

CHEMISTRY AND KINETICS OF THE HYDRO-DESULFURIZATION OF COAL

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INTRODUCTION

Most of the published data on the hydro-desulfurization of coal are unsuitable for detailed kinetic interpretation because equilibrium conditions were partially or wholly achieved. Forty years ago Snow (1) showed almost ten-fold less desulfurization with "fast" heating versus "slow" heating. The present paper describes the theoretical extension and experimental application of the non-isothermal method of Juntgen (2) to the hydro-desulfurization of ten bituminous coals ranging from 1 to 5% sulfur.

This powerful method overcomes the above difficulty by treating temperature as a controlled variable. Essentially continuous measurements of reaction products in a flow system provide experimental functions whose theoretical interpretations identify sets of chemical reactions which are responsible for desulfurization. The kinetics of desulfurization of all ten coals are accounted for satisfactorily by five chemical reaction systems. This method gives activation energies and frequency factors for each chemical reaction.

Independent or idealized experiments were also conducted to test separately these results. In addition, the kinetics of a series of back reactions were also measured including the scavenging of hydrogen sulfide by calcium oxide. In this paper, the theory is summarized, the experimental conditions are described, and the results are summarized, together with a discussion of their significance to processes for control of environmental pollution.

THEORY

The non-isothermal kinetic method circumvents the uncontrolled occurrence of chemical reactions during the time that a sample is being heated to a desired isothermal reaction temperature. This is accomplished by maintaining a constant rate of heat during the experiment. Consider a solid gas reaction in a flow system which produces a new gas as a reaction product. Under the conditions of a constant heating rate of M degrees per minute the usual Arrhenius equations, $k = k_0 \exp(-E/RT)$, can be expressed in terms of the temperature rate of evolution of the new product gas, dV/dT , and the total volume of product gas when the reaction has gone to completion, V_0 .

$$\frac{dV}{dT} = \frac{V_0 k_0}{M} \exp \left\{ - \left[\frac{E}{RT} + \frac{k_0 R T^2}{M E} \right] \right\} \quad (1)$$

where R is the usual gas constant T is the absolute temperature.

The graphical expression of this function of Equation (1) is shown in Figure 1. Three important experimental parameters are obtained from this function, the integral of evolved gas V_0 which is shown as the cross-hatch area under the graph, the temperature of the maximum T_0 , and the temperature rate of evolution of the product chemical at the temperature maximum, $(dV/dT)_{T_0}$. In order to solve this equation for the activation energy, E , and the frequency factor, k_0 , it is convenient to introduce two dimensionless parameters,

$$a = E/RT_0 \text{ and } b = T_0/V_0 (dV/dT)_{T_0} \quad (2)$$

when these dimensionless parameters are substituted in the transcendental Equation (1), we obtain the following relationship

$$a = b \exp(1 - 2/a) \quad (3)$$

which by taking logarithms may be written as

$$\ln a + 2/a = 1 + \ln b \quad (4)$$

We may immediately compute b and, therefore, $1 + \ln b$ from the experimental measurement of the curve in Figure 1. Equation (4) may then be solved graphically by plotting this equation. We can read directly the value of a corresponding to the experimentally determined value of $1 + \ln b$.

Knowing a the activation energy and frequency factors are given by:

$$E - RT_0 a \text{ and } k_0 = (M a/T_0) e^a \quad (5)$$

This derivation is given in greater detail together with extensions to reversible and for back reactions in reference (3).

EXPERIMENTAL

Ten samples of bituminous coal ranging from 1 to 5 percent sulfur were provided by the Illinois Geological Survey and the U.S. Bureau of Mines. These include coals from Illinois, Ohio, Maryland, Pennsylvania and Kentucky. A.S.T.M. analyses were done on these coals for forms of sulfur, mineral analyses, proximate analyses, and sulfur in ash and fixed carbon.

Heating was done with flow hydrogen in a furnace controlled by a linear temperature programmer. Continuous analyses were done with a special mass spectrometer designed and built for this purpose. The experimental set up is shown schematically in Figure 2.

HYDROGEN SULFIDE EVOLUTION FROM COAL

In a hydrogen atmosphere the sulfur in the coal reacts with hydrogen to produce hydrogen sulfide. A typical H_2S evolution curve for a non-isothermal experiment on coal heated in hydrogen is given in Figure 3. These results were obtained using a hydrogen flow rate of 1 litre per minute over a 250 mg sample of Illinois coal No. 4, as identified in our report, reference (3). The heating rate

was 4°C per minute. Clearly the H₂S evolution does not occur by a single process. Since sulfur exists in coal in many different forms, e.g. pyrite, sulfide, sulfate and several different types of organic sulfur, this result is expected. Each individual reaction of the form, coal + H₂ → H₂S, should yield an H₂S evolution curve similar to that shown in Figure 1. The parameters characterizing that curve T₀, V₀, and (dV/dT)_{T₀} should reflect the kinetics for the individual process. The overall H₂S evolution curve will be composed of the sum of the set of overlapping curves characterizing each of the individual reactions. In the absence of any knowledge on the individual processes an experimental result such as given in Figure 3 can be resolved into individual processes in infinitely many ways. However, if the kinetics of the individual processes are known a priori, a unique resolution of the experimental results can be achieved.

Since iron pyrite is known to be a major source of sulfur in coal, we conducted non-isothermal experiments on samples of iron pyrite obtained from the U.S. Bureau of Mines. In these experiments the back reaction of H₂S with iron was suppressed by using a very high hydrogen flow rate and a very small sample of iron pyrite. The heating rate employed was 4°C per minute. The experimental data on the non-isothermal evolution of H₂S from pyrite are shown in Figure 4. These results clearly indicate two reactions producing hydrogen sulfide; firstly the reduction to FeS and secondly to Fe.

These experimental results on pyrite may be analyzed in a straight forward manner to yield the kinetic parameters for the two reactions. The procedure used is as follows: First we sketch in two peaks of the type shown in Figure 1 which give a reasonable fit to the experimental points. The values of the parameters characterizing the curves are read off of these curves. These parameters are the temperature corresponding to each of the peaks, T₀(°K), the area of the peak, V₀, and the amplitude of the peak at T₀. From these values a dimensionless parameter b as given by Equation (2) is computed and used to graphically obtain a. The values of the activation energies E and pre-exponential factor k₀ are then computed using Equation (5). The results are then double checked by recomputing the H₂S evolution peak corresponding to these parameter values using Equation (1). The calculated peaks are then replotted with the experimental data and the accuracy of the fit is checked. By these procedures we find for the pyrite reaction E = 47 kilocalories per mole and k₀ = 2.8 × 10¹² (atm H₂)⁻¹ min⁻¹ and for the sulfide reduction E = 55 kilocalories per mole k₀ = 2.1 × 10¹³ (atm H₂)⁻¹ min⁻¹. The calculated H₂S evolution curves for these two reactions are compared with the experimental data in Figure 5. The calculated H₂S evolution for the sum of the two processes is shown in the dash line in the figure. The fit between calculation and experimental could obviously be improved by slightly adjusting the amplitudes of the two peaks. However, the amplitudes reflect the stoichiometries of the reaction while the locations and shapes of the peaks reflect the kinetics. These results suggest that the pyrite sample was not pure FeS₂ but rather initially contained a small amount of sulfide.

DESULFURIZATION KINETICS FOR ORGANIC SULFUR

The pyrite sulfur clearly accounts for most of the inorganic sulfur found in coal, but there is also generally substantial amounts of organic sulfur and it is well known that this sulfur may exist in many different kinds of bonding arrange-

ments within the coal. In an attempt to investigate behavior of the organic sulfur on a somewhat simpler, but, related system, we prepared artificially some organic sulfur-containing material. A sample of essentially mineral free charcoal was reacted with hydrogen sulfide in a stream of helium to produce a sulfurated carbon which contained approximately 2.5% sulfur. Non-isothermal measurements on the desulfurization of this material in both hydrogen and helium were carried out. The results of one such experiment are given in Figure 6. In this experiment the sample size and flow rate of hydrogen used were the same as that employed on the major series of non-isothermal experiments on coals. It is clear from the results of studies to date on the sulfurated carbon that a single simple reaction does not account for the behavior of this material. Pending the completion of the kinetic investigation on the complex sequence of reactions involved in the desulfurization of these relatively stable organic sulfur species the empirical result corresponding to the smooth curve shown in Figure 8 has been used in the analysis on the results on coal. We have designated this form of organic sulfur as Organic III.

To proceed further in our analysis of the experimental result given in Figure 3 it is necessary to consider the results on all ten coals studied. The results of non-isothermal kinetic experiments for ten coals studied under similar experimental conditions are summarized in Figures 7 and 8. Certain points in common and certain differences should be noted in these results. All of the H_2S evolution curves show a peak in the range between $380^\circ C$ and $430^\circ C$. All of the coals high in pyrite show secondary peaks very close to those found experimentally for the sample of pyrite as illustrated in Figure 5. However, in general for these coals these peaks appear to occur at slightly lower temperatures typically from $10 - 20^\circ C$. If we assume that results on the pyrite are valid for coal we would expect that the presence of the carbon should have little effect on the activation energies for these reactions. But, because of both the production of hydrogen from within the coal and the possibility of the absorption of hydrogen on the carbon surface, we might expect that the pre-exponential factor which is expressed in terms of the concentration of hydrogen in the bulk gas stream might be increased in the case of the coal by these effects increasing surface concentration of hydrogen for a given bulk gas concentration of hydrogen. A downward shift in the temperature corresponding to the peak in the H_2S evolution from pyrite of $20^\circ C$ corresponds to an increase in the pre-exponential factor of about 40%. Data obtained by us and by Powell in his earlier work on the forms of sulfur in char, as a function of carbonizing temperature, support the hypothesis that the secondary peaks in these non-isothermal results do correspond to the reaction of the pyritic and sulfide sulfurs. Similarly this work suggests that the low temperature peaks in the non-isothermal results correspond to the reaction of relatively unstable organic sulfur compounds in coal. A single reaction cannot account for the variation in the location and shape of the low temperature peak for all of these ten coals. However, we have found that two processes, one with T_0 corresponding to $380^\circ C$ and a second with T_0 corresponding to $430^\circ C$ satisfactorily account for the low temperature peak in all ten coals. The kinetic parameters for these two processes which we have designed as Organic I and Organic II are as follows: ORGANIC I, $E = 34.5$ kcal/mole, $K_0 = 3.1 \times 10^{10}$ (atm H_2) $^{-1}$ min $^{-1}$; ORGANIC II : $E = 41.5$ kcal/mole, $K_0 = 2.8 \times 10^{11}$ (atm H_2) $^{-1}$ min $^{-1}$. It is, of course, possible that more than two processes contribute to this low temperature peak, however, only the two are required to account for the experimental

results.

We will now discuss the resolution of the experimental result given in Figure 3 into individual processes. The five processes we have identified in the preceding discussion are three forms of organic sulfur, pyrite, and sulfide. This result in the individual processes were performed graphically by drawing in the peaks corresponding to the individual processes and adjusting the amplitude of the peak without changing the peak location until a best fit to the experimental data is obtained. The fit is determined by comparing the sum of all of the H_2S evolution peaks with the experimental data. The result of this analysis is shown in Figure 9. In the figure the dotted line represents the sum of the individual processes with the amplitudes shown in the figure and the agreement with the experimental points is quite satisfactory with one exception. In the region about $530^\circ C$ there appears to be a significant amount of sulfur evolution which is not accounted for by these five processes. This discrepancy occurs in most of the coals studied but is particularly prominent in coal No. 7, the Maryland coal. This discrepancy may indicate that an additional desulfurization process occurs which we have not taken into account, however, our recent experiments, in an attempt to further understand the Organic III set of reactions, have indicated that the results obtained on the artificial sample of sulfurated carbon may not be directly applicable to coal. It now appears that a proper representation of the Organic III sulfur removal may remove this discrepancy.

One additional point that should be mentioned concerning this analysis of Illinois No. 4 coal is that the total amount of sulfur evolved from the pyrite and sulfide processes appears rather lower than would be expected from the amount of iron pyrite in the coal from the ASTM analysis. However, this coal contains an unusually high calcium content. Our separate experiments on the reaction of H_2S with calcium oxide and calcium carbonate have shown that the reaction of H_2S with these materials in the temperature range above 500° is extremely fast so that nearly one half of the sulfur, which might otherwise be evolved in the pyrite and sulfur peaks, is converted to calcium sulfide and retained in the char. Similar procedures to those described above have been employed in analyzing all ten of the coals studied.

KINETICS OF DESULFURIZATION

We may summarize the chemical reactions and the rate data of coal desulfurization in hydrogen atmospheres by listing our measured kinetics parameters for the five major reactions and two back reactions, as shown in Table I.

Non-isothermal studies were also made of the removal of H_2S by calcined dolomites and limestones and the regeneration kinetics of the resulting calcium sulfide. The kinetic parameters for these rate data are shown in Table II.

The significance of these results to considerations of sulfur control can be seen by expressing them as rate constants versus temperature over the range of engineering interest. The rate constants for these reactions are shown from $400^\circ C$ to $1000^\circ C$ in Figure 10. There emerges a desulfurization band which encompasses the desulfurization reactions which account for the hydrodesulfurization of the ten bituminous coals studied.

TABLE I

CHEMICAL REACTIONS AND RATE DATA OF COAL DESULFURIZATION
IN HYDROGEN ATMOSPHERES

<u>No.</u>	<u>Reaction</u>	<u>E^{kcal}/mole.</u>	<u>k₀</u>
1	(Org-S) _I + H ₂ → H ₂ S	34.5	3.1 × 10 ¹⁰ (atm H ₂) ⁻¹ min ⁻¹
2	(Org-S) _{II} + H ₂ → H ₂ S	41.5	2.8 × 10 ¹¹ " "
3	FeS ₂ + H ₂ → H ₂ S + FeS	47	2.8 × 10 ¹² " "
4	FeS + H ₂ → Fe + H ₂ S	55	2.1 × 10 ¹³ " "
5	(C-S) + H ₂ → H ₂ S	52	~2 × 10 ¹³ " "
6	Fe + H ₂ S → H ₂ + FeS	18	6.5 × 10 ⁶ (atm H ₂ S) ⁻¹ min ⁻¹
7	Coke + H ₂ S → (C-S) + H ₂	32	2.3 × 10 ⁸ " "

TABLE II

8	CaO + H ₂ S → CaS + H ₂ O	38	4.7 × 10 ¹³ (atm H ₂ S) ⁻¹ min ⁻¹
9	CaS + H ₂ O → CaO + H ₂ S	55	1.0 × 10 ¹⁴ (atm H ₂ O) ⁻¹ min ⁻¹
10	CaCO ₃ → CaO + CO ₂	58	3.0 × 10 ¹² min ⁻¹
11	CaO + CO ₂ → CaCO ₃	17	5.0 × 10 ⁴ (atm CO ₂) ⁻¹ min ⁻¹

ACKNOWLEDGMENTS

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3. (a) Scientific Research Instruments Corporation Report No. SRIC 68-13 (1969), (b) Scientific Research Instruments Corporation Report No. SRIC 69-10 (1969).

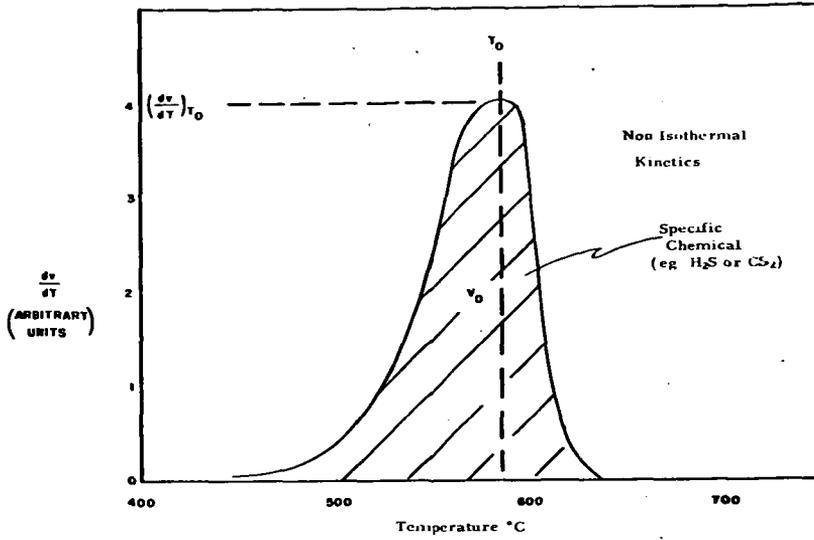


Figure 1. Typical outgassing kinetics curve vs. temperature. T_0 is temperature at peak. $(\frac{dv}{dT})_{T_0}$ is peak height, V_0 is area.

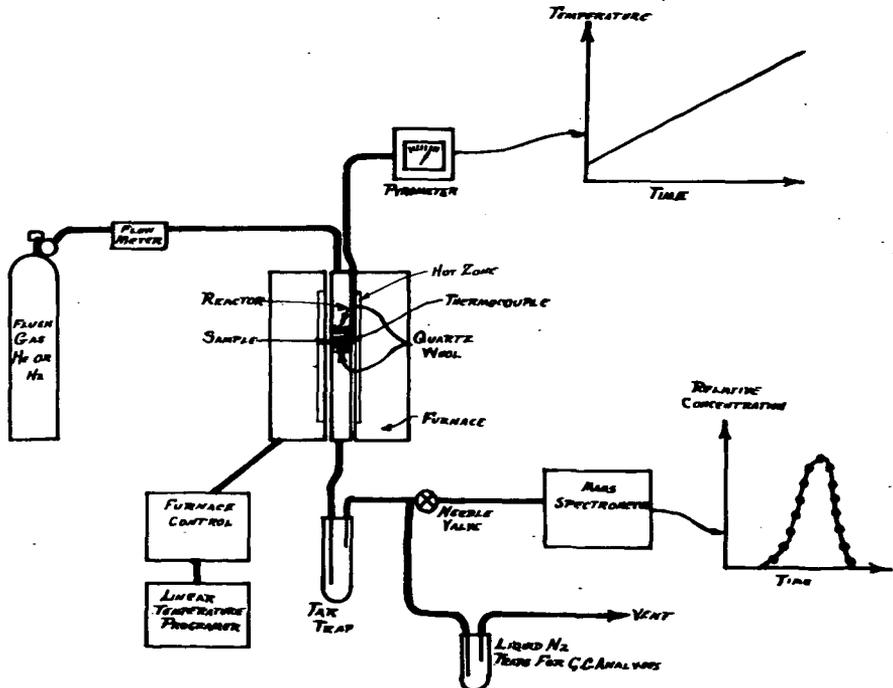


Figure 2. Schematic diagram of experimental apparatus.

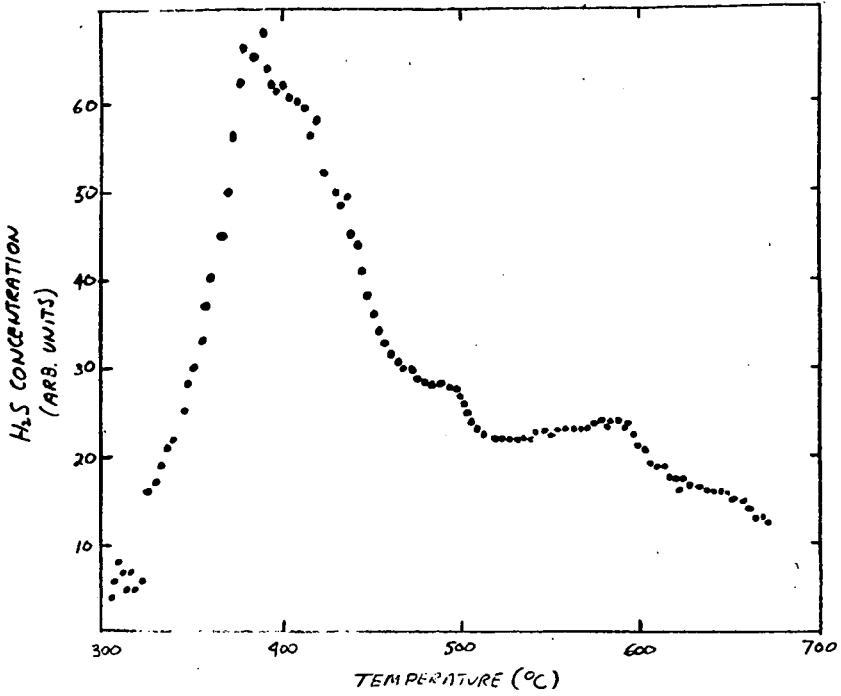


Figure 3. H₂S evolution in a non-isothermal experiment at one atmosphere of hydrogen on Illinois 5% sulfur coal, SRI No. 4.

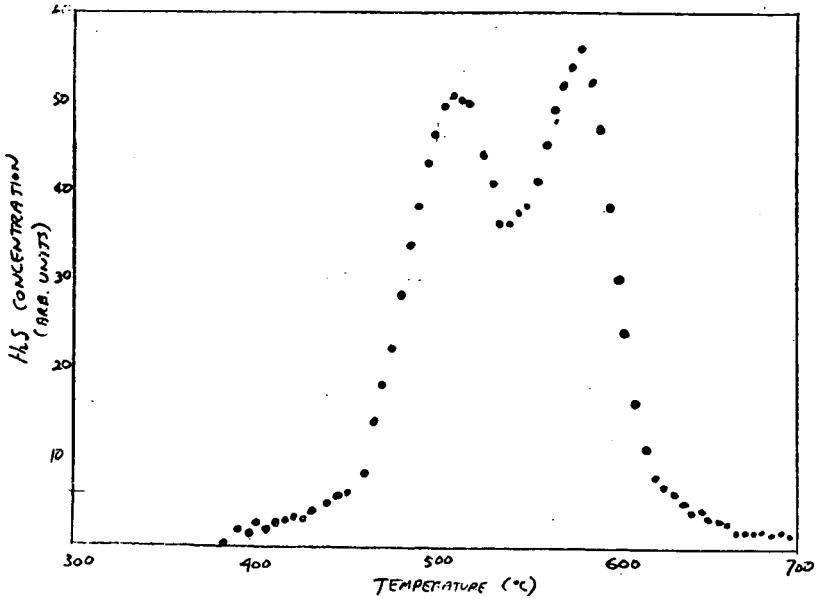


Figure 4. H₂S evolution in a non-isothermal experiment at one atmosphere of hydrogen on pyrite.

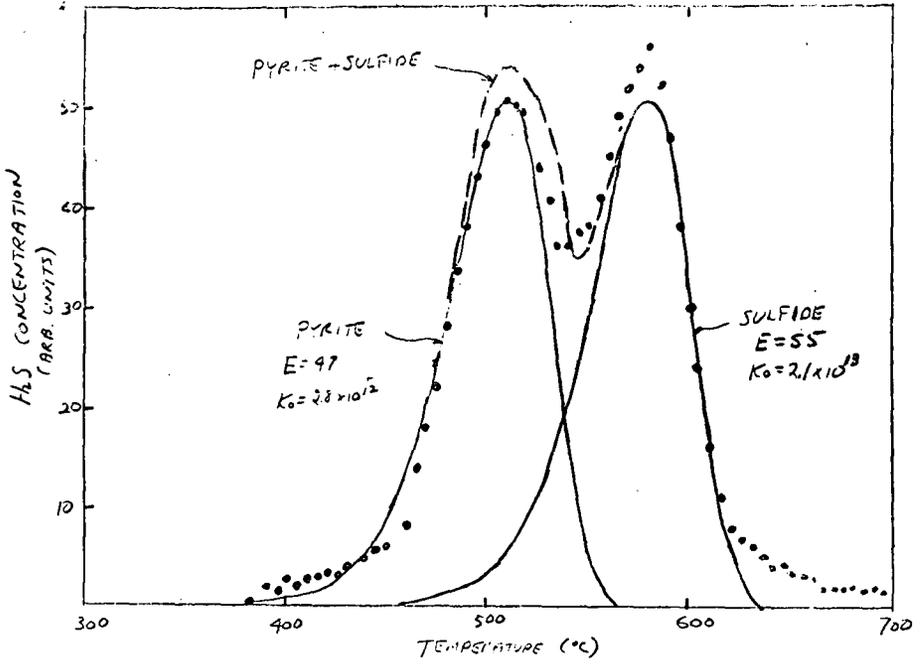


Figure 5 . Kinetic analysis of the non-isothermal measurement on pyrite.

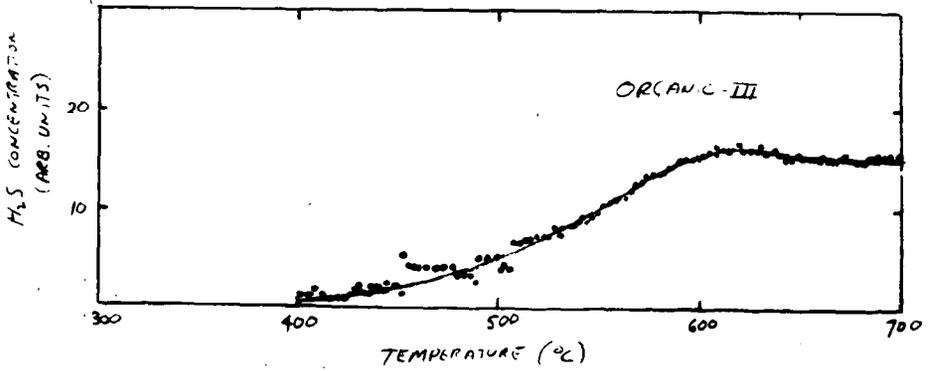


Figure 6. H_2S evolution in non-isothermal experiment at one atmosphere of hydrogen on sulfurated carbon prepared from charcoal.

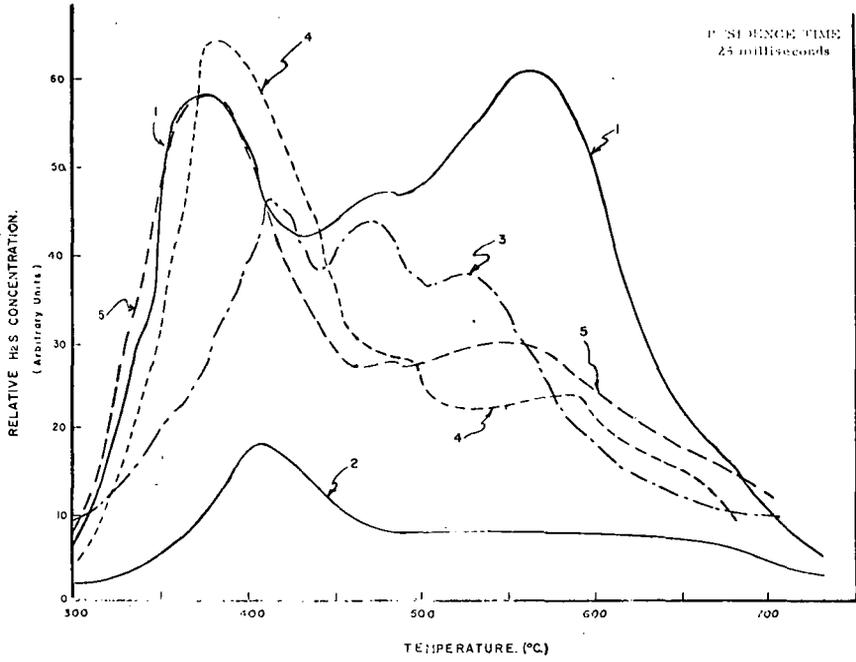


FIGURE 7. NON-ISOTHERMAL H_2S EVOLUTIONS IN H_2 FROM COALS SRI NUMBERS 1 THROUGH 5.

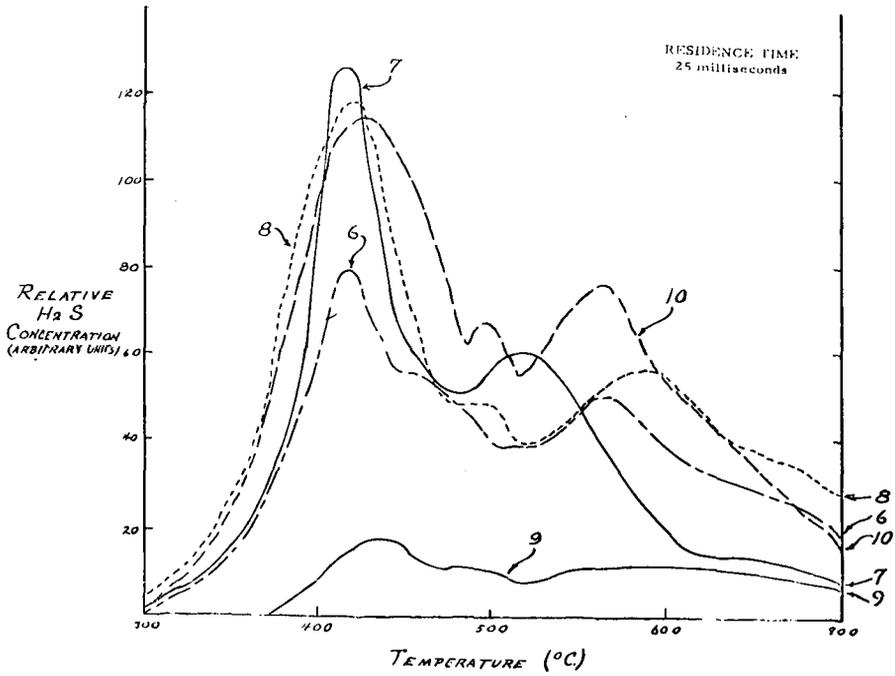


FIGURE 8. NON-ISOTHERMAL H_2S EVOLUTIONS IN H_2 FROM COALS SRI NUMBERS 6 THROUGH 10.

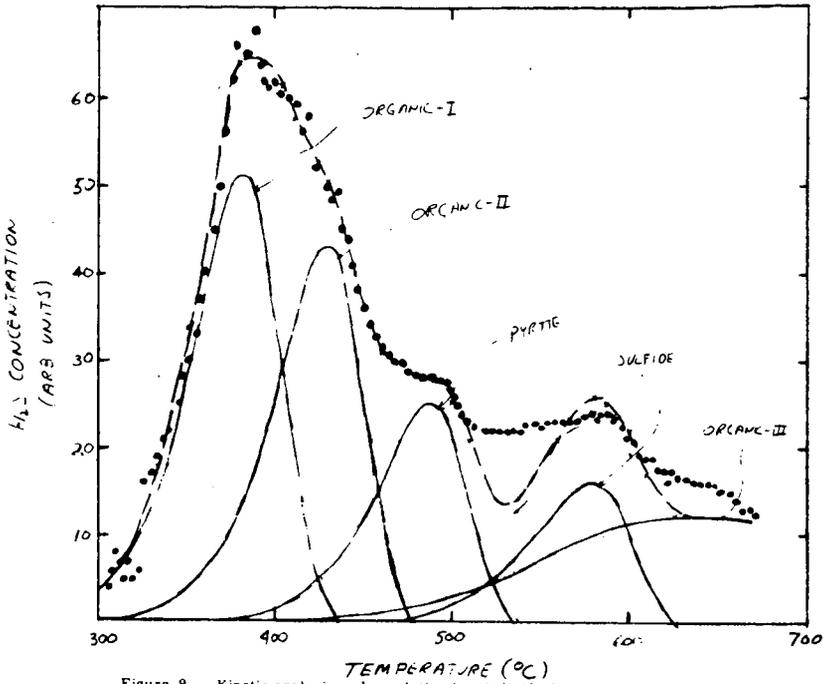


Figure 9. Kinetic analysis and resolution into individual processes of the H_2S evolution in a non-isothermal experiment at one atmosphere of hydrogen on Illinois 5% sulfur coal, SRI No. 4.

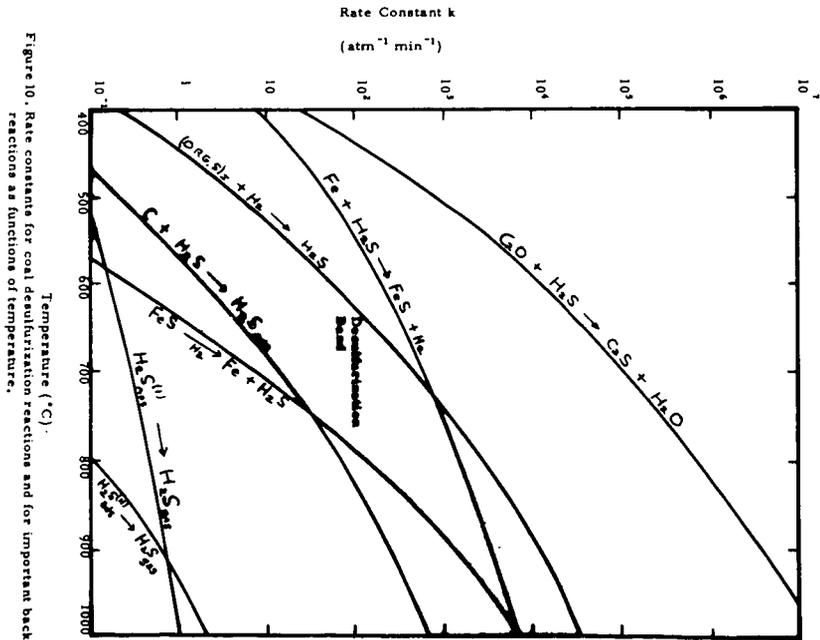


Figure 10. Rate constants for coal desulfurization reactions and for important back reactions as functions of temperature.

MANUFACTURE OF ACTIVATED CARBON AND ITS APPLICATION
TO AIR, WATER, AND NUCLEAR POLLUTION CONTROL

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ABSTRACT

Activated Carbon in the United States is mainly made by the steam activation process and important variables in the manufacture and resulting end properties are considered particularly temperature, gas mixtures, and residence time. Economic of granular activated carbon pollution control is primarily dependent on the adsorption properties, both static and dynamic, and the various variables affecting the mass transfer characteristics are illustrated. Practical use of granular activated carbon generally will require on site regeneration and the knowledge of working capacity with various regeneration techniques (furnace, heated solvents, internal, chemical and biological) are required for the most efficient plant design. Size and growth of various end use areas are reviewed.

THERMAL REGENERATION OF ACTIVATED CARBONS

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Introduction

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

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

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

Laboratory Studies to Improve Carbon Regeneration

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

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

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

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

Carbon input rate is generally 450 cc/hr and gas input rate about 10 ft³/hr (stp).

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

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

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

TABLE 1 - PROPERTIES OF SPENT AND VIRGIN
FILTRASORB 400

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

Step-wise Nature of Carbon Regeneration

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

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

The activating step was found to be more sensitive to the operating conditions. For instance, CO₂ activation produced regenerated carbons of lower iodine number than pure steam activation. Activation at high temperature of 1650° to 1700°F gave better results than activation at 1600°F and lower, although at about 1500°F, activation rate was too slow to be of any importance in the regenerations.

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

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

Effect of Metallic Elements on Regeneration

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

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

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

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

TABLE 3 - ACTIVATING GAS INPUT REQUIRED ON SUCCESSIVE ACTIVATIONS

Cycle No	Gas input, ft ³ /hr (stp)		
	N ₂	CO ₂	H ₂ O
1	3.6	0.36	1.0
2	1.27	0.17	0.18

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

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

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

Activation run no	Bulk density, g/cc	Not HCl treated		HCl treated	
		I ₂ no, mg/g	Mol no	I ₂ no, mg/g	Mol no
(virgin)	(0.468)	(1090)	(250)		
30	0.469	960	290		
32	0.467	950	---		
34	0.478			1020	230
36	0.484			1040	230
39	0.461	930	270		
40	0.468	950	250		
41	0.476	950	260		
47	0.468			1050	230
53	0.472			1020	250
77	0.468	930	250		
79	0.480	---	---	1040	230
	means	945	264	1034	234

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

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

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

TABLE 5 - BAKING AND ACTIVATING CONDITIONS

Run no.	Regenerating step	Temperature, °F			Gas input, ft ³ /hr (stp)	
		1	2	3	N ₂	CO ₂
29	dry OSF 400 baked	750	1330	1550	7.0	0.90
30	Run 29 activated	1550	1650	1700	4.0	0.51
78	dry, HCl treated, baked	800	1350	1550	7.0	0.93
79	Run 78 activated	1550	1650	1700	6.0	0.50
						H ₂ O
						2.26
						1.48
						1.96
						1.94

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

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

Ash Analyses

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

Run 67 shows a considerable increase in the oxides, Fe₂O₃, CaO, MgO, K₂O, Na₂O and Cr₂O₃. As is evident from Run 79, these oxides are considerably reduced by the HCl acid leach, hence one or more of these oxides contribute to lowered recovery of the iodine number and over recovery of the molasses number.

TABL 6 - 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 ₂ O ₃	2.51	1.94	1.62
Fe ₂ O ₃	0.42	0.80	0.59
CaO	0.17	1.23	0.05
MgO	0.14	0.34	0.09
K ₂ O	0.06	0.40	0.20
Na ₂ O	0.04	0.15	0.07
TiO ₂	0.03	----	----
Cr ₂ O ₃	0.01	0.12	0.12
Total ash in carbon	5.7	7.2	5.0

Effect of Regeneration on Pore Size Distribution

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

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

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

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

A further study was conducted to determine the manner in which the surface area changes occurred. Pore size distribution curves were determined for selected carbons, using the water adsorption method³ and mercury porosimetry. In preparation for the water isotherm determinations (and also porosimetry), the carbons were HCl acid and pure water leached to remove hydrophilic compounds from the carbon surface. The validity of the water adsorption method depends on the water being adsorbed by capillary condensation, with negligible monolayer adsorption. The adsorption method is applicable to maximum pore diameter of 500 to 1000 Å.

Pores in the larger diameter range are measured by mercury porosimetry⁴. These measurements cover the diameter range 30 to 100,000 Å, hence the two methods overlap in the range 30 to 500 Å. For some of the pore size distributions, the agreement in the overlap range is good while for others, some discrepancy exists. The trend is for the mercury porosimeter to measure a larger pore diameter at a given volume. Figure 5 presents two distribution curves, Run 68 showing the best agreement and F 400 the poorest. A possible explanation for the discrepancy is that the carbons are slightly compressed by the mercury at the higher pressures. Maximum pressure at 30 Å is 60,000 lb/in².

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

Those in Figure 6 show the effects of acid leach, steam activation and CO₂ activation. The virgin F 400 is uppermost in pore volume at the 28 Å diameter, and then Runs 79, 67 and 68 in descending order. The iodine numbers were respectively, 1090, 1040, 940 and 840 mg/g, while the molasses numbers were quite close to each other.

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

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

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

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

From Figure 8, the surface areas of pores larger than 10 Å in diameter for the carbons F 400, Runs 79, 67 and 68 are 965, 925, 860 and 805 m²/g, respectively. The surface areas of pores larger than 28 Å are respectively, 120, 100, 110 and 100 m²/g. Likewise from Figure 9, the surface areas of pores larger than 10 Å in diameter for the carbons Runs 36, 67 and 46 are 915, 860 and 840 m²/g, respectively. Surface areas of pores larger than 28 Å in diameter are, respectively, 85, 110 and 150 m²/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 7.

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

Carbon	Iodine number, mg/g		Molasses number	
	test	calc	test	calc
Filtrisorb 400	1090	1040	250	250
Run 79 (HCl)	1040	1010	230	230
Run 67	940	940	260	240
Run 68 (CO ₂)	840	880	250	230
Run 46	920	920	320	280
Run 36 (HCl)	1040	1000	230	210

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

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

Summary

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

References

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2. R. J. Grant, "Basic Concept of Adsorption on Activated Carbon", Pittsburgh Activated Carbon Company.
3. E. O. Wiig and A. J. Juhola, JACS 71 2069, 2078 (1949).
4. Measurements made by American Instrument Co, Inc, Silver Springs, Maryland.

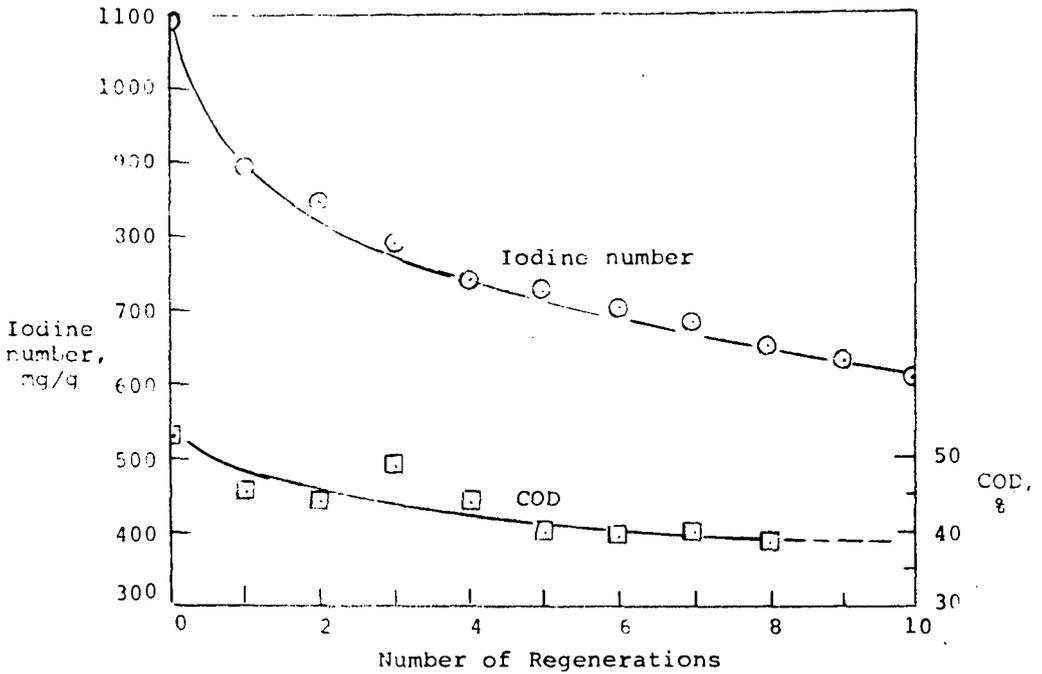


FIGURE 1 - DECREASE IN IODINE NUMBER AND COD ADSORPTIVE CAPACITY WITH SUCCESSIVE REGENERATIONS

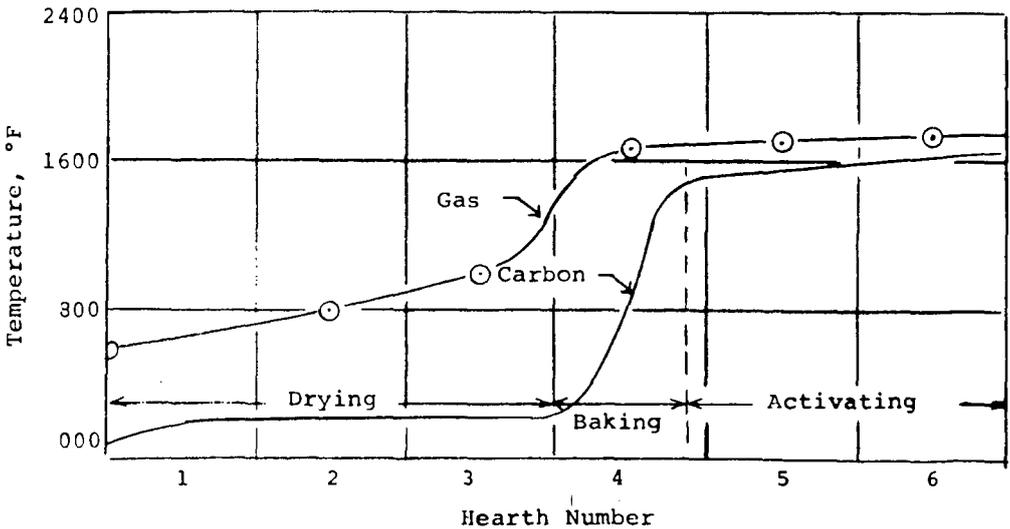


FIGURE 3 - TEMPERATURE PROFILES FOR GAS AND CARBON IN MULTIPLE HEARTH FURNACES, REGENERATION OF WET SPENT CARBON

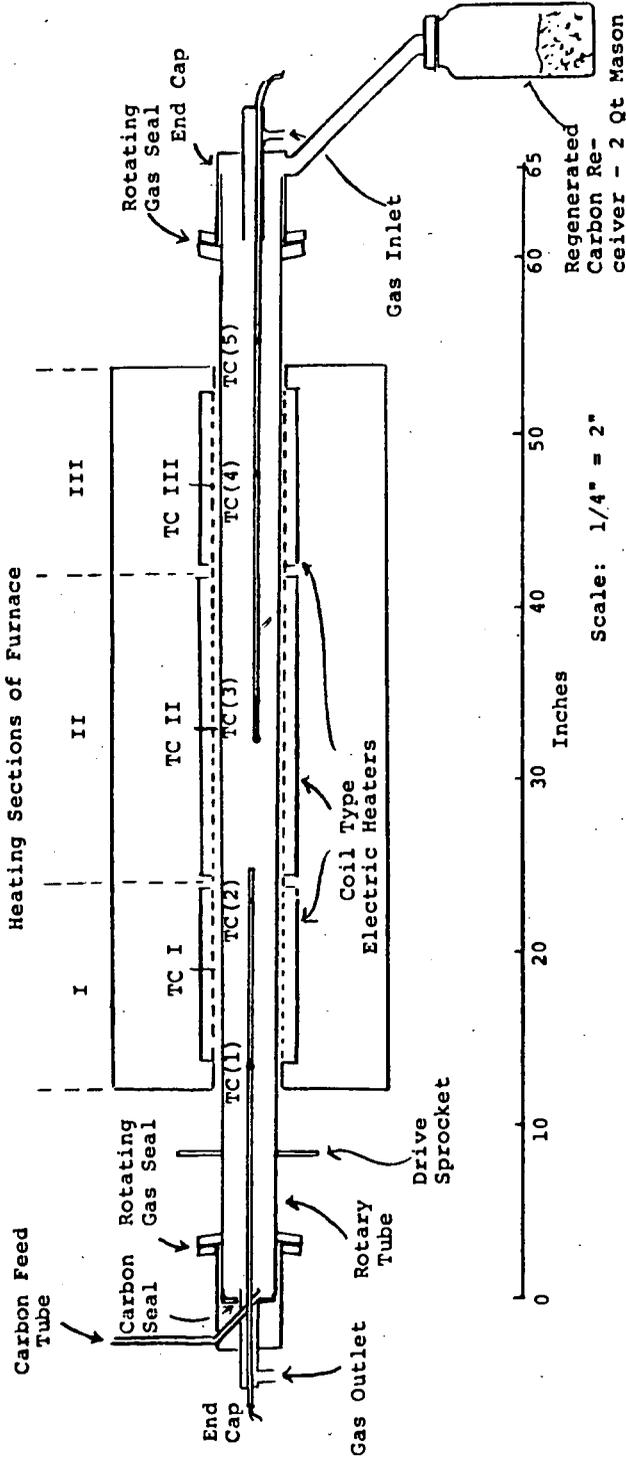


FIGURE 2 - CROSS SECTIONAL VIEW OF ROTATING TUBE, END CAPS AND HEATING FURNACE

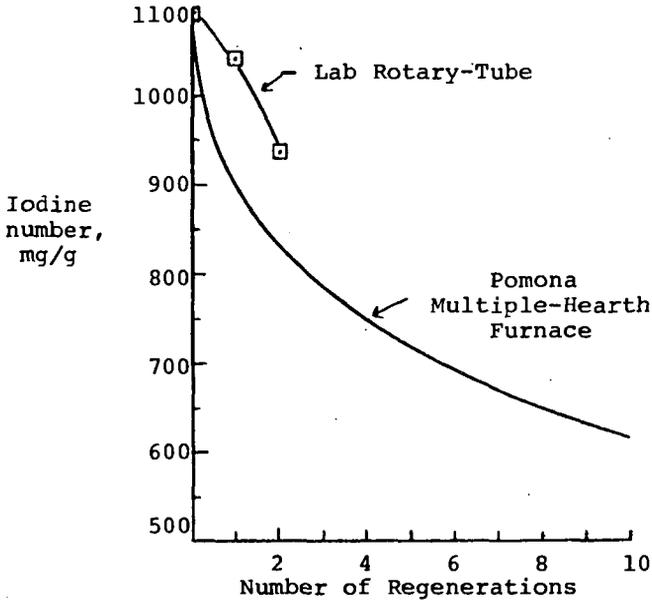


FIGURE 4 - DECREASE OF IODINE NUMBER WITH SUCCESSIVE REGENERATIONS

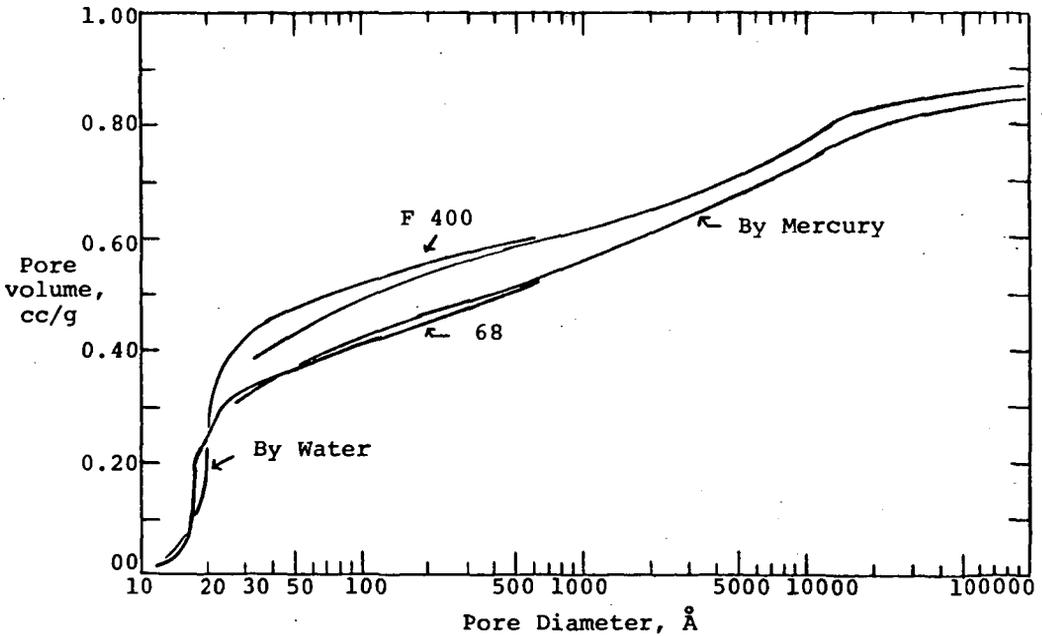


FIGURE 5 - PORE SIZE DISTRIBUTION MEASURED BY WATER ADSORPTION AND BY MERCURY PENETRATION

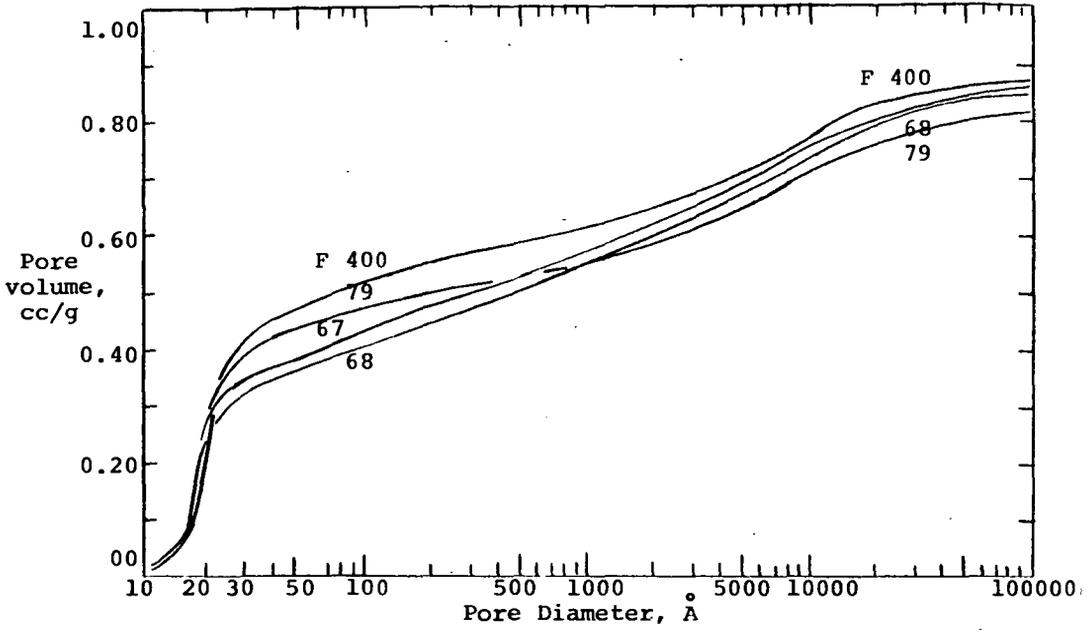


FIGURE 6 - PORE SIZE DISTRIBUTIONS OF REGENERATED CARBONS

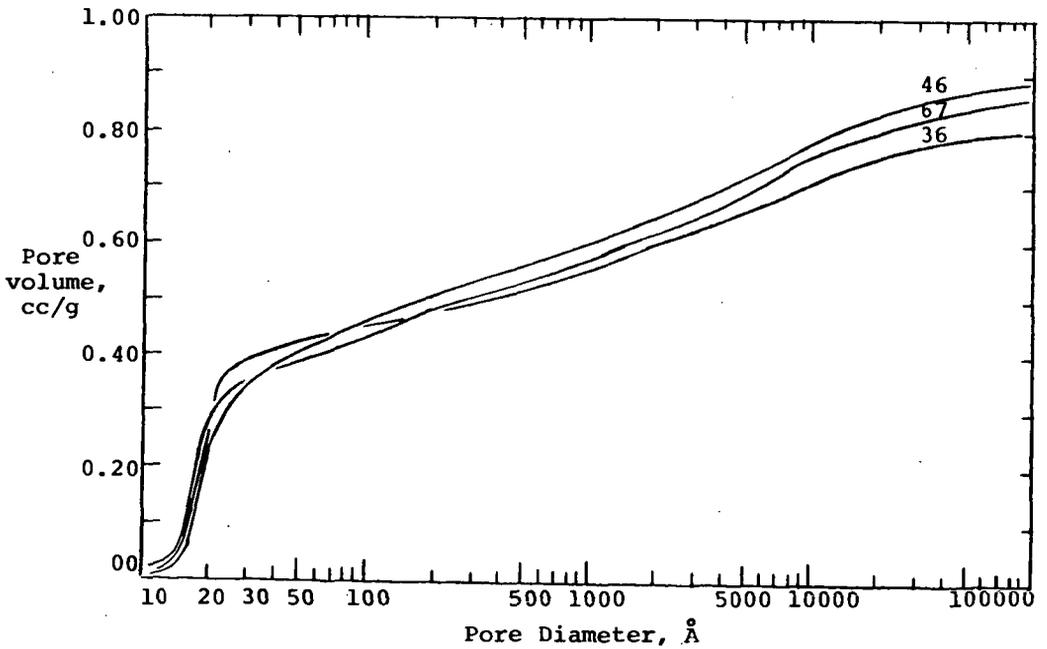


FIGURE 7 - PORE SIZE DISTRIBUTIONS OF REGENERATED CARBONS

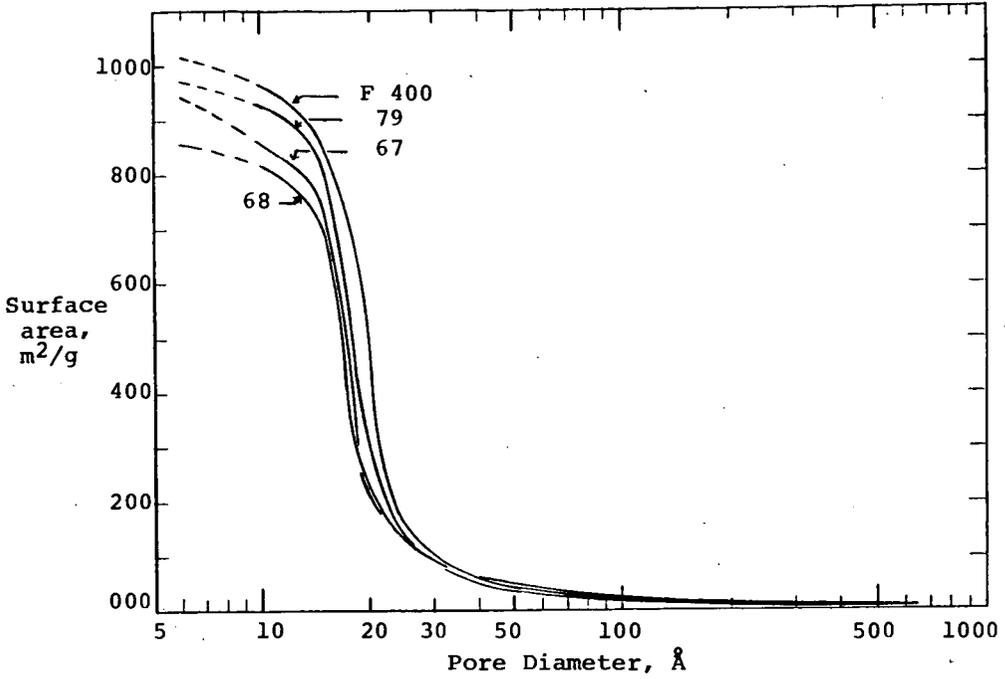


FIGURE 8 - CUMULATIVE SURFACE AREAS OF REGENERATED CARBONS

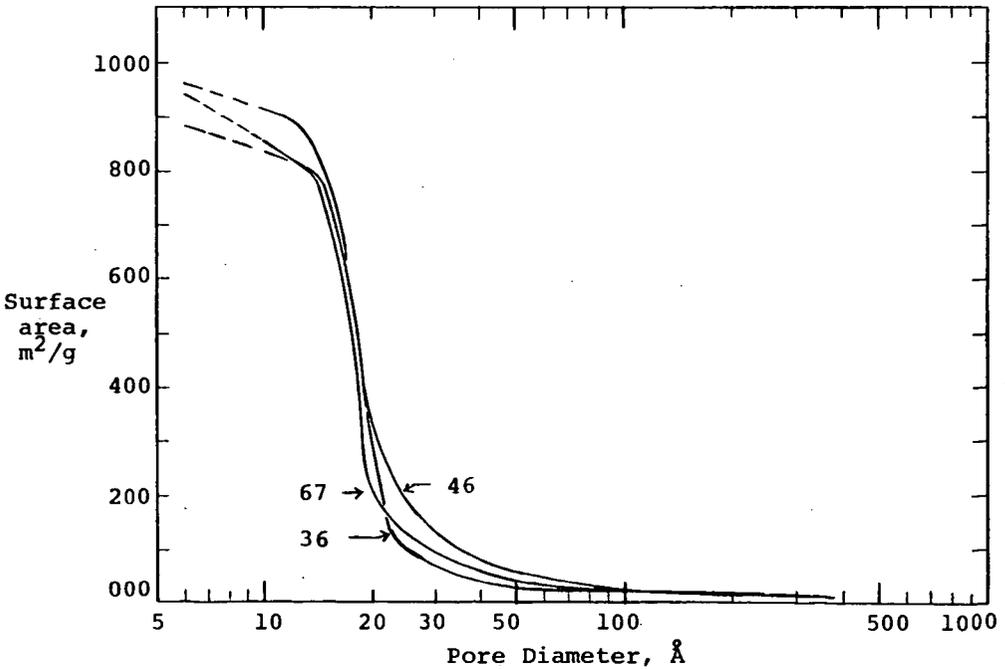


FIGURE 9 - CUMULATIVE SURFACE AREAS OF REGENERATED CARBONS

TREATMENT OF PRIMARY EFFLUENT*
BY LIME CLARIFICATION AND GRANULAR CARBON

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Introduction

Conventional systems for treating wastewater are usually composed of two processes: a primary treatment process which removes the bulk of the settleable solids from the wastewater by sedimentation, and a secondary treatment process which removes the bulk of the soluble organic matter by biological oxidation. These processes in combination have shown to be an effective and economical means of improving the discharge quality of wastewater. However, the processes are not without certain disadvantages.

First, the processes require considerable operating control and often generate operating problems of a complex nature. Second, they are easily upset and require time to regain efficient operation. And finally, they produce sludge at such a rate that it poses an ultimate sludge disposal problem of considerable magnitude.

Conceivably, each of these disadvantages could be largely eliminated if wastewater were treated by a system that utilized solely physical and chemical methods. Such a system is shown schematically in Figure 1.

In Figure 1, primary treatment is replaced by lime clarification with the added bonus of phosphate removal and secondary

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treatment is replaced by activated carbon adsorption. Recalcination of the spent lime and regeneration of the carbon make the system essentially closed loop. The most intriguing aspect of the system as a whole is that there are no large volumes of waste sludge to contend with.

The results of applying activated carbon adsorption and lime clarification techniques to wastewater renovation have been widely reported in the literature (1) (2) (3) (4) (5). However, virtually all the work has been done on secondary effluent. The number of reported instances in which lime clarification and carbon adsorption have been applied to raw or primary wastewater are few.

Recently, a system utilizing lime clarification followed by biological treatment was applied to raw wastewater (6). Results showed that lime clarification with subsequent recalcination and collateral combustion of the primary sludge solids was economically competitive with conventional methods of removing suspended matter from wastewater by sedimentation and ultimate disposal by incineration. The process had the added benefit of phosphate removal.

In another study, raw wastewater was lime clarified at high pH and then carbon treated (7). The results presented were interpreted as showing that the removal of soluble organic matter by carbon is enhanced by the hydrolytic breakdown at high pH of large molecular weight organic compounds into lower weight ones which are more readily adsorbable. The results also give final effluent COD values that compare favorably with those associated with good secondary effluent.

Thus, to fully assess the feasibility of the system shown in Figure 1, it will be necessary to answer two key questions. First, can activated carbon adsorption compete with biological oxidation as an economical method of removing soluble organics from lime clarified raw wastewater, and second, can a complete physical and chemical system of wastewater treatment produce water of a quality at least equal to that produced by good conventional treatment.

Work addressed to answering these questions is presently underway at the Lebanon, Ohio pilot plant facility of the Federal Water Pollution Control Administration. The purpose of this interim project report is to give the preliminary results of the work.

Methods and Procedures

A flow diagram for the experimental system is shown in Figure 2. Primary effluent from the Lebanon Municipal Treatment Plant is fed to a lime clarification process for removal of suspended matter and phosphates. A schematic of the lime clarification process is given in Figure 3 and its operation is described in detail elsewhere (1). Except for a brief operational period during which the

pH was greater than 11.5, lime clarification was carried out at a pH of 9.5. Following lime clarification and filtration through parallel dual-media filters, the clarified water is pumped through three carbon contactors for removal of soluble organic matter.

Each carbon contactor is 4 ft in diameter and contains 2400 lbs of 8x30 mesh granular activated carbon (a). This quantity of carbon fills the contactor to a depth of 8 ft. The contactors are operated downflow and in series.

Prior to dual-media filtration, the clarified effluent is adjusted to pH 8 with sulfuric acid to minimize calcium carbonate incrustation of the filter media. Following filtration, the clarified effluent is further adjusted to pH 7.5 with sulfuric acid prior to carbon treatment.

The lime clarification process is operated at a steady flow rate of 75 gpm. Part of this flow is stored for use in backwash of the dual-media filters, the remainder goes into a holding tank from which it is pumped at a constant rate of 48 gpm to the carbon contactors. During backwash of the dual-media filters, the water stored in the holding tank serves as feed to the carbon contactors.

At the flow rate of 48 gpm, contactor residence time based on an empty bed is 15 minutes each or 45 minutes total. This and other contactor constants are given in Figure 4.

Operation of the system is continuous over a 24-hour period and over run lengths of roughly one-month duration. During runs, the lime clarification process normally never requires shutdown; however, the carbon contactors require periodic shutdown which normally occurs when the headloss in the lead contactor is such that a flow of 48 gpm cannot be attained. When this occurs, the contactor is shut down, backwashed and then returned to service.

System performance was monitored initially by both grab sampling and composite sampling. Grab samples normally were taken manually every 3 hours at first, and later by automatic samplers every hour. Grab sampling was discontinued midway in the study and only composite sampling done.

Samples of the lime clarification process feed and product were taken for TOC, BOD, COD, turbidity, suspended solids, and phosphate determination. The feed and product of the carbon contactors were sampled for TOC, BOD, COD, and turbidity measurements. In addition, the product from carbon contactor one and two was sampled for TOC, BOD, and COD determinations. Late in the study, nitrogen forms around the system were determined. After establishing

- (a) Filtrasorb 300, Calgon, Inc. Mention of specific proprietary equipment or products throughout this paper is for information purposes only and does not constitute endorsement by the Federal Water Pollution Control Administration and the U. S. Department of the Interior.

a ratio between TOC and BOD, and TOC and COD, only TOC was monitored around the system.

All samples were analyzed by Standard Methods (a).

Results and Discussion

Results will be presented in three parts: first those pertaining to carbon contactor performance; second, those pertaining to lime clarification at high pH; and last, those pertaining to the performance of the system as a whole.

Data on nitrogen and ratio results between TOC and BOD, and TOC and COD are given in the Appendix.

Carbon Contactor Performance

TOC profiles through the carbon contactors for increments of one million gallon throughput are given in Figure 5. The average TOC of the feed was 25 mg/l and the average product TOC was 11 mg/l. The range in feed TOC values was 20 to 33 mg/l. As can be noted, the effect of this variation in feed TOC on product TOC was damped by increased removal of TOC by contactor one. It is apparent that the lead contactor serves the important function of buffering increased TOC loadings.

In Table 1, the percent organic matter removed by the carbon contactors is given as TOC, BOD, and COD. As can be seen, organic removal was about the same regardless of the organic parameter utilized as a quantitative measure.

TABLE 1 - TOTAL PERCENT ORGANICS
REMOVED BY CONTACTORS

TOC (1)	57
BOD (2)	59
COD (2)	60

(1) Based on 5 MG

(2) Based on 3 MG

Organic removal as a function of contactor residence time is shown in Figure 6. The data suggest that the percent of the soluble organic matter removed cannot be substantially improved by increasing contactor residence time.

(a) Standard Methods for the Examination of Water and Wastewater 12th Edition, 1965, American Public Health Association, Inc. 1790 Broadway, New York, N. Y. 10019

Contactor loading data are given in Table 2. The loading in lbs TOC per lb of carbon shown for contactor one is considered very good since the contactor is only partially exhausted. In gallons of primary effluent treated, this loading in gallons treated per pound of carbon is roughly 2000. It appears realistic to project a treatment of 4000 gallons per pound of carbon (250 lb carbon/MG) before the carbon requires changing. This suggests carbon replacement costs of less than \$0.07 per thousand gallons for one-time usage of the carbon and, if carbon regeneration is considered, the costs look economically attractive.

TABLE 2 - CARBON TOC LOADING - 5 MG

<u>Contactor Number</u>	<u>Lbs TOC Removed</u>	<u>Lbs TOC Removed per Lb Carbon</u>
1	367	0.153
2	169	0.070
3	51	0.021

TOC removed per lb of carbon as a function of TOC applied per lb of carbon is shown in Figure 7 for each contactor. These data represent the cumulative TOC applied and removed per million gallon increment of flow through the contactors. As can be seen, the TOC removal rate by contactor one decreased as the carbon became loaded with TOC. However, the TOC removal rate by contactor two increased as the carbon became loaded with TOC. This suggests that as contactor one becomes progressively exhausted it progressively passes an increasing amount of adsorbable organics to contactor two. TOC removal by contactor three was essentially constant at all loading rates. This seems to indicate that contactor two passes a relatively constant amount of adsorbable TOC to the third contactor.

Carbon Contactor Operational Problems

The carbon contactors became anaerobic early in the operational period. This was evident by the odor of hydrogen sulfide gas in the contactor effluent. The amount of hydrogen sulfide present was not measured quantitatively. An attempt was made midway in the study to operate the contactors in an aerobic condition. The first method used was to aerate the holding tank prior to the carbon contactors. Air was used first and then oxygen. Neither method injected enough oxygen into the feed to maintain the lead carbon contactor aerobic. Oxygen was then injected directly into the feed stream at the inlet to the lead contactor. This eliminated the hydrogen sulfide from the contactor effluent after a short operational period which indicated the contactors were operating aerobically. After a period of less than a day running time, however, a large leadloss developed in the lead contactor and maintaining the desired

flow rate through the contactor became impossible. The contactors were shut down, the lead contactor backwashed, and then all contactors put back into operation.

Rapid buildup of headloss across the lead contactor continued despite frequent backwash. The lead contactor was again shut down, partially drained, and its surface layer inspected. The layer was found to be greatly impregnated with calcium carbonate. The holding tank prior to the contactor was then drained and inspected and a heavy deposit of calcium carbonate was found at the bottom. This deposit probably accumulated during the high pH run when large quantities of lime were used to raise the pH above 11.5 in the clarifier. During backwash of one of the dual-media filters, the volume of water entering the holding tank is decreased by a half and the holding tank level drops to half or less. The momentum of the incoming water is probably sufficient enough at low water levels to create a bottom turbulence in the tank and the turbulence puts bottom deposits such as calcium carbonate into the feed to the contactor.

The holding tank was thoroughly flushed out with water, the lead contactor acid rinsed with 40 gallons of pH 2.0 sulfuric acid solution and backwashed, and then the contactor was returned to service. At this point the contactor throughput was approximately 1.5 million gallons. Headloss across the contactor was then normal. It was decided to cease feeding oxygen to the contactors and thereby let them become anaerobic. It was felt that the oxygen was promoting the growth of aerobic slime-producing microorganisms and contributing to leadloss buildup.

Following the acid rinse of the lead contactor and the cessation of oxygenation of the contactors, headloss buildup assumed a reasonable magnitude.

Lime Clarification at pH >11.5

As previously mentioned, it has been reported that lime clarification of raw wastewater at a high pH results in the hydrolytic breakdown of organic matter which subsequently enhances its removal by carbon adsorption (7). In an effort to evaluate this, the lime clarifier was operated at a pH greater than 11.5 over an eleven day operational period. The lime clarifier pH range for the period was 11.10 to 11.75 and the pH averaged 11.59. To achieve this pH level, lime dosages in excess of 1100 mg/l were necessary as compared to 200 to 300 mg/l to achieve pH 9.5. All other operational procedures and methods as previously described were the same. Operational sequence of the high pH run relative to the low pH runs was: 31 days at pH 9.5, 11 days at pH greater than 11.5, and 30 days at pH 9.5.

Removal of organic matter from primary effluent clarified at a pH greater than 11.5 is shown in Table 3. For comparative purposes similar data are given for the pH 9.5 runs. The high pH results were averaged over a throughput of 0.7 million gallons while

the low pH results were averaged over a throughput of 5.0 million gallons. Since a low pH run preceded and followed the high pH run, it is reasonable to assume that prior history of the carbon contactors did not prejudice the results to any significant extent.

As can be seen in Table 3, the pH level did not have a significant effect on product quality as measured by BOD, COD, and TOC, nor did it affect a greater percentage removal of organic matter.

TABLE 3 - CARBON ADSORPTION OF ORGANICS FROM PRIMARY EFFLUENT CLARIFIED AT pH 9.5 and pH >11.5

	<u>TOC</u>	<u>BOD</u>	<u>COD</u>
pH 9.5: % Removed	56.0	58.7	60.4
Product Average, mg/l	11.0	10.0	31.0
Product Range, mg/l	2.9-22	2.0-23	11-70.6
pH >11.5% Removed	53	56.2	59.6
Product Average, mg/l	9.8	14.5	31.0
Product Range, mg/l	6.4-12.2	6.6-19.4	12.0-42.6

Some improvement in the turbidity of the effluent from the lime clarifier was noted at the higher pH. This was probably because of the removal of fine turbidity matter by the magnesium hydroxide floc which forms at a pH above 11.

Overall System Performance

Organic matter removed by the complete system as determined by TOC, BOD, and COD measurements is given in Table 4. As shown, lime clarification removed 76 percent of the organic matter. This suggests that the amount of organic matter present in Lebanon primary effluent that is amenable to removal by clarification and adsorption mechanisms is, on the average, 76 percent suspended and 24 percent soluble in form.

TABLE 4 - TOTAL ORGANIC REMOVAL FROM PRIMARY EFFLUENT BY LIME CLARIFICATION AND CARBON TREATMENT

	<u>TOC</u> (1)	<u>BOD</u> (2)	<u>COD</u> (2)
Total Organic Removal			
mg/l	66	66	165
lbs/MG	550	550	1376
Percent Removed by Lime Clarification	76	76	76
Percent Removed by Carbon Adsorption	24	24	24

(1) Based on 5 MG
 (2) Based on 3 MG

The percent removal distribution of the applied organic loading between the processes and that remaining in the product is shown in Table 5. As can be noted, 66 percent of the applied organic matter was removed by clarification, 21 percent by adsorption, and 13 percent was not removed by either process and remained in the product water. Assuming that essentially no soluble organic matter is removed by lime clarification, the data indicates that roughly 34 percent of the applied organic loading was soluble in form and, surprisingly, 13 percent of the soluble organics were not removed by carbon adsorption.

TABLE 5 - THE DISTRIBUTION OF THE APPLIED ORGANIC LOADING

	TOC (1)	BOD (2)	COD (2)
Removed by Lime Clarification, %	66	66	65
Removed by Carbon Adsorption, %	21	21	21
Remaining in Product, %	13	13	14

(1) Based on 5 MG

(2) Based on 3 MG

NOTE: Overall removal by lime clarification and carbon adsorption was 87% TOC, 87% BOD and 86% COD based on primary effluent. If 35% removal of BOD in the primary tanks is assumed, the overall BOD removal by primary treatment, lime clarification and carbon adsorption is 91.5%.

It is anticipated that raw wastewater could be fed directly to the lime clarifier (without primary treatment) without affecting product quality.

Turbidity, suspended solids, and phosphate removal data for the system are given in Figure 8. Removal in each instance was good. As would be expected, the carbon contactors tend to remove suspended matter and thus turbidity, that escapes the dual-media filters. Phosphates are not removed by activated carbon.

Organic concentrations of the feed and product stream as shown in Figure 8 indicate that overall system performance was quite good. The quality of the water obtained solely by lime clarification of primary effluent is probably equal to that discharged by many conventional treatment plants today plus the added benefit of phosphate removal. Final product water quality is equal to that required for direct discharge and for many reuse purposes.

In Table 6, a comparison is made between wastewater quality attainable by good conventional treatment and that attained in the present study by lime clarification and carbon adsorption. The data given for activated sludge treatment was obtained from measurements made on secondary effluent from a pilot plant activated sludge

unit operating at a constant feed rate. This unit utilizes primary effluent from the Municipal Treatment Plant and treats it by conventional activated sludge methods. The secondary effluent from this unit is normally of good quality with an organic carbon content of 20 mg/l or less and a turbidity of 10 or less JTU. As shown in Table 6, the quality of effluent produced by lime clarification and carbon adsorption was slightly better than that of the secondary effluent used as the standard, and probably significantly better in quality than the effluent produced by the majority of treatment plants now in operation that utilize conventional treatment methods.

TABLE 6 - COMPARISON OF CONVENTIONAL TREATMENT AND PHYSICAL AND CHEMICAL TREATMENT

<u>Treatment</u>	<u>BOD</u> ⁽¹⁾	<u>TOC</u> ⁽¹⁾	<u>JTU</u>
Activated Sludge	79-13 (a)	59-12 (b) 72-12	2.4
Lime and Carbon	76-10	76-10	1.1

(1) Based on 1 MG

(a) First group of figures are influent, second group effluent

(b) Results from two separate sampling periods.

General Comments

In assaying the results presented, two factors must be considered. First, the system under study was operated at a steady flow. The effect of diurnal variation in the flow of wastewater on the performance of the system was not determined. However, there is some evidence that several magnitudes of change in flow rate through a carbon contactor do not materially affect product quality (9)(10). The effect of variation in flow on the performance of the lime clarification process is not known.

Second, the primary effluent used as the feed to the system is highly domestic in nature and is weak to moderate in strength. Conceivably the results would be significantly altered if a strong strength wastewater were used as the feed.

The results must also be considered in light of certain deficiencies in the system. For one, the carbon contactors were not designed for efficient backwash. This most likely resulted in the establishment of a microbial population in the contactors, particularly the first one. Undoubtedly, some of the organic matter removed in the contactors was removed through biological metabolic activity. This poses the question as to whether or not the organic matter that survives carbon treatment is qualitatively and quantitatively the same whether or not the contactors are operated anaerobically or aerobically. It probably is not since the metabolic pathways are different and result in different end products. Possibly then, the magnitude of the

organic content in carbon treated effluent could be influenced by operating conditions imposed on the contactors.

Second, operation of the contactors anaerobically is probably not desirable because of the ultimate problem of removing the hydrogen sulfide gas in the effluent. Air stripping would create odor problems. Oxidation to sulfate with chlorine or ozone could be costly. Costs involved, however, could be compared to the costs of oxygenating the contactors.

Summary and Conclusions

The results of the work thus far show that the treatment of primary effluent by lime clarification and activated carbon produces an effluent of good quality suitable for discharge. Averaged over a five million gallon throughput, effluent TOC and BOD were 10 mg/l with an overall range of 2-23 mg/l. Effluent turbidity averaged less than 2 Jackson turbidity units. Phosphate removals were consistently 90 percent or better. These characteristics are consistent with those associated with good quality secondary effluent plus the added bonus of phosphate removal.

Carbon contactor performance to date suggests that the lead contactor will treat 4000 gallons of lime clarified primary effluent per pound of carbon before requiring replacement. This projects a carbon make-up cost of \$0.07/1000 gallons without recovery of carbon, and, possibly, less than \$0.01/1000 gallons if the carbon is regenerated. These costs suggest that carbon treatment may be competitive with biological treatment as a means of removing soluble organics from primary or raw wastewater. However, sufficient information is not presently available to positively conclude this.

The results presented must be considered in the light of certain factors. First, the system was run at steady flow. Second, the feed to the system was a weak to moderate strength domestic wastewater. How the system would respond to a number of magnitudes of change in these factors is presently only speculative.

It is concluded that: (1) wastewater treatment to a quality level comparable to that achieved by good conventional methods is technically feasible using lime clarification and activated carbon treatment, and (2) projected costs based on carbon contactor performance thus far suggest that the removal of soluble organics from raw wastewater by activated carbon will be economically attractive.

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APPENDIX

Nitrogen Data

Some nitrogen data were gathered during the latter part of the study to determine the magnitude of the nitrogen forms present in lime clarified and carbon treated primary effluent. These data are given in Table 7. As can be seen, there was a substantial increase in ammonia nitrogen during carbon treatment. This is probably attributable to the ammonia produced by the hydrolysis of cellular matter present in the suspended organic matter reaching the carbon contactors. This is evidenced by the decrease in organic nitrogen across the carbon contactors. Nitrite and nitrate content of the final product was always less than 0.2 mg/l.

The amount of ammonia nitrogen present is typical of that found in most good quality secondary effluents since few conventional activated sludge treatment plants nitrify. Probably the organic nitrogen is somewhat less than that found in conventional secondary effluent.

TABLE 7 - NITROGEN BALANCES AROUND SYSTEM⁽¹⁾

	<u>NH₃-N</u>	<u>Org-N</u>
Primary Effluent	11.5	4.2
Lime Clarified Primary	13.2	2.1
Lime Clarified-Carbon Treated Primary	16.8	1.0

(1) Based on 2 MG. All data in mg/l.

TABLE 8 - ORGANIC PARAMETER RATIOS

<u>BOD/TOC Ratio</u>		
Lime Clarified Primary	$\frac{25.8}{22.0} = 1.17$	$\frac{26.5}{23.2} = 1.14$
Carbon Contactor No. 1 Product	$\frac{15.5}{15.5} = 1.00$	$\frac{12.7}{11.2} = 1.13$
Carbon Contactor No. 2 Product	$\frac{11.4}{10.9} = 1.05$	$\frac{11.0}{9.6} = 1.15$
Carbon Contactor No. 3 Product	$\frac{11.9}{11.6} = 1.03$	$\frac{9.0}{9.6} = 0.94$

Average of all ratio results = 1.08 = $\frac{\text{BOD}}{\text{TOC}}$

COD/TOC Ratio

Lime Clarified Primary	$\frac{79}{22} = 3.59$	$\frac{72.0}{23.2} = 3.10$
Carbon Contactor No. 1 Product	$\frac{37.3}{15.5} = 2.4$	$\frac{40.2}{11.2} = 3.57$
Carbon Contactor No. 2 Product	$\frac{27.7}{11.6} = 2.39$	$\frac{36.4}{9.6} = 3.79$
Carbon Contactor No. 3 Product	$\frac{27.4}{10.9} = 2.51$	$\frac{35.5}{9.6} = 3.68$

Average of all ratio results = 3.13 = $\frac{\text{COD}}{\text{TOC}}$

TABLE 9 - TOC DATA PER MILLION GALLON INCREMENT OF THROUGHPUT

Gallons Throughput	Feed TOC, mg/l	Contactor Product TOC, mg/l		
		1	2	3
1035000	25.8	13.1	11.3	10.6
2005000	21.3	14.0	11.6	10.8
3040000	18.7	12.9	9.1	8.4
4058000	24.3	19.6	14.8	13.4
5024000	32.9	19.6	11.8	9.6
Average	24.6	15.8	11.7	10.6

TABLE 10 - LBS TOC APPLIED, REMOVED, AND REMAINING
PER MILLION GALLON OF THROUGHPUT

LBS TOC APPLIED PER MILLION GALLON INCREMENTS OF THROUGHPUT						
	1	2	3	4	5	Total
Contactore 1	223	173	161	206	265	1028
Contactore 2	113	113	111	166	158	661
Contactore 3	98	94	79	126	95	492

LBS TOC REMOVED PER MILLION GALLON INCREMENTS OF THROUGHPUT						
	1	2	3	4	5	Total
Contactore 1	110	60	50	40	107	367
Contactore 2	15	19	32	40	63	169
Contactore 3	7	7	7	12	18	51

LBS TOC REMAINING PER MILLION GALLON INCREMENTS OF THROUGHPUT						
	1	2	3	4	5	Total
Product	91	87	72	114	77	441

$$\text{TOC Removed, \%} = \frac{\text{Total Removed}}{\text{Total Applied}} = \frac{587}{441 + 587} = 57$$

TABLE 11 - LBS TOC APPLIED AND REMOVED PER LB CARBON
PER MILLION GALLON INCREMENT OF THROUGHPUT

LBS TOC APPLIED PER LB OF CARBON FOR MILLION GALLON INCREMENTS OF THROUGHPUT						
	1	2	3	4	5	Total
Contactora 1	.043	.072	.067	.086	.110	.430
Contactora 2	.047	.047	.046	.069	.066	.275
Contactora 3	.041	.039	.033	.053	.040	.205

LBS TOC REMOVED PER LB OF CARBON FOR MILLION GALLON INCREMENTS OF THROUGHPUT						
	1	2	3	4	5	Total
Contactora 1	.046	.025	.021	.017	.045	.153
Contactora 2	.006	.008	.013	.017	.026	.070
Contactora 3	.0029	.0029	.0029	.005	.008	.021

ADVANCED WASTE TREATMENT OF
SECONDARY EFFLUENT WITH ACTIVATED CARBON

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Introduction

The past decade has seen a fundamental change in our concepts of waste treatment and pollution control. Originally, the treatment of municipal wastes was primarily concerned with the preservation of public health. Next we became concerned with esthetic concepts such as the elimination of visible signs of pollution and the maintenance of oxygen levels for sustenance of marine life in receiving waters. In the last decade two new concepts have been developed. The first is that in many areas water is becoming scarce so that it may be necessary to use water more than once. The second is that natural waters should be maintained in a condition of purity so that the overall impact of water use on the environment is minimized. Both of these concepts require treatment of wastewaters that is fundamentally different from the treatment that was acceptable at a time when our only concerns were with public health, esthetics, and oxygen depletion. In this context activated carbon adsorption is the key unit process in the treatment of wastewater to produce effluents meeting our present requirement for effluent quality and receiving water preservation.

The use of coal in water treatment goes back to the last century. In 1883, 22 water plants in the United States were reported to be employing charcoal filters. These were later abandoned because of the low adsorptive capacity of the charcoal. The production of activated carbon was started in 1913 by a predecessor of Westvaco. However, its first recorded application to municipal water treatment was not until 1927 when two Chicago meat packing companies used powdered activated carbon to remove tastes from their water supplies. During the 1930's, the use of powdered activated carbon to remove tastes and odors caused by traces of dissolved organics spread rapidly.

In 1960, the U. S. Public Health Service embarked on the Advanced Waste Treatment Research Program with two stated goals - to help abate water pollution problems and, more startling in concept, to renovate water for direct and deliberate reuse. The program focused early on adsorption as the most promising process for achieving its stated goals, and on activated carbon as the most feasible adsorbant. A series of studies were commissioned by the Public Health Service and, since 1966, the Federal Water Pollution Control Administration, to evaluate the feasibility of activated carbon adsorption for wastewater renovation. These studies concentrated on two aspects - the physical configuration for the

most economical use of the adsorptive properties of the carbon and the reactivation of the carbon for reuse.

Based on results of these studies, several demonstration plants were designed to obtain data from commercial equipment. One of these plants is a joint effort of the County Sanitation Districts of Los Angeles County and the Federal Water Pollution Control Administration and is located at Pomona, California. The plant includes five carbon contactors and has a capacity of 400 gpm. A second plant is located at Lake Tahoe, California and is operated by the South Tahoe Public Utility District. The plant has a capacity of 7.5 mgd. A third plant, located on Long Island, New York, is the subject of this paper.

Background

Nassau County occupies 291 sq. mi. of Long Island immediately adjacent to the City of New York. During the last two decades, the County has experienced an explosive growth of population and water consumption. Since the County's only source of water supply is the local ground water, whose safe yield is limited by its rate of recharge, the continuation of this growth presages a crisis in water supply. Over-pumping results in lowering of the ground water levels and intrusion of salt water in the aquifer.

Development of the County has also decreased the rate of recharge of the ground waters. The installation of public sewer system diverts wastewater previously recharged into the ground through septic tanks and cesspools to ocean outfalls. Present projections indicate that, if present trends continue, the net amount of water withdrawn from the aquifers will exceed the rate of recharge by 1977.

One plan to increase the permissible withdrawals is to create a hydraulic barrier in the aquifer. This barrier would prevent a natural outflow in the aquifer, estimated to be of the order of 30 mgd which is now lost to the sea. It would also prevent the intrusion of salt water into the aquifer which is already becoming a problem in some areas of Nassau County. The barrier would be formed by injecting tertiary treated wastewater through a series of recharge wells along the southern perimeter of Nassau County.

Water Quality Requirements

In order to provide water of a quality necessary for injection into public water supply aquifers, the effluent of the existing sewage treatment plant must receive additional treatment to meet the following requirements:

1. U. S. Public Health Service Standards for drinking water.
2. Economical operation of injection system.
3. Chemical compatibility with natural ground water.

The drinking water standard was adopted primarily in order to gain public acceptance of the concept of injecting treated wastewater into an aquifer which is used as a source of public water supply. Present plans provide for maintaining at least one mile separation between injection and water supply wells. This distance will insure that no particulates or bacteria will reach the water supply wells. Nevertheless, it was decided as a policy matter that the water as injected must meet the standards for drinking water.

Advanced Waste Treatment Process

The advanced waste treatment process used to achieve these water quality criteria consists of coagulation with alum, filtration, adsorption on activated carbon and disinfection with chlorine.

Standards of water quality for economical operation of the injection system are being developed as part of the demonstration project. From injection tests conducted thus far, it is apparent that particulates must be maintained at the lowest possible level. Turbidity levels of less than 0.5 J.U. appear to be desirable. Low levels of dissolved gases were considered desirable during the early stages of the project but do not appear to be as critical as they were thought to be. Turbidities in excess of 1.0 Jackson Units result in rapid buildup of pressure required to inject at a given rate of flow.

The principal problems of compatibility involve iron and phosphate concentrations. Iron precipitates in the aquifer, causing irreversible clogging of the formation. The role of phosphates is not yet fully understood. However, changes in phosphate concentration between water injected and injected water recovered have been observed, leading to the conclusion that phosphates interact with the fine clayey sands that comprise the aquifer.

Effluent from the final sedimentation tanks of the Bay Park Sewage Treatment Plant is pumped into a clarifier, where alum and coagulant aids are added. Sludge recirculation is employed to improve coagulation and overcome sudden changes in water quality. Flow then passes by gravity to two mixed media filters operated in parallel, each containing a 36-inch bed of anthracite above a 12-inch layer of sand. Filter backwash is automatic, and includes facilities for air scour, surface wash, and high and low rate backwashing.

Filter effluent is pumped through four granular activated carbon adsorbers operating in series. Adsorber piping is arranged so that the order of the vessels can be rotated to change the sequence of flow and insure the most efficient utilization of carbon. Upon exhaustion, carbon is moved hydraulically to a regeneration system. Here the carbon is restored to its original activity by controlled burning off of the adsorbed organics in a multi-hearth furnace.

The renovated water is disinfected with chlorine prior to being pumped about one half mile to the test injection site. The injection facilities consist of a storage tank, degasifier for removal of residual chlorine and dissolved gases, injection and redevelopment pumps, the injection well

and 12 observation wells. The injection well is 36 inches in diameter by 500 ft. deep, and contains an 18 inch casing which supports a 16 inch screen set between elevations - 420 and 480 ft. The annular space surrounding the screen has been backfilled with graded sand and contains an observation well and geophysical probes. Other observation wells are located up to 200 ft. from the injection well.

Carbon Adsorption System

The design of a carbon adsorption system for the treatment of wastewaters involves consideration of the following parameters:

Type of carbon - granular or powdered
Physical configuration - upflow or downflow, or mixed
number of stages, parallel or series, packed bed or expanded
bed, external regeneration or continuous flow
Carbon capacity - detention time, dosage rate
Method of operation - pure adsorption, filtration, biochemical

For the Nassau County project, granular carbon was selected over powdered carbon primarily because of the state of the art of carbon regeneration. Powdered carbon has some advantages over granular carbon. Its initial cost is lower, 7½ cents per pound against 30 cents for granular carbon. It reacts faster and more completely, and its dosage can be adjusted to meet changes in the composition of the influent to the system. On the other hand, even the cost of powdered carbon is not sufficiently low to permit its discard after a single use. Some experimental work is now in progress on powdered carbon regeneration, but it has not yet reached the stage where a full scale demonstration plant can be designed. Dewatering and incineration are the most feasible methods of disposal of waste powdered carbon.

Granular carbon has been in industrial use for many years and the technology for its regeneration is well established. It has the additional advantage of providing a margin of safety in operation that powdered carbon does not provide. Sudden changes in influent composition are common in wastewater treatment. If the dosage of powdered carbon is not adjusted to meet these changes, the effluent quality will reflect the insufficient dosage. Granular carbon has the capacity to withstand substantial changes in the influent composition with a much reduced effect on the effluent quality. This aspect and the availability of the regeneration technology were the major factors in the selection of granular carbon for the Bay Park project.

Even after the choice has been made between granular and powdered carbon, some further selectivity is required. Activated carbons are manufactured from a variety of raw materials such as coal, wood, nut shells and pulping wastes. A carbon that must undergo multiple regenerations must have the capability of being handled with a minimum of deterioration or abrasion. Since coal derived carbons are harder and denser than other carbons, this type of carbon was specified for the Bay Park project.

As a result of operating experience the additional requirement that the carbon contain less than 0.5% of iron by weight has been added.

The limit on the iron also forced a change in the gradation, so that the specifications for carbon could be met with a commercially available product. The original carbon had a size range of 8 x 30 (passing a standard No. 8 mesh sieve, but retained on a No. 30 sieve). The replacement carbon has a size range of 14 x 40.

A number of physical configurations have been suggested for activated carbon adsorption systems. These include upflow-expanded bed, upflow-compacted bed, downflow-single stage, downflow-multistage, and a quasi-countercurrent system, in which the flow is down in the first unit and up in the second unit, exhausted carbon being continuously removed in the first unit and regenerated or makeup carbon being added continuously in the second.

Upflow systems have the advantages of being less susceptible to plugging and more adaptable to continuous countercurrent operations, which in theory yield the most efficient carbon utilization. Downflow systems require periodic backwashing to prevent the buildup of headloss and multistaging to approach countercurrent operation. The differences in equipment costs are of a second order compared with the costs of regeneration and makeup. Downflow systems are mechanically simpler and have greater flexibility as to rates of flow that can be applied. For the Nassau County project, a four-stage downflow system was selected. The four vessels containing the carbon are piped so that they are in series, with each unit capable of being the lead unit. In normal operation, the flow is applied to the vessel containing carbon closest to exhaustion. As it passes from unit to unit, it encounters successively more active carbon, until in the last unit it passes through the most recently regenerated carbon.

When the organic content of the product water starts to exceed the desired level, the first unit is taken off the line and the carbon in this unit is transferred hydraulically to the dewatering tank of the carbon regeneration system. As soon as the transfer is completed, regenerated and makeup carbon from the storage tank is pumped back into the unit. The unit is then put back on the line, but in the last position in the sequence. In this manner, the countercurrent mode of the operation is maintained.

Laboratory bench and pilot plant studies were relied upon to furnish other design data. Laboratory bench studies were used to derive adsorption isotherms, which give some indications as to carbon dosage. Column tests were then used to determine the required contact time. The hydraulic loading then becomes a matter of convenience for the design of the equipment. For the Nassau County project, the following design parameters were adopted, based on over a year's pilot plant operations:

Total contact time (empty bed volume) 24 min
Hydraulic Loading (approach velocity) 7.5 gpm/sq ft.

The combination of these factors resulted in a vessel diameter of 8 ft and a bed depth of 6 ft in each vessel. Each of the vessels contains 300 cu ft or about 9,000 lb of carbon. The rate of exhaustion has been about 800 gal per pound of carbon or 1.25 lb per 1000 gal treated.

Economics

Unit costs for the advanced waste treatment process are given in the following table. The table is based on a COD reduction 90% from 50 mg/l in the secondary effluent to 5 mg/l in the product water and a phosphate reduction of 90% from 30 mg/l (as PO₄) to 3 mg/l.

Estimated Unit Costs

Cents per 1000 gal	Plant Capacity		
	1 mgd	10 mgd	100 mgd
Process costs, less labor			
Coagulation	4.9	3.5	3.2
Filtration	1.8	1.1	1.0
Carbon adsorption	<u>6.3</u>	<u>4.5</u>	<u>4.0</u>
	13.0	9.1	8.2
Operating labor	<u>28.0</u>	<u>5.6</u>	<u>1.8</u>
	41.0	14.7	10.0

Annual charges have been assumed at 8.5% of the capital costs and include both debt service and an allowance for maintenance, repair and replacement. Unit costs also assume continuous operation at design capacity (100% load factor). The costs are for treatment only and do not include transmission or injection facilities.

Conclusions

The Nassau County project is demonstrating the feasibility of treating secondary effluent with a physiochemical process sequence involving activated carbon to remove organics resistant to biological treatment. The product water meets U.S. Public Health Service Standards for drinking water and has physical properties such as turbidity, color or odor equivalent to those of the domestic water supply. It can be recharged into the ground without causing any deterioration of the aquifer. Based on test operations now in progress, it is believed that the concept of using treated wastewater for hydraulic barriers against seawater intrusion is technically feasible.

The project opens up new potentials for water reuse in areas where fresh water supplies are scarce. Wastewater is always available where there are public water supply and sewerage systems. Newly adopted water quality standards will require many communities to provide more than conventional secondary treatment. With activated carbon treatment, the product water can now be made available for many forms of beneficial reuse requiring high quality water.

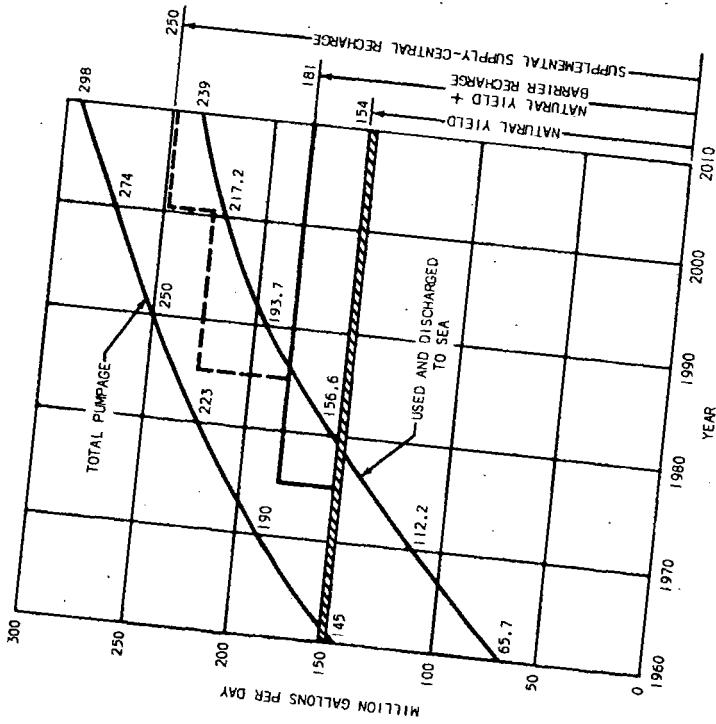


Figure 1
Water Requirements and Supply

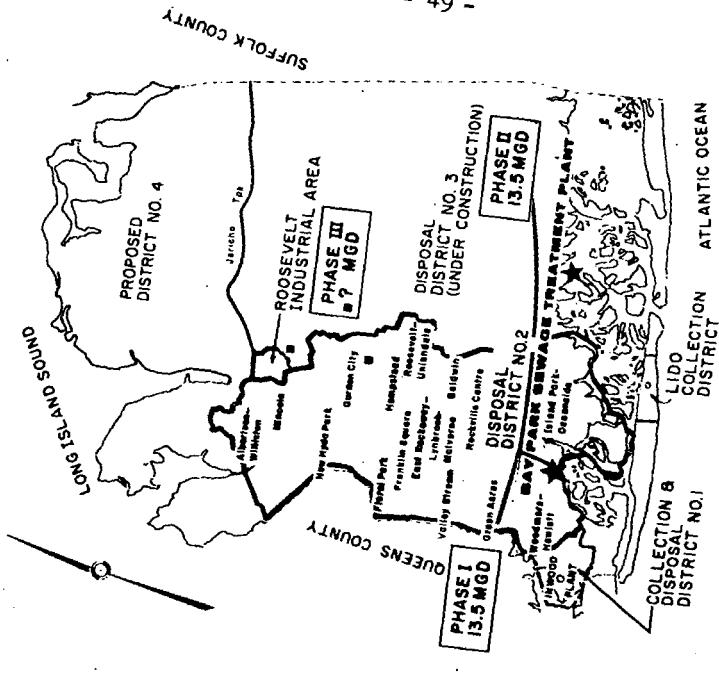


Figure 2
Proposed Recharge System

USE OF ACTIVATED CARBON FOR MINE WATER TREATMENT

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ABSTRACT

Extremely rapid oxidation of the ferrous iron in raw acid mine water is possible without the use of costly oxidants and precipitating agents. This was achieved by catalytic oxidation in an activated carbon-air-mine water system. The ferrous iron content of an acid mine water flowing through aspirated, granular, activated carbon was reduced from about 700 to 10 ppm in less than 1 minute. Incorporating a catalytic oxidation step in the treatment of acid mine water containing ferrous iron would facilitate treatment by virtual elimination of aeration equipment and precise stoichiometric control of pH. Limestone would replace expensive alkaline reagents, thus lowering reagent costs. Finally, smaller settling ponds would result through sludge volume reduction. The process would essentially consist of oxidation, neutralization, and settling of solids.

INTRODUCTION

Mine drainage is now classified as an industrial waste. Although mine waters vary widely in chemical composition, the most damaging constituents--acid sulfate and/or iron--are invariably present, and economical removal of these pollutants constitutes the problem of mine water treatment at the present time. From an economic standpoint, one of the most difficult technical aspects of mine water treatment is iron removal. If the iron is in the ferric state (Fe^{+++}), removal would be relatively simple and inexpensive. Iron, aluminum, and acid could be effectively removed from mine water by raising the pH to about 6 with a cheap alkaline agent such as limestone. However, in most mine waters the iron is predominantly in the ferrous form (Fe^{++}). Ferrous iron is more difficult and more expensive to remove, especially when present in appreciable quantity.

Conventional mine-water treatment processes consist of lime neutralization, aeration, and sludge settling. Aeration is utilized primarily to oxidize ferrous iron because less sludge results when iron is in the ferric form, and savings in reagent costs can be realized with the use of lower pH. If aeration were not applied, a high pH (about 9) would be needed to guarantee a low soluble iron content (<7 ppm) in the treated water. Larger sludge volumes would result because of a more flocculent precipitate and thus further complicate the sludge disposal problem.

An inherent disadvantage to this mode of treatment is the difficulty of process control. Neutralization of acidity is not achieved until most of the iron has been converted to the insoluble ferric state. Therefore, regulation of the alkaline reagent feed cannot be established by a set pH limit for efficient operation without continuous monitoring of acidity and ferrous iron load. Some semblance of control is possible if the raw mine water feed is equilibrated in holding ponds and aeration equipment capabilities and performance are firmly established. But sudden changes in the acid and iron load may result in excess alkalinity or acidity in the treated water. Only experience and trial and error, therefore, can provide some degree of control in such a mine water treatment process.

When acid mine water is exposed to the atmosphere the ferrous iron oxidizes to ferric iron. The oxidation rate, however, is exceedingly slow, even with the aid of aeration (1).^{1/} To accommodate large volumes of mine water having appreciable ferrous iron, prohibitively large basins and aeration facilities would be required. Chemical oxidants can be used to accelerate the rate of oxidation, but a brief analysis of the stoichiometric requirements and the unit cost of oxidants show that such oxidation would be too costly. Certain substances (2) enhance the oxidation of ferrous iron, but none are used in practice.

The best approach to acid mine water treatment is to convert the ferrous iron to the ferric form prior to neutralization. Complete iron removal would then readily be achieved by simply increasing the pH above 4.5.

Recent developments (2) in the Bureau of Mines Pittsburgh Mining Research Center laboratory indicate that extremely rapid ferrous iron oxidation in an acid mine water is possible without the use of high-priced chemical oxidants, without expensive precipitating agents, and without extensive aeration equipment. This catalytic oxidation reaction was achieved in an activated carbon-air-mine water system. Activated carbon accelerates the rate of oxidation of ferrous iron in sulfuric solutions (4). Acid mine water effluents are dilute solutions of sulfuric acid and acid salts. Although only an exploratory effort was made with granular activated carbon as a means of catalyzing the air oxidation of ferrous iron in acid mine water, the initial results are promising. The brevity of this study did not allow defining the reaction kinetics or resolving the factors affecting the activated carbon-air-acid mine water system. Therefore, only a general description of the test and the test results can be made.

EXPERIMENTAL WORK

The carbon used throughout the tests was a commercial-type, coal-base, activated carbon sized 12 by 40 mesh. Mine water containing 613 to 945 ppm Fe⁺⁺, 810 to 960 ppm total Fe, 2,100 to 2,400 ppm total acidity, and with a pH ranging from 2.70 to 3.15 was used for the tests. A typical analysis of the mine water is shown in table 1.

TABLE 1. - Typical mine water analysis

pH	3.10
Eh	6.05
Total acidity	ppm 2,370
Fe ⁺⁺	ppm 830
Total Fe	ppm 965
Ca ⁺⁺	ppm 220
Mg ⁺⁺	ppm 66
SO ₄	ppm 4,512
Dissolved solids	ppm 7,080

The experimental apparatus consisted of a glass cylinder with a fritted disk connected to a filtering flask. The disk supported the granular carbon and allowed passage of air and water. A side tube in the filtering flask was connected to an aspirator. The same batch of activated carbon (200 grams, 12 by 40 mesh) was used in all the tests. Two different glass cylinders were used: In one the carbon column was 6.5 cm in diameter and 12.5 cm in depth; in the other (used in later tests) the carbon column was 3.8 cm in diameter and 42 cm in depth. The longer cylinder was used to increase flow through time. A synthetic porous sponge supported the granular carbon in the cylinder and prevented the loss of

^{1/} Underlined numbers in parenthesis refer to items in the list of references at the end of this report.

carbon particles. A sketch of the activated carbon oxidation apparatus is shown in figure 1.

Air was aspirated through the carbon column before the mine water was added and continuously throughout the test until most of the water had passed through the carbon. The mine water volumes flowing through the carbon column ranged from 175 to 1,070 cu cm per batch (test); airflow rates ranged from 0 to 3,500 cu cm per min.

Prior to testing, the batches of raw mine water were analyzed for pH, ferrous iron, and total iron. Identical analyses were made immediately after testing on the effluent from the activated carbon column. All tests were conducted at room temperature. A total of 65 separate runs, consisting of about 25 liters of raw mine water, were made in the same carbon column over a period of about 2 weeks.

TEST RESULTS

The pH of a suspension of the activated carbon in distilled water was about 6.6. With successive additions of the acid mine water (pH 2.70 to 3.15), the pH of the effluent decreased steadily and appeared to level off at a pH of 2.3 to 2.5 when ferrous iron oxidation was virtually complete. The raw mine water was practically colorless, but the effluent from the carbon column was a deep amber color owing to the presence of a hydroxylated ferric sulfate.

The ferrous iron content (635 to 920 ppm) of the raw mine water was reduced to about 10 ppm after flowing through the carbon column for less than 1 minute. By contrast, aeration of an acid mine water (1) in the absence of an oxidizing agent, except for bacteria which may have been present, reduced the ferrous iron concentration from 261 to about 10 ppm in 168 hours. While a direct comparison cannot be made between these results, they do indicate the enormous increase in the ferrous iron oxidation rate that can be achieved with activated carbon.

The test results are summarized in table 2. These preliminary results indicate that activated carbon catalyzed the air oxidation of ferrous iron in a ferruginous acid mine water. The initial tests also show that the activated carbon must be preconditioned to an acidic state for the catalytic reaction to take place. The low ferrous iron content in the effluent, beginning with run 26, was consistently maintained to the end of the experiment. It was likely that the activated carbon was adequately conditioned at this time. For these tests the total iron (practically all in the ferric form) in the effluent represents about 65 percent of the total iron in the feed.

After 25 liters of a ferruginous mine water had passed through the carbon column, there was no appreciable loss in catalytic efficiency and no visible sign of surface fouling or solids deposition on the surface of the carbon particles, although a portion of the iron was adsorbed by the carbon. It is possible that only an insignificant amount of iron would be held by the carbon in a continuous flow operation. If the pH of the system were maintained below 2.5, ferric hydrolysis would be negligible. The air requirements for oxidation of ferrous iron might be minimal. Run 60, conducted without aspirating air through the carbon column, produced equally effective ferrous iron removal.

TABLE 2. - Batch test results of catalytic oxidation of ferrous iron in acid mine water with activated carbon

Date, 1969	Run	pH	Feed			Feed time, min	Volumic collected, cu cm	Total aspi- rating time, min	Flow through time, min ¹	Air aspi- rating rate, cu cm per min ²	Effluent			
			Fe ⁺⁺ , ppm	Total Fe, ppm	Vol- ume, cu cm						pH	Fe ⁺⁺ , ppm	Total Fe, ppm	
April 15	1	2.80	613	-	260	3.0	250	5	-	-	4.50	417	-	
	2	2.80	613	-	260	4.0	250	5	-	-	4.30	230	-	
	3	2.80	613	-	260	5.0	250	5	-	-	4.10	272	-	
April 16	4	2.80	613	-	260	3.0	250	6	-	-	3.95	175	-	
	5	2.80	613	-	260	3.0	250	7	-	-	3.75	125	-	
	6	2.80	613	-	260	3.0	260	8	-	-	3.60	130	-	
	7	2.80	613	-	260	3.5	235	8	-	-	3.45	105	-	
	8	2.80	613	-	260	3.5	220	8	-	-	3.35	75	-	
	9	2.80	613	-	260	3.0	225	9	-	-	3.50	80	-	
	10	2.80	613	-	260	3.0	230	10	-	-	3.35	85	-	
	Extracted excess water						-	125	9	-	-	3.15	190	-
	11	2.80	613	-	260	3.0	175	10	-	-	3.05	205	-	
	12	2.80	613	-	260	1.5	225	20	-	-	2.90	220	-	
13	2.80	613	-	260	1.5	210	20	-	-	2.70	165	-		
14	2.80	613	-	260	1.0	200	18	-	-	2.60	145	260		
Cleaned fritted disk														
April 17	15	2.75	745	-	260	1.5	260	5	-	-	2.55	245	-	
	16	2.75	745	-	260	2.0	260	5	-	-	2.55	270	-	
	17	2.75	745	-	260	3.5	260	9	-	-	2.50	275	575	
	18	2.75	745	-	260	3.0	260	5	-	-	2.50	90	-	
	19	2.75	745	-	260	3.0	260	6	-	-	2.45	72	-	
	20	3.15	945	-	260	3.0	260	8	-	-	2.45	70	-	
	21	2.85	920	-	260	3.0	260	10	-	-	2.45	10	215	
Cleaned fritted disk														
April 21	22	2.90	920	-	260	1.5	250	4	-	-	2.45	35	420	
	23	2.90	920	-	750	-	750	12	-	-	2.45	85	-	
	24	2.90	920	-	260	-	250	5	-	-	2.40	70	-	
	25	2.90	920	-	260	-	240	4	-	-	2.40	55	-	
	26	2.70	660	-	260	.5	240	8	-	-	2.50	5	-	
	27	2.70	660	-	260	2.0	250	10	-	-	2.45	2	250	
	28	2.70	660	-	260	.8	250	15	-	-	2.35	2	280	
Cleaned fritted disk														
April 23	29	2.70	900	-	260	1.0	260	4	-	-	2.35	5	-	
	30	2.70	900	-	260	1.0	260	6	-	-	2.30	5	550	
	31	2.70	900	-	260	2.0	250	8	-	-	2.40	5	-	
	32	2.90	800	960	260	3.0	250	11	-	-	2.40	<2	365	
	33	2.90	800	960	260	3.0	250	14	-	-	2.45	<2	430	
	Cleaned fritted disk													
	34	2.90	800	960	260	1.0	260	5	-	-	2.40	5	510	
	35	2.90	800	960	260	3.0	260	10	-	-	2.35	5	540	
	36	2.90	800	960	260	3.0	260	13	-	-	2.35	<2	490	
	37	2.90	800	960	260	4.0	260	21	-	-	2.35	<2	535	

See footnotes at end of table.

TABLE 2. - Batch test results of catalytic oxidation of ferrous iron in acid mine water with activated carbon--Continued

Date, 1969	Run	Feed				Feed time, min	Volume collected, cu cm	Total aspirating time, min	Flow through time, min ¹	Air aspirating rate, cu cm per min ²	Effluent		
		pH	Fe ⁺⁺ , ppm	Total Fe, ppm	Volume, cu cm						pH	Fe ⁺⁺ , ppm	Total Fe, ppm
Cleaned fritted disk													
April 23	38	2.90	800	960	260	0.8	260	3	-	-	2.45	15	560
	39	2.90	800	960	260	1.5	260	4	-	-	2.40	12	653
	40	2.90	800	960	260	1.8	260	4	-	-	2.45	10	647
	41	2.90	800	960	260	2.0	250	5	-	-	2.45	<2	410
	42	2.90	800	960	260	2.0	260	6	-	-	2.40	<2	445
April 24	43	2.80	720	865	260	1.3	-	3	-	-	2.50	<2	420
	Installed long cylinder (3.8-cm-diam, 42-cm-long carbon column)												
April 25	44	2.80	720	865	260	2.0	250	5	-	-	2.35	<2	510
	45	2.80	720	865	260	1.8	260	5	-	2,000	2.45	<2	445
	46	2.80	720	865	260	.6	250	2	0.25	3,500	2.40	15	505
	47	2.80	720	865	245	1.3	225	3	.5	2,000	2.40	<2	520
	48	2.80	720	865	260	1.7	240	3	.6	2,000	2.40	<2	585
	49	2.80	720	865	1,000	5.0	990	8	.5	2,000	2.40	7	710
	50	2.80	720	865	720	3.5	710	6	.5	2,000	2.40	15	715
April 28	51	2.80	720	865	260	1.0	250	3	.5	2,000	2.45	15	550
	52	2.75	655	855	260	1.2	240	3	.6	2,000	2.40	<2	560
	53	2.75	655	855	1,050	5.0	1,035	8	.5	2,000	2.30	10	670
	54	2.75	655	855	1,020	5.0	1,000	8	.5	2,000	2.35	32	710
	55	2.75	655	855	1,070	5.5	1,055	8	.5	2,000	2.45	12	620
May 1	56	2.75	655	855	260	1.5	250	4	.5	2,000	2.35	5	635
	57	2.85	635	810	260	1.3	240	3	.6	2,000	2.45	10	315
	58	2.85	635	810	1,040	5.0	1,020	8	.6	2,000	2.40	10	560
May 2	59	2.85	635	810	995	5.0	980	8	.6	2,000	2.40	35	605
	60	2.85	635	810	260	1.8	250	None	.75	None	2.45	<2	320
	61	2.85	635	810	1,090	5.0	1,075	8	.6	2,000	2.40	25	620
	62	2.85	635	810	635	3.0	615	6	.6	500	2.45	7	490
	63	2.85	635	810	510	2.5	495	5	.6	500	2.50	10	470
	64	2.85	635	810	500	2.5	475	4	.6	3,500	2.45	7	490
	65	2.85	635	810	535	2.6	520	5	.6	250	2.45	15	525

¹Not determined for runs 1-45.

²Approximately 2,000 cu cm per min of air drawn through carbon column for runs 1-44.

DISCUSSION

The exploratory tests conducted with activated carbon and a ferruginous acid mine water indicate that ferrous iron oxidation takes place catalytically at an extremely rapid rate. Further investigation is necessary to determine the factors that may limit the effectiveness of the carbon, to determine the efficiency and effective life of the carbon in a continuous flow system, and to determine whether acid regeneration will restore the carbon to its original efficiency when the surfaces become fouled with solids. Cost and performance standards need to be established also.

Rapid oxidation in a carbon-air-acid mine water system to convert ferrous iron to ferric iron prior to neutralization would greatly facilitate the mine water treatment process and reduce costs to a minimum. Catalytic oxidation would provide distinct advantages:

1. Limestone, the least costly alkaline agent, would supplant the more expensive alkaline agents in common use for neutralization.
2. Stoichiometric relations could be precisely controlled at a pH level which would ensure optimum use of alkaline agent.
3. Aeration after neutralization would be eliminated.
4. The dense, small volume of sludge produced at near neutral pH conditions would significantly reduce the cost of sludge separation and sludge handling.

Other potential advantages include production of practically pure iron oxide by fractional precipitation; maintenance of optimum ferrous-ferric ratios, by means of controlled oxidation, to form dense, low-volume sludges; and the use of more reactive alkaline agents, which can be justified if significant reductions in sludge volume can be attained.

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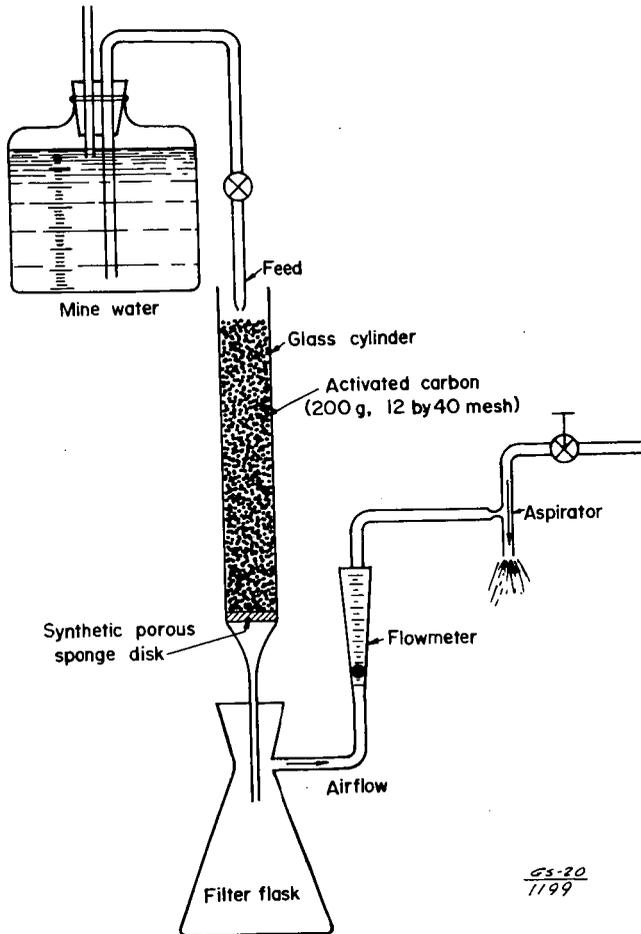


FIGURE 1. - Activated Carbon Oxidation Apparatus.

TREATMENT OF PULPING WASTES BY PERCOLATION
THROUGH GRANULAR BITUMINOUS COAL

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ABSTRACT

A group of experiments on the removal of suspended solids, lignins and their derivatives, and other soluble components causing chemical oxygen demand (C.O.D.) from industrial pulping wastes are summarised. An HVCB coal from Nova Scotia was used for most work. Percolation of a ground wood white water waste (total solids - 1850 ppm) through 28/48 mesh ground coal gave about 80% reduction of suspended solids and 20% removal of the soluble components exerting a C.O.D. Percolation of a sulphite residual cooking liquor (total solids 106,000 ppm) containing mainly lignin derivatives show substantial adsorption of lignins. Reduction of the C.O.D. of a Kraft bleachery effluent was also found. Batch adsorption measurements show Nova Scotia coal capable of adsorping lignins up to 4% of its weight. Coal based treatment may be feasible when suspended solids are the important pollutant, but when lignin content or the soluble C.O.D. is to be lowered this treatment is probably feasible only when coal is used as a pulp mill fuel.