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VAPOR PHASE IMPREGNATION OF ACTIVE CARBONS

Quarterly Progress Report No. 2

April through June 1969

by

D. Marshall Andrews

July 1969

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010

Contract DAAA15-69-C-0302

COMMONWEALTH SCIENTIFIC CORPORATION
500 Pendleton Street
Alexandria, Virginia 22314

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COMMONWEALTH SCIENTIFIC CORPORATION
500 Pendleton Street
Alexandria, Virginia

FOREWORD

The work described in this report was authorized under Project 1B662706A095, CB Physical Protection Investigations (u). This report covers work completed in the period April to June 1969.

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SUMMARY

Work during this period was concerned mainly with the deposition of copper and chrome to produce an impregnated carbon with activity similar to that of an ASC whetlerite. Samples were prepared using the procedures detailed in the first progress report (1) and subjected to various post impregnation treatments in an attempt to illicit CK activity. A laboratory scale break through test apparatus, using HCl gas as the agent, was constructed and used to evaluate the effect of post impregnation treatments on the activity of the copper. Using this test, a treatment was devised which gives vapor impregnated copper coated carbons HCl activity equal to or better than whetlerites.

Nitrogen adsorption isotherms were performed on samples of plain PCC grade CWS carbons, 8% by weight copper vapor impregnated carbons and ASC whetlerite carbons, and pore-size distribution computations made to determine coating penetration. Concentration of impregnants was determined from emmission spectrographic analysis and X-ray diffraction patterns were run in an attempt to identify the chemical structure of the impregnant. Photomicrographs were taken of the carbons surface using the scanning electron microscope as a meansto further determine coating distribution.

A method was developed for depositing chrome as the metal in the pores of the carbon from dicumene chromium. Samples were prepared by this method and treated to oxidize the chrome. Samples were prepared containing copper vapor deposited from CuAA and chrome deposited from dicumene, and sent to Edgewood for CK testing.

Work was also done during this report period on Phase III of the program, the vapor deposition of platinum on activated carbons. A method similar to that developed for vapor impregnation with copper was used to deposit platinum from platinum acetyl acetonate (PAA). Several samples containing platinum in various weight percents were prepared and sent to Edgewood for testing.

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POST IMPREGNATION TREATMENTS

In Progress Report Number 1,(1) a method for the vapor impregnation of active carbons with chromium trioxide and copper was described. Samples prepared using this method, although containing copper and chrome in the proper oxidation states, failed to show any CK activity on toxic agent breakthrough tests performed at Edgewood Arsenal. As a result, post impregnation treatments were performed on the samples in an attempt to produce the CK active form as it exists on whetlerite impregnated carbons. The actual form necessary to produce this activity is now known, however, previous work (2) indicates that the most likely form is that of the basic copper chromate, $CuCrO_4 \cdot 2CuO$ and post treatments were used which by duplicating as much as possible in vapor phase the conditions existing on the whetlerite, gave the best possible chance of forming this compound.

Atmospheric Pressure Treatment

The constituents of the whetlerite solution are: basic copper carbonate, chromic acid, ammonium carbonate, and aqua ammonia. The first attempts at activating the vapor deposited copper and chrome consisted of saturating the 4% copper, 2% chrome trioxide impregnated carbon with ammonia, carbon dioxide and water vapor (Run 17, Table 1) and heating the treated carbon to 150°C in air. In addition, a sample of laboratory prepared Type A whetlerite (Run 16, Table 1) was vapor impregnated with 2% CrO_3, saturated from vapor phase with NH_3 and H_2O and heated to 150° in air. Samples of both preparations were sent to Edgewood Arsenal for CK and PS testing.

Copper is vapor deposited as the metal from CuAA and must be oxidized to the +2 state in order to be active against CK. Although heating the carbon in air should oxidize the copper, a stronger oxidizing compound would insure that the reaction was complete. Hydrogen peroxide was chosen as the oxidizing agent because it can be easily vaporized into the carbon. Samples of 4% copper vapor impregnated carbons were placed in a tube connected at one end to a heated vaporizer containing 3% hydrogen peroxide in water. The peroxide solution was heated and the vapors passed through the carbon. When the carbon was seen to be saturated, the vaporizer was disconnected and carbon dioxide followed by NH_3 gas was passed through the bed. The material was then dried at 150°C, vapor impregnated with CrO_3 (Run 24, Table 1) and once again saturated with NH_3 and H_2O vapor. A final heating to 150°C removed the excess NH_3 and H_2O. Samples prepared by this method were sent to Edgewood Arsenal for CK and PS testing.

TABLE 1

Run #	Date	Carbon History	Reactants	Conc.	Post Treatment	Remarks
16	4/29/69	Plain	Type A Whetlerite Sol.	8%	Heat at 150°C for 3 hrs.	
16(a)	5/5/69	From Run 16	CrO_2Cl_2 vapor	2%	NH_3 & H_2O Sat. from vapor phase, heat at 150°C for 3 hr	Sample sent to Edgewood Arsenal
17	5/6/69	4% Cu vap. impregnated	CrO_2Cl_2 vapor	2%	Same as 16(a) + CO_2	Sample sent to Edgewood Arsenal
18	5/15/69	Plain	CuAA vapor	4%	None	
18(a)	5/19/69	From Run 18	CO_2, H_2O, H_2O_2 NH_3 vapor	Sat.	Heat at 150°C for 3 hr.	
19	5/27/69	Plain	CuAA vapor	4%	None	
20	5/28/69	From Run 18	O_2 + 80°C	30 psi	None	
21	5/29/69	From Run 19	$(NH_4)_2CO_3$ Solid + 80°C	Pressure 100 psi	Heat at 150°C for 3 hr	
22	6/2/69	From Run 19	H_2O_2, H_2O, CO_2 NH_3 vapor	Sat.	Heat at 150°C for 3 hr	
23	6/3/69	From Run 19	H_2O, $(NH_4)_2CO_3$	Sat. Pressure 100 psi	Heat at 150°C for 3 hr	
24	6/3/69	From Run 22	CrO_2Cl_2 vapor	1%	H_2O, NH_3 + heat at 150° for 3 hr	Sample sent to Edgewood Arsenal
25	6/3/69	Plain	Type AC whetlerite Sol.	--	Heat at 150°C for 3 hr	Sample sent to Edgewood Arsenal
26	6/4/69	From Run 23	CrO_2Cl_2 vapor	1%	NH_3 & H_2O sat from vapor phase Heat at 150° for 3 hr	Sample sent to Edgewood Arsenal
27	6/6/69	Plain	CrO_2Cl_2 vapor	1.5%	None	
28	6/6/69	From Run 27	CuAA vapor	4%	NH_3 + H_2O + heat at 150° for 3 hr	Sample sent to Edgewood Arsenal

High Pressure Treatments

The final method of post treatment used to activate the vapor impregnated copper and chrome involved the use of pressure to increase the concentration of the reactants. A piece of galvanized pipe, 2" in diameter, 6" long, was capped at one end and lined with teflon. A valve and a 0-100 psi pressure gauge were fitted to the other end cap. The carbon could now be placed in the tube, sealed, pressurized and placed in an oven. Excess pressure which might build up in the tube was released through the valve.

For the first run using this tube (Number 20, Table I), 4% copper impregnated carbon was pressurized to 30 psi with oxygen and placed in an oven at 80°C for 24 hr. During this time, pressure in the tube rose only slightly. The next run (No. 21, Table I), was made using powdered ammonium carbonate mixed with copper impregnated carbon. Ammonium carbonate decomposes above 58°C at atmospheric pressure to give ammonia, carbon dioxide and water according to the reaction $(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$. By placing ammonium carbonate in the tube, sealing it and heating it above 58°C, this decomposition can be brought about, with the result that the atmosphere in the tube will contain the same constituents as a whetlerite.

Run No. 21 was also made using the sealed tube, however, the copper impregnated carbon was first saturated with water vapor at atmospheric pressure, mixed with powdered ammonium carbonate, and pressurized to 30 psi with oxygen. During heating, pressure in the tube rose above 100 psi and had to be bled off several times. After 24 hr. at 100°C, the sample was removed from the tube and placed in an oven at 150°C for 3 hr, evacuated and vapor impregnated with CrO_3. Following impregnation, the material was saturated with NH_3 and H_2O vapor at atmospheric pressure and heated to 150°C to dry. A sample of this material was sent to Edgewood Arsenal for CK and PS testing.

Initial Cr Deposition

Previously, all vapor impregnated samples were made by first depositing copper and then depositing the CrO_3. Simultaneous deposition could not be achieved because of the imcompatibility of CuAA and CrO_2Cl_2. Initial deposition of CrO_3, followed by deposition of Cu is unfavorable because the high temperature (300°C) necessary for the complete decomposition of CuAA, may cause reduction of the chrome. One sample (No. 27-28) was prepared by this procedure, however, as a test of effects the presence of CrO_3 may have on the deposition of copper.

Plain PCC grade CWS carbon was out gassed under vacuum and was 1.5% by weight CrO_3 vapor impregnated from CrO_2Cl_2. The amount of CuAA necessary to give a 4% by weight Cu impregnation was dry mixed with the CrO_3 coated carbon, placed in a vacuum and heated. At 150°C, a dark brown liquid began to collect in the cold trap, indicating some oxidation of acetyl acetone was occurring. At approximately 250°C, reddish violet crystals, which were later identified as chrome +3 acetyl acetonate, began to appear on the cool neck of the reaction flask. This material is very stable, and does not decompose at 350°C.

When the reaction was complete, indicated by a drop in pressure in the reaction flask, the sample was cooled down and restored to atmospheric pressure. Water vapor followed by NH_3 was bled into the flask to saturate the carbon. The material was then heated to 150° to dry and a sample sent to Edgewood Arsenal for CK and PS testing.

CHROME IMPREGNATION FROM DICUMENE CHROMIUM

The chrome impregnations using dicumene chromium (DCCr), a dark brown liquid at room temperature, were done in the same apparatus used for impregnation with copper. Because of the air and moisture instability of DCCr, the liquid was transfered onto dry, outgassed carbon in a nitrogen atmosphere. A vacuum of approximately 500 μ was drawn on the carbon and heat applied by an oil bath.

Carbon showed the same affinity for DCCr that it has shown for CuAA. At a temperature of approximately 90°C, all of the DCCr had been adsorbed. Decomposition of the reactant began at approximately 150°C and was complete at 350°C. Very little of the DCCr was lost through vaporization out of the reaction flask. A summary of the various runs made with DCCr is in Table II.

Tests on carbon impregnated from DCCr showed that chromium was present as the metal, and would have to be oxidized to the +6 state known to be necessary for CK activity. One sample was prepared (Run #29) and sent to Edgewood for CK testing in the as-plated condition. The other samples were treated in various ways in an effort to oxidize the chrome, and tested for the presence of Cr +6.

Treatment with H_2O and NH_3 in air failed to oxidize the chrome either on

TABLE II

Run #	Date	Carbon History	Reactants	Conc.	Post Treatment	Remarks
29	6/17/69	From Run 23	DCCr	1%	None	Sample sent to Edgewood Arsenal
30	6/18/69	Plain	DCCr	1.5%	None	
31	6/20/69	Plain	CuAA	4%	None	
32	6/23/69	From Run 30	H_2O, NH_3	Sat.	None	No CrO_3
33	6/23/69	From Run 30	$(NH_4)_2CO_3$ solid + 100°C	100 psi	None	No CrO_3
34	6/23/69	From Run 31	DCCr	1%	Sat. with H_2O & NH_3	No CrO_3
35	6/24/69	From Run 31	DCCr	2%	$(NH_4)_2CO_3$ solid 100°C & 100 psi	No CrO_3
36	6/24/69	From Run 31	$(NH_4)_2 CO_3$ solid + 100°C $+O_2$	100 psi	None	
37	6/25/69	From Run 32	CuAA	4%	None	
38	6/26/69	From Run 36	CrO_3, NH_4OH $(NH_4)_2 CO_3$ H_2O sol. 24 hr soak	1%	150°C for 3 hr	Sample sent to Edgewood Arsenal
39	6/26/69	From Run 35	Boiled in H_2O_2 sol.	30%	150°C for 3 hr	Sample sent to Edgewood Arsenal
40	6/26/69	From Run 35	$(NH_4)_2 CO_3$ sol. $+H_2O, O_2$-100°C	100 psi	40 psi O_2 for 24 hr 150°C for 3 hr	Sample sent to Edgewood Arsenal

plain carbon (Run #32) or in the presence of copper (Run #34). Treatment in the sealed tube under pressure also failed to accomplish the necessary oxidation either on plain carbon (Run #33) or in the presence of copper (Run #35).

Finally, a sample of Cu - Cr impregnated carbon was boiled in 30% H_2O_2 solution and heated to 150°C to dry (Run #39). Another sample of the same material was placed in the tube under oxygen pressure of 40 psi for 24 hr. (Run #40) and then dried at 150°C. A third sample of Cu coated carbon was soaked in whetlerite solution containing all of the constituents except $CuCO_3$ (Run #38) and dried at 150°C. All three samples were sent to Edgewood Arsenal for CK testing.

HCl TESTS

The actual mechanism for the removal of CK by ASC whetlerite is unknown, however, the following reaction has been postulated:(3)

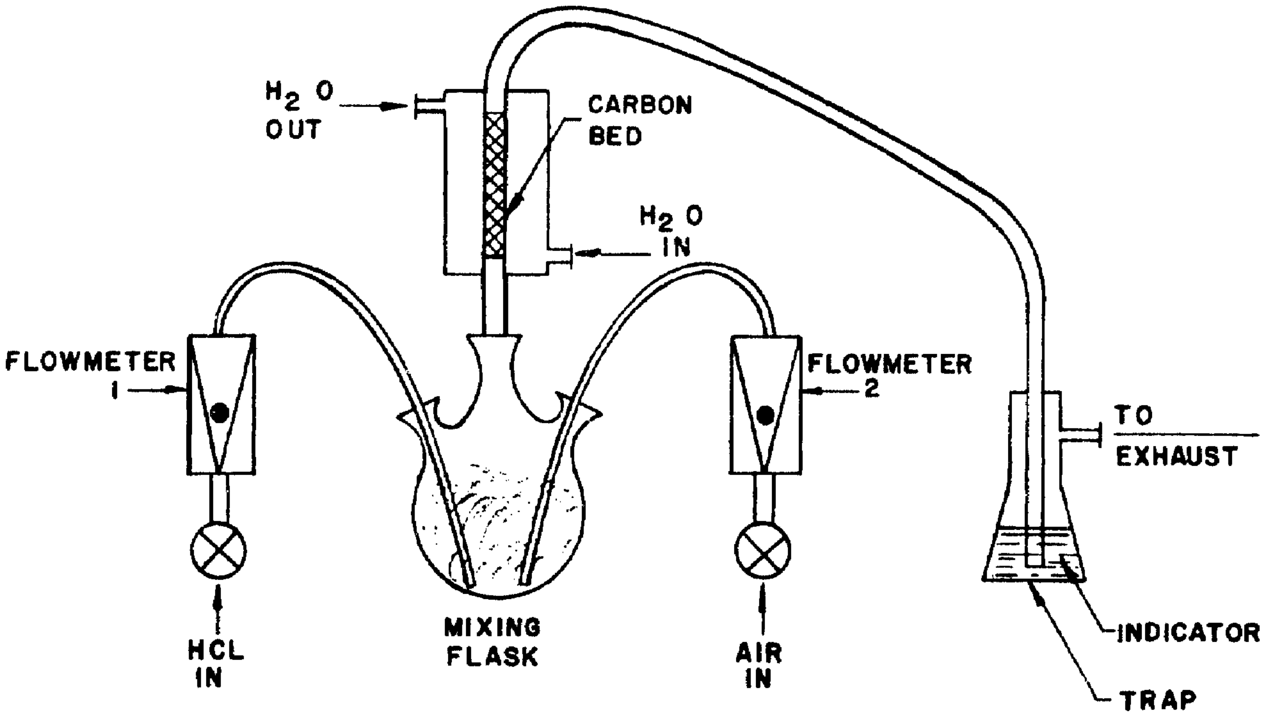
1. $5CNCl + 5H_2O \rightarrow 5HOCN + 5HCl$
2. $2HCl + CuO \rightarrow CuCl_2 + H_2O$
3. $3HCl + Cr \rightarrow 3/2\ Cl_2 + Cr^{+3} + 3H^+$

The first step is catalyzed by +6 chrome in combination with the copper. It can be seen from these reactions that the amount of HCl adsorbed by the impregnated carbons is a measure of the activity of copper, and tests for HCl adsorption should give a means of determining the effect of post impregnation treatment on vapor deposited copper.

The apparatus used for this test can be seen in Fig. 1. Reagent grade HCl gas is brought in through flowmeter 1, while breathing quality compressed air is bled in through flowmeter 2. Both gasses enter the mixing flask containing glass wool to aid homoginization. From the mixing flask, the gasses pass into the carbon bed which is maintained at a constant temperature by the circulation of water around the outside of the tube. When the carbon becomes saturated with HCl, excess gas passes into the trap containing a 0.04% solution of methyl orange indicator in 500 ml H_2O. The break point is indicated by a change in color from orange to red.

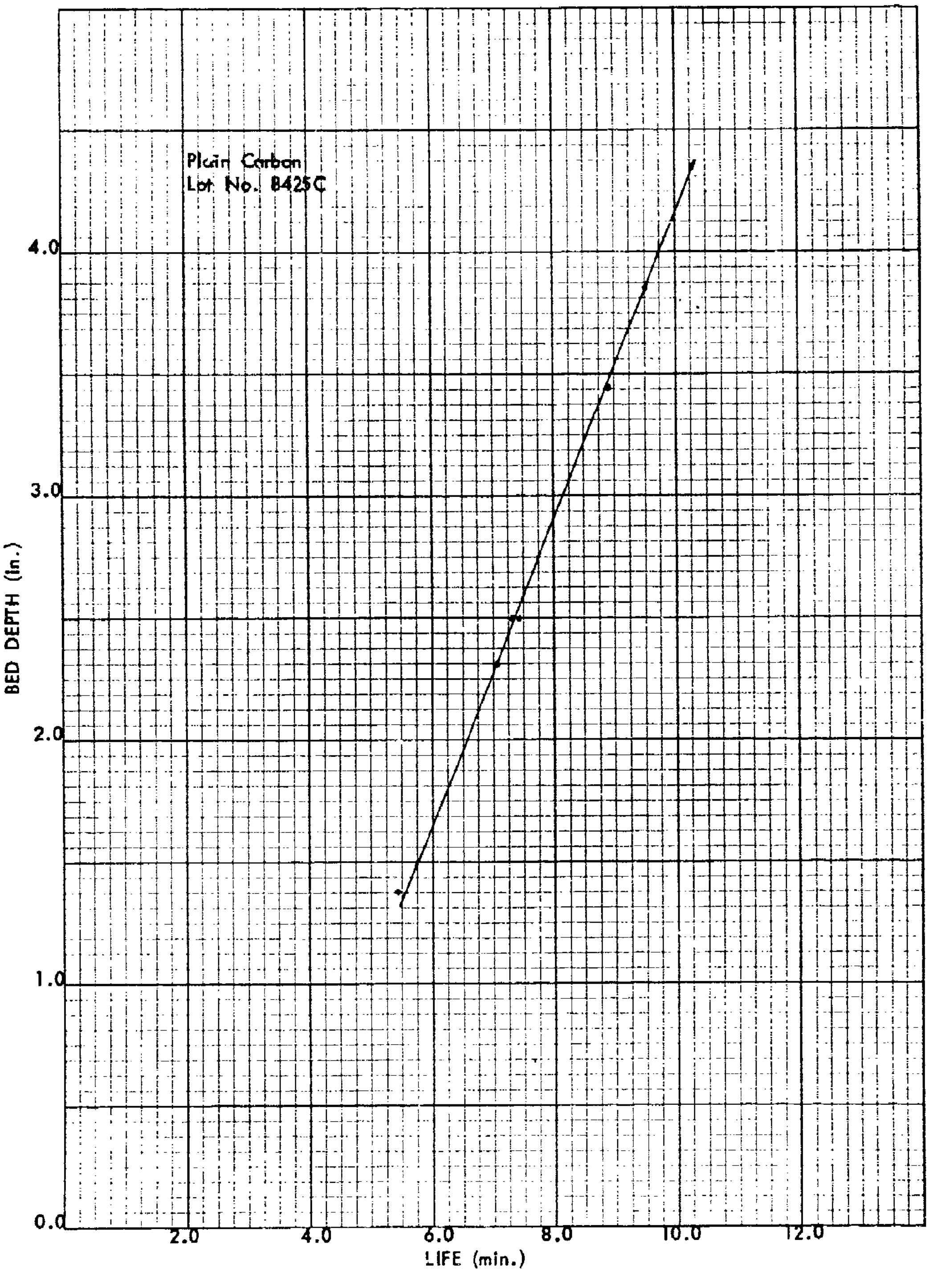
Runs were made using untreated PCC grade CWS carbon, Lot #8425C, as a means

FIGURE I



HCL TEST APPARATUS

FIG. 2 HCL TEST



of comparing the effects of impregnated samples as well as a check on the performance of the system. All samples were heated in an oven at 150°C for 3 hr. before testing in order to minimize the effects of adsorbed water on HCl pick-up. Figure 2 shows the results of tests on blank carbon. The graph is linear and shows a minimum scattering of points, indicating that the system is sufficiently sensitive to yield meaningful data.

Table III is a summary of results of tests performed on samples of treated carbons. Each sample was heated to 150°C for 3 hr. prior to testing and a minimum of 3 runs were performed on each sample. These samples represent each of the treatments given vapor impregnated samples as well as comparative tests on liquid impregnated types A and ASC carbons. The type A whetlerite is a laboratory prepared impregnation (Run 16, Table I), while the type ASC is a sample of production run whetlerite supplied by Edgewood Arsenal.

Comparison of the results is done by two methods. First, the weight percent HCl adsorbed is calculated according to the formula: (grams HCl per minute X life) $\div$ weight carbon = weight % HCl adsorbed. This allows for a direct comparison of samples by eliminating the effects of varying bed depth. Second, the % theoretical HCl pick-up is calculated assuming the reaction #2 above. From this reaction, the theoretical HCl pick-up is equal to: (wt. copper on carbon $\div$ molecular wt. copper) x molecular wt. HCl. The theoretical HCl pick-up is then divided into the amount of HCl adsorbed by the impregnated sample minus the amount adsorbed by the blank carbon, giving the percent of theoretical pick-up.

Tests on vapor impregnated carbons of 1/2%, 2%, and 4% by weight copper show an increase in weight percent adsorbed with increasing copper concentration, as would be expected. However, only a little over half of the theoretical amount of HCl is adsorbed. This would indicate that complete oxidation of the copper to the +2 state is not achieved by heating the carbon to 150°C in air, and a more vigorous oxidation process is necessary.

Runs made on type A and ASC whetlerite, showed a marked increase in weight percent adsorbed. In addition, these carbons picked up about 1-1/2 times the theoretical amount of HCl. The additional HCl is believed to have been picked up by ammonia which is either adsorbed on the carbon and not driven off by heating at 150°C, or is chemically combined in some form with the copper. These results do show that the presence of chrome on the ASC does not significantly increase the HCl pick-up when compared to the type A containing no chrome.

TABLE III

HCl BREAKTHROUGH TEST

TUBE AREA: 1.04 Cm^2

Run #	Date	Inlet conc. g/l	Vol. flow l/min	Linear vol. cm/min	Carbon weight g	Life min	Bed depth	Wt. % Adsorbed	% Theoretical HCl pick-up
Plain carbon B425 C	4/24/69	0.50	0.10	96.2	3.24	8.87	3.46	13.7	--
15 - 1/2% Cu	5/5/69	0.50	0.10	96.2	3.38	9.37	3.61	13.9	--
14 - 2% Cu	5/5/69	0.50	0.10	96.2	3.40	9.92	3.51	14.6	61.5
18	5/16/69	0.50	0.10	96.2	3.60	10.98	3.61	15.3	63.2
19	5/27/69	0.50	0.10	96.2	3.50	10.42	3.53	14.9	55.5
ASC Whetlerite	5/20/69	0.50	0.10	96.2	4.30	15.17	3.40	17.6	158.0
Type A Whetlerite	5/1/69	0.50	0.10	96.2	4.17	14.87	3.48	17.8	155.0
18(a)	5/21/69	0.50	0.10	96.2	3.70	11.02	3.52	14.9	69.5
20	5/29/69	0.50	0.10	96.2	3.74	11.07	3.53	14.8	64.0
23	6/4/69	0.50	0.10	96.2	3.80	13.88	3.53	18.3	143.0
26	6/6/69	0.50	0.10	96.2	3.82	13.92	3.63	18.1	144.0

Based on these results, samples of 4% copper vapor impregnated carbons were tested in such a way as to promote complete oxidation of the copper and adsorption of ammonia. Samples 18a and 20 were subjected to oxidizing conditions and in addition the former was saturated with ammonia vapor. HCl tests of these samples however, failed to show any significant improvement over untreated impregnants, further indicating that ammonia must be chemically combined with copper on the whetlerite.

Samples were then subjected to ammonia, carbon dioxide and water vapor under pressure in a sealed tube as described in the previous section, in order to promote a chemical combination of copper and ammonia. These samples (Run 23) showed an HCl pick-up equal to that of a whetlerite, approximately 1-1/2 times that due to Cu^{++} alone. Furthermore, vapor impregnation with CrO_3 had no effect on the HCl activity as seen from Sample 26.

ANALYTICAL TESTS

Emission Spectrograph

Semiquantitative spectrographic analysis was run on samples of plain PCC grade CWS carbon, 8% copper vapor impregnated carbon, 8% copper 3% CrO_3 vapor impregnated carbon and ASC liquid impregnated carbon as a means of varifying the presence and concentration of impregnants. The results of these analysis can be seen in Table IV.

The concentration of impregnants on the two vapor deposited samples are within the expected range: 7% Cu rather than 8% Cu and 2% Cr (or 4% CrO_3) rather than 3% CrO_3. The solution impregnated ASC, however, contains only half of the expected concentration of impregnants. A whetlerite solution contains approximately 8% Cu and 3% CrO_3, but the impregnated carbon contains 3.5% Cu and 0.7% Cr (or 1.4% CrO_3). These findings led to the use of 4% Cu and 1.5% CrO_3 concentrations in future vapor impregnation.

Nitrogen Adsorption Isotherms

Surface area calculations using nitrogen adsorption isotherms showed a significant drop in total surface area for all three samples (Table V).

TABLE IV

SPECTROGRAPHIC ANALYSIS OF CARBON SAMPLES

CONCENTRATION
(PERCENT BY WEIGHT)

Element	Plain Carbon	8% Cu	8% Cu - 8% CrO_3	ASC
Cu	0.005	7.0	7.0	3.5
Cr	0.004	0.004	2.0	0.7
Ag	---	---	---	0.05
B	0.004	0.004		
Mn	0.005	0.008		
Mg	0.04	0.004		
Ca	0.03	0.03		
Be	0.0003	0.0003		
Ti	0.03	0.04		
Al	0.7	0.7		
Na	0.4	0.4		
Y	0.003	0.003		
Zr	0.004	0.004		
Ni	0.008	0.009		
Co	0.004	0.004		
Sr	0.03	0.03		
Ba	0.02	0.02		
V	0.01	0.01		
Fe	0.2	0.2		
Sc	0.002	0.002		
Si	0.7	0.7		

"OTHER ELEMENTS SAME AS PREVIOUS SAMPLES"

TABLE V

SAMPLE	Surface Area (M^2/gm)	% Drop
Plain	1125	0.0
8% Cu	952	15.4
8% Cu-3% CrO_3	764	32.0
ASC	788	30.0

The data showed also that the vapor impregnated carbon had approximately the same surface area as the ASC whetlerite, although having twice as much material on it. This could be due to deposition inside small carbon pores by vapor processes rather than plugging of these pores as might occur with solution impregnation.

To test this, calculations of pore size distribution were made for the four carbons, by the Cranston method.(4) Since these calculations are long and involved, a computer program was written at Edgewood Arsenal and the calculations done on their computer.

As of this report, calculations for the ASC sample are not complete. Results for the impregnated carbon, the 8% copper vapor impregnated sample and the 8% copper -3% CrO_3 vapor impregnated sample are summarized in Table VI.

TABLE VI

	Surface Area (M^2/g) of pores		Material Deposited on pores (%)		Loss of Surface Area (%)	
Sample	>12 Å	<12 Å	>12 Å	<12 Å	>12 Å	<12 Å
Blank	697.1	427.9	--	--	--	--
8% Cu	664.3	287.7	4.7	95.3	5.0	33.0
8% Cu-3% CrO_3	511.5	252.5	26.6	73.4	27.0	40.5

The Cranston method of calculating pore-size distribution assumes that the amount of surface area in pores larger than 300 Å in diameter is insignificant compared to the surface area of pores less than 300 Å. Although the calculations with these samples cannot be made for pores less than 12 Å in diameter, the difference between nitrogen adsorption isotherms surface area calculations and surface area calculated by the Cranston method is due to the contribution of pores less than 12 Å in diameter. Thus by comparing surface area distributions for the plain carbon and the 8% Cu impregnated carbon, it is seen that 95% of the copper is deposited in pores less than 12 Å in size, while only 5% is deposited in pores larger than 12 Å. This can also be seen by comparing the surface area loss caused by deposition to the original surface area distribution. There was a 5% loss of surface area in pores greater than 12 Å and 33% loss in pores less than 12 Å.

Deposition of CrO_3 from vapor phase causes a change in the distribution, indicating that the CrO_3 is not being deposited in the same pores as copper. The CrO_3 impregnated sample had 26.6% of the CrO_3 deposited in pores larger than 12 Å and 73.4% deposited in pores less than 12 Å in diameter. This resulted in surface area loss due to CrO_3 deposition of 23% in the pores greater than 12 Å and 6.5% in pores less than 12 Å.

Scanning Electron Microscope

Samples of plain carbon, 8% copper vapor impregnated carbon and ASC whetlerite were viewed with a scanning electron microscope in an effort to determine coating distribution by visual observation. Samples of photographs taken at a magnification of 1000X can be seen in Fig. III.

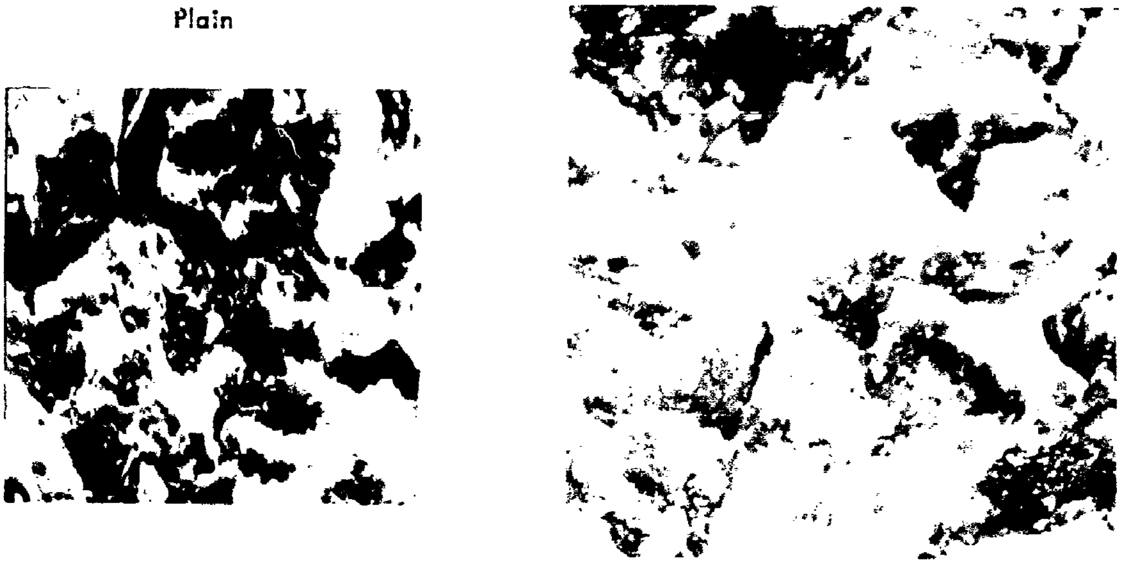
The major differences which appear at this magnification are the lack of sharp edges on the carbon crystallites and lack of cracks in the surface of the ASC sample. Both cracks and sharp contours can be seen on the plain carbon and the copper coated sample. This is perhaps due to the greater penetration of the vapor process which seems to deposit most of the material in the small pores of the carbon, rather than on the surface. Observations at greater magnification may give a better view of the coating.

DETOXIFICATION TESTS

Samples sent to Edgewood Arsenal were tested for CK activity and compared to ASC whetlerite, and PS adsorption capacity was compared to an unimpregnated carbon. The results of runs made during this report period can be seen in the appendix.

FIGURE III

SCANNING ELECTRON PHOTOMICROGRAPHS OF CARBON SAMPLES
MAGNIFICATION 1000X



8% Cu Vapor Impregnated

Plain

ASC Whetlerite

PS Tests

Removal of PS by active carbons is accomplished by surface adsorption only, thus any loss in surface area caused by impregnation would be reflected in a loss of PS adsorption capacity. Samples of 8% copper impregnated carbon had a PS life 32% less than unimpregnated carbon, while an ASC whetlerite has a 31% drop in PS life. Samples of 4%, 2% and 1/2% copper showed losses of 6.3%, 4.1% and 2.1%, respectively.

CK Tests

Carbons impregnated from an ASC whetlerite solution can remove 3 to 4 times the amount of CK removed by an unimpregnated carbon. Only one vapor impregnated sample however, showed more activity than plain carbon. This sample (Run #38, Table VI) removed about twice as much CK as plain carbon. Previously, samples had been prepared similarly to #38 (vapor deposited copper and solution deposited CrO_3) however, these samples remained in contact with the CrO_3 solution only 20 to 30 min., and showed no CK activity. Run #38 was allowed to soak in the solution 24 hr. This result further indicates that vapor deposition is taking place in the small pores of the carbon, since time was required for the CrO_3, to reach the copper and form the active complex.

PHASE III - PLATINUM DEPOSITION

This phase of the program calls for the vapor deposition of platinum, as the metal, onto activated carbon. The good results achieved with the deposition of copper from the acetyl acetonate led to the search for a similar compound containing platinum, and platinum acetyl acetonate (PtAA) was chosen for initial deposition studies. This compound is a light yellow powder which can be sublimed in a vacuum at 180°C, and decomposes at 350°C to yield platinum metal and acetyl acetone.

The same system and procedure outlined in progress report #1 for use with copper deposition was used for the deposition of platinum. Adsorption of PtAA by carbon was seen to take place at about 75°C at a pressure of 240 microns. Decomposition began at 190°C but was rather slow up to 250°C. A temperature of 325°C was necessary to complete the decomposition.

Samples containing three different weight percentages of platinum, 1%, 1/2%

and 1/4%, were prepared using the method described above. Back flow of oil from the vacuum pump contaminated the 1/4% sample, but the 1% and 1/2% carbons were sent to Edgewood Arsenal for testing.

CONCLUSIONS AND RECOMMENDATIONS

The results of post impregnation treatments, as evaluated by the HCl tests, indicate that a simple oxidation of the vapor deposited copper is not sufficient to duplicate the activity of copper on a whetlerite impregnated carbon. The copper must be reacted with ammonia. This is accomplished with vapor impregnated carbons by exposing them to an atmosphere of NH_3, CO_2 and H_2O under pressure at a temperature of 100°C for several hours, and produces a copper vapor impregnated carbon of equal activity to a type A whetlerite.

Computations of pore size distribution from nitrogen adsorption isotherms show that vapor deposited CrO_3 does not occupy the same pores as vapor deposited copper. This accounts for the failure of vapor impregnated samples to show CK activity, since it is known that copper and chrome must be combined to be active. Deposition of chrome from DCCr, which because of its similarity to CuAA would be expected to deposit in similar pores, also failed to elicit CK activity due to the difficulty encountered in oxidizing the deposited chrome to the +6 state. Future work will be concerned with methods of bringing about impregnation with CrO_3 from CrO_2Cl_2 in such a way that deposition will occur in the pores occupied by copper. In addition, studies will be made of methods designed to bring about diffusion of CrO_3 on the carbon into copper occupied pores.

Generally, physical tests have shown that vapor impregnation results in deposition of a more uniform film, combined with penetration into the small pores of the carbon. Nitrogen adsorption isotherms showed that twice as much material could be deposited from vapor phase as could be deposited by solution impregnations, with the same loss of surface area. These results indicated that once the CK active complex is produced, a carbon superior to whetlerites can be made by vapor impregnation processes.

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APPENDIX

EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulk Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm^3	Carbon Weight g	Protective Life Min. As is	Protective Life Min. corrected	Bed Depth cm	Gas
Control												
8425C PCC	4/1/69	50.01	50	75	365	1.07	7.5	2.91	26.6	26.6	2.40	PS
8425C PCC	4/1/69	50.01	50	75	365	1.07	7.5	3.05	28.6	28.6	2.60	PS
CSI-II 5-2/17 P-I (8) Cu	4/1/69	50.01	50	75	365	1.07	10.0	4.69	0.3	0.3	3.35	PS
CSI-II 5-2/17 P-I (8) Cu	4/1/69	50.01	50	75	365	1.07	10.0	5.05	0.3	0.3	3.50	PS
CSI-II 10-3/4 P-I (4) Cu	4/1/69	50.01	50	75	365	1.07	10.0	4.29	36.6	36.6	3.40	PS
CSI-II 10-3/4 P-I (4) Cu	4/1/69	50.01	50	75	365	1.07	10.0	4.61	37.8	37.8	3.40	PS
CSI-II 10-3/4 P-I (4) Cu (1.5) Cr NH$_4$OH	4/1/69	50.01	50	75	365	1.07	7.5	3.50	25.3	25.3	2.50	PS
CSI-II 10-3/4 P-I (4) Cu (1.5)Cr NH$_4$OH	4/1/69	50.01	50	75	365	1.07	7.5	3.50	25.2	25.2	2.50	PS
CSI-II 10-3/4 P-I (4)Cu (1.5)Cr NH$_4$OH	4/2/69	4.22	80	80	575	1.68	10.0	4.52	2.8	2.9	3.50	CK
CSI-II 10-3/4 P-I (4)Cu (1.5)Cr NH$_4$OH	4/2/69	4.22	80	80	575	1.68	10.0	4.65	2.7	2.8	3.50	CK
8425C PCC	4/2/69	4.22	80	80	575	1.68	10.0	4.05	2.3	2.4	3.00	CK
8425C PCC	4/2/69	4.22	80	80	575	1.68	10.0	3.90	2.1	2.1	3.00	CK

*Bed Area is 2.93 cm^2.

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*Bed Area is 2.93 cm^2.

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Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulk Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm^3	Carbon Weight g	Protective Life Min. As is	Protective Life Min. corrected	Bed Depth cm	Gas
CSI-II 14-3/24 P-I (2) Cu	4/16/69	50.48	48	78	365	1.07	10.0	4.27	35.5	35.15	3.4	PS
CSI-II 14-3/24 P-I (2) Cu	4/16/69	50.48	48	78	365	1.07	10.0	4.50	38.2	37.82	3.4	PS
CSI-II 15-3/31 P-I (I/2) Cu	4/16/69	50.48	48	78	365	1.07	10.0	3.86	33.2	32.87	3.4	PS
CSI-II 15-3/31 P-I (I/2) Cu	4/16/69	50.48	48	78	365	1.07	10.0	4.46	35.2	34.85	3.6	PS
Sol. Imp. Carbon 4/7/69	4/16/69	50.48	48	78	365	1.07	10.0	5.39	29.3	29.01	3.7	PS
Sol. Imp. Carbon 4/7/69	4/16/69	50.48	48	78	365	1.07	10.0	5.37	33.5	33.16	3.6	PS
8425C PCC	4/16/69	50.48	48	78	365	1.07	5.0	2.00	16.6	16.43	1.9	PS
8425C PCC	4/16/69	50.48	48	78	365	1.07	7.5	3.21	30.5	30.19	2.6	PS
8425C PCC	4/21/69	3.66	75	67	575	1.68	10.0	4.41	2.5	2.73	3.4	CK
8425C PCC	4/21/69	3.66	75	67	575	1.68	10.0	4.65	2.6	2.84	3.5	CK
Sol. Imp. Carbon 4/7/69	4/21/69	3.66	75	67	575	1.68	10.0	5.31	14.6	15.95	3.5	CK
Sol. Imp. Carbon 4/7/69	4/21/69	3.66	75	67	575	1.68	10.0	4.91	20.0	21.86	3.4	CK
8425C PCC	4/25/69	3.80	70	66	575	1.68	22.5	9.13	26.0	24.70	7.5	CK
8425C PCC 4/7/69	4/25/69	3.975	80	66	575	1.66	10.0	5.55	52.7	52.38	3.4	CK
Sol. Imp. AC Carbon 4/7/69	4/25/69	3.975	80	66	575	1.68	10.0	5.02	39.2	38.96	3.4	CK

*Bed Area is 2.93 cm^2.

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EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulk Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm^3	Carbon Weight g	Protective Life Min.		Bed Depth cm	Gas
									As is	corrected		
11-17-5/6 P-1 (4)Cu 1.5 Cr Vapor Imp. 4%Cu 1.5% Cr.	5/8/69	3.80	80	78	575	1.68	10.0	4.99	2.6	2.47	3.2	CK
11-17-5/6 P-1(4)Cu 1.5 Cr Vapor Imp. 4%Cu 1.5%Cr	5/8/69	3.80	80	78.	575	1.68	10.0	4.67	2.1	2.00	3.1	CK
11-16-5/5 P-1(8)Cu$_3$Cr Sol.imp. Cu Vapor imp. cr.	5/8/69	3.80	80	78	575	1.68	10.0	5.11	3.6	3.42	3.2	CK
11-16-5/5 P-1(8)Cu$_3$Cr. Sol.imp. Cu Vapor imp. cr.	5/8/69	3.80	80	78	575	1.68	10.0	4.33	2.6	2.47	3.2	CK
8425C PCC	5/8/69	3.80	80	78	575	1.68	20.0	8.18	12.5	11.87	6.8	CK
8425C PCC	5/8/69	3.80	80	78	575	1.68	20.0	8.66	10.5	9.98	6.7	CK
8425C PCC	5/14/69	51.09	48	78	365	1.07	5.0	2.14	16.7	17.0	1.9	PS
11-16-5/5 P-A(8)Cu$_3$Cr Sol.imp. Cu Vapor imp. Cr	5/14/69	51.09	48	78	365	1.07	5.0	2.81	9.4	9.5	1.8	PS
11-16-5/5 P-A(8)Cu$_3$Cr Sol.imp. CuVapor imp. Cr.	5/14/69	51.09	48	78	365	1.07	5.0	2.50	8.9	9.0	1.9	PS
11-17 5/6P-1(4)Cr 1.5Cr Vapor imp.4%Cu 1.5%Cr	5/14/69	51.09	48	78	365	1.07	5.0	2.45	14.1	14.3	1.8	PS
11-17 5/6P-1(4)Cr 1.5Cr Vapor imp.4%Cu 1.5%Cr	5/14/69	51.09	48	78	365	1.07	5.0	2.38	15.5.	15.8	1.9	PS
8425C PCC	5/20/69	4.07	80	73	575	1.68	20.0	8.51	12.0	12.2	7.1	CK
8425C PCC	5/20/69	4.07	80	73	575	1.68	20.0	8.27	11.8	12.0	7.2	CK
11-19 5/15 P-1 1/2Cu, 1/2Cr	5/20/69	4.07	80	73	575	1.68	10.0	4.40	4.4	4.5	3.5	CK
11-19 5/15 P-1 1/2Cu, 1/2Cr	5/20/69	4.07	80	73	575	1.68	10.0	4.21	3.2	3.3	3.5	CK

*Bed Area is 2.93 cm^2.

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EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulk Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm^3	Carbon Weight g	Protective Life Min		Bed Depth cm	Gas
									As is	corrected		
Control 8425C PCC	7/10/69	4.16	80	79	575	1.68	20.0	8.23	7.4	7.6	6.8	CK
8425C PCC	7/10/69	4.16	80	79	575	1.68	20.0	8.22	8.1	8.4	6.5	CK
11-29 6/17/69 (4) Cu $NH_4)_2CO_3$(1Cr)	7/10/69	4.16	80	79	575	[illegible]	10.0	4.93	1.2	1.2	3.7	CK
11-29 6/17/69 (4) Cu $(NH_4)_2CO_3$(1Cr)	7/10/69	4.16	80	79	575	1.68	10.0	4.96	1.2	1.2	3.7	CK
11-38 6/26/69 (4) Cu $(NH_4)_2CO_3$+ liq. Cr	7/10/69	4.16	80	79	575	1.68	20.0	10.60	32.4	33.6	6.6	CK
11-38 6/26/69 (4)Cu $(NH_4)_2CO_3$+ liq. Cr.	7/11/69	4.36	80	77	575	1.68	20.0	10.59	35.2	38.1	6.6	CK
11-39 6/24/69 (4)Cu $(NH_4)_2CO_3$(2)Cr H_2O_2	7/14/69	4.16	80	79	575	1.68	20.0	9.66	15.5	16.1	6.9	CK
11-39 6/24/69 (4)Cu $(NH_4)_2CO_3$(2)CrH_2O_2	7/14/69	4.38	80	77	575	1.68	20.0	9.41	14.0	15.2	6.7	CK
11-40 6/27/69 (4)Cu $(NH_4)_2CO_3$(2)Cr	7/16/69	4.16	80	79	575	1.68	20.0	10.67	14.4	14.9	7.0	CK
11-40 6/27/69 (4)Cu $(NH_4)_2CO_3$(2)Cr	7/16/69	4.16	80	79	575	1.68	20.0	10.36	14.7	15.2	6.8	CK
8425C PCC	7/11/69	4.36	80	77	575	1.68	20.0	8.51	10.0	10.9	6.6	CK
8425C PCC	7/11/69	4.36	80	77	575	1.68	20.0	8.50	9.2	10.0	6.8	CK

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13. ABSTRACT

Work during this period was concerned mainly with the deposition of copper and chrome to produce an impregnated carbon with activity similar to that of an ASC whetlerite. Samples were prepared using the procedures detailed in the first progress report (1) and subjected to various post impregnation treatments in an attempt to illicit CK activity. A laboratory scale break through test apparatus, using HCl gas as the agent, was constructed and used to evaluate the effect of post impregnation treatments on the activity of the copper. Using this test, a treatment was devised which gives vapor impregnated copper coated carbons HCl activity equal to or better than whetlerites.

Nitrogen adsorption isotherms were performed on samples of plain PCC grade CWS carbons, 8% by weight copper vapor impregnated carbons and ASC whetlerite carbons, and pore-size distribution computations made to determine coating penetration. Concentration of impregnants was determined from emmission spectrographic analysis and X-ray diffraction patterns were run in an attempt to identify the chemical structure of the impregnant. Photomicrographs were taken of the carbons surface using the scanning electron microscope as a means to further determine coating distribution.

A method was developed for depositing chrome as the metal in the pores of the carbon from dicumene chromium. Samples were prepared by this method and treated to oxidize the chrome. Samples were prepared containing copper vapor deposited from CuAA and chrome deposited from dicumene, and sent to Edgewood for CK testing.

Work was also done during this report period on Phase III of the program, the vapor deposition of platinum on activated carbons.

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Vapor Phase						
Active Carbons						
Metals						
Metal Salts						
Toxic Gas Removal						
Copper Deposition						
CWS Carbon						
Ammonolysis						
Hydrolysis						
Chromyl Chloride						
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