.6	3.9	0.72
90 (HCl)	-9.3	50.4	35.1	9.5	13.4	3.9	2.8	1.00
98	58.8	66.7	62.1	2.3	9.2	6.9	3.6	1.21
104 (HCl)	-5.5	55.4	39.6	8.9	13.9	5.0	8.2	1.15
105 (HCl)	12.5	50.6	40.7	7.3	12.7	5.4	1.5	0.79
106 (HCl)	1.8	36.2	25.7	8.4	11.0	2.6	4.2	0.70
108 (HCl)	-6.3	33.5	23.1	13.0	15.7	2.7	5.3	0.74
					mean	3.7	3.9	

(1) Weight decrease calculated from particle volume decrease

and the correlation is shown graphically in Figure 19. No logical explanation can be offered for this correlation.

Rate of Carbon Oxidation - The rate of carbon oxidation was calculated from the rates of CO_2 and steam utilizations, with CO_2 utilization rate calculated according to Equation 6. The oxidation rates based on gas analysis were then compared to oxidation rates based on direct weight of carbon before and after the activating step. It was found that the oxidation rates based on weight measurements were consistently larger and that the differences were approximately equal to the weight decreases associated with particle volume decreases. The results of these calculations are summarized in Table XXXVII. The mean weight of carbon oxidized, as obtained by difference, was 3.7 g/hr while the mean weight based on particle volume decrease was 3.9 g/hr. This fact suggests that particle volume decreases may be due to formation of sub-micron size fines which are then carried out of the regenerator by the vent gas.

For Runs 36, 70 and 79, the calculated CO_2 utilizations were negative, indicating that CO_2 was actually produced rather than consumed. This is possible if steam input rate is large, in view of Equation 7 and equilibrium constants K.

Gas Analysis Without Carbon in Regenerator - Because of some of the apparent discrepancies in the gas analyses, a number of tests were conducted in which gas mixtures were passed through the regenerator under activating conditions but without carbon. These tests were primarily a check on the accuracy of the gas concentration measurements.

The results of the measurements are reported in Appendix B, and Table XXVIII presents an analysis of the results. Except for Test 5, these show a self consistency of 0.01 to 0.02 ft^3/hr in the consumed and produced gas volumes, hence the apparent discrepancy observed in the gas analyses of the activation runs are not due to errors in measurements.

Tests 3, 4 and 5 show formation of CO_2 when CO is added to the gas mixture, indicating that with high steam and CO concentration, CO_2 can be formed as per Equation 7.

Table XXXIX presents the K values for these tests. Except for Test 1, they fall in the range 0.65 to 1.36. Because of the very small CO concentration in Test 1, the high value of K = 1.69 is due to lack of instrumental accuracy.
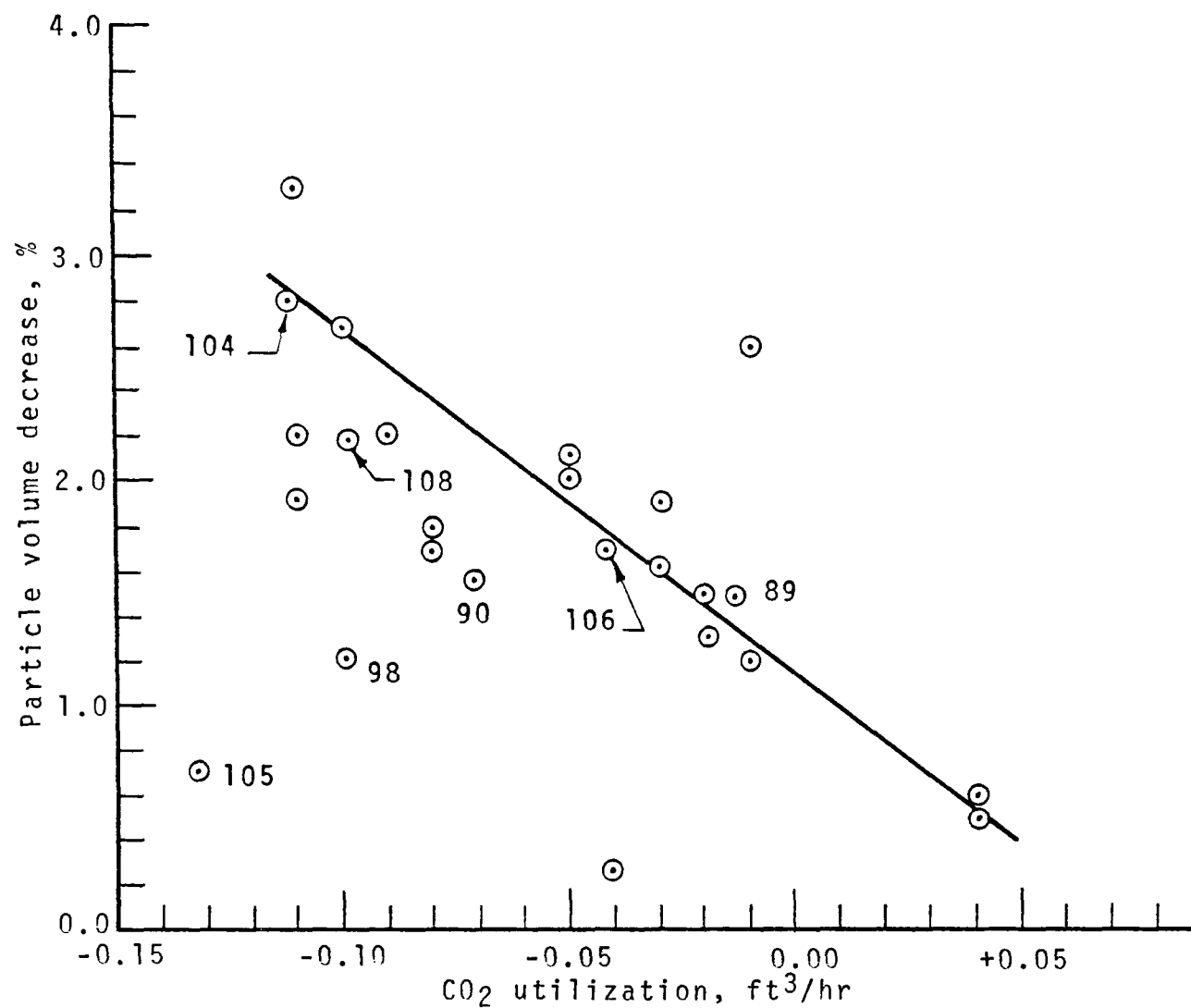
FIGURE 19 - PARTICLE VOLUME DECREASE DURING ACTIVATION AS FUNCTION OF DIFFERENCE IN CO_2 UTILIZATION AS DETERMINED BY DIRECT MEASUREMENT AND BY $CO-H_2$ ANALYSIS

TABLE XXXVIII - REACTIONS ASSOCIATED WITH
EACH GAS ANALYSIS

Test 1

CO_2 + metal ⟶ metal oxide + CO
  CO_2 consumed 0.92 - 0.93 = -0.01 ft^3/hr
  CO produced 0.01 - 0.00 = 0.01 ft^3/hr

H_2O + metal ⟶ metal oxide + H_2
  H_2 produced 0.02 - 0.00 = 0.03 ft^3/hr
  H_2 consumed = (-.03 ft^3/hr)
  (from H_2 prod)

Test 2

H_2 + CO_2 ⟶ CO + H_2O
  H_2 consumed 0.58 - 0.79 = -0.21 ft^3/hr
  CO_2 consumed 0.72 - 0.93 = -0.21 ft^3/hr
  CO produced 0.20 - 0.00 = 0.20 ft^3/hr
  H_2O produced
  (from H_2 prod) 0.20 - 0.00 = (0.20 ft^3/hr)

Test 3

CO + H_2O ⟶ CO_2 + H_2
  CO consumed 0.49 - 0.90 = -0.41 ft^3/hr
  H_2O consumed = (-0.41 ft^3/hr)
  (from CO cons)
  CO_2 produced 1.35 - 0.93 = 0.42 ft^3/hr
  H_2O produced 0.38 - 0.00 = 0.38 ft^3/hr

Test 4

CO + H_2O ⟶ CO_2 + H_2
  CO consumed 0.23 - 0.50 = -0.27 ft^3/hr
  H_2O consumed = (-0.27 ft^3/hr)
  (from CO cons)
  CO_2 produced 1.21 - 0.93 = 0.28 ft^3/hr
  H_2 produced 0.25 - 0.00 = 0.25 ft^3/hr

Test 5

CO + H_2O ⟶ CO_2 + H_2
  CO consumed 0.10 - 0.20 = -0.10 ft^3/hr
  H_2O consumed = (-0.10 ft^3/hr)
  (from CO cons)
  CO_2 produced 1.00 - 0.93 = 0.07 ft^3/hr
  H_2 produced 0.17 - 0.00 = 0.17 ft^3/hr

TABLE XXXIX - K FOR TESTS 1 THROUGH 5

Test	K
1	1.69
2	0.98
3	0.72
4	0.97
5	1.06

Task 7 - Regeneration of 25 lb Quantities of Spent Carbon

The object of this task was to carry out larger quantity re-
generations after the optimum operating conditions had been
worked out in Task 1. Regenerations of Darco and WVP&P were
to be carried out. Darco is a 14 x 30 mesh granular carbon
manufactured by Atlas Powder Company and the WVP&P is an
8 x 30 mesh granular carbon manufactured by West Virginia
Pulp and Paper Company.

As has already been learned, the work of Task 1 during the
first 12 months of the program did not yield optimum con-
ditions which would reproduce the initial properties in the
regenerated carbon, hence confirming runs of larger duration
could not be carried out during that period.

Exploratory regeneration runs were, however, carried out
with the WVP&P and Darco carbons. The Darco regeneration
followed a drastically different pattern from that of Fil-
trasorb 400; it regenerated to the virgin bulk density or
lower during the baking step, although the iodine number
did not always come up to the initial value. No activating
step appeared necessary, but variations were tried in baking
conditions.

The regeneration conditions and results for these two car-
bons are given in Tables XL and XLI.

For the Darco carbon, in Run 58, a gas mixture approximating
a flue gas was used as sweep gas and carbon residence time
was 34 min. This brought the bulk density below the virgin
carbon bulk density and the iodine number came up to the
level of the virgin carbon. On Run 59, the residence time
was shortened to 21 min in an attempt to raise the bulk
density. In Run 60, N_2 sweep gas was used and the baking
temperature was raised. In this case, the bulk density
matched the virgin carbon density but the iodine number was
now below that of the virgin carbon. Run 75 is similar to
Run 59 but with lower temperature; the results were not sat-
isfactory. Run 73 was HCl pretreated and produced a regen-

TABLE XL - REGENERATION CONDITIONS, WVP&P AND DARCO

Run no.	Regenerating step	Temperature, °F 1	2	3	Gas input,ft^3/hr (stp) N$_2$	CO$_2$	H$_2$O	Residence time, min
58	Darco, baked	850	1350	1550	7.0	0.90	1.49	34
59	Darco, baked	850	1350	1550	7.0	0.90	1.71	21
60	Darco, baked	170C	1700	1600	3.7	none	none	35
--	spent Darco HCl leached	---	---	---	---	---	---	---
73	above, baked	800	1350	1550	7.0	0.93	1.50	38
75	Darco, baked	850	1250	1450	7.0	0.93	2.05	34
74	WVP&P, baked	800	1350	1550	7.0	0.93	1.96	30
76	Run 74 act	1550	1650	1700	3.3	0.41	0.78	16
---	spent Darco HCl thermal reg	---	---	---	---	---	---	---
99		850	1360	1600	7.0	0.93	2.14	27
	Large Darco run - 10.9 lb feed, 21.7 hr thermal regeneration time							
---	spent Darco HCl thermal reg	---	---	---	---	---	---	---
100		880	1400	1600	7.0	0.93	1.76	34
---	spent WVP&P,HCl above baked	---	---	---	---	---	---	---
101		880	1350	1550	7.0	0.93	1.67	26
106	Run 101 act	1550	1650	1700	4.0	0.67	1.49	9
	Large WVP&P run - 15.5 lb feed, 48.3 hr thermal regeneration (includes baking and activating)							
---	spent WVP&P,HCl above baked	---	---	---	---	---	---	---
107		880	1350	1550	2.0	0.93	1.74	
108	Run 107 act	1550	1650	1700	7.6	1.00	2.68	

TABLE XLI - REGENERATION RESULTS, WVP&P AND DARCO

Run no.	Bulk density, g/cc	Weight decrease, %	Bulk volume decrease, %	Particle volume decrease, %	Pore volume, cc/cc	Iodine number, mg/g	Molasses number
spent Darco	0.450	---	---	---	0.585	310	---
spent WVP&P	0.597	---	---	---	0.522	---	180
virgin Darco	0.408	---	---	---	---	570	---
virgin WVP&P	0.504	---	---	---	---	1070	---
58	0.380	17.2	3.2	3.7	0.686	580	366
59	0.390	16.0	3.2	7.0	0.669	540	330
60	0.408	13.1	4.2	6.8	0.664	510	300
Darco HCl leach	0.433	4.4 ⎤ 18.0	-0.1 ⎤ 3.9	4.1 ⎤ 8.0	0.592	---	---
73	0.387	14.2 ⎦	4.0 ⎦	4.1 ⎦	0.677	630	310
75	0.402	13.7	2.0	6.0	0.662	530	320
74	0.531	12.4 ⎤ 17.3	1.3 ⎤ 1.9	2.9 ⎤ 4.5	0.603	590	210
76	0.509	5.5 ⎦	0.6 ⎦	1.6 ⎦	0.619	970	250
spent Darco HCl leach	0.502	---	---	---	0.562	330	260
	0.472	6.3 ⎤ 20.3	0.4 ⎤ 4.0	0.3 ⎤ 2.1	0.581	360	270
99	0.419	14.9 ⎦	3.6 ⎦	1.8 ⎦	0.667	660	305
spent Darco HCl leach	0.496	---	---	---	0.562	330	250
	0.471	5.3 ⎤ 20.2	0.2 ⎤ 4.4	-0.6 ⎤ 2.1	0.585	360	270
100	0.415	15.7 ⎦	4.2 ⎦	2.7 ⎦	0.665	700	310
spent WVP&P, lot 1	0.582	---	---	---	0.554	---	230
HCl leached	0.568	2.3 ⎤	0.0 ⎤	-0.3 ⎤	0.574	800	
101	0.535	7.8 ⎰ 14.1	2.2 ⎰ 2.9	2.2 ⎰ 3.6	0.617	950	
106	0.517	4.6 ⎦	0.7 ⎦	1.7 ⎦	0.628	1070	
spent WVP&P, lots 2 to 6	0.582	---	---	---	0.554		
HCl leached	0.568	2.8 ⎤	0.2 ⎤	-0.5 ⎤	0.576		
107	0.531	9.5 ⎰ 17.5	3.1 ⎰ 4.7	3.9 ⎰ 5.5	0.618	805	250
108	0.512	6.1 ⎦	1.4 ⎦	2.1 ⎦	0.637	1120	280

erated carbon with a low bulk density but also a high iodine number. This is a favorable position since it will now be possible to adjust baking conditions to increase bulk density while decreasing the iodine number to match those of the virgin carbon.

After the effectiveness of the HCl leach procedure had been established, regeneration of these two carbons was resumed during the extension period, but on new batches of carbons received from Pomona. The conditions of regeneration and results are included in the lower halves of Tables XL and XLI, Runs 99, 100, 101, 106, and 107 and 108.

About 13.7 lb of (dried) spent Darco were available for the extended regenerations which now consisted of (1) an HCl pretreatment according to the standardized procedure and (2) thermal regeneration normally designated as the baking step. Of the 13.7 lb, 2.8 lb was used in Run 99 to establish the regeneration conditions. The remaining 10.9 lb were then regenerated in a continuous run over a 22 hr period.

Other conditions of operation not given in Table XL are:

Feed rate   - 0.016 ft^3/hr; 450 cc/hr

Tube rotation   - 1.1 rpm

Tube inclination   - 3.75 in. per 42 in. length

No problems that could not be easily corrected were encountered during the run. The carbon losses, 4.4% by bulk volume and 2.1% by particle volume decrease, are lower than had been expected as based on results of the previous runs, Runs 59, 60 and 73. The iodine number is higher than the value reported for the virgin carbon (of lower density). Some of these differences may be due to different initial properties of the carbons, since these results are now on a different batch from Pomona.

The great ease with which the Darco can be regenerated is due to its open pore structure, i.e., a large portion of the total pore volume is in pores greater than 30Å diameter.

Carbons with a large portion of large pores also tend to be softer and therefore subject to greater attrition and this is reflected in the generally larger decrease in particle volume during the regeneration. For Darco the particle volume decrease ranged from 3.7% to 8.0% for the first batch, while on the extended regeneration run of the second batch, the particle volume decrease was only 2.1%.

The regeneration of WVP&P carbon was expected to follow a pattern very similar to that of Filtrasorb 400 since they are both activated by a similar method from bituminous coal. In the spent WVP&P regenerations, a baking and an activating step are necessary and also the required conditions are very similar to that for Filtrasorb 400. Run 74-76 of Tables XL and XLI shows the regeneration results when no acid pretreatment was employed. The iodine number was 970 relative to 1070 mg/g for the reported virgin carbon. Table XVII, Runs 88, 89 and 90, shows the effect of HCl acid pretreatment. For these regenerated carbons the iodine numbers were in the 1010 to 1070 mg/g range. On the new batch acquired for the extended run, Runs 107 and 108, the spent carbon was HCl pretreated as routine procedure. Iodine numbers of 1070 and 1120 were attained. A large excess of steam was used on Run 108 in the attempt to bring the bulk density down to 0.504 g/cc, the density reported for the virgin carbon. The excess steam did not accomplish this. However, the steam utilization was low, about 23.5%, and particle volume decrease was abnormally large, 5.5%.

Other conditions not given in Table XL for WVP&P runs are:

Feed rate   - 0.016 ft^3/hr

Tube rotation   - 1.2 rpm for bake; 24 rpm for
                       activation

Tube inclination   - 3.75 in. per 42 in. length

Figure 20 shows the various carbons studied in perspective. The Darco carbons have much lower densities and iodine numbers than Filtrasorb 400 and WVP&P carbons. There is some indication that absorbate pick up may be slightly less for the Darco since the weight loss of the Darco during regeneration ranged from 13% to 20% while the weight loss of Filtrasorb 400 varied between 18% and 24%. This may not be an entirely valid comparison since the absorbate concentration in the waste water varies and the Darco may have been spent at a lower concentration.

HCl leach of the spent Darco, prior to baking, increased the iodine number from 560 to 630 mg/g for the first batch received from Pomona. This increase is proportionately the same as observed with acid leached Filtrasorb carbons. The iodine numbers of the regenerated second batch are much higher.

In the Filtrasorb 400 regenerations, the attempt has been to regain the 0.469 g/cc bulk density and 1090 mg/g iodine num-
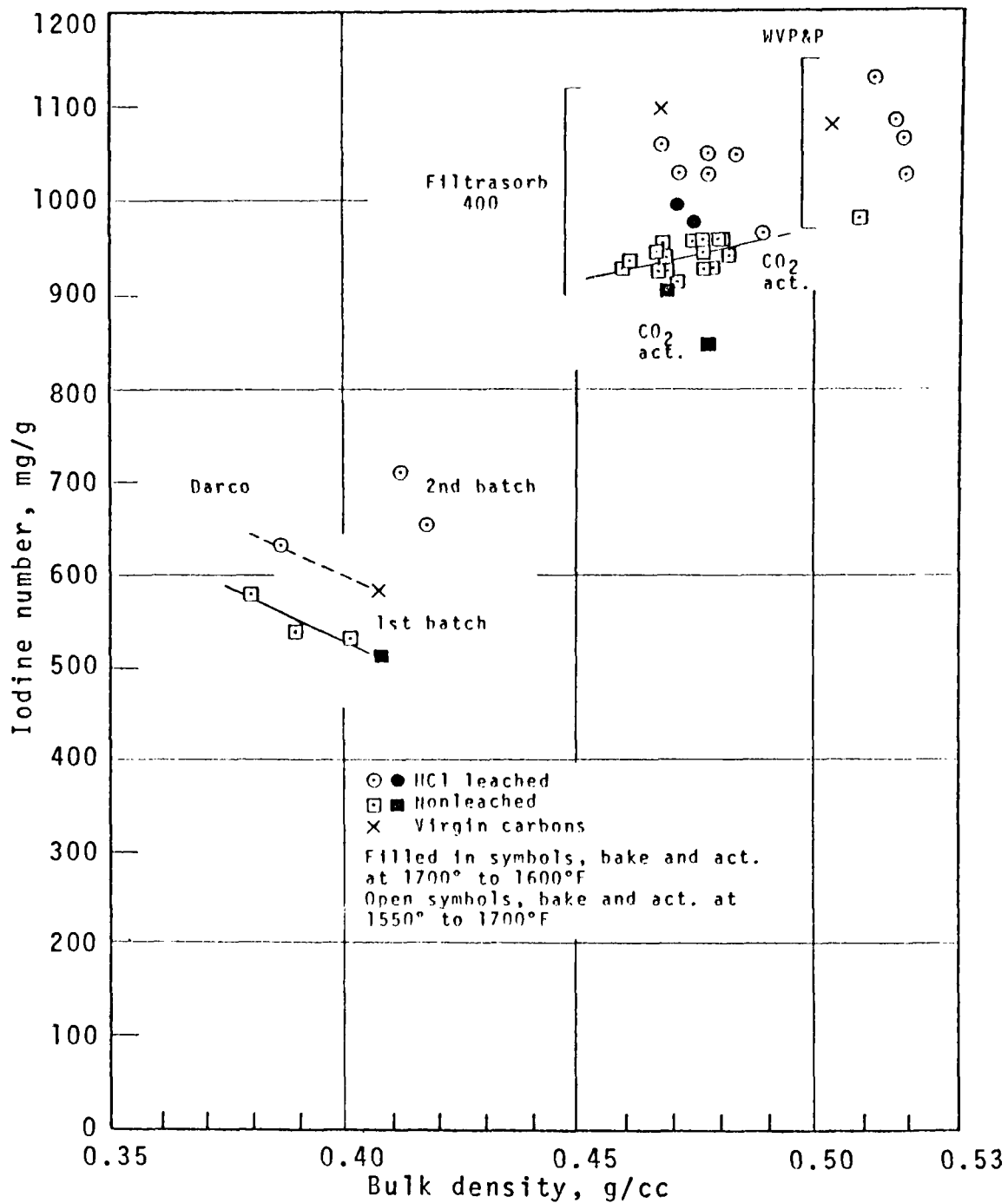
FIGURE 20 - IODINE NUMBERS OF REGENERATED DARCO, F 400 AND
WVP&P CARBONS AS FUNCTION OF BULK DENSITIES

ber. Densities in the 0.460 to 0.484 g/cc range were attained but the high iodine number of the virgin carbon was never reached. A straight line through the nonleached carbon iodine number points indicates that the virgin carbon iodine number cannot be attained by extrapolation of densities in either direction. It is felt that the parameters; temperature, residence time, gas composition and input rate, both during baking and activating have been adequately covered. It is beginning to appear as an impossibility to regain the original iodine number simultaneously with all other initial properties of the carbon when the metallic elements, brought in with the adsorbate, are in the carbon during baking and activating. When these were removed by HCl leach, the iodine number increased from the 930 to the 1030 mg/g level, which is still below the virgin carbon iodine number.

SECTION VI

ACKNOWLEDGMENTS

APPENDIX A
INPUT AND OUTPUT GAS COMPOSITIONS OF ACTIVATION RUNS

Run	Gas	Input ft³/hr (stp)	Input % Comp	Output ft³/hr (stp)	Output % Comp
	N_2	4.00	71.2	4.00	59.2
	CO	---	---	1.36	20.1
32	CO_2	0.51	9.1	0.29	4.3
	H_2	---	---	0.89	13.2
	H_2O	1.11	19.7	0.22	3.3
		5.62	100.0	6.76	100.1
	N_2	7.16	73.0	7.16	67.6
	CO	---	---	0.78	7.4
34	CO_2	0.81	8.2	0.81	7.6
	H_2	---	---	0.73	6.9
	H_2O	1.84	18.8	1.11	10.5
		9.81	100.0	10.59	100.0
	N_2	8.30	70.3	8.30	64.1
	CO	---	---	0.99	7.6
36	CO_2	1.10	9.3	1.23	9.5
	H_2	---	---	1.03	8.0
	H_2O	2.41	20.4	1.38	10.7
		11.81	100.0	12.93	99.9
	N_2	8.26	72.5	8.26	64.2
	CO	---	---	1.39	10.8
39	CO_2	1.00	8.8	1.07	8.3
	H_2	---	---	1.35	10.5
	H_2O	2.14	18.8	0.79	6.1
		11.40	100.1	12.86	99.9
	N_2	5.36	77.1	5.36	68.3
	CO	---	---	1.03	13.1
40	CO_2	0.64	9.2	0.50	6.4
	H_2	---	---	0.70	8.9
	H_2O	0.95	13.7	0.25	3.2
		6.95	100.0	7.84	99.9
	N_2	8.3	68.9	8.3	60.7
	CO	---	---	1.53	11.2
41	CO_2	1.10	9.1	1.22	8.9
	H_2	---	---	1.55	11.3
	H_2O	2.63	21.9	1.08	7.9
		12.03	99.9	13.68	100.0

Run	Gas	Input ft^3/hr (stp)	% Comp	Output ft^3/hr (stp)	% Comp
	N_2	5.80	70.1	5.80	63.7
	CO	---	---	0.76	8.3
47	CO_2	0.77	9.3	0.84	9.2
	H_2	---	---	0.74	8.1
	H_2O	1.70	20.6	0.96	10.5
		8.27	100.6	9.10	99.8
	N_2	3.33	74.3	3.33	63.7
	CO	---	---	0.90	17.2
51	CO_2	0.41	9.2	0.26	5.0
	H_2	---	---	0.54	10.3
	H_2O	0.74	16.5	0.20	3.8
		4.48	100.0	5.23	100.0
	N_2	3.24	76.2	3.24	63.7
	CO	---	---	1.08	21.4
52	CO_2	0.44	10.3	0.20	3.9
	H_2	---	---	0.47	9.2
	H_2O	0.57	13.4	0.10	2.0
		4.25	99.9	5.09	100.2
	N_2	3.12	70.0	3.12	59.9
	CO	---	---	0.73	14.0
53	CO_2	0.41	9.2	0.43	8.2
	H_2	---	---	0.61	11.7
	H_2O	0.93	20.8	0.32	6.1
		4.46	100.0	5.21	99.9
	N_2	4.00	66.2	4.00	56.3
	CO	---	---	1.18	16.6
66	CO_2	0.55	9.1	0.44	6.2
	H_2	---	---	1.04	14.6
	H_2O	1.49	24.7	0.45	6.3
		6.04	100.0	7.11	100.0
	N_2	4.00	58.7	4.00	48.0
	CO	---	---	1.00	12.0
67	CO_2	---	---	0.53	6.3
	H_2	---	---	2.05*	24.6
	H_2O	2.81	41.3	0.76	9.1
		6.81	100.0	8.34	100.0

*Estimated from CO and CO_2 analyses, H_2 concentration off scale on analyses

Run	Gas	Input		Output	
		ft^3/hr (stp)	% Comp	ft^3/hr (stp)	% Comp
	N_2	9.22	73.3	9.22	67.2
	CO	---	---	1.07	7.8
69	CO_2	1.10	8.8	1.19	8.7
	H_2	---	---	1.03	7.5
	H_2O	2.24	17.8	1.21	8.8
		12.56	99.9	13.72	100.0
	N_2	10.14	72.2	10.14	67.7
	CO	---	---	0.84	5.6
70	CO_2	1.21	8.6	1.31	8.7
	H_2	---	---	0.95	6.3
	H_2O	2.69	19.1	1.74	11.6
		14.04	99.9	14.98	99.9
	N_2	3.3	73.5	3.3	64.4
	CO	---	---	0.71	13.9
76	CO_2	0.41	9.1	0.33	6.4
	H_2	---	---	0.49	9.6
	H_2O	0.78	17.4	0.29	5.7
		4.49	100.0	5.12	100.0
	N_2	7.6	68.2	7.6	62.1
	CO	---	---	1.16	9.5
77	CO_2	1.01	9.1	0.94	7.7
	H_2	---	---	1.09	8.9
	H_2O	2.53	22.7	1.44	11.8
		11.14	100.0	12.23	100.0
	N_2	6.00	68.7	6.00	62.5
	CO	---	---	0.78	8.1
79	CO_2	0.80	9.1	0.88	9.2
	H_2	---	---	0.84	8.7
	H_2O	1.94	22.2	1.10	11.5
		8.74	100.0	9.60	100.0
	N_2	3.50	69.1	3.50	62.4
	CO	---	---	0.54	9.6
88	CO_2	0.43	8.5	0.44	7.7
WVP&P	H_2	---	---	0.48	8.6
	H_2O	1.13	22.3	0.65	11.6
		5.06	99.9	5.61	99.9

Run	Gas	Input ft^3/hr (stp)	Input % Comp	Output ft^3/hr (stp)	Output % Comp
89 WVP&P	N_2	3.50	69.0	3.50	62.2
	CO	---	---	0.55	9.8
	CO_2	0.43	8.5	0.44	7.8
	H_2	---	---	0.54	9.6
	H_2O	1.14	22.5	0.60	10.7
		5.07	100.0	5.63	100.1
90	N_2	3.50	67.5	3.50	59.9
	CO	---	---	0.55	9.4
	CO_2	0.43	8.3	0.54	9.2
	H_2	---	---	0.63	10.8
	H_2O	1.25	24.1	0.62	10.6
		5.18	99.9	5.84	99.9
98 Task 2	N_2	1.27	81.4	1.27	69.0
	CO	---	---	0.28	15.2
	CO_2	0.17	10.9	0.17	9.2
	H_2	---	---	0.08	4.3
	H_2O	0.12	7.8	0.04	2.2
		1.56	100.1	1.84	99.9
104 Task 2A	N_2	2.19	59.5	2.19	50.1
	CO	---	---	0.55	12.6
	CO_2	0.37	10.0	0.51	11.7
	H_2	---	---	0.62	14.2
	H_2O	1.12	30.4	0.50	11.4
		3.68	99.9	4.37	100.0
105 Task 2B	N_2	2.19	65.0	2.19	54.9
	CO	---	---	0.56	14.0
	CO_2	0.37	11.0	0.43	10.8
	H_2	---	---	0.41	10.3
	H_2O	0.81	24.0	0.40	10.0
		3.37	100.0	3.99	100.0

APPENDIX A (Continued)

Run	Gas	Input		Output	
		ft³/hr (stp)	% Comp	ft³/hr (stp)	% Comp
	N_2	4.00	65.0	4.00	59.1
106	CO	---	---	0.57	8.4
WVP&P	CO_2	0.67	10.9	0.70	10.4
	H_2	---	---	0.54	8.0
	H_2O	1.49	24.2	0.95	14.0
		6.16	100.1	6.76	99.9
	N_2	7.60	67.4	7.60	62.1
108	CO	---	---	0.79	6.5
WVP&P	CO_2	1.00	8.9	1.15	9.4
	H_2.	---	---	0.90	7.4
	H_2O	2.68	23.7	1.78	14.6
		11.28	100.0	12.22	100.0

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APPENDIX B
GAS ANALYSES WITH NO CARBON IN REGENERATOR

TEST 1 - APPROXIMATE FLUE GAS MIXTURE THROUGH HEATED REGENERATOR

Gas	Input		Output	
	ft^3/hr (stp)	% Comp	ft^3/hr (stp)	% Comp
N_2	7.0	73.0	7.0	73.0
CO	---	---	0.01	0.1
CO_2	0.93	9.7	0.92	9.6
H_2	---	---	0.03	0.3
H_2O	1.66	17.3	1.63	17.0
	9.59	100.0	9.59	100.0

TEST 2 - APPROXIMATE FLUE GAS MIXTURE THROUGH HEATED REGENERATOR WITH HYDROGEN ADDED

Gas	Input		Output	
N_2	7.0	65.7	7.00	65.7
CO	---	---	0.20	1.9
CO_2	0.93	8.7	0.72	6.8
H_2	0.79	7.4	0.58	5.4
H_2O	1.93	18.1	2.14	20.1
	10.65	99.9	10.64	99.9

TEST 3 - APPROXIMATE FLUE GAS MIXTURE THROUGH HEATED REGENERATOR WITH 0.90 ft^3/hr CO ADDED

Gas	Input		Output	
N_2	7.0	65.7	7.0	65.7
CO	0.90	8.4	0.49	4.6
CO_2	0.93	8.7	1.35	12.7
H_2	---	---	0.38	3.6
H_2O	1.83	17.2	1.45	13.6
	10.66	100.0	10.67	100.2

TEST 4 - APPROXIMATE FLUE GAS MIXTURE THROUGH
HEATED REGENERATOR WITH 0.50 ft^3/hr CO ADDED

Gas	Input ft^3/hr (stp)	% Comp	Output ft^3/hr (stp)	% Comp
N_2	7.0	69.7	7.0	69.7
CO	0.50	5.0	0.23	2.3
CO_2	0.93	9.3	1.21	12.0
H_2	---	---	0.25	2.5
H_2O	1.61	16.0	1.35	13.4
	10.04	100.0	10.04	99.9

TEST 5 - APPROXIMATE FLUE GAS MIXTURE THROUGH
HEATED REGENERATOR WITH 0.20 ft^3/hr CO ADDED

Gas	Input ft^3/hr (stp)	% Comp	Output ft^3/hr (stp)	% Comp
N_2	7.0	70.8	7.0	70.9
CO	0.20	2.0	0.10	1.0
CO_2	0.93	9.4	1.00	10.1
H_2	---	---	0.17	1.7
H_2O	1.77	17.9	1.60	16.2
	9.90	100.1	9.87	99.9

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1	Accession Number	2	Subject Field & Group 10 A	**SELECTED WATER RESOURCES ABSTRACTS** INPUT TRANSACTION FORM

5	Organization

Mine Safety Appliances Research Corporation
Evans City, Pennsylvania

6	Title

OPTIMIZATION OF THE REGENERATION PROCEDURE
FOR GRANULAR ACTIVATED CARBON

10	Author(s)	16	Project Designation Program #17020 DAO

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25	Identifiers (Starred First)

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27	Abstract

Spent granular activated carbons from tertiary water treatment, on multiple-hearth furnace regenerations, suffer a volume loss of 5% to 10% per regeneration. On the first regeneration, activity loss is as high as 13% but diminishes on subsequent cycles. Laboratory studies to improve regeneration have demonstrated that on regeneration of wet spent carbon three steps occur; (1) drying at about $220^\circ F$, (2) pyrolysis of adsorbed pollutants at 500° to $1500^\circ F$ (baking step) and (3) activation with flue gas and steam at 1600° to $1700^\circ F$. Alkaline and iron oxides accumulate in the carbon and catalyze oxidation of pores in the 18Å to 28Å diameter range. When metallic elements are leached from the carbon, prior to regeneration, less carbon and activity loss occurs. Steam regeneration is more effective than that with CO_2. Carbon volume decreases during laboratory baking and activation average 2% and 1.8%, respectively. The apparent volume decrease during baking is due to pyrolysis of colloidal pollutants on the particle surfaces; true carbon loss is then 1.8%. The latter proceeds as submicron fines formation from particle surfaces. Regeneration attempts by leaching with solutions of NaOH, H_2O_2 and CCl_4 were ineffective and/or uneconomical. Report contains 41 tables and 20 figures.

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