

NRL Memorandum Report 4006
NUREG/CR-0771
RQ

Effects of Weathering on Impregnated Charcoal Performance

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May 10, 1979

Prepared for
Division of Safeguards, Fuel Cycle and Environmental Research
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Under Interagency Agreement No. AT(49-24)-9006
NRC FIN No. B-6003



NAVAL RESEARCH LABORATORY
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| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|--|---|---|
| 1. REPORT NUMBER NRL Memorandum Report 4006 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) EFFECTS OF WEATHERING ON IMPREGNATED CHARCOAL PERFORMANCE | 5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL problem. | |
| | 6. PERFORMING ORG. REPORT NUMBER | |
| 7. AUTHOR(s) Victor R. Deitz | 8. CONTRACT OR GRANT NUMBER(s) | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375 | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NRL Problem C08-39E | |
| 11. CONTROLLING OFFICE NAME AND ADDRESS | 12. REPORT DATE May 10, 1979 | |
| | 13. NUMBER OF PAGES 77 | |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | 15. SECURITY CLASS. (of this report) UNCLASSIFIED | |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE | |
| 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | |
| 18. SUPPLEMENTARY NOTES | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The useful life of activated charcoal filters in engineered-safety-feature and normal ventilation systems of nuclear power stations is slowly impaired by the contaminants accumulated from the large volume of air being processed. The weathering of eight commercial impregnated activated carbons have now been studied by a two-fold approach: (1) Exposure to unmodified outdoor air for periods up to nine months, followed by measurements of methyl iodide-131 penetration, and (2) exposure of the same type charcoals to air flows of known pollutant species and concentrations under controlled laboratory conditions, also followed by measurements of the (Continues) | | |

20. Abstract (Continued)

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Acknowledgements

The technical guidance of J. T. Collins and his Staff and the overall program guidance of C. B. Bartlett and D. Solberg of the U.S. Nuclear Regulatory Commission are very much appreciated.

The important contribution to the laboratory work by J. B. Romans of the Surface Chemistry Branch, Naval Research Laboratory, is gratefully acknowledged. A. Stamulis of the Radiological and Environmental Protection Branch has been most helpful in advising on contaminant evaluation and the Branch has generously permitted the use of unpublished results.

Thanks are due to the several manufacturers and suppliers who kindly provided the samples of commercial charcoals.

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Abstract

The useful life of activated carbon filters in engineered-safety-feature and normal ventilation systems of nuclear power stations is slowly impaired by the contaminants accumulated from the large volume of air being processed. The weathering of eight commercial impregnated activated carbons have now been studied by a two-fold approach: (1) Exposure to unmodified outdoor air for periods up to nine months, followed by measurements of methyl iodide-131 penetration, and (2) exposure of the same type charcoals to air flows of known pollutant species and concentrations under controlled laboratory conditions, also followed by measurements of the methyl iodide-131 penetration. The influence of moisture in laboratory air flows of 50, 70, and 90% RH has been studied in detail for the eight charcoals. The exposures of the charcoals to outdoor air have now been extended to nine months and the results show a progressive decrease in iodine trapping efficiency. There is evidence from both the laboratory and outdoor exposure tests that moisture can enhance charcoal degradation. An adverse synergistic influence of moisture and hydrocarbon vapors has also been observed. All samples were layered to permit a determination of the profile in properties along the line of flow. The entrance layer, first of four equal layers, was found to be most significantly affected by the exposure insult. It is believed that local meteorological conditions of high humidity combined with atmospheric pollutants in the test vicinity contribute jointly to the degradation of impregnated activated carbons.

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I. Introduction

The use of activated and impregnated charcoals by the nuclear industry for periods of two to three years without regeneration is an adsorbent application with new and undefined maintenance problems. These relate to the effect of environmental contaminants on the useful life of the charcoal. During the period in service the charcoal must be ready to serve its role in the retention of radioiodine should an incident occur, or in the continuous removal of low concentration levels of radioactive iodine. The immediate objective of this investigation is to determine the extent to which atmospheric contaminants degrade the efficiency of impregnated activated carbons for trapping methyl iodide, an organic species found in nuclear power plant operations.

In the first reports (1,2) from NRL the many complex factors involved in weathering of charcoal were discussed. Results of initial tests were then reviewed wherein the trapping efficiency for methyl iodide-131 was determined for a few charcoals after exposure to ozone, sulphur dioxide, carbon monoxide and water vapor. The present report describes tests, carried out on a greater variety of charcoals, which utilized water vapor and/or hydrocarbons as the principle weathering agents. The results to be described illustrate the properties of certain base charcoals with particular impregnations and should not be interpreted as an endorsement or recommendation of any particular manufacturer's product.

The impregnated activated carbons installed in engineered-safety-features and in normal ventilation systems of nuclear power plants are subject to a continuous interaction with ambient and local contaminants found in air. The ambient contaminants include volatile hydrocarbons, ozone, sulfur dioxide, nitric oxides and carbon monoxide which are widely distributed in the environment. Local contaminants are materials drawn into air ducts leading to the charcoal filters as a result of solvent spills, evaporation of lubricating agents, and volatilization

Note: Manuscript submitted April 10, 1979.

of paint components. The prolonged exposure of charcoals to these contaminants has a degrading influence on the trapping efficiency for methyl iodide-131. Methyl iodide is generally considered as representative of the organic iodides present in nuclear power operations and these compounds may be generated by a series of chemical reactions between elemental iodine, a fission product, and the organic compounds present in the containment space. The adsorption sites of a charcoal can be occupied by atmospheric contaminants and thus prevent a reaction with methyl iodide. Also, the specific chemical sites in the interface between the base charcoal and the impregnants, where chemical reactions with methyl iodide molecules take place, can be physically damaged or destroyed. Both categories of change occur in "weathering" of charcoals by exposure to contaminants, and there has not been hitherto (as of January 1977) an in-depth engineering analysis of the problem.

The commercial impregnated charcoals used in this study (Table 1) include both coconut and coal as source materials for the base charcoals. The impregnations include a mixture of KI and elementary iodine, and a tertiary amine, either alone or with iodine salts. The first report (1) dealt mainly with BC 727 and G 615 and the present report extends the number to those shown in Table 1. Additional properties of the eight charcoals are given in Appendix 1.

A two-fold approach has been followed in these studies to obtain the necessary data. First, charcoal samples were exposed to unmodified outdoor air for various periods of time, and then examined for changes in methyl iodide retention capability, weight changes, and pH of the water extract. This approach is representative of conditions which might exist in the charcoal service life, but allows no control over the concentration or type of atmospheric contaminant. Second, additional samples of the same charcoals were exposed under controlled laboratory conditions in various known pollutant combinations. In this way pollutant types, concentration and combinations can be varied under the discretion of the investigator.

Table 1: Impregnated Charcoals Under Investigation

| Charcoal | Nominal Size | CCl ₄ Activity* | Source | Impregnation |
|--------------------------|--------------|----------------------------|---------|----------------------------------|
| BC 727 | 8 x 16 | 90 | Coconut | KI + I ₂ |
| BC 717 | 8 x 16 | 60 | Coconut | KI + I ₂ |
| G 615 | 8 x 16 | 60 | Coconut | KI + TEDA |
| G 617 | 8 x 16 | 95 | Coconut | KI + I ₂ |
| MSA (463563) | 8 x 16 | 60 | Coconut | KI + I ₂ |
| AAF 2701 | 8 x 16 | 60 | Coconut | KI + I ₂ |
| KITEG | 8 x 16 | 60 | Coal | Iodine Salts and Tertiary Amines |
| Sutcliffe, Speakman & Co | 8 x 16 | 60 | Coal | 5% TEDA |

* ASTM D3467; TEDA ≡ triethylenediamine

Since the initiation of this investigation (1), the ambient contaminants encountered in the outdoor air at NRL have varied over the four seasons of the year. The absolute humidity (dew point) was maximum in July and August and minimum in January and February. These trends are similar to previous years (see Appendix 2, 1970-1978) and appear to be a general characteristic of the climatological location of which NRL is a part. From the NRL Air Quality Data (3,4) for 1976, 1977 and 1978 the monthly average concentrations of five common pollutants (Appendix 3) may be seen to have uniform trends. The NO₂ concentrations were fairly uniform over the year; the SO₂ was greater in the first and fourth quarters than in the second and third; the total hydrocarbons including methane were uniform over the year. The oxidants (mainly ozone) were higher in the second and third quarters. These are some of the facts that have to be considered in any attempt to correlate the weathering behavior of charcoals in outdoor air during long periods of exposure.

Tests under controlled laboratory weathering conditions have been beneficial in identifying water vapor as a very important factor. The influence of moisture on the subsequent methyl iodide-131 penetration was demonstrated in the previous report (1) by the action of the 16-hour prehumidification in the testing of new coconut-base charcoals. In fact, the interfering behavior of water vapor led to the introduction of the triethylenediamine impregnation of charcoals developed by Collins, Taylor and Taylor (5).

Since a water vapor-air mixture can be characterized by relative humidity and the dew point, a question may be raised as to which measurement is the more helpful parameter in understanding the water vapor-charcoal interaction of a long duration. It appears that both parameters are important. The physical adsorption of water vapor at a specified temperature is determined by the relative humidity which controls the mass transfer of the water vapor from a continuous air flow into the activated carbon. On the other hand, the actual partial pressure of water vapor is the measure of chemical reactivity in any kinetic rate process and thus determines the rate of chemical reaction of water vapor with the charcoal. Hence, dew point, a measure of absolute humidity, is of value in a consideration of the long-range weathering reactions. The methyl iodide-131 trapping efficiency of a charcoal after relatively short contact times (24 - 48 hours) with high humidity air (95% RH) can be recovered by drying the charcoal in warm air of lower relative humidity, but prolonged exposures to high relative humidities may lead to a degradation that is non-reversible at ambient temperatures (unpublished results, NRI). The above behaviors suggest strongly that both relative humidity and absolute humidity must be taken into account in the charcoal weathering processes.

The slow oxidation of an activated carbon at ambient temperatures by the oxygen content of air is also a factor to be considered in weathering processes of long duration. Unfortunately, little work has been reported on this topic. In 1956, some research was reported at

NRL (6) in which laboratory-prepared activated carbons were exposed to oxygen and to oxygen-water vapor mixtures. It was shown that a steady uptake of oxygen occurred at 24°C and that this adsorption was enhanced in the presence of moisture. The results in Figure 1 indicate that the increase in oxygen adsorption was approximately proportional to the moisture content of the activated carbon. In view of the constant proportion of oxygen in air, this parameter will not be varied in the weathering experimentation. However, it remains to be considered as an additional chemical reactant, along with the pollutants, in the mechanism of weathering.

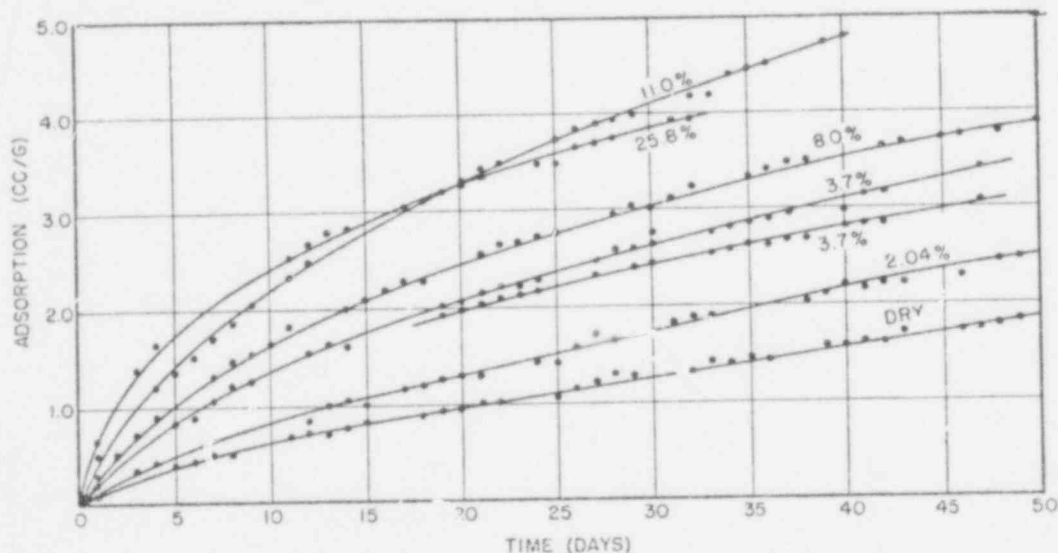


Figure 1: Adsorption of Oxygen by a Charcoal at the Designated Moisture Content, dry basis (6)

It may be helpful to repeat the several questions raised at the beginning of this investigation (1) and to review these based on the data obtained since then. The following queries were submitted:

(1) How can a judgment be made on when the charcoal must be replaced?

(2) What precursor behavior and information can be used to anticipate the need for a replacement?

(3) How can the useful lifetime of the charcoal be increased?

It appears that a judgment might be made based on the profile of contaminants along the normal flow direction through the charcoal bed. The observations with all of the charcoals have demonstrated that the entrance layer of the charcoal behaves as a "guard" bed and after a few months exposure this layer permits several-fold greater penetration of methyl iodide than the remainder of the charcoal. However, the subsequent layers are not as efficient as an equivalent amount of the unexposed charcoal. It appears that a charcoal bed has a chromatographic behavior along the direction of the air flow and also displacement phenomena can occur in which one contaminant may displace another which had been previously adsorbed. In view of these facts, it may be feasible to judge when to replace the charcoal by measurements in the effluent air in real time on an on-line basis of these displaced contaminants. Ultimately, of course, the charcoal must be evaluated by a methyl iodide penetration test and it is then necessary to preserve the actual profile present in the bed of weathered charcoal.

Minimizing the moisture influence by decreasing the air flow during high humidity periods and enhancing the flow during dry periods may extend the useful life of a carbon adsorber. The engineering aspects of this practice would have restrictions local to every installation. Intermittent exposure of charcoal to air flows of high

and low humidity has been studied as part of this project in order to establish the effects of such a method of operation on laboratory-scale filters.

It has been mentioned above that superimposed on the normal weathering of charcoal by the pollutants of the air is the action of organic vapors derived from local solvent spills and/or the solvent vapors from large paint operations conducted within a facility. These are special situations, but are very important to the efficient operation of carbon filters. Pertinent laboratory experiments are now in progress to follow the methyl iodide trapping efficiency of charcoals after exposure to concentrations of organic vapors greater than ambient total hydrocarbons (Appendix 3). It may be noted that considerable methane (1 to 2 ppm) is always present in outdoor air and in the presence of ozone, the products derived from a methane-ozone reaction may also contribute to the degradation of the activated carbon.

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II. Problems in Testing Weathered Charcoals

1. Weathering and Testing Procedures

Uniform procedures for the determination of iodine and methyl iodide penetrations for new impregnated activated carbons are being established for the nuclear industry by Subcommittee D-28.04 of the American Society of Testing Materials (ASTM) and a summary tabulation of these is given in Appendix 4. The specified parameters of the tests are the bed dimensions, flow rates, temperatures, relative humidities, pre-equilibration times, the methyl iodide-131 feed period (temperature, relative humidity, concentration and duration of feed), and the elution period (temperature, relative humidity, flow rate, and duration).

Three test modes, or configurations, containing the weathered charcoals have been used (1) in the determination of the methyl iodide-131 penetration:

Mode 1 - Measurement of the penetration through each of the four charcoal layers, exposed in beds 2-inch diameter and 2-inch depth.

Mode 2 - Measurements of the penetration using one-fourth of the weathered charcoal from each layer, reconstructed in the same sequence of entrance-to-exit as in the exposed sample.

Mode 3 - Measurements of penetration after the charcoal was weathered in standard test beds and do not require the transfer of the charcoal after the exposures.

It is essential to keep in mind that the experimental weathering parameters are distinct from the charcoal testing procedures. The test bed (Appendix 4) is specified as 2 inches (5.08 cm) in diameter and

2 inches high and it is packed with a uniform sample of the charcoal. In the present study the weathered samples have to be of sufficient quantity to make all of the desired determinations. Therefore, the charcoals were exposed in large stainless steel containers in beds 4-inch diameter (10.16 cm) and 2-inch height (5.08 cm). Each sample was introduced in four equal layers, each 0.5 inch deep (1.27 cm) and separated by perforated stainless steel discs (see Figure 2, NUREG/CR-0025, page 8). After exposure, the four layers were handled separately. In this manner, the vertical profile in the weathering of the charcoal could be determined.

The use of the ASTM testing procedures, designed to qualify new material, raises uncertainties when they are applied to weathered samples. The problem may be examined by noting the following general objectives and requirements of test procedures for activated carbons used in nuclear applications:

- (1) A means must be provided to make a decision when the activated carbon must be replaced.
- (2) The test must be demonstrated to be relevant to plant operation and simulate as close as practical accident conditions.
- (3) The test must provide a capability to attain reproducible results between laboratories.
- (4) The test results must not be negated by the action of specific contaminants that accumulate during service.

In adapting the ASTM procedures to weathered samples, it has been suggested that weathered charcoals not be subjected to the 16-hour prehumidification with 95% RH air which is prescribed for new material. It is thought that the elimination of the prehumidification is a better

simulation of accident conditions since a carbon filter must be ready at all times to serve its role as an engineered safety feature. Several investigators do not recommend any pretreatment in order to prevent a partial regeneration of the carbon which would increase the measured trapping efficiency. Should the regeneration be appreciable, the test results would be invalidated. Another suggested pretreatment is to store the sample as received in a static enclosure at 30°C over water for 24 hours, followed by a rapid transfer to the test container. In the present study, the testing of weathered samples has not been made with the 16-hour prehumidification. The procedures used will be discussed in the next section.

2. Temperature Excursions during Testing

Charcoals weathered at NRL with outdoor air are exposed on a time basis and accordingly are removed under the meteorological conditions existing at that time. The final days of an exposure may, therefore, occur during a very wet or a very dry period. A record of the dew points at NRL (7) over the past eight years, shown in Appendix 2, combined with the changing daily temperature, establishes a variability in relative humidity that is beyond prediction. Charcoals from exposures completed during a period of dry weather have a small weight increase due chiefly to lack of adsorbed water. When these samples are exposed to the 95% RH air during the methyl iodide testing, a significant temperature rise occurred. The rise was recorded by inserting a thermocouple in the air flow between the sample and back-up beds. The temperature rise can be ascribed to the release of the heat of adsorption of water vapor on charcoal. Some typical examples are given in Figure 2 for a 30°C test and in Figure 3 for a 130°C test. Because of the temperature gradients within the charcoal test sample, there is a corresponding change in the linear air flow velocity and in the calculated contact time within the bed. These are estimated to be approximately 1 to 3% for a temperature change of 10°C. The above observations are instructive for an understanding of the source of the temperature

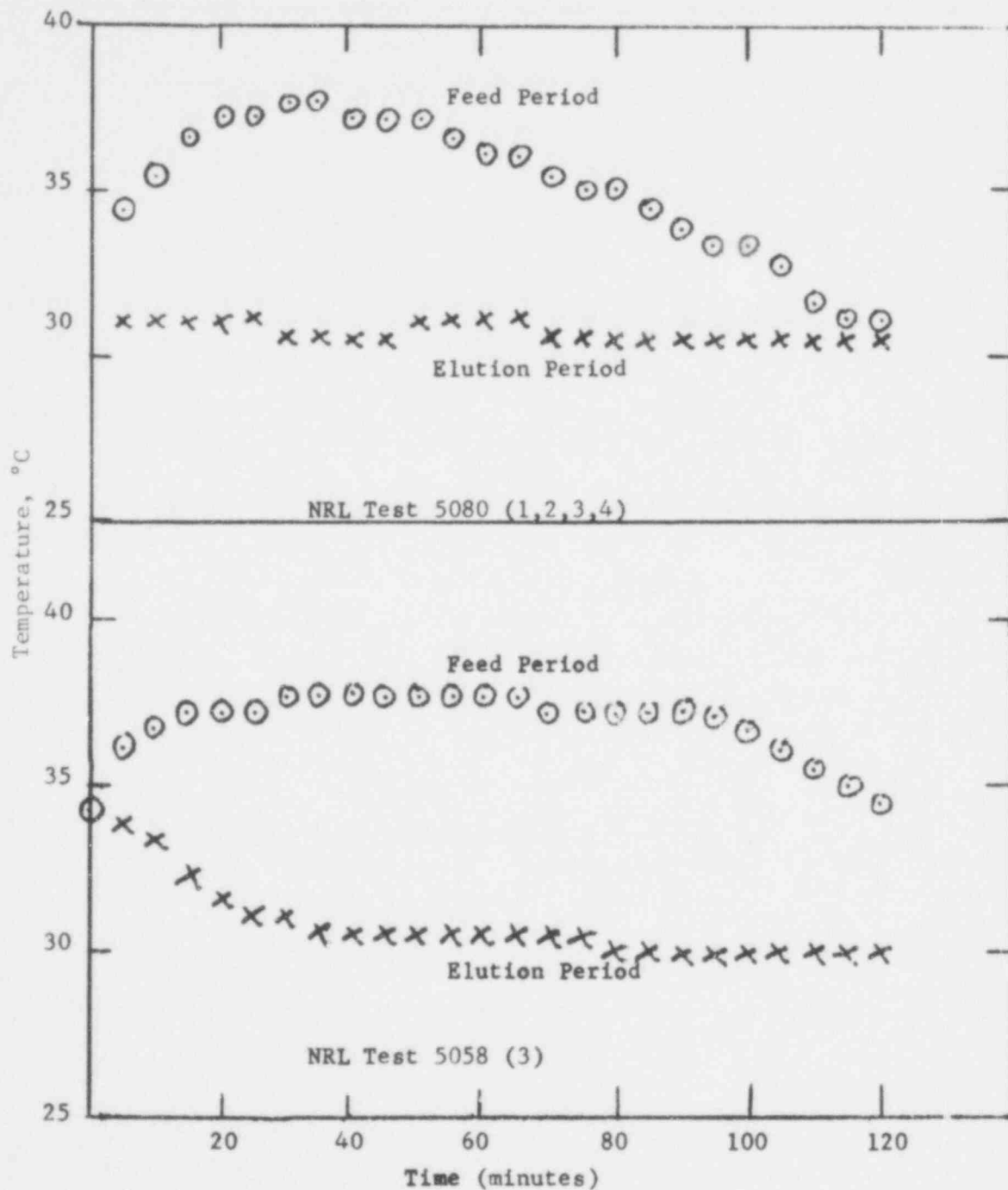


Figure 2: Temperature Excursion in Testing Weather Charcoals
 at 30°C with air at 95% RH
 (thermocouple located between sample and back-up beds)

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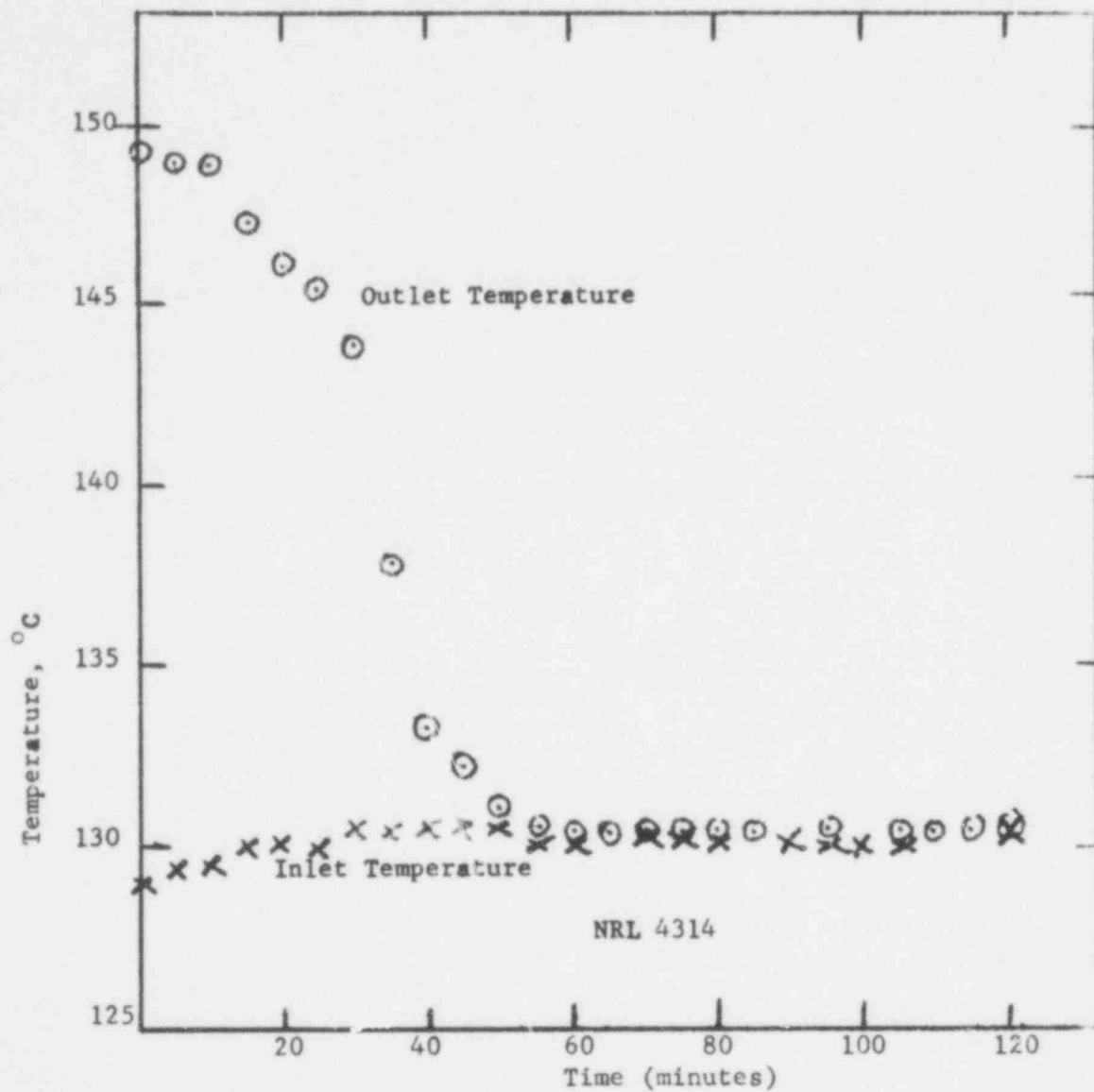


Figure 3: Temperature Excursions in Testing Weathered Charcoal at 130°C, the elution temperatures remained 130 - 130.5°C (thermocouple located between sample and back-up beds)

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excursions within a test bed. When the charcoal sample had been exposed to 90% RH air before testing, no temperature increase was observed as shown by the tabulated data for NRL Test 5088 given in Appendix 5. Relative to other sources of uncertainties, for example, the charcoal sampling error, the influence of the temperature gradient in the bed may not be significant. However, the temperature control specified by the ASTM test procedures need not be as precise for weathered samples as that specified for new charcoals. It also should be noted that the designated control conditions specified by the ASTM Test Procedures (Appendix 4) apply only to the inlet air flow.

Using weathered charcoals completed during periods of low relative humidity (< 30% RH), it was possible to ameliorate the rise in temperature observed during methyl iodide testing by first placing the test sample in a stainless steel wire basket and keeping it overnight over water in static storage in a closed container. The procedure was successful in substantially minimizing the temperature rise in testing at 30°C; however, it is not known to what extent the procedure had influenced the observed value for penetration. Moreover, its significance to plant-scale carbon bed operation is not known. The consensus mentioned in a previous paragraph, namely to seek in a testing procedure the best simulation of accident conditions, would require that a pre-humidification technique not be used. Accordingly, after a number of tests to be described later, the above prehumidification technique in the wire basket was no longer used.

Milham and Jones (8) observed a partial regeneration of BC 416, a non-impregnated coconut charcoal, when the test bed was heated to 60°C for about 48 hours with purified air at 7.5 ft/min. After these conditions some improvement was noted in the elementary iodine trapping efficiency. It may be noted that an air flow of 95% RH at 30°C drops to 22% RH at 60°C which presents a different set of test parameters relative to that employed in the standard 30°C test procedure. Temperatures well above 60°C are necessary to reach a level of regeneration

equivalent to new charcoal, as shown in 1947 in a detailed study of kilns (Herreshoff Kiln, a Rotary Kiln, and a Kiln with Stationary Retorts) for the regeneration of char (9).

3. Testing Charcoals With and Without Prehumidification

The accumulated experiences with weathered charcoals at NRL indicate that any prehumidification before testing at 90% RH and above contributes to a further lowering in trapping efficiency relative to that observed without prehumidification. Thus, the use of a high relative-humidity in the prehumidification of weathered charcoals can confuse the results of the subsequent methyl iodide efficiency. Table 2 summarizes some penetration results for a number of charcoals weathered at NRL and also a few charcoals received after plant service. These were determined with and without prehumidification (16 hours in 95% RH air at 25 L/min, see Appendix 4). In all cases, the penetration is greater after prehumidification. When compared with the ASTM suggested performance requirements of new activated carbon (Appendix 7), six of the ten samples would not qualify when tested after preconditioning. There are several possible changes that could occur in nuclear charcoals during the prolonged exposure at high humidity air flows. Chemically, there are hydrolytic reactions and hydration changes among the impregnation constituents. Physically, the base charcoal adsorbs water vapor in a strongly increasing amount with increase of relative humidity above about 40-50% (1). The behavior for a coconut activated carbon is shown in Figure 4. A charcoal filter, exposed accidentally to the vapors from solvent spills or to organic vapors from plant operations, is subject to a synergistic interaction with water vapor. This behavior requires additional understanding before a judgment can be made as to charcoal replacement. The above facts will be discussed in following sections.

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Table 2: Methyl Iodide Penetration of Weathered Activated Carbon and those Removed from Service Tested with and without Prehumidification at 95% RH and 30°C

| Activated Carbon | Exposure | CH ₃ I-131 Penetration % Prehumidification | |
|-----------------------|------------------------|--|------|
| | | Yes | No |
| NRL 4289 on G202 | 4-29 Oct 76 | 6.74 | 0.73 |
| NRL 4258 on MBV | 1-30 Nov 76 | 1.10 | 0.22 |
| SS (KI on 207B) | 2-29 Dec 76 | 18.7 | 14.6 |
| G-618 | 10-31 Jan 77 | 0.62 | 0.05 |
| NRL 4230 on MBV | 1 Feb - 1 Mar 77 | 1.75 | 0.30 |
| GX 176 | 2-31 Mar 77 | 0.89 | 0.45 |
| BC 717 | 1 Apr - 2 May 77 | 3.79 | 0.67 |
| GX 176 | Paint Fumes, 1 week | 13.6 | 9.4 |
| Used (Not Identified) | Removed from Plant | 5.45 | 2.36 |
| G 615 | Removed from Plant | 2' | 17. |

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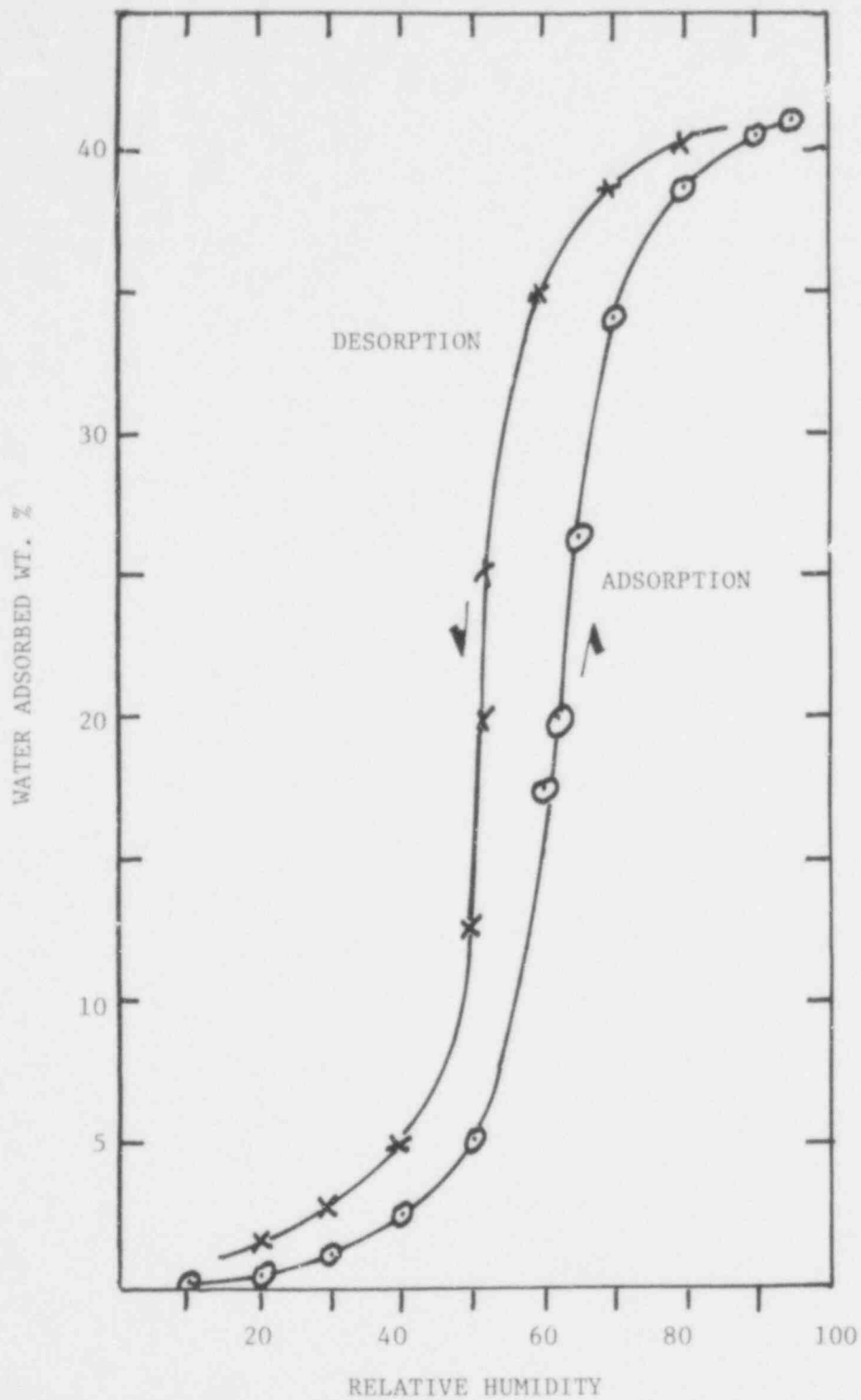


Figure 4: Dynamic Adsorption and Desorption of Water by Coconut Activated Carbon (NACAR G 210) at 25°C (Kindly furnished by Frank Schwartz, Jr.)

III. Laboratory Weathering

1. Air Flows at Three Levels of Relative Humidity

The controlled exposures of seven commercial charcoals to air flows at three levels of relative humidity (50, 70, 90% RH) have been completed. The air flow was continuous at a flow rate of 100 L/min for 100 hours. The residence time was 0.25 sec and the linear flow rate was 12.3 m/min. The total flow was thus 600 M^3 and the total weight of water (calculated at 22°C) to which each charcoal was exposed, was 0.97, 1.74, and 2.61 kg at 50, 70, and 90% RH, respectively. The exposures of the charcoals (Table 3) and the sequence of relative humidities were random in sequence. The temperature of the air conditioned laboratory was kept in the range 21 to 23°C . The relative humidity in each of the two independent exposure systems was monitored by a dewpoint hygrometer (General Eastern, Series 1211 P Sensor) and the air temperature was measured simultaneously with a platinum resistance thermometer (General Eastern, 1212 P). The measurements illustrated in Figure 5 are continuous recordings of dew points and air temperature as the air flow from the two systems was alternately passed through the instrument. The control, experimentally based on thermostated water supplies, was calculated to realize an overall standard deviation of 1-8% RH over the 100-hour laboratory exposure.

The results for pH, weight increase, and methyl iodide-131 penetration are given in Table 4 for the above exposures. The pH remained about the same throughout the four layers of each charcoal (see detailed results given in Appendix 6). The weight increases (also given in Appendix 6) followed a behavior consistent with the water adsorption isotherm of the charcoal. The latter has the characteristic curvature of Figure 4 which accounts for the non-linearity of weight increase with relative pressure (see also Figure 5 of NUREG/CR-0025); the weight increases of all seven charcoals were greatest at the highest humidity. The profile of weight increase through the four layers of each charcoal

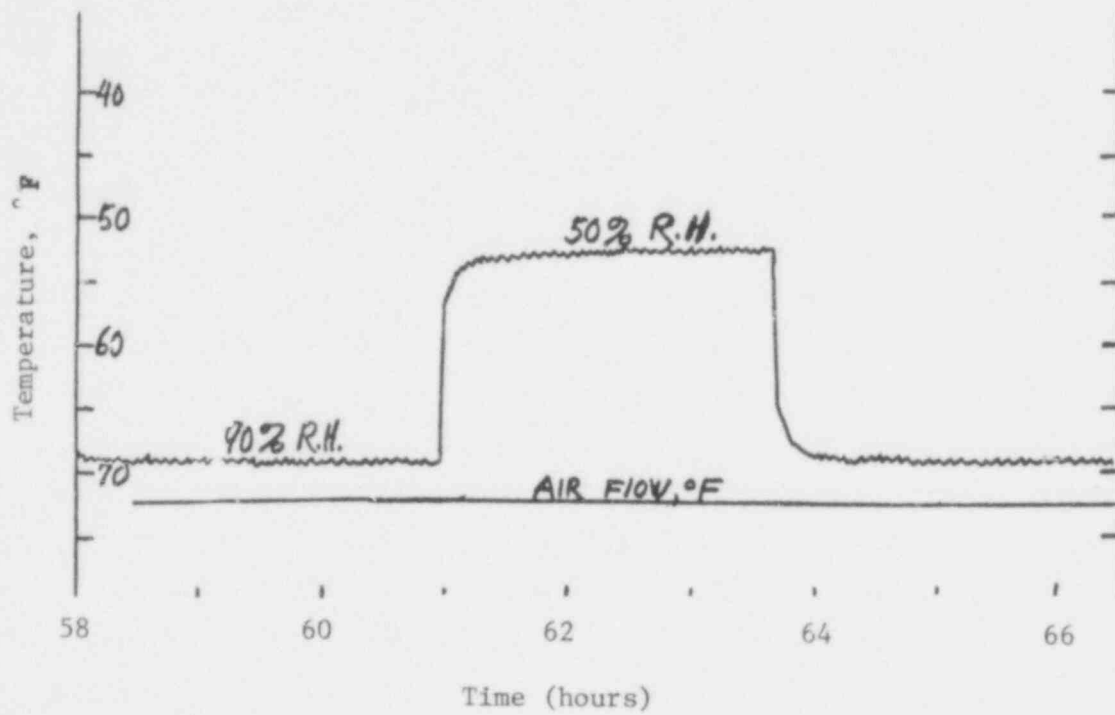


Figure 5: Temperature Record of Dew Point and Air Flow in Laboratory Weathering

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can be obtained from the results given in Appendix 6, since the dry weights (initially dried at 100°C) of charcoal introduced into each of the four layers were equal. The results at 50% RH showed a much greater gradient than the weight increases at 70 and 90% RH. It may be noted that the weight increase at 90% RH was 30 wt.% or above for all charcoals under investigation (Table 4) and at 50% RH the weight increase was below 25% or less in all cases.

Table 3: Exposure Schedule of Charcoals with Air-Water Vapor of Designated Constant Humidity for 100 Hours

| Charcoal | Constant Humidity Maintained During Entire Exposure | | |
|----------|---|-------------------------|-------------------------|
| | 50% RH | 70% RH | 90% RH |
| BC 727 | 4-8 Oct 1977 5053* | 1-5 Aug 1977 5030* | 15-19 Aug 1977 5036* |
| G 615 | 11-15 Oct 1977 5054* | 8-12 Aug 1977 5035* | 22-26 Aug 1977 5037* |
| MSA | 24-28 Apr 1978 5073* | 5-9 Jun 1978 5100* | 8-12 May 1978 5086* |
| S&S | 8-12 May 1978 5085* | 7-11 Jun 1978 5101* | 18-22 Apr 1978 5072* |
| 2701 | 18-22 Apr 1978 5071* | 12-16 Jun 1978 5102* | 15-19 May 1978 5088* |
| G 617 | 15-19 May 1978 5087* | 12-16 Jun 1978 5103* | 24-28 Apr 1978 5074* |
| KITEG | 1-5 May 1978 5075* | 13-19 Jun 1978 5104* | 1-5 May 1978 5076* |

*Indicates the NRL Test Number

The methyl iodide-131 penetrations (Table 4) increased for all seven charcoals with increase in the relative humidity of the air flow. The increase from 50 to 70% RH was greater than the increase from 70 to 90% RH. The differences among the different charcoals, seen in Figure 6, vary to some extent, but it is important to remember that these

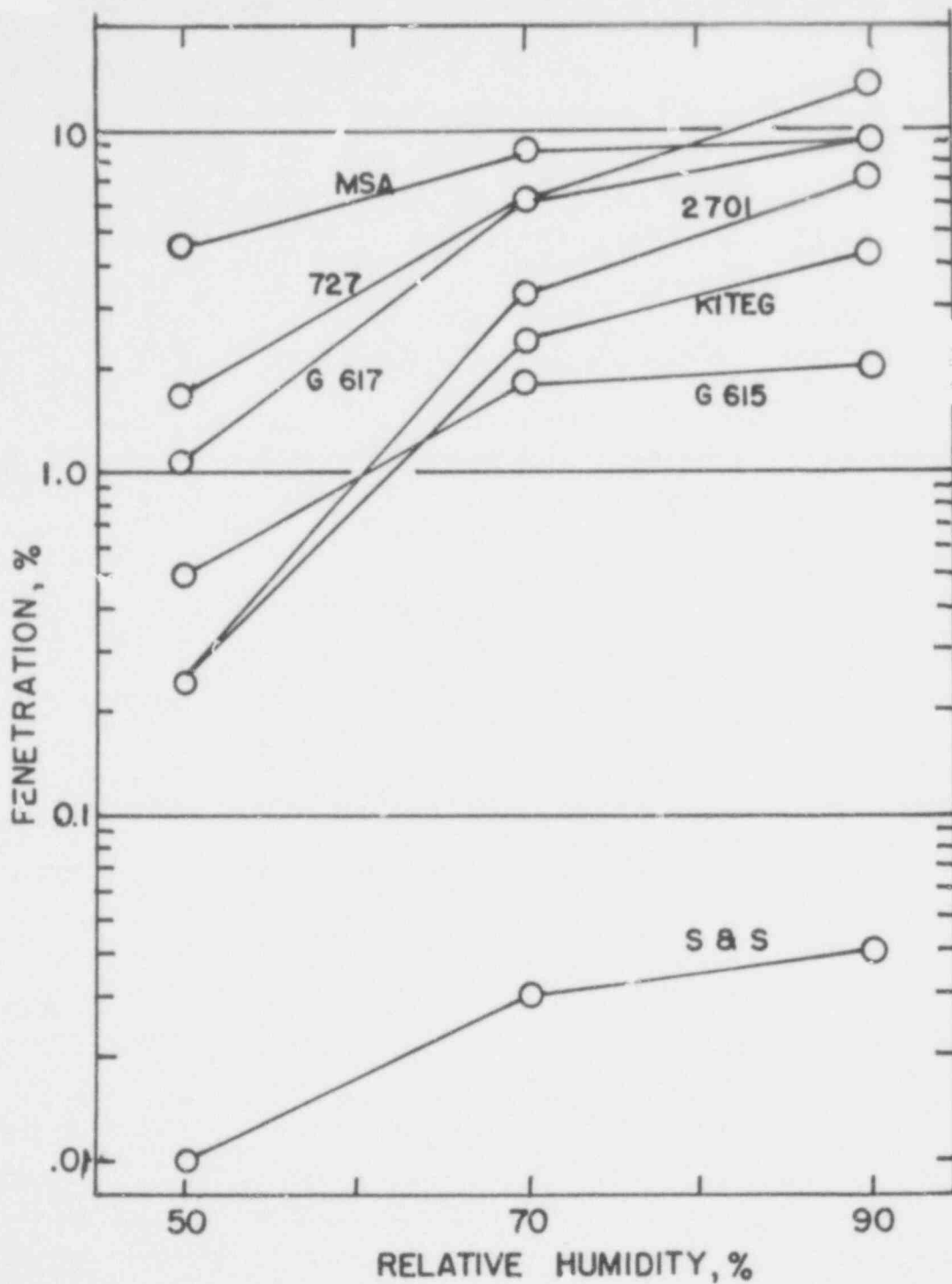


Figure 6: Methyl Iodide-131 Penetration for Charcoals Weathered at Constant Relative Humidity (21-23°C) for 100 Hrs at 100 L/min

measurements are based on a single production sample (25 pounds) of each type. The behavior of the S&S, 5% TEDA, according to these measurements is outstanding for weathering in water vapor only. Mixtures of pollutants and water vapor will be discussed in another section.

Table 4: Results for Charcoals Exposed at Constant Humidity for 100 Hours at a Rate of 100 L/min

| Charcoal | Relative Humidity % | pH (av) | Average of Weight Increase % | Methyl Iodide-131 Penetration % |
|------------------|---------------------|---------|------------------------------|---------------------------------|
| BC 727 | 50 | 9.5 | 25.8 | 1.9 |
| | 70 | 8.7 | 45.4 | 6.3 |
| | 90 | 8.9 | 47.6 | 13.6 |
| G 615 | 50 | 9.9 | 20.0 | 0.56 |
| | 70 | 9.4 | 28.6 | 1.8 ± .04 |
| | 90 | 9.3 | 29.9 | 2.0 |
| MSA 463563 | 50 | 8.3 | 21.4 | 4.66 ± .09 |
| | 70 | 8.1 | 36.1 | 8.6 ± .09 |
| | 90 | 8.3 | 39.0 | 9.27 ± .06 |
| S&S (5% TEDA) | 50 | 8.4 | 15.4 | <.01 |
| | 70 | 8.4 | 26.7 | <.03 |
| | 90 | 8.7 | 31.9 | .04 ± .01 |
| AAF 2701 | 50 | 9.1 | 18.9 | 0.24 ± .02 |
| | 70 | 8.6 | 43.6 | 3.29 ± .04 |
| | 90 | 8.7 | 51.5 | 7.21 ± .05 |
| G 617 | 50 | 9.4 | 20.3 | 1.10 ± .02 |
| | 70 | 9.2 | 57.4 | 6.20 ± .05 |
| | 90 | 9.6 | 61.5 | 9.10 ± .13 |
| FITEG | 50 | 7.7 | 18.6 | 0.25 ± .03 |
| | 70 | 7.7 | 29.1 | 2.45 ± .03 |
| | 90 | 7.7 | 40.0 | 4.37 ± .27 |

The general behavior of the seven charcoals was found to be reproducible. For example, two samples of BC 727 were exposed in August 1977 and in October 1978 and the results are given below:

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| Test | Exposure | RH% | % Penetration |
|------|----------------|-----|---------------|
| 5030 | 1-5 Aug 1977 | 70 | 6.3 |
| 5131 | 16-20 Oct 1978 | 70 | 6.12 ± .076% |
| 5036 | 15-19 Aug 1977 | 90 | 13.6 |
| 5132 | 16-20 Oct 1978 | 90 | 13.7 ± .127% |

The good reproducibility obtained for BC 727 may be due in part to the close control possible in laboratory weathering and to the good reproducibility of the charcoal samples withdrawn from the master stock supply.

2. Exposures to Two Sequential Air Flows of Different Relative Humidity

Since the actual relative humidity of an air flow is never constant during an exposure to outside air, the question was raised as to how rapidly a charcoal filter responds to air flows of different relative humidity. The laboratory exposure-schedule detailed in Table 5 was carried out in which the 100-hour exposure was replaced by two 50-hour periods. Each of two charcoals (G 615 and BC 727) was exposed in the following sequence of relative humidity: 50 → 90, 90 → 50, and 90 → dry air (dew point < 2°F).

Table 5: Exposure Schedule of Charcoals with Air-Water Vapor at Two Levels of Relative Humidity (each 50 hours)

| NRL Test | Charcoal | First Exposure | | Second Exposure | |
|----------|----------|----------------|-----|-----------------|---------|
| | | Date | %RH | Date | %RH |
| 5089 | G 615 | 22-24 May 78 | 50 | 24-26 May 78 | 90 |
| 5090 | G 615 | 22-24 May 78 | 90 | 24-26 May 78 | 50 |
| 5108 | G 615 | 3-5 July 78 | 90 | 5-7 July 78 | dry air |
| 5106 | BC 727 | 26-28 Jun 78 | 50 | 28-30 Jun 78 | 90 |
| 5107 | BC 727 | 26-28 Jun 78 | 90 | 28-30 Jun 78 | 50 |
| 5109 | BC 727 | 3-5 July 78 | 90 | 5-7 July 78 | dry air |

The quantity of water retained by a charcoal at a given relative humidity (see example in Figure 4) is greater on the desorption than on the adsorption branch of the isotherm. This hysteresis is reproducible only under the steady state conditions reached in static systems. In flow systems pertinent to the present studies, the rates of adsorption and desorption that modify the weight-gain and weight-loss behavior depends on the duration of the exposure. Deitz and Blachly (16) showed that the largest weight-gains were obtained within the first 10 hours and increased only slowly after 50 hours. A study of the results (Table 6) indicate that the highest relative humidity of a two-stage exposure may be the controlling factor in the weight-gain observed. These results are plotted in Figure 7 and an arrow indicates the direction of the approach to steady-state values. The change from 90% RH to 50% RH or the change from 50% RH to 90% RH yields approximately the same weight-gain of adsorbed water. However, the change from 90% RH to 0.8% RH does result in almost complete water removal. This behavior demonstrates the need to use low humidity air to dry charcoals which have been exposed to air flows of high relative humidity.

The penetration of methyl iodide was also studied by Deitz and Blachly (16) as a function of the duration of prehumidification (air at 25 L/min and 95% RH) and the penetration was found to increase with increased times of prehumidification. It required about 100 hours before the penetration leveled off; the penetration doubled on extending the prehumidification from 50 to 100 hours. A study of the present results (Table 6) show a similar dependence on exposure time. The penetration after the 100-hour contact times are given, Figure 8, for G 615 and BC 727. It is evident that the two additional exposures for each charcoal that had received only 50 hours at 90% RH did not result in as much penetration. The increased penetration with increased times of prehumidification was quite unexpected when first observed in 1976 with experimental charcoals, and it is important to note that the same effect is present for commercial charcoals.

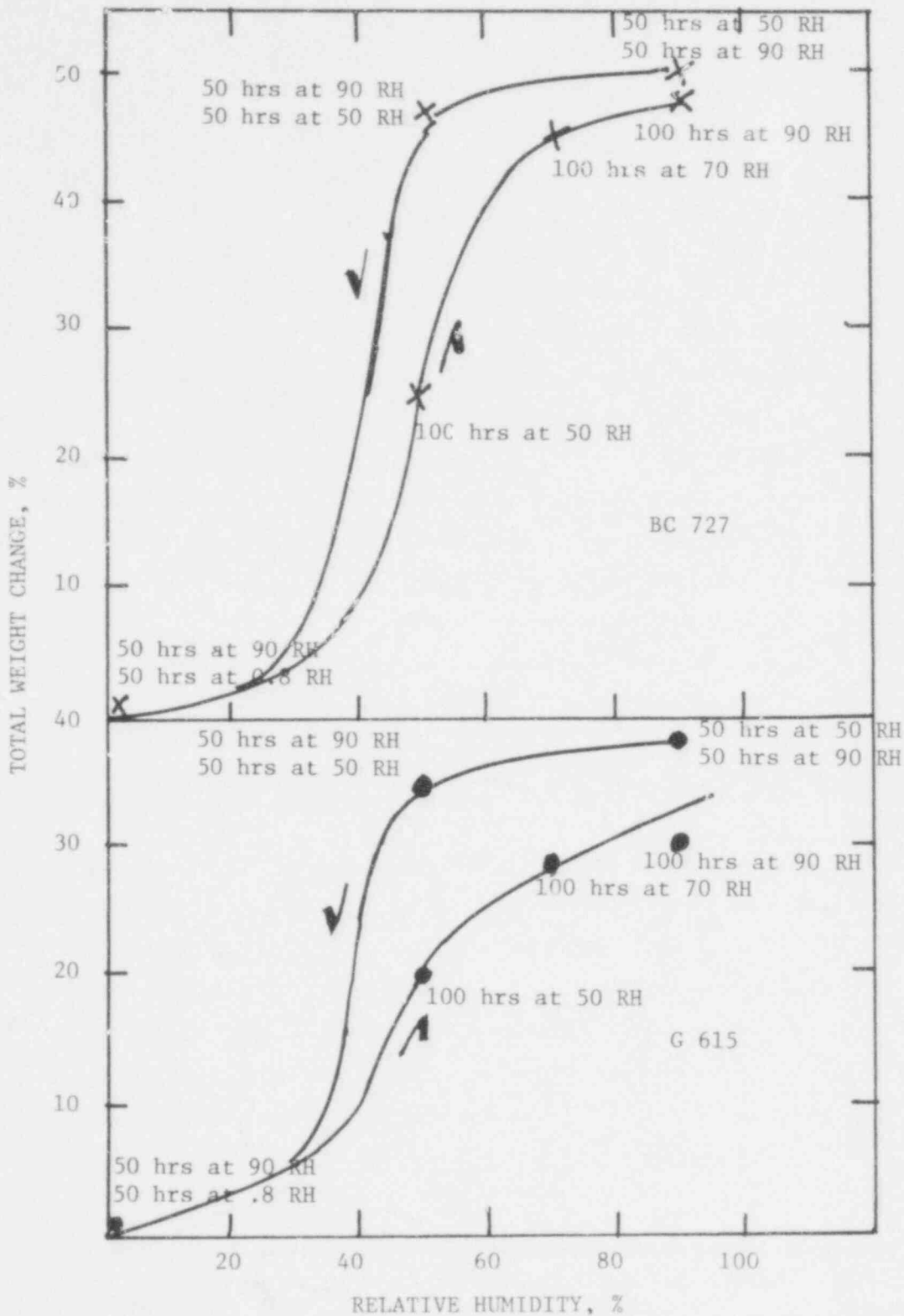


Figure 7: Exposures to Two Sequential Air Flows of Different Relative Humidity

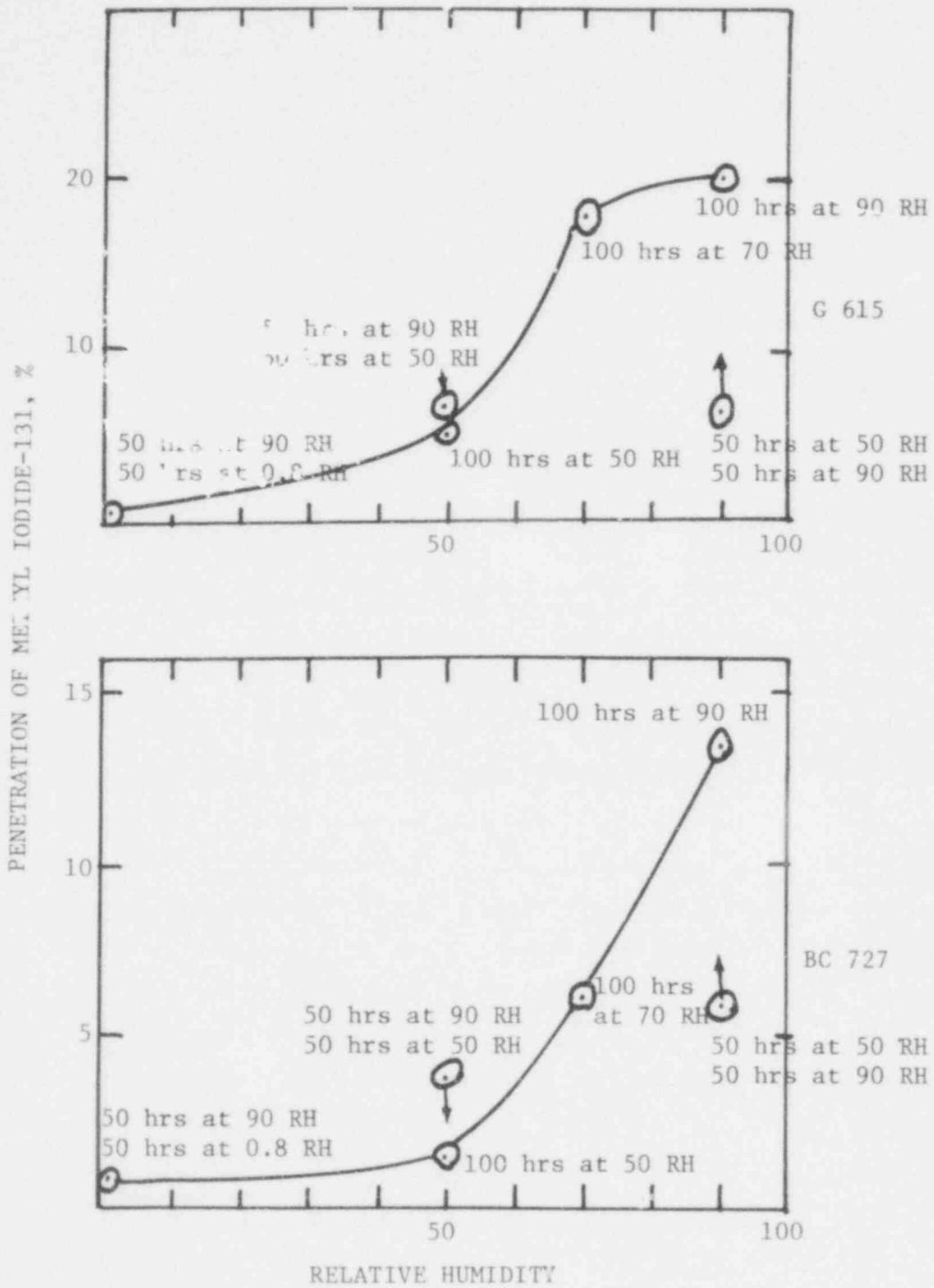


Figure 8: Penetration on Exposure to Sequential Changes in Relative Humidity

Table 6: Results after Exposure at Two Levels of Relative Humidity (Total Time 100 hours)

| Charcoal | Exposure | | pH | Total Wt Change % | Penetration % |
|----------|------------|---------|-----|-------------------|---------------|
| | Time (hrs) | % RH | | | |
| G 615 | 50 | 50 | 9.5 | 38.8 | 0.66 ± .02% |
| | 50 | 90 | | | |
| G 615 | 50 | 90 | 9.4 | 34.8 | 0.69 ± .06 |
| | 50 | 50 | | | |
| G 615 | 50 | 90 | 9.3 | 0.84 | 0.06 ± .01 |
| | 50 | dry air | | | |
| G 615 | 100 | 90 | 9.3 | 29.9 | 2.00 |
| G 615 | 100 | 50 | 9.9 | 20.0 | 0.50 |
| BC 727 | 50 | 50 | 9.2 | 50.1 | 5.88 ± .05 |
| | 50 | 90 | | | |
| BC 727 | 50 | 90 | 9.0 | 46.9 | 3.95 ± .04 |
| | 50 | 50 | | | |
| BC 727 | 50 | 90 | 8.9 | 0.78 | 1.02 ± .05 |
| | 50 | dry air | | | |
| BC 727 | 100 | 90 | 8.9 | 47.6 | 13.6 |
| BC 727 | 100 | 50 | 9.5 | 25.8 | 1.69 |

The above examples of the exposure of charcoals to two levels of relative humidity are only a small approximation to the great variability encountered in practice. The charcoal filter in service is subjected to relatively short periods of high and low relative humidity; periods of dry air will be favorable to high charcoal efficiency and periods of wet weather will steadily increase the moisture content of the charcoal. These preliminary results indicate that it could be advantageous to introduce a flow of air in dry weather to dehydrate effectively charcoal filters which otherwise may not be in operation at that time.

3. Hydrocarbon-Air-Water Vapor Mixtures

Of the contaminants studied, the normally occurring total hydrocarbon fraction (including methane) of the environment is second in

magnitude only to water vapor. The adverse influence of extraneous organic materials on methyl iodide penetration was reported several years ago by Bennett and Strege (10). Assuming a concentration of 5 ppm hexane, for example, and a flow of 100 L/min, the amount of hydrocarbon entering a 2-inch charcoal test filter in 100 hours is 10.3g. Depending on the density of the charcoal, this quantity corresponds to a potential loading of 5 to 7 wt. percent of the charcoal. In some preliminary experiments at NRL, a number of nuclear grade charcoals were first allowed to adsorb a known quantity and type of hydrocarbon and the penetrations of methyl iodide-131 were then determined. In one series, the charcoals were then prehumidified (16 hours exposure to air of 95% RH at a flow of 25 L/min) and in the second series the same charcoals were not prehumidified. The objective was to observe the magnitude of the synergistic influence of water vapor and hydrocarbon on the efficiency of the charcoal. The results (Table 7) give the methyl iodide-131 trapping efficiencies of four charcoals with and without prehumidification after the hydrocarbon contamination and these results may be compared with the behavior after exposure to water vapor alone. Without prehumidification, there is an increase in penetration relative to the original charcoal, but the efficiencies remain within the ASTM suggested acceptable performance requirements for nuclear grade charcoals (Appendix 7). After the prehumidification of the charcoals, the penetration was markedly increased.

All of the combinations of charcoals and pollutants in Table 7 were not studied since the results already demonstrated the synergistic influence of water vapor and hydrocarbon. For example, the penetration for BC 727 was 4.8% for water vapor alone, 0.63% for 2% $C_{14}H_{30}$ alone, and 9.5% for both water vapor and 2% $C_{14}H_{30}$. Also, the penetration for MSA 463563 was 2.5% for water vapor alone, 1.01% for 2% $C_{14}H_{30}$ alone, and 7.5% for both water vapor and 2% $C_{14}H_{30}$. The weathering exposures now in progress involve the insult mixture of organic vapor and 95% RH air going continuously to the charcoal and this is followed by the determination of methyl iodide-131 penetration. The compounds selected include n-hexane, methanol, cyclohexanone and methyl isobutyl ketone.

The last two compounds are found in paint formulations. Some pertinent data helpful in the preparation of the vapor mixture of the desired concentrations are given below:

| | MW | d(g/cc) | bp°C | Temp at 10 torr (°C) |
|------------------------|--------|---------|---------|----------------------|
| n-hexane | 86.17 | 0.659 | 68.7 | -25.0 |
| methanol | 32.04 | 0.792 | 64.7 | -16.2 |
| cyclohexanone | 98.14 | 0.947 | 155.7 | - |
| methyl isobutyl ketone | 100.16 | 0.804 | 117-119 | - |

In these exposures the air flow is 100 L/min (residence time 0.25 sec) and the duration 100 hours. Calibrated permeation tubes are used as standards for n-hexane and methanol air mixtures and diffusion tubes are used for the higher boiling liquids.

The above organic vapors in air mixtures without water vapor were added to one of the charcoals to a level of 11 wt.%. The results are:

| Test | Charcoal | Contaminant | CH ₃ I-131 Penetration |
|------|----------|------------------------|-----------------------------------|
| - | BC 727 | None | 0.014 |
| 5114 | BC 727 | Hexane | 2.04 ± .04 |
| 5115 | BC 727 | Methanol | 0.77 ± .05 |
| 5116 | BC 727 | Methyl Isobutyl Ketone | 1.19 ± .10 |

The addition of 11 wt.% of these compounds did not degrade the charcoal below the allowable performance requirements. However, based on the results presented in Table 7, unacceptable methyl iodide penetration can be expected when a combined flow of water vapor and organic vapor is allowed to enter the charcoal. As detailed above, such experiments are now in progress.

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Table 7: Influence of Prehumidification on Trapping Efficiency
After Hydrocarbon Contamination

| Charcoal | *Prehumidification | % Penetration CH ₃ I-131 | | | |
|--|--------------------|-------------------------------------|-----------|---------------|----------|
| | | BC 717 | BC 727 | MSA 463563 | G 615 |
| Orig. | No | .05 | .014 | 0.13 | 0.05 |
| Orig. | Yes | 1.0 | 4.8 | 2.5 | 0.27 |
| +10% Octane | No | | | 0.37 | |
| | Yes | | | 9.2 | |
| +10% C ₁₄ H ₃₀ | No | 1.2 | 0.33 | 0.80 | |
| | Yes | 5.3 | 15.6 | 15.9 | |
| +2% C ₁₄ H ₃₀ | No | 0.63 | 0.63 | 1.01 | 0.18 |
| | Yes | 8.8 | 9.5 | 7.5 | 1.5 |
| +0.2% C ₁₄ H ₃₀ | No | | | | 0.09 |
| | Yes | | | | 0.81 |

*Prehumidification: 16 hrs, 25 L/min, 95% RH.

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IV. Weathering of Charcoals in Unmodified Outdoor Air at NRL

1. The Scheduling of the Exposures

The study in outdoor air weathering has now been extended to include the same seven commercial charcoals used in the laboratory work. When completed, all of these will have been exposed continuously for 1, 2, 3, 6, or 9 months. One of these charcoals (BC 727) will be weathered in each month of the year in a series of 1-month exposures to cover seasonal changes (for example, the dew point variations, Appendix 2). The contaminants in air exist with a considerable variation in concentration (Appendix 3). Moreover, a charcoal filter behaves as a chromatographic column and the different contaminants vary widely in the retention time in the filter. Those contaminants that are irreversibly held by the charcoal can be expected to modify the chromatographic behavior in a progressive manner. The successful use of any impregnated charcoal by the nuclear industry (for two or three years without regeneration) must somehow be dependent on the reversible adsorption of some of the contaminants and the non-reversibility of the iodine trapping.

The weathering schedule of the charcoals exposed to outdoor air at NRL (still in progress) is summarized in Table 8. The volume of air in each case was determined by the integrating gas meter placed directly downstream from the charcoal; there is a separate meter and a separate air pump for each sample of charcoal. From the time (t) and the volume (V), the number of filter displacements, n , and the average residence times, τ , can be estimated:

$$n = \frac{V}{v} \quad \text{and} \quad \tau = \frac{v}{Q}$$

where v is the volume of the charcoal container and Q is the average flow rate of the air, namely V/t . Table 8 contains the calculated values for n and τ in addition to the exposure dates, V , and the corresponding times, t . The large magnitude of n results from the huge volume

of air that is passed through a charcoal filter. A contaminant concentration of 1 ppm becomes a significant insult when integrated over the total flow.

Table 8: Weathering Schedule for the Charcoals Exposed to Unmodified Outdoor Air at NRL

| Test | Period (Months) | Time (Hours) | Volume (10 ⁶ cu. ft.) | Exposure Date | n ₆ (10 ⁶) | τ (sec.) |
|-----------|-----------------|--------------|----------------------------------|-----------------------|-----------------------------------|----------|
| NACAR 615 | | | | | | |
| 5016 | 1 | 667 | 0.1018 | 2-30 Jun 77 | 7.0 | .34 |
| 5031 | 2 | 1506 | .2209 | 29 Jul - 30 Sep 77 | 15.2 | .36 |
| 5022 | 3 | 2178 | .3302 | 1 Jul - 30 Sep 77 | 22.8 | .34 |
| 5097 | 3 | 2151 | .3077 | 3 Jun - 1 Sep 78 | 21.2 | .36 |
| 5098 | 3 | 2151 | .3130 | 3 Jun - 1 Sep 78 | 21.6 | .36 |
| 5099 | 3 | 2151 | .3124 | 3 Jun - 1 Sep 78 | 21.5 | .36 |
| 5058 | 6 | 3982 | .6288 | 16 Nov - 1 May 78 | 43.4 | .33 |
| 5057 | 9 | 6552 | 1.0379 | 16 Nov - 16 Aug 78 | 71.6 | .33 |
| NACAR 617 | | | | | | |
| 5017 | 1 | 667 | 0.1044 | 2-30 Jun 77 | 7.2 | .33 |
| 5023 | 1 | 668 | .1017 | 1-29 Jul 77 | 7.0 | .34 |
| BC 727 | | | | | | |
| 5014 | 1 | 667 | 0.1100 | 2-30 Jun 77 | 7.6 | .32 |
| 5070 | 1 | 599 | .0919 | 7 Apr - 2 May 78 | 6.3 | .34 |
| 5081 | 1 | 743 | .1143 | 2 May - 2 Jul 78 | 7.9 | .34 |
| 5082 | 1 | 745 | .1076 | 2 May - 2 Jul 78 | 7.4 | .36 |
| 5083 | 1 | 745 | .1110 | 2 May - 2 Jul 78 | 7.7 | .35 |
| 5113 | 1 | 717 | .1097 | 2 Aug - 1 Sep 78 | 7.6 | .34 |
| 5121 | 1+ | 1009 | .1623 | 1 Sep - 13 Oct 78 | 11.2 | .32 |
| 5124 | 1 | 764 | .1248 | 13 Oct - 14 Nov 78 | 8.6 | .32 |
| 5032 | 2 | 1505 | .2274 | 29 Jul - 30 Sep 77 | 15.7 | .34 |
| 5065 | 2 | 1366 | .2065 | 9 Feb - 7 Apr 78 | 14.2 | .34 |
| 5096 | 2 | 1409 | .2159 | 3 Jun - 1 Aug 78 | 14.9 | .34 |
| 5020 | 3 | 2200 | .3422 | 1 Jul - 30 Sep 78 | 23.6 | .34 |
| 5056 | 6 | 3984 | .6575 | 16 Nov 77 - 1 May 78 | 45.3 | .32 |
| 5055 | 9 | 6552 | 1.0105 | 16 Nov 77 - 16 Aug 78 | 69.7 | .34 |

Table 8 (Continued)

| Test | Period (Months) | Time (Hours) | Volume (10 ⁰ cu. ft.) | Exposure Date | n ₆ (10 ⁶) | τ (sec.) |
|---|--------------------|-----------------|-------------------------------------|----------------------|--------------------------------------|-------------|
| BC 717 | | | | | | |
| 5084 | 1 | 745 | .1085 | 2 May - 2 Jun 78 | 7.5 | .36 |
| 5013 | 1 | 667 | .09930 | 2 Jun - 30 Jul 77 | 6.8 | .35 |
| 5010 | 1 | 741 | .08262 | 1 Apr - 2 May 77 | 10.1 | .26 |
| 5024 | 1 | 668 | .1057 | 1-29 Jul 77 | 7.3 | .33 |
| 5019 | 1 | 668 | .1001 | 1-29 Jul 77 | 6.9 | .35 |
| AAF 2701 | | | | | | |
| 5039 | 1 | 696 | 0.1071 | 1-30 Sep 77 | 7.4 | .34 |
| 5040 | 1 | 696 | .1131 | 1-30 Sep 77 | 7.8 | .32 |
| 5061 | 3 | 1920 | .3088 | 16 Nov - 4 Feb 78 | 21.3 | .32 |
| 5118 | 6 | incomplete | | | | |
| 5120 | 9 | incomplete | | | | |
| KITEG (Nuclear Consulting Services, Inc.) | | | | | | |
| 5042 | 1 | 644 | .0954 | 3-30 Sep 77 | 6.6 | .35 |
| 5069 | 3 | 1968 | .2952 | 3 Feb - 2 May 78 | 20.4 | .35 |
| 5119 | 6 | incomplete | | | | |
| 5117 | 9 | incomplete | | | | |
| Sutcliff & Speakman (5% TEDA) | | | | | | |
| 5033 | 1 | 786 | 0.1204 | 29 Jul - 30 Aug 77 | 8.3 | .34 |
| 5034 | 1 | 786 | .1259 | 29 Jul - 30 Aug 77 | 8.7 | .33 |
| 5078 | 1 | 743 | .1234 | 1 May - 1 Jun 78 | 8.5 | .31 |
| 5079 | 1 | 743 | .1189 | 1 May - 1 Jun 78 | 8.2 | .33 |
| 5080 | 1 | 726 | .1138 | 2 May - 1 Jun 78 | 7.8 | .33 |
| 503 | 1+ | 1077 | .1746 | 2 Jun - 17 Jul 78 | 12.0 | .32 |
| 5110 | 1 | 740 | .1200 | 18 Jul - 18 Aug 77 | 8.3 | .32 |
| 5063 | 3 | 1946 | .3160 | 9 Feb 78 - 1 May 78 | 21.8 | .32 |
| 5064 | 6 | 3623 | .6736 | 9 Feb 78 - 10 Aug 78 | 46.5 | .28 |
| 5066 | 9 | 6670 | 1.0104 | 9 Feb 78 - 14 Nov 78 | 69.7 | .34 |
| MSA (463563) | | | | | | |
| 5015 | 1 | 667 | 0.1025 | 2 Jun - 30 Jun 77 | 7.1 | .34 |
| 5021 | 1 | 668 | .0912 | 1 Jul - 29 Jul 77 | 6.3 | .38 |
| 5060 | 3 | 1920 | .3263 | 16 Nov 77 - 4 Feb 78 | 22.5 | .31 |
| 5059 | 6 | 3982 | .6276 | 16 Nov 77 - 1 May 78 | 43.3 | .33 |
| 5077 | 9 | incomplete | | | | |

2. Depth Profile of Properties in Weathered Charcoals

The pH of the water extract of charcoal from the entrance layer was always lower than the remaining charcoal and was also lower than the unexposed material. Table 9, in which the tests are arranged in the same sequence as in Table 8, shows that the pH of the entrance layers generally decreases with exposure time (months) and these values are listed below:

| Month | 615 | 727 | 2701 | S&S | MSA | KITEG |
|-------|-----|-----|------|-----|-----|-------|
| 1 | 9.3 | 8.5 | 7.6 | 8.1 | 7.5 | 6.7 |
| 2 | 8.2 | 7.5 | - | - | - | - |
| 3 | 7.8 | 7.0 | 3.6 | 4.5 | 3.4 | 2.8 |
| 6 | 3.8 | 3.1 | 2.4 | 4.0 | 2.5 | 2.4 |
| 9 | 4.1 | 3.3 | - | 3.2 | 2.7 | - |

The pH values of the remaining three layers of charcoal in the test beds did not differ significantly from each other until about the ninth month of weathering at which time some penetration of the pH-lowering contaminants was detectable.

The observed weight-increases varied considerably with the dew point of the outdoor air supply. The majority of the 48 weathering tests (Table 9) showed a two-digit weight increase, but 11 of these were definitely smaller, having average increases of only 2.5 to 6.0 wt.%. The exceptions grouped in Table 10, include weathered charcoals sampled at four different times in 1978; five completed exposures on 1 May and 2 May, three on 1 June, two on 4 February, and one on 10 August. Using the published observations given every 3 hours (7) of the relative humidity and dew points in the immediate vicinity of NRL, the averages were obtained for the immediate 24 hours before termination and also for the period 24 to 48 hours before termination (see also data given in Appendix 8). The results (Table 10) indicate no correlation among the various kinds of charcoal (one exception) and no correlation with the duration of weathering. However, five charcoals (BC 727, KITEG, G 615, MSA, and 2701) have in common the fact that the relative humidity was

below 50% and the dew points were 24°F and less. Thus, the small increase in weight correlates with the known small adsorption of water vapor for these five charcoals under these conditions. The remaining four charcoals in this set of exposures were manufactured by Sutcliffe and Speakman and constitute an anomaly.

The results on S&S (5% TEDA) (Table 10) could indicate that the expected gain in weight due to water adsorption might be offset by some loss in weight, possibly the impregnant. The impregnation of this charcoal is nominally 5 wt.% TEDA (triethylenediamine). Some volatilization might have taken place in detectable amounts during the long exposure times, since the vapor pressure of TEDA is about 0.2 torr at 25°C. However, even in the unlikely loss of all TEDA, the weight gain on weathering would have been decreased by only 5 wt.% below the nominal increase due to water vapor adsorption. The average dew points during the final days of the exposure (1 May - 1 June 1978) were not exceptionally low and consequently, it is not known what could have prevented the expected weight increases of the S&S samples. As will be shown in the next section, the corresponding values for methyl iodide-131 penetration for the S&S charcoal were of a satisfactory low level.

Table 9: Profile Along Line of Flow on Weathering Charcoals in Unmodified Outdoor Air - pH and Weight Increase

| Test | Months | pH of Layers | | | | % Weight Increase of Layers | | | |
|-----------|--------|--------------|-----|------|------|-----------------------------|------|------|------|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| NACAR 615 | | | | | | | | | |
| 5016 | 1 | 9.3 | 9.5 | 9.6 | 9.7 | 21.7 | 19.8 | 17.0 | 14.7 |
| 5031 | 2 | 8.2 | 9.8 | 10.0 | 10.0 | 21.3 | 20.7 | 20.5 | 17.7 |
| 5022 | 3 | 7.5 | 9.8 | 10.0 | 10.0 | 25.9 | 26.2 | 26.6 | 25.7 |
| 5097 | 3 | 7.9 | 9.2 | 9.2 | 9.3 | 35.8 | 35.4 | 35.4 | 36.1 |
| 5098 | 3 | 7.9 | 9.2 | 9.2 | 9.2 | 36.7 | 35.3 | 35.5 | 35.1 |
| 5099 | 3 | 7.9 | 9.2 | 9.3 | 9.2 | 36.0 | 36.1 | 36.2 | 37.1 |
| 5058 | 6 | 3.8 | 9.4 | 9.6 | 9.6 | 6.5 | 4.0 | 3.2 | 2.9 |
| 5057 | 9 | 4.1 | 8.5 | 9.2 | 9.2 | 36.4 | 35.0 | 35.2 | 35.6 |
| NACAR 617 | | | | | | | | | |
| 5017 | 1 | 8.8 | 9.4 | 9.4 | 9.4 | 22.2 | 20.3 | 18.8 | 16.9 |
| 5023 | 1 | 8.4 | 9.2 | 9.2 | 9.2 | 45.9 | 46.3 | 44.9 | 42.6 |
| BC 727 | | | | | | | | | |
| 5014 | 1 | 8.8 | 9.3 | 9.3 | 9.3 | 25.2 | 24.0 | 22.0 | 20.5 |
| 5070 | 1 | 8.3 | 9.2 | 9.2 | 9.2 | 4.9 | 5.6 | 5.8 | 5.8 |
| 5081 | 1 | 8.4 | 9.2 | 9.2 | 9.2 | 11.4 | 19.1 | 27.8 | 28.4 |
| 5082 | 1 | 8.5 | 9.3 | 9.3 | 9.3 | 12.8 | 20.0 | 26.1 | 26.2 |
| 5083 | 1 | 8.4 | 9.2 | 9.2 | 9.2 | 12.9 | 19.1 | 19.6 | 19.9 |
| 5113 | 1 | 8.6 | 9.0 | 9.0 | 9.0 | 46.6 | 47.0 | 46.8 | 46.8 |
| 5121 | 1+ | 8.0 | 9.1 | 9.0 | 9.0 | 31.1 | 36.0 | 36.6 | 37.0 |
| 5124 | 1 | 7.5 | 8.9 | 8.8 | 8.8 | 33.3 | 34.7 | 35.6 | 35.6 |
| 5032 | 2 | 7.3 | 9.2 | 9.5 | 9.5 | 34.8 | 35.6 | 34.7 | 32.2 |
| 5065 | 2 | 7.3 | 9.3 | 9.2 | 9.4 | 27.0 | 24.6 | 22.2 | 19.5 |
| 5096 | 2 | 8.0 | 9.3 | 9.4 | 9.4 | 46.8 | 46.6 | 47.2 | 48.0 |
| 5020 | 3 | 7.0 | 9.4 | 9.5 | 9.5 | 34.5 | 36.0 | 35.0 | 33.0 |
| 5056 | 6 | 3.1 | 8.9 | 9.1 | 9.0 | 9.1 | 3.0 | 2.6 | 2.5 |
| 5055 | 9 | 3.3 | 8.5 | 8.8 | 8.8 | 47.4 | 45.1 | 45.1 | 44.7 |
| BC 717 | | | | | | | | | |
| 5084 | 1 | 8.2 | 9.1 | 9.1 | 9.1 | 16.0 | 23.7 | 29.0 | 30.0 |
| 5013 | 1 | 8.8 | 9.2 | 9.3 | 9.3 | 24.1 | 21.8 | 20.1 | 17.8 |
| 5010 | 1 | 8.5 | 8.9 | 9.0 | 9.2 | 37.0 | 36.7 | 35.5 | 34.0 |
| 5024 | 1 | 8.6 | 8.6 | 8.9 | 9.0 | 35.3 | 35.5 | 35.6 | 35.6 |
| 5019 | 1 | 8.1 | 8.6 | 8.9 | 8.8 | 13.2 | 11.6 | 11.8 | 9.9 |

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Table 9 (Continued)

| Test | Months | pH of Layers | | | | % Weight Increase of Layers | | | |
|---|--------|--------------|------|------|-----|-----------------------------|------|------|------|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 2701 (American Air Filter) | | | | | | | | | |
| 5039 | 1 | 7.6 | 8.5 | 9.1 | 9.1 | 27.4 | 30.2 | 28.2 | 25.0 |
| 40 | 1 | 7.6 | 8.7 | 9.1 | 9.1 | 26.7 | 29.4 | 26.7 | 22.2 |
| 61 | 3 | 3.6 | 8.2 | 8.5 | 8.6 | 5.5 | 2.0 | 1.8 | 1.7 |
| 5118 | 6 | 2.4 | 7.0 | 8.0 | 8.0 | 27.0 | 18.9 | 16.5 | 14.8 |
| 5120 | 9 | not finished | | | | | | | |
| KITEG (Nuclear Consulting Services, Inc.) | | | | | | | | | |
| 5042 | 1 | 6.7 | 9.2 | 9.6 | 9.6 | 16.8 | 16.2 | 16.7 | 17.3 |
| 5069 | 3 | 2.8 | 7.2 | 7.3 | 7.4 | 9.2 | 5.2 | 5.0 | 4.7 |
| 5119 | 6 | 2.4 | 5.7 | 6.9 | 7.0 | 27.0 | 20.0 | 19.1 | 18.4 |
| 5117 | 9 | not finished | | | | | | | |
| Sutcliff & Speakman (5% TEDA) | | | | | | | | | |
| 5033 | 1 | 7.1 | 7.9 | 7.8 | 7.9 | 21.2 | 15.8 | 14.7 | 14.2 |
| 5034 | 1 | 7.2 | 8.0 | 8.1 | 8.0 | 14.5 | 13.7 | 14.4 | 14.3 |
| 5078 | 1 | 8.2 | 8.6 | 8.6 | 8.6 | 1.0 | 1.5 | 6.0 | 9.4 |
| 5079 | 1 | 8.1 | 8.6 | 8.6 | 8.6 | 0.4 | 1.3 | 5.8 | 9.4 |
| 5080 | 1 | 8.2 | 8.6 | 8.6 | 8.6 | 0.0 | 2.3 | 6.8 | 9.8 |
| 5093 | 1+ | 7.7 | 8.2 | 8.3 | 8.3 | 25.7 | 26.9 | 26.3 | 26.4 |
| 5110 | 1 | 8.0 | 8.3 | 8.3 | 8.4 | 19.5 | 20.8 | 21.9 | 21.5 |
| 5063 | 3 | 4.5 | 8.7 | 8.9 | 8.9 | 5.9 | 2.4 | 2.1 | 2.0 |
| 5064 | 6 | 4.0 | 8.1 | 8.3 | 8.4 | 30.7 | 28.7 | 28.5 | 28.6 |
| 5066 | 9 | 3.2 | 7.4 | 7.9 | 8.1 | 26.5 | 22.2 | 22.0 | 22.0 |
| MSA (463563) | | | | | | | | | |
| 5015 | 1 | 7.45 | 7.65 | 7.65 | 7.8 | 19.8 | 17.3 | 14.6 | 11.8 |
| 5021 | 1 | 6.7 | 8.2 | 8.2 | 8.2 | 30.0 | 30.3 | 30.1 | 30.3 |
| 5060 | 3 | 3.4 | 7.5 | 7.7 | 7.8 | 5.0 | 1.9 | 1.6 | 1.6 |
| 5059 | 6 | 2.5 | 6.9 | 7.8 | 8.0 | 8.0 | 2.4 | 1.7 | 1.6 |
| 5077 | 9 | 2.7 | 6.4 | 6.9 | 7.3 | 9.2 | 1.6 | 0.92 | 0.06 |

Table 10: Correlation of Weight Increases with the Relative Humidity and Dew Point of the Air

| Test | Charcoal | Months | Termination Date | Wt. Increase % (Av.) | Average Relative Humidity | | Average (°F) Dew Point | |
|------|----------|--------|------------------|----------------------|---------------------------|--------|------------------------|--------|
| | | | | | 48 - 24 | 24 - 0 | 48 - 24 | 24 - 0 |
| 5070 | 727 | 1 | 2 May 78 | 5.5 | 26 | 35 | 23 | 24 |
| 5069 | KITEG | 3 | 2 May 78 | 6.0 | 26 | 35 | 23 | 24 |
| 5058 | 615 | 6 | 2 May 78 | 4.2 | 26 | 35 | 23 | 24 |
| 5056 | 727 | 6 | 1 May 78 | 4.3 | 26 | 35 | 23 | 24 |
| 5059 | MSA | 6 | 1 May 78 | 3.4 | 26 | 35 | 23 | 24 |
| 5060 | MSA | 3 | 4 Feb 78 | 2.5 | 59 | 46 | 15 | 8 |
| 5061 | 2701 | 3 | 4 Feb 78 | 2.8 | 59 | 46 | 15 | 8 |
| 5079 | S&S | 1 | 1 Jun 78 | 4.2 | 73 | 64 | 66 | 63 |
| 5080 | S&S | 1 | 1 Jun 78 | 4.7 | 73 | 64 | 66 | 63 |
| 5063 | S&S | 6 | 10 Aug 78 | 3.1 | 72 | 78 | 72 | 69 |
| 5078 | S&S | 1 | 1 Jun 78 | 4.4 | 73 | 64 | 66 | 63 |

NOTE: 24-0 signifies the 24 hours before termination.

48-24 signifies the period between 48 and 24 hours before termination of the exposures.

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3. Results for the Penetration of Methyl Iodide-131

Of the three test-modes or configurations for conducting the methyl iodide-131 test for weathered charcoals (see page 8), it is possible to calculate a result for Mode 2 from the four values of penetration obtained by Mode 1. Using the expression for penetration

$$\frac{C_i}{C_o} = \exp(-k_v \tau) \quad (1)$$
$$k_v = -1/\tau \ln \frac{C_i}{C_o}$$

where C_i = penetration concentration and C_o = initial concentration, τ = residence time and k_v reaction rate constant, the values of k_v are first calculated with the data of Mode 1. In each of these cases, $\tau = 0.25$ sec. Since $\tau = .0625$ in each layer of Mode 2, the penetration is then calculated for each of the four layers using the corresponding value of k_v . Third, the product is calculated for the desired penetration, namely

$$\text{Product} = \frac{C_1}{C_o} \times \frac{C_2}{C_1} \times \frac{C_3}{C_2} \times \frac{C_4}{C_3} = \frac{C_4}{C_o} \quad (2)$$

Some examples are given in Table 11 using the data for weathered charcoals.

It was not possible to make a comparison between calculated and observed penetrations in Mode 2 of the weathered charcoal examples given in Table 11 because all of the weathered sample was required for the four determinations of Mode 1. Accordingly, two additional samples were weathered under the same conditions with the laboratory control previously used (air at 100 L/min for 100 hours at 70% RH and at 90% RH). The results given in detail in Table 12 show excellent agreement between calculated and observed penetrations of methyl iodide-131 for

Table 11: Calculation of Penetration in Mode 2 Configuration
From the Results in Mode 1

| Test | Weathered Layer | Depth (cm) | Penetration Fraction | τ | k_v | τ | $e^{-k_v \tau}$ | Product* |
|------|-----------------|------------|----------------------|--------|--------|--------|-----------------|----------|
| 5016 | 1 | 5.08 | .0177 | 0.25 | 16.137 | .0625 | 0.365 | 0.72% |
| | 2 | 5.08 | .0064 | 0.25 | 20.206 | .0625 | .283 | |
| | 3 | 5.08 | .0034 | 0.25 | 22.736 | .0625 | .241 | |
| | 4 | 5.08 | .0070 | 0.25 | 19.847 | .0625 | .289 | |
| 5031 | 1 | 5.08 | .0342 | 0.25 | 13.502 | .0625 | 0.430 | 1.41% |
| | 2 | 5.08 | .0132 | 0.25 | 17.310 | .0625 | .339 | |
| | 3 | 5.08 | .0086 | 0.25 | 19.024 | .0625 | .305 | |
| | 4 | 5.08 | .0102 | 0.25 | .341 | .0625 | .318 | |
| 5022 | 1 | 5.08 | .0862 | 0.25 | 9.804 | .0625 | 0.542 | 1.84% |
| | 2 | 5.08 | .0138 | 0.25 | 17.132 | .0625 | .343 | |
| | 3 | 5.08 | .0119 | 0.25 | 17.725 | .0625 | .330 | |
| | 4 | 5.08 | .0081 | 0.25 | 19.264 | .0625 | .300 | |
| 5014 | 1 | 5.08 | .0267 | 0.25 | 14.492 | .0625 | 0.404 | 1.30% |
| | 2 | 5.08 | .0120 | 0.25 | 17.691 | .0625 | .331 | |
| | 3 | 5.08 | .0068 | 0.25 | 19.963 | .0625 | .287 | |
| | 4 | 5.08 | .0131 | 0.25 | 17.341 | .0625 | .338 | |
| 5032 | 1 | 5.08 | 0.0581 | 0.25 | 11.382 | .0625 | 0.491 | 3.56% |
| | 2 | 5.08 | .0258 | 0.25 | 14.630 | .0625 | .401 | |
| | 3 | 5.08 | .0309 | 0.25 | 13.908 | .0625 | .419 | |
| | 4 | 5.08 | .0345 | 0.25 | 13.467 | .0625 | .431 | |
| 5020 | 1 | 5.08 | 0.216 | 0.25 | 6.130 | .0625 | 0.682 | 7.6% |
| | 2 | 5.08 | .054 | 0.25 | 11.675 | .0625 | .482 | |
| | 3 | 5.08 | .050 | 0.25 | 11.983 | .0625 | .473 | |
| | 4 | 5.08 | .057 | 0.25 | 11.459 | .0625 | .488 | |

*Product determined from equation (2).

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2.40

the same charcoal (BC 727). The reproducibility of the laboratory weathering procedure is also established by these measurements.

Table 12: Comparison of the Penetrations of Methyl Iodide-131 for the Same Charcoal Weathered in Mode 1 and Mode 2

| Test | Weathered Layer | Depth (cm) | Penetration Fraction | τ (sec) | k_v | τ (sec) | $e^{-k_v \tau}$ | Penetration Calc (%) | Penetration Obsvd (%) |
|------------------------------|-----------------|------------|----------------------|--------------|--------|--------------|-----------------|----------------------|-----------------------|
| 5030 (Mode 1) (90% RH) | 1 | 5.08 | .163 | 0.25 | 7.256 | .0625 | .6354 | 13.6 | |
| | 2 | 5.08 | .132 | 0.25 | 8.100 | .0625 | .6028 | | |
| | 3 | 5.08 | .152 | 0.25 | 7.535 | .0625 | .6244 | | |
| | 4 | 5.08 | .107 | 0.25 | 8.940 | .0625 | .5719 | | |
| 5132 (Mode 2) | 1,2,3,4 | 5.08 | .137 | 0.25 | | | | | 13.7 |
| 5036 (Mode 1) (70% RH) | 1 | 5.08 | .127 | 0.25 | 8.254 | .0625 | .5970 | 6.3 | |
| | 2 | 5.08 | .051 | 0.25 | 11.904 | .0625 | .475 | | |
| | 3 | 5.08 | .073 | 0.25 | 10.469 | .0625 | .5198 | | |
| | 4 | 5.08 | .034 | 0.25 | 13.526 | .0625 | .4293 | | |
| 5131 | 1,2,3,4 | 5.08 | .0612 | 0.25 | | | | | 6.12 |

NOTE: The two columns headed 1,2,3,4 signify that the test column was assembled with equal volumes of carbon from the four weathered layers and arranged in the same sequence.

The results for the penetration of methyl iodide-131 after weathering in outdoor air are summarized in Table 13. These include all data for the different commercial charcoals at the specified exposure times listed in monthly increments. These times have now been extended sufficiently to see the seasonal influence of the environment.

A considerable amount of information is contained in Table 13. For example, the results in weathering NACAR 615 are assembled in Table 14.

Table 13: Methyl Iodide-131 Penetration Through Channels
After Weathering in Unmodified Outdoor Air

| Test | Period (Months) | % Penetrations | | | | Calcd. 1,2,3,4 | Observed 1,2,3,4 |
|-----------|--------------------|----------------|------|------|------|-------------------|---------------------|
| | | 1 | 2 | 3 | 4 | | |
| NACAR 615 | | | | | | | |
| 5016 | 1 | 1.77 | 0.64 | 0.34 | 0.70 | 0.72 | |
| 5031 | 2 | 3.42 | 1.32 | 0.86 | 1.02 | 1.41 | |
| 5022 | 3 | 8.62 | 1.38 | 1.19 | 0.81 | 1.84 | |
| 5097 | 3 | | | | | | 3.13 ± .03 |
| 5098 | 3 | | | | | | 1.83 |
| 5099 | 3 | | | | | | 3.10 ± .049 |
| 5058 | 6 | 8.33 | 0.27 | 0.34 | 0.18 | 0.61 | |
| 5057 | 9 | | | | | | 6.62 ± .20 |
| NACAR 617 | | | | | | | |
| 5017 | 1 | 1.90 | 0.62 | 0.32 | 0.64 | 0.70 | |
| 5023 | 1 | 12.91 | | | 5.40 | | |
| BC 727 | | | | | | | |
| 5014 | 1 | 2.67 | 1.20 | 0.68 | 1.31 | 1.30 | |
| 5070 | 1 | | | | | | 1.13 |
| 5081 | 1 | | | | | | 0.92 |
| 5082 | 1 | | | | | | 0.69 |
| 5083 | 1 | | | | | | 0.83 |
| 5113 | 1 | | | | | | 13.2 |
| 5121 | 1+ | | | | | | 3.31 |
| 5124 | 1 | | | | | | 0.81 |
| 5032 | 2 | 5.81 | 2.58 | 3.09 | 3.45 | 3.56 | |
| 5065 | 2 | 15.4 | 4.8 | 5.1 | 5.8 | 6.84 | |
| 5096 | 2 | | | | | | 3.79 ± 0.16 |
| 5020 | 3 | 21.6 | 5.4 | 5.0 | 5.7 | 7.59 | |
| 5056 | 6 | 13.3 | 0.97 | 1.50 | 0.97 | 2. | |
| 5055 | 9 | | | | | | 15.6 |
| BC 717 | | | | | | | |
| 5084 | 1 | | | | | | |
| 5013 | 1 | 0.83 | 0.44 | 1.68 | 0.92 | 0.87 | |
| 5010 | 1 | | | | | | 0.67 |
| 5024 | 1 | 11.7 | 3.75 | 3.75 | 4.86 | 5.32 | |
| 5019 | 1 | 13.2 | 11.6 | 11.8 | 9.86 | 11.55 | |

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Table 13 (Continued)

| Test | Period (Months) | % Penetrations | | | | Calcd. 1,2,3,4 | Obserd. 1,2,3,4 |
|---|--------------------|----------------|------|------|------|-------------------|--------------------|
| | | 1 | 2 | 3 | 4 | | |
| MCI (American Air Filter) | | | | | | | |
| 5039 | 1 | 5.95 | 3.9 | 2.6 | 1.75 | 3.21 | |
| 5040 | 1 | 4.38 | 2.8 | 1.75 | 1.11 | 2.21 | |
| 5061 | 3 | | | | | | 0.287 ± .051 |
| 5118 | 6 | | | | | | |
| 5120 | 9 | | | | | | |
| KITEG (Nuclear Consulting Services, Inc.) | | | | | | | |
| 5042 | 1 | | | | | | 0.73 |
| 5069 | 3 | | | | | | 3.22 ± .09 |
| 5119 | 6 | | | | | | |
| 5117 | 9 | | | | | | |
| Sutcliff and Speakman | | | | | | | |
| 5033 | 1 | 8.63 | | | 0.52 | | |
| 5034 | 1 | 3.88 | 0.87 | 0.4 | 0.45 | 0.90 | |
| 5078 | 1 | | | | | | .05 |
| 5079 | 1 | | | | | | <.02 |
| 5080 | 1 | | | | | | .02 |
| 5093 | 1+ | | | | | | .13 ± .02 |
| 5110 | 1 | | | | | | 0.39 |
| 5063 | 3 | 1.93 | .05 | .13 | .08 | 0.18 | |
| 5064 | 6 | | | | | | 0.82 ± 0.12 |
| 5066 | 9 | | | | | | 0.46 ± .02 |
| MSA (463563) | | | | | | | |
| 5015 | 1 | 4.03 | 1.86 | 3.61 | 2.06 | 2.73 | |
| 5021 | 1 | 15.5 | 8.0 | 8.81 | 8.39 | 9.78 | |
| 5060 | 3 | | | | | | 0.659 ± .020 |
| 5059 | 6 | | | | | | |
| 5077 | 9 | | | | | | |

NOTE: The two columns headed 1,2,3,4 signify that the test column was assembled with equal volumes of carbon from the four weathered layers and arranged in the same sequence.

Table 14: The Penetration of NACAR 615 and Duration of Exposure

| NRL Test | Time (Months) | Termination Date | Dew Points °F | | | Penetration % |
|----------|---------------|------------------|---------------|-----|-----|---------------|
| | | | S-2 | S-1 | S | |
| 5022 | 3 | 30 Sep 77 | 52° | 45° | 51° | 1.84 |
| 5097 | 3 | 1 Sep 78 | 71 | 72 | 69 | 3.13 ± .03 |
| 5099 | 3 | 1 Sep 78 | 71 | 72 | 69 | 3.10 ± .049 |
| 5058 | 6 | 1 May 78 | 35 | 38 | 19 | 0.61 ± .17 |
| 5057 | 9 | 16 Aug 78 | 75 | 77 | 77 | 6.62 ± .20 |

The two samples (5097, 5099), exposed during the same three-month period ending 1 September 1978, gave the reproducibility indicated in Table 14 for the penetration values. Included are the uncertainties of sampling the starting material, those inherent in weathering and those in the determination of the penetration. The mean value for penetration of 3.12 is based on too few measurements for statistical analysis. The test 5022 also for three-months ending 30 September 1977 showed less penetration, but this behavior may be correlated with the lower dew point just before sampling. In Table 14, the Column S-2 gives the dew points two days before termination of the exposure, S-1 gives values one day before, and Column S corresponds to the day of termination. Sample 5058 weathered for six months terminated on 1 May 1978 during a period of rather dry weather (very low dew point) and showed only 0.61% penetration. After 9 months of weathering the sample of G 615 showed a high penetration (6.62% in Mode 2) and a corresponding low acidity of the entrance layer (pH = 4.1).

The above results are yet another example of the effect of water adsorption on charcoal and the subsequent penetration of methyl iodide-131. The separate contributions of contaminants and water vapor and their synergistic influence on the weathering of charcoal are important and critical factors. The reduction in the partial pressure of water during the period of low humidity weather may function as a

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regeneration process with respect to a partial recovery of the methyl iodide trapping efficiency.

The weight-gain of a charcoal was found to respond to the meteorological conditions during the exposure. For example, NACAR 617 was exposed for one month in June 1977 and in July 1977. The data for the two tests with the charcoal are summarized in Table 15.

Table 15: The One-Month Performance of NACAR 617 in June and July 1977

| | June | July |
|---------------------------|-------|-------|
| Average Temperature (°F) | 74° | 80.9° |
| Average Dew Point (°F) | 59° | 67° |
| Weight Increase - Layer 1 | 22.2% | 45.9% |
| 2 | 20.3 | 46.3 |
| 3 | 18.8 | 44.9 |
| 4 | 16.9 | 42.6 |
| Penetration - Layer 1 | 1.9% | 12.9% |
| 2 | 0.62 | - |
| 3 | 0.32 | - |
| 4 | 0.64 | 5.4 |

The moisture content of the air was less in June than in July and accounts for the two-fold increase in adsorbed moisture of the July sample. By reference to Figure 8, however, it is seen that the increase comes in the critical region where the penetration increases sharply with relative pressure. As a result a 7- to 8-fold increase in penetration was realized.

The attempts to correlate the one-month exposures of BC 727 with meteorological data are summarized in Figure 9. The monthly-average dew point and temperature for each exposure are given in Table 16 with the observed penetration of methyl iodide-131. The latter is plotted (Figure 9) as a function of dew point, relative humidity and the quantity

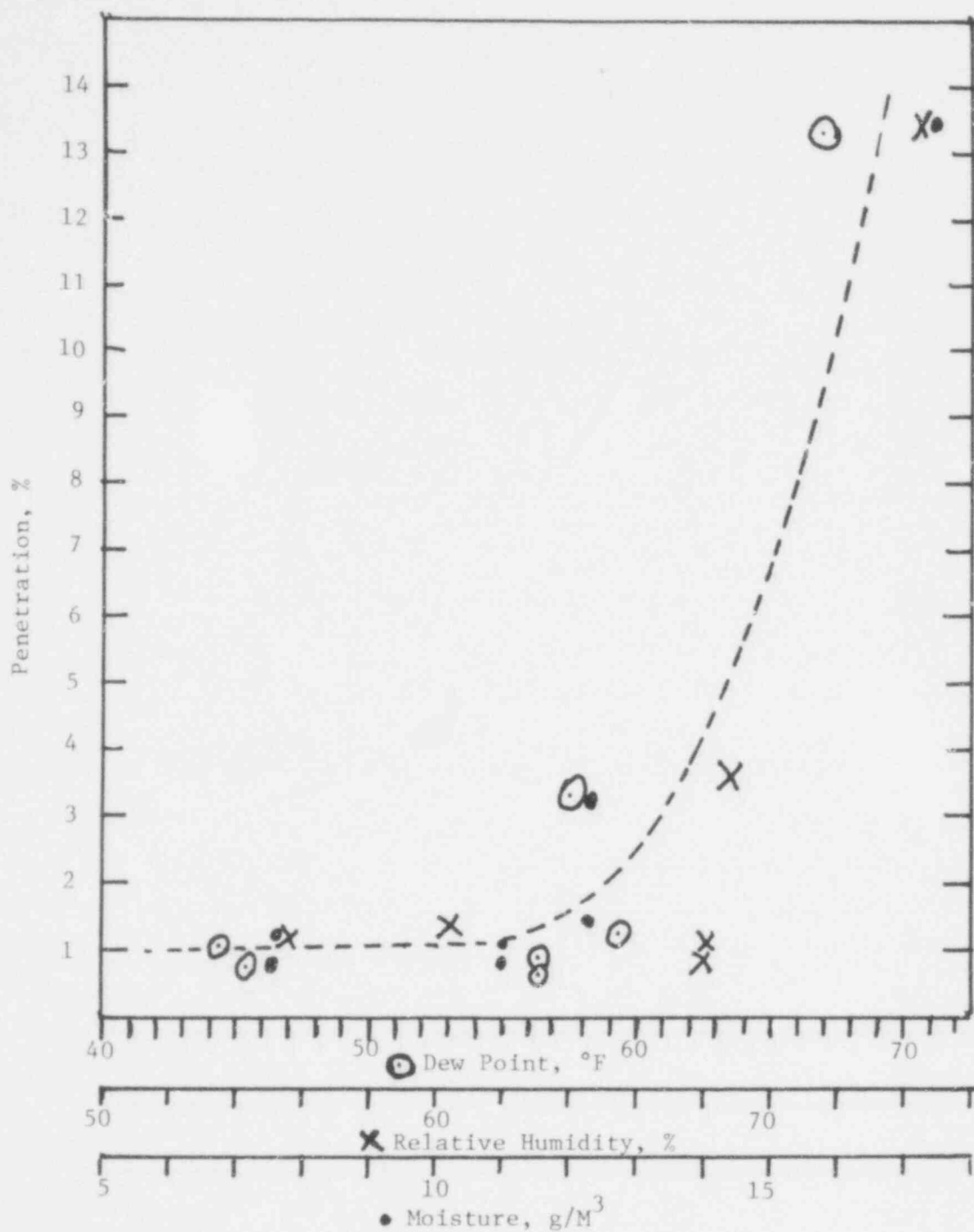


Figure 9: Penetration of Methyl Iodide-131 through BC 727
After One-Month Exposure to Outdoor Air (Table 13)

of water vapor that were present during exposure. The penetration increased sharply within the same range since these parameters are inter-related. The behavior is similar to that previously reported (Figure 7) for laboratory exposures with water vapor-air flows.

Table 16: One-Month Exposures of BC 727

| Sample | Date | Average Temp. °F | Average Dew Point | Penetration % |
|--------|--------------------|------------------|-------------------|---------------|
| 5014 | 2-30 Jun 77 | 74 | 59 | 1.30 |
| 5070 | 7 Jan - 2 May 78 | 60 | 44 | 1.13 |
| 5081 | 2 May - 2 Jul 78 | 69 | 56 | 0.92 |
| 5082 | 2 May - 2 Jul 78 | 69 | 56 | 0.69 |
| 5083 | 2 May - 2 Jul 78 | 69 | 56 | 0.83 |
| 5113 | 2 Aug - 1 Sep 78 | 79 | 68 | 13.2 |
| 5124 | 13 Oct - 14 Nov 78 | 58 | 45 | 0.81 |
| 5121 | 1 Sep - 13 Oct 78 | 70 | 57 | 3.31 |

4. Behavior in Intermittent Air Flows

Frequently, a charcoal filter is placed on a stand-by basis and thus is used with intermittent air flows. One result of such operations may be to redistribute the adsorbed contaminants through surface mobility on the large area of the activated carbon. Adsorbed molecules are known to diffuse in directions parallel to the surface and the extent varies with the potential energy barrier that exists. Low boiling hydrocarbons, for example, may diffuse with less restraint than a strongly held contaminant like ozone.

In order to observe the possible influence of "resting" impregnated activated carbons, three samples (BC 727, NACAR G 615, and Sutcliffe and Speakman 5% TEDA) were exposed for known periods of outdoor air flow and stand-by. The weathering was conducted for one month, then held inactive by a secure closure of the inlet and outlet, and then again exposed for an additional month. An additional off-on cycle was

Table 17: Schedule for Intermittent Weathering in Exposure to Unmodified Outdoor Air at NRL

| Test | Charcoal | Time (Hours) | Volume (10 ⁶ cu ft) | Exposure Dates 1978 | Total Exposure (Months) | n (10 ⁶) | t (sec) | Pene. |
|------|----------|--------------|--------------------------------|---------------------|-------------------------|----------------------|---------|--------------|
| 5094 | BC 727 | On 1077 | .1704 | 2 Jun - 17 Jul | 2.5 | 11.7 | .33 | (11.8±.302)% |
| | | Off 768 | - | 17 Jul - 18 Aug | | | | |
| | | On 744 | .1155 | 18 Aug - 18 Sep | | | | |
| | Total | On 1821 | .2859 | | | | | |
| 5095 | BC 727 | On 1077 | .1677 | 2 Jun - 17 Jul | 3.7 | 11.6 | .34 | (12.0±.106)% |
| | | Off 768 | - | 17 Jul - 8 Aug | | | | |
| | | On 745 | .1186 | 18 Aug - 18 Sep | | | | |
| | | Off 720 | - | 18 Sep - 18 Oct | | | | |
| | | On 888 | .1450 | 18 Oct - 24 Nov | | | | |
| | Total | On 2710 | .4313 | | | | | |
| 5112 | S&S | On 740 | .1150 | 18 Jul - 18 Aug | 3.0 | 7.91 | .34 | (.019±.002)% |
| | | Off 744 | - | 18 Aug - 18 Sep | | | | |
| | | On 720 | .1162 | 18 Sep - 18 Oct | | | | |
| | | Off 720 | - | 18 Oct - 18 Nov | | | | |
| | | On 672 | .0985 | 18 Nov - 18 Dec | | | | |
| | Total | On 2132 | .3297 | | | | | |
| 5111 | G 615 | On 740 | .1156 | 18 Jul - 18 Aug | 2.0 | 7.95 | .34 | (.089±.014)% |
| | | Off 744 | - | 18 Aug - 18 Sep | | | | |
| | | On 720 | .1165 | 18 Sep - 18 Oct | | | | |
| | Total | On 1460 | .2321 | | | | | |

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added in two cases. The schedule of these exposures is summarized in Table 17, where n is the number of filter displacements and t is the average residence time during the exposure periods.

Although not all of these measurements have been completed, the intermittent weathering of BC 727 appears to be more degrading than continuous operations with the same carbon. A summary of the results for BC 727 is given in Table 18.

Table 18: Intermittent Exposures with BC 727

| Test | Operation | Total Exposure Time (months) | Penetration % |
|------|--------------|------------------------------|---------------|
| 5032 | Continuous | 2 | 3.56 |
| 5065 | " | 2 | 6.84 ± .12 |
| 5096 | " | 2 | 3.79 ± .16 |
| 5020 | " | 3 | 7.59 |
| 5094 | Intermittent | 2.5 | 11.8 ± .302 |
| 5095 | " | 3.7 | 12.0 ± .106 |

Incomplete results for another charcoal, NACAR G 615, which contained TEDA as part of the impregnation, indicate a different behavior (Table 19).

Table 19: Intermittent Exposures with NACAR G 615

| Test | Operation | Time (Months) | Penetration % |
|------|--------------|---------------|---------------|
| 5031 | Continuous | 2 | 1.41 |
| 5022 | Continuous | 3 | 1.84 |
| 5111 | Intermittent | 2 | 0.09 |

The "resting" of the filter in this case appeared to reduce the subsequent penetration of methyl iodide. The difference in behavior may be due to the type of impregnation. The G 615 contains among other things some TEDA and the BC 727 contains KI_x in the impregnation. The TEDA of the

impregnation appears to be stable in the environment of the adsorbed contaminants and in fact improves during "resting". Additional work is obviously needed to include the influence of the changing concentrations of moisture that existed during the exposures to outside air and in the period just before the termination of the weathering. Future experimentations may be more amenable to the control available in laboratory exposures rather than in outside air.

V. Concluding Remarks

1. Moisture Influence on Charcoal Efficiency

It has been shown in this report that the interaction of water vapor with impregnated charcoals, as judged by methyl iodide trapping efficiency, depends on relative pressure and contact time. In the laboratory exposures (Appendix 6), the water retained by the charcoals was approximately 1% of the water introduced during the 100 hours. After this period in air flows of 50% RH, a gradient in the water retained was observed in the four layers (see Figure 10). The dynamic adsorption behavior of the charcoals for water vapor is thus shown. In air flows of 70% RH and 90% RH, gradients in water-retained are not observed which demonstrates the greater surface mobility of adsorbed water at high humidities. The hysteresis behavior of water adsorption and desorption explains why it is difficult to dry an activated carbon bed after exposure to humidities greater than 50% RH.

In addition to this mass transport factor, the adsorptivity deteriorates after long exposures to air of high dew point relative to air of low dew point. In the environment of NRL, the dew point in the last three years has been above 70°F for only 30 to 40% of a year (see Appendix 2). In the southeastern areas of the country, the percentage is larger and in the desert areas it is less. It remains to be demonstrated to what extent the useful life of a charcoal installation (without local abnormal loading) depends on the existing meteorological conditions.

2. Moisture and Contaminant Influence on Charcoal Efficiency

The adsorption isotherms of organic compounds on activated carbons are of the Langmuir type and the quantity adsorbed at low partial pressures is large. This behavior is quite different than a water adsorption isotherm. The removal efficiency in a flow of air through a

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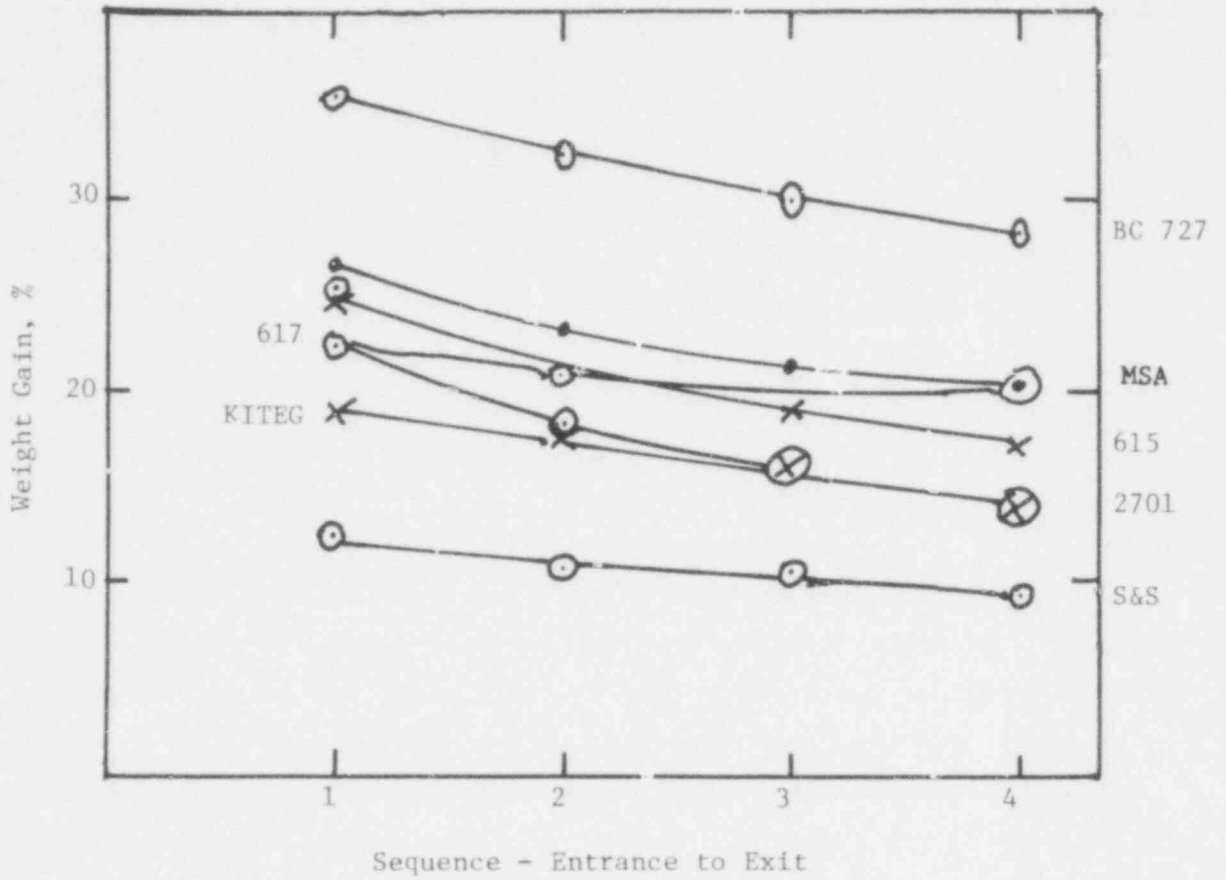


Figure 10: Weight-Gains (%) of the Four Layers Exposed 100 Hours at 50% RH

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charcoal depends on the molecular species as well as the source of activated carbon. In a flow system the concentration in the first effluent air is much less than steady-state adsorption. Eventually, the steady-state value finally breaks through as indicated by general sigmoidal dependence in Figure 11.

When moisture and contaminant are both present, the removal of the contaminant is independent of moisture at low relative humidities since this is the region of small water adsorption. The testing conditions that specify 95% RH, however, correspond to high surface coverage by moisture and in this region there is a competition of the water molecule and methyl iodide for the available surface. A successful impregnated charcoal of high trapping efficiency must interact strongly with the remaining surface and some mechanism must be present that is highly efficient in doing so. Deitz and Jonas (17) have proposed a catalytic trapping of methyl iodide at specific sites on the impregnated charcoal and the observed kinetics have been tested over a ten-fold change in residence time.

A general observation in the profile of the methyl iodide penetration measurement through the four-layer test bed is not only a definite greater penetration through the entrance layer relative to the remaining three layers, but also a somewhat greater penetration through the exit layer relative to the second and third layers. This behavior is compatible with a chromatographic separation among the several components of the gaseous contaminants in the air flow and perhaps to a differential surface mobility of a component of the impregnation.

Superimposed on the normal weathering of charcoal by atmospheric contaminants and moisture in the air flow to a filter are organic vapors derived from local solvent spills and/or solvent vapors from large paint operations conducted within a facility (11). These are special and isolated occurrences that can, however, accumulate and involve a considerable surface coverage of the charcoal. The desorption of a highly

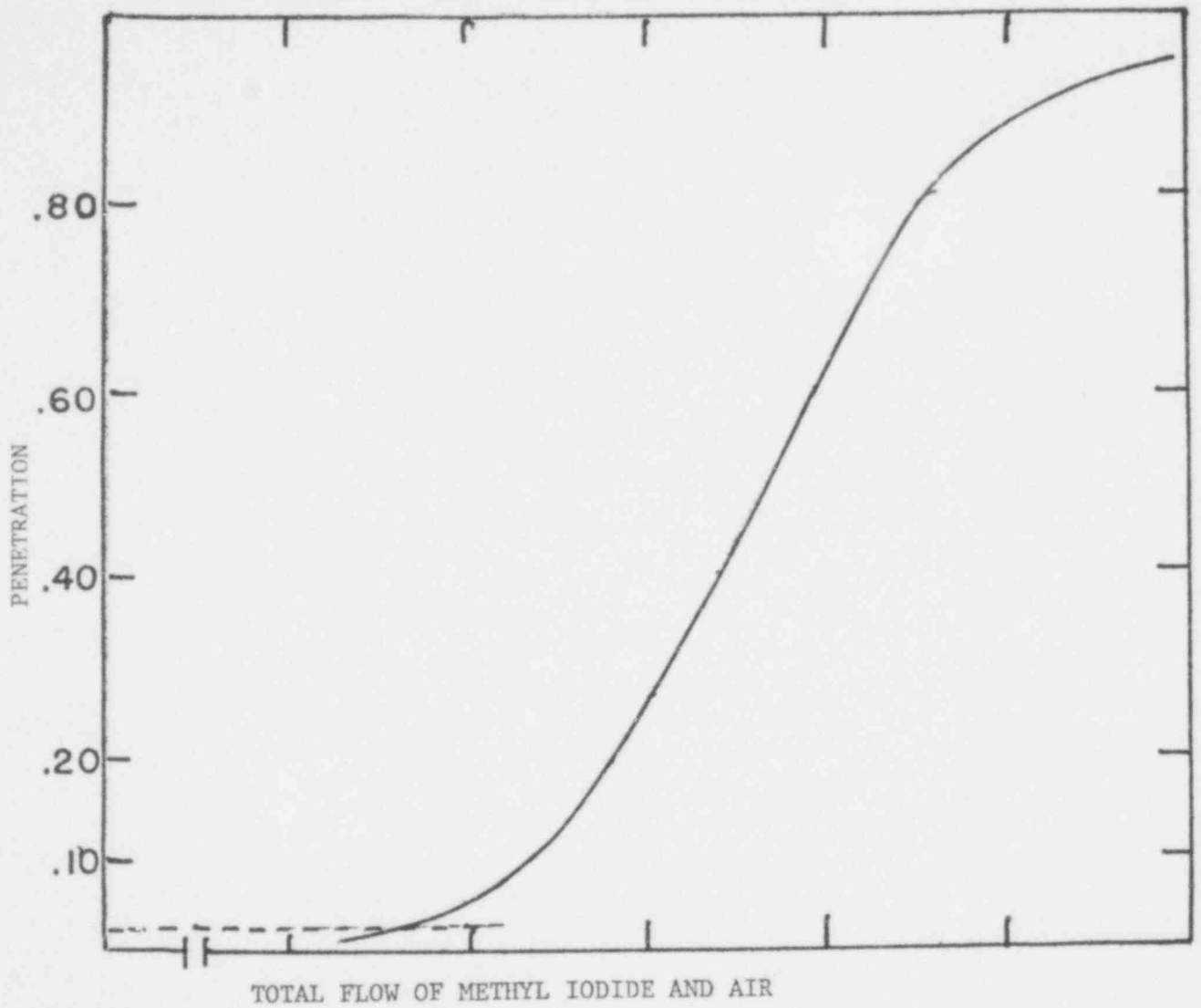


Figure 11: General Dependence of Fractional Penetration Over the Complete Range of Breakthrough Concentration

volatile material into flowing air (12) may be effective in removing some of the adsorbed vapor; also, the removal would be enhanced during a test procedure which uses a temperature of 80° or 130°C. However, the experience to date given in Table 7 has shown that at ambient temperatures, the recovery level of the methyl iodide trapping efficiency upon pre-humidification is not realized. In fact, it is further degraded. The program of weathering with untreated outdoor air is now being supplemented by pertinent laboratory experiments designed to weather charcoals at high organic concentrations. These measurements now in progress in FY79 should yield useful information as to the influence of accidental solvent spills on charcoal efficiency.

The possibility of obtaining precursor information that could be used to anticipate a need for charcoal replacement was raised at the beginning of this report. To this end, it might be helpful to integrate the quantities of organic vapors that get into the air ducts leading to a charcoal filter. Any excessive hydrocarbon loading on the charcoal could then be determined and thus, it would be possible to anticipate the need for replacement due to such sources of contamination.

3. Future Plans for FY79

The following basic tasks will be performed during the continuation of the research activities in FY79:

- (1) Laboratory controlled exposures of commercial charcoals to air mixtures with water vapor and pollutant.
- (2) Weathering of charcoals in ambient un-modified outdoor air at the NRL site and at two additional locations selected for different environmental conditions.
- (3) Laboratory examination of spent charcoals of known history.

Laboratory-Controlled Exposures

One significant observation in the research in progress is the important contribution of water vapor of high relative humidity to the degradation of impregnated charcoals. Furthermore, a synergistic influence of the water vapor in mixtures with hydrocarbon vapors exists which has an important bearing on the degradation. It is planned, therefore, to weather three of the charcoals now being studied (BC 727, G 615 and S&S-5% TEDA) with air mixtures which will contain n-hexane, methanol, cyclohexanone, or methylisobutyl ketone. The exposures will be in air flows of 100 L/min for 100 hours at ambient temperature (22-23°C). The air will be maintained at 90% RH and a hydrocarbon concentration will be selected to yield a weight increase of the charcoal that will result in significant loss in trapping efficiency for methyl iodide-131. These measurements will establish the magnitude of organic loading that is compatible with good methyl iodide trapping under the conditions of the exposures.

In the previous report for FY77 (see pp. 16-17(1)) the laboratory measurements with ozone were completed at a concentration of 2.5 to 2.7 ppm. The ozone generator has now been adjusted to produce lower concentrations in the total air flow of 100 L/min. A lower concentration of about 0.1 ppm will be used and exposures will be repeated in 50%, 70% and 90% RH during FY79. The lower concentration is desired for weathering the charcoal since it is a closer approximation to actual environmental conditions.

In the real world the environment contains, of course, complex mixtures of pollutants in variable proportion. It is planned to make a few charcoal exposures in the laboratory with an air flow containing water vapor, hydrocarbon, ozone or sulphur dioxide. This spot check with a multi-component pollutant mixture in 90% RH air may indicate the presence of factors that might cancel each other in the influence on methyl iodide-131 trapping.

Exposure to Outdoor Air at NRL

The exposures of the six commercial charcoals started in FY78 will be completed to include 6 and 9 month periods. Exposures of BC 727 and G 615 of 12-month duration will also be completed. One charcoal, BC 727, will be exposed for one month in each of twelve consecutive months in order to establish the seasonal influence on the trapping efficiency of one particular charcoal. In connection with intermittent exposures, the BC 727 and the S&S-5% TEDA charcoals will each be exposed for three one-month periods with one month rests between each exposure. In all cases the weathered bed of charcoal will be divided into four equal layers for analysis of the methyl iodide penetration in each of the four successive layer in the flow direction. There is a gradient of pollutants in a weathered bed and this gradient is responsible for the profile observed in the methyl iodide-131 penetration. A continued study will be made during FY79 of the meteorological conditions during the last few days before terminating an exposure to outdoor air. When the desorption of adsorbed water is favored by a continuous period of dry weather, the subsequent efficiency for methyl iodide-131 trapping should increase, provided the accumulation of pollutants has not exceeded a specified surface coverage to be determined from laboratory experiments. The data will be examined from this point of view.

Exposures to Outdoor Air at Other Sites

There are two categories of contaminants that have a changing influence on the weathering of charcoals: (1) local meteorological conditions that define the water content of the air, and (2) the concentrations of pollutants that vary in the vicinity of the weathering. It is planned, therefore, to expose charcoal samples to the environmental conditions at locations other than NRL. One site is the Argonne National Laboratory near Chicago and another is a dry area in the far west.

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It has been pointed out (Appendix 2) that the monthly average dew points observed at the National Airport Weather Station showed a pattern of similar variations for the period 1970-1978. A similar compilation has been made for the Chicago O'Hare International Airport (Appendix 9) for the period 1971-1978. The two locations differ in that the time when the dew point is above 50°F at O'Hare is half that of National. The O'Hare airport is in the general vicinity of the Argonne National Laboratory. The second location will be sought where a drier climate exists.

It is also necessary to have additional information at these other locations on the pattern of pollutants that exist during the weathering. The Chicago location is in a more industrialized area than NRL and published records assembled by U.S. Environmental Protection Agency (14) for the Chicago area show a high sulfur dioxide emission. Contact will be made with the Chicago EPA stations and the records of the pollutant concentrations in the immediate area of the Argonne Laboratory will be obtained. From the records comparisons will be made to characterize the pollutant concentrations with respect to the influence on methyl iodide-131 penetration data (15).

The field units will be assembled to be capable of exposing two samples of charcoal in each unit. Separate air flow meters and blowers will be used for each sample. The only facility required in the field is a source of 120 volts AC. Samples of BC 727 and G 615 charcoals will be exposed for periods of one-month and six-months at each site.

Service Charcoals

With the cooperation of the research staff of Nuclear Regulatory Commission, a number of charcoal samples will be obtained that have been used in commercial operations and which have well defined exposures. Laboratory tests will be performed at NRL to determine those charcoal properties that are pertinent to residual efficiency for methyl iodide-131 trapping.

References

1. "Effects of Weathering on Impregnated Charcoal Performance" by Victor R. Deitz, Naval Research Laboratory, NUREG/CR-0025 (1977).
2. R. R. Bellamy and V. R. Deitz, "Confirmatory Research Program - Effects of Atmospheric Contaminants on Commercial Charcoals," Proc. 15th DOE Nuclear Air Cleaning Conference 1978.
3. A. Stamulus, "The 1976 NRL Air Quality Data," NRL Memo Report 3652, 41 pp.
4. A. Stamulus, "The 1977 NRL Air Quality Data," NRL Memo Report 3764, 27 pp.
5. D. A. Collins, L. R. Taylor and R. Taylor, "The Development of Impregnated Charcoals for Trapping Methyl Iodide at High Humidity," TRG Report 1300 (W), U.K.A.E.A. (1967).
6. R. E. VanderVennen, "The Oxidation of Activated Carbons at Room Temperature," NRL Report 4823 (24 August 1956).
7. Local Climatological Data, National Weather Service Office, Washington National Airport, Monthly Summary Reports for 1978, N.O.A.A., Ashville, North Carolina.
8. R. C. Milham and L. R. Jones, "Iodine Retention Studies," DP 1213 and DP 1234, Savannah River Laboratory (1969).
9. Victor R. Deitz, "Survey of Char Revivification and Filtration," 301 pp., National Bureau of Standards, Washington, D.C. (1947).
10. E. C. Bennett and D. E. Strege, "Evaluation of Weathered Impregnated Charcoals for Retention of Iodine and Methyl Iodide," UNI-251 (August 8, 1974) and UNI-425 (November 7, 1975), United Nuclear Industries, Inc., Richland, Washington.
11. A. G. Evans, "Personal Communication," Publication Pending in 1978 Report from the Savannah River Laboratory.
12. J. Louis Kovach and L. Rankovic, "Evaluation and Control of Poisoning of Impregnated Carbons Used for Organic Iodide Removal," Proc. 15th DOE Nuclear Air Cleaning Conference, 1978
13. D. R. Muhlbaier, "Standard Non-Destructive Test of Carbon Beds for Reactor Confinement Applications - Final Progress Report," Feb - Jun 1966, DP 1082.
14. National Air Quality and Emissions Trends Report, 1976. EPA-450/1-77-002 December 1977, EPA Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina 27711.

15. A. Stamulis, "The Characterization of Pollutant Concentration by a Relative Measure of Variability," NRL Memorandum Report 3659, (1977).
16. Victor R. Deitz and Charles H. Blachly, "The Effect of Exposure Times in the Prehumidification of Impregnated Charcoals," Proc. 14th DOE Air Cleaning Conference, Volume 2, 836-843 (1976).
17. Victor R. Deitz and Leonard A. Jonas, "Catalytic Trapping of Methyl Radioiodide by Beds of Impregnated Charcoal," Nuclear Tech. 37, 59-64 (1978).

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Appendix 1: Physical Properties of Impregnated Charcoals

| Charcoal | Weight Percent on Each Sieve | | | | | | | Nom. Size | Hard. ¹ (ASTM) % | Particle ² Diameter Change | Bulk ³ d. | Dusting ⁴ Coef. |
|-----------------|------------------------------|------|------|------|------|-----|-----|-----------|-----------------------------------|---|-------------------------|-------------------------------|
| | #8 | 10 | 12 | 14 | 16 | 20 | PAN | | | | | |
| BC 727 | 0.4 | 10.0 | 36.0 | 36.2 | 16.1 | 1.3 | 0.2 | 8x16 | 94.8 | 88.1 | 0.46 | 0.20 |
| BC 717 | 0.9 | 6.6 | 27.2 | 41.2 | 21.8 | 2.2 | 0.1 | 8x16 | 97.3 | 94.1 | 0.51 | 0.20 |
| G 615 | 1.4 | 10.5 | 30.8 | 40.5 | 15.4 | 1.0 | 0.3 | 8x16 | 97.4 | 96.4 | 0.54 | 0.04 |
| G 617 | 0.5 | 6.9 | 35.4 | 43.5 | 11.6 | 1.8 | 0.2 | 8x16 | 96.8 | 93.5 | 0.43 | 0.06 |
| MSA (463563) | 0.9 | 7.5 | 30.8 | 42.2 | 17.4 | 1.0 | 0.2 | 8x16 | 98.6 | 97.4 | 0.56 | 0.01 |
| AAF 701 | 1.4 | 12.0 | 33.4 | 36.2 | 14.0 | 2.8 | 0.3 | 8x16 | 90.6 | 80.0 | 0.44 | 0.22 |
| KITEG | 0.2 | 9.9 | 40.3 | 34.4 | 13.4 | 1.2 | 0.6 | 8x16 | 95.7 | 94.6 | 0.42 | 0.13 |
| SS (5% TEDA) | 0 | 2.3 | 36.2 | 51.9 | 6.4 | 1.4 | 1.8 | 10x16 | 85.4 | 82.0 | 0.51 | 1.6 |

¹ASTM Hardness

²(Av. Particle Dia. After Hardness Test/Av. Dia. Before Test) x 100

³Density A.S.T.M. Procedure D-2854

⁴Dusting Coefficient (method developed at NRL to be published in 1979)

NOTE: Measurements made at NRL by Poonsuk Pongpat, IAEA Fellow, 1978-1979.

Appendix 2: Dew Points, °F (Monthly Average) at the Washington National Airport

| | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 | 1978 |
|-----------|------|------|------|------|------|------|------|------|------|
| January | 17 | 19 | 27 | 23 | 31 | 29 | 20 | 12 | 18 |
| February | 22 | 25 | 23 | 23 | 23 | 28 | 29 | 23 | 15 |
| March | 28 | 25 | 30 | 40 | 31 | 29 | 35 | 36 | 28 |
| April | 41 | 33 | 39 | 42 | 41 | 34 | 38 | 44 | 35 |
| May | 54 | 49 | 53 | 50 | 51 | 56 | 49 | 56 | 52 |
| June | 61 | 64 | 59 | 65 | 60 | 62 | 60 | 59 | 61 |
| July | 65 | 64 | 67 | 66 | 64 | 66 | 64 | 67 | 67 |
| August | 65 | 64 | 65 | 67 | 67 | 67 | 66 | 68 | 71 |
| September | 61 | 63 | 61 | 60 | 59 | 59 | 60 | 63 | 60 |
| October | 51 | 57 | 44 | 48 | 42 | 52 | 46 | 44 | 45 |
| November | 39 | 36 | 35 | 36 | 36 | 41 | 29 | 40 | 40 |
| December | 28 | 34 | 33 | 29 | 31 | 28 | 22 | 26 | 28 |

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Appendix 3: Monthly Average Concentrations in ppmv of Pollutants
During 1976 and 1977 at NRL

| Month | O ₃ | | | SO ₂ | | | NO ₂ | | | RHC* | | | CO | | |
|-------------------|----------------|-------|------|-----------------|-------|------|-----------------|-------|------|---------------------------|------|------|------|------|------|
| | 1976 | 1977 | 1978 | 1976 | 1977 | 1978 | 1976 | 1977 | 1978 | 1976 | 1977 | 1978 | 1976 | 1977 | 1978 |
| January | .013 | 0.007 | .013 | .042 | 0.052 | .028 | .038 | 0.018 | .011 | 0.11 | 0.28 | .04 | 1.58 | 1.92 | .45 |
| February | .012 | 0.010 | -- | .038 | 0.029 | -- | .046 | 0.055 | -- | .09 | 0.48 | -- | 1.32 | 1.22 | -- |
| March | .014 | 0.012 | -- | .027 | 0.023 | -- | .036 | 0.079 | -- | .05 | 0.24 | -- | 0.98 | 3.77 | -- |
| April | .010 | 0.013 | .034 | .024 | 0.023 | .016 | .028 | 0.051 | .087 | .20 | 0.40 | .02 | 0.68 | 0.63 | 1.10 |
| May | .008 | 0.015 | .037 | .017 | 0.020 | .013 | .024 | 0.047 | .031 | .25 | 0.22 | .10 | 0.54 | 0.32 | 1.24 |
| June | .022 | 0.020 | .052 | .015 | 0.020 | .014 | .020 | 0.116 | .006 | .49 | 1.06 | .05 | 0.33 | 0.98 | 1.06 |
| July | .040 | 0.040 | .035 | .026 | 0.023 | .014 | .044 | 0.078 | .025 | .53 | 0.07 | .07 | 1.23 | 0.95 | 1.06 |
| August | -- | -- | .038 | .026 | -- | .015 | .029 | -- | .011 | .47 | -- | .06 | 1.81 | -- | 1.25 |
| September | .013 | -- | .030 | .035 | -- | .024 | .035 | -- | -- | 0.29 | -- | .02 | 1.92 | -- | 1.14 |
| October | .008 | 0.018 | .055 | .019 | 0.015 | .024 | .050 | 0.075 | -- | -- | 0.08 | .09 | 1.65 | 1.14 | 1.56 |
| November | .010 | 0.013 | .012 | .035 | 0.015 | .029 | .057 | 0.028 | -- | 0.11 | 0.04 | .28 | 2.67 | 1.17 | 2.25 |
| December | .006 | 0.012 | .006 | .036 | 0.022 | .017 | .084 | 0.061 | .015 | 0.49 | 0.06 | .89 | 1.79 | 1.62 | 1.52 |
| Yearly Average | .013 | 0.014 | .031 | .027 | 0.024 | .019 | .043 | 0.058 | .027 | *excludes CH ₄ | | | 1.42 | 1.33 | 1.36 |

"The 1976 NRL Air Quality Data" by A. Stamulis, NRL Memo Report 3652, 41 pp.

"The 1977 NRL Air Quality Data" by A. Stamulis, NRL Memo Report 3764, 27 pp.

"The 1978 NRL Air Quality Data" by A. Stamulis, unpublished data.

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Appendix 4: Proposed Radioiodine/Methyl Iodide Standard Test
Conditions of ASTM D 28.04, 1978

| Section | 3.1 | 3.2 | 3.3 | 3.4 | 3.5 | | |
|------------------------------|---|---------------------------------------|--|---|----------------------------|-------------------|-------|
| Test Description | Methyl Iodide Penetration 30°C 95% RH | Methyl Iodide Penetration 80°C 95% RH | Methyl Iodide Penetration 130°C 95% RH | Elemental Iodine Penetration 30°C 95% RH | Elemental Iodine Retention | Units | |
| Test Adsorbate | (CH ₃ ¹²⁷ I + CH ₃ ¹³¹ I) | | | (¹²⁷ I ₂ + ¹³¹ I ₂) | | | |
| Test Adsorbate Concentration | 1.75±0.25 | 1.75±0.25 | 1.75±0.25 | 17.5±0.5 | 75±5 | mg/m ³ | |
| Equilibration Period: | Temp | 30.0±0.5 | 80.0±1.0 | 130±2 | 30.0±1.0 | 30±5 | °C |
| | RH | 95±2 | (Note a) | 95±3 | 95±2 | (Note a) | % |
| | Duration | 16.0±0.5 | 0 | (Note b) | 16.0±0.5 | 0 | hr |
| Feed Period | Temp | 30.0±0.5 | 80.0±0.5 | 130±2 | 30.0±0.5 | 30±5 | °C |
| | RH | 95±2 | 95±1 | 95±3 | 95±1 | Ambient | % |
| | Duration | 120±1 | 60±1 | 60±1 | 120±1 | 10.0±0.2 | min |
| Elution Period: | Temp | 30.0±0.5 | 80±0.5 | 130±2 | 30.0±0.5 | 180±3 | °C |
| | RH | 95±1 | 95±1 | 95±3 | 95±1 | NA | % |
| | Duration | 240±1 | 240±1 | 240±1 | 240±1 | 240±1 | min |
| Absolute Pressure | (Note c) | 104±5 | 104±5 | 104±5 | 104±5 | 104±5 | kPa |
| Gas Velocity | | 12.2±0.5 | 12.2±0.5 | 12.2±0.5 | 12.2±0.5 | 12.2±5 | m/min |
| Bed Depth | (Note d) | 50±1 | 50±1 | 50±1 | 50±1 | 25±1 | mm |

Above list is standard for adsorption media used in 50 mm bed depth tray filters, as described in AACC CS-8 and for media used in other bed depths and operated at the same gas velocity (12.2±0.5 m/min). For other operating velocities and for all media to operate at conditions substantially different from the above, any deviations from the above list must be specified.

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NOTES:

- a. For each of these tests, the test bed is brought to the listed equilibration temperature without air flow before other phases of the test begin. For tests 3.2 and 3.5 this thermal equilibration is the only equilibration. For tests 3.1, 3.3 and 3.4, humid air at the stated temperature and humidity is passed through the beds for the stated period following bed warm-up.
- b. For test 3.3, humid air flow is maintained for 2.0 ± 0.1 hr, or until the upstream/downstream dry-bulb temperature differential is less than 2°C .
- c. $101 \text{ kPa} = 1 \text{ atm}$. Tests 3.1, 3.2, 3.4 and 3.5 are run slightly above one atmosphere to allow for a blow-through system with flow measurement, demister, etc.
- d. The test bed for tests 3.1 - 3.4 may be a single canister of full depth, or two 25 mm deep canisters in series. For test 3.5, a single 25 mm deep canister is used.

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Appendix 5: Temperatures Observed Between Sample and Back-up Beds
 during Methyl Iodide-131 Penetration Test for Sample #5088
 (1,2,3,4), Weathered at 90% RH

| | TIME | TEMPERATURE °C | | %RH | | TIME | TEMPERATURE °C | | %RH |
|------------------------|------|----------------|--------|------|-----------|------|----------------|--------|------|
| | | INLET | OUTLET | | | | INLET | OUTLET | |
| FEED CH ₃ I | 1300 | 29.5 | 30.0 | 94.4 | PURGE ON | 1500 | 30.0 | 30.0 | 94.4 |
| | 1305 | 29.5 | 30.0 | 94.4 | | 1505 | 30.0 | 30.0 | 94.4 |
| | 1310 | 29.5 | 29.5 | 94.4 | | 1510 | 30.0 | 30.0 | 94.4 |
| | 1315 | 29.5 | 29.5 | 94.0 | | 1515 | 30.0 | 30.0 | 94.4 |
| | 1320 | 29.5 | 29.5 | 94.0 | | 1520 | 30.0 | 30.0 | 94.4 |
| | 1325 | 29.5 | 29.5 | 94.0 | | 1525 | 30.0 | 30.0 | 94.4 |
| | 1330 | 30.0 | 30.0 | 94.4 | | 1530 | 30.0 | 30.0 | 94.4 |
| | 1335 | 30.0 | 30.0 | 94.4 | | 1535 | 30.0 | 30.0 | 94.4 |
| | 1340 | 30.0 | 30.0 | 94.4 | | 1540 | 30.0 | 30.0 | 94.4 |
| | 1345 | 30.5 | 30.5 | 94.4 | | 1545 | 30.0 | 30.0 | 94.9 |
| | 1350 | 30.5 | 30.5 | 94.9 | | 1550 | 30.0 | 30.0 | 94.5 |
| | 1355 | 30.5 | 30.5 | 94.9 | | 1555 | 30.0 | 30.0 | 94.4 |
| | 1400 | 30.5 | 30.5 | 94.9 | | 1600 | 30.0 | 30.0 | 94.0 |
| | 1405 | 30.5 | 30.5 | 94.4 | | 1605 | 30.0 | 29.5 | 94.4 |
| | 1410 | 30.5 | 30.5 | 94.4 | | 1610 | 30.0 | 30.0 | 94.9 |
| | 1415 | 30.5 | 30.5 | 94.4 | | 1615 | 30.0 | 30.0 | 94.4 |
| | 1420 | 30.5 | 30.5 | 94.4 | | 1620 | 30.0 | 30.0 | 94.4 |
| | 1425 | 30.5 | 30.5 | 94.4 | | 1625 | 30.0 | 30.0 | 94.4 |
| | 1430 | 30.0 | 30.5 | 94.9 | | 1630 | 30.0 | 30.0 | 94.4 |
| | 1435 | 30.0 | 30.5 | 94.9 | | 1635 | 30.0 | 29.5 | 94.4 |
| 1440 | 30.0 | 30.5 | 94.4 | 1640 | 30.0 | 30.0 | 94.4 | | |
| 1445 | 30.0 | 30.5 | 94.4 | 1645 | 30.0 | 30.0 | 94.9 | | |
| 1450 | 30.0 | 30.0 | 94.4 | 1650 | 30.0 | 30.0 | 94.9 | | |
| 1455 | 30.0 | 30.0 | 94.9 | 1655 | 30.0 | 30.0 | 94.9 | | |
| FEED OFF | 1500 | 30.0 | 30.0 | 94.9 | PURGE OFF | 1700 | 30.0 | 30.0 | 94.9 |

NRL SAMPLE = 0.140 (1) $\mu\text{Ci}\pm 0.23\%$

Backup A = 0.108 (0) $\mu\text{Ci}\pm 0.39\%$

Backup B = 0.723 (-3) $\mu\text{Ci}\pm 4.34\%$

NRL Penetration = (7.21 \pm 0.05)%

Appendix 6: Dependence of Weight Increase and the pH of the Water Extract after 100 hr Exposure at Designated Relative Humidity at a Flow of 100 L/min

| Charcoal | % RH | % Wt. Increase in Layer | | | | pH in Layer | | | |
|------------------|------|-------------------------|------|------|------|-------------|-----|-----|-----|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| BC 727 | 50 | 27.7 | 26.3 | 25.1 | 24.2 | 9.4 | 9.5 | 9.5 | 9.6 |
| | 70 | 45.4 | 45.3 | 45.5 | 45.3 | 7.7 | 9.2 | 9.1 | 8.8 |
| | 90 | 47.7 | 47.7 | 47.5 | 47.3 | 8.2 | 9.1 | 9.1 | 9.2 |
| G 615 | 50 | 22.3 | 19.6 | 19.5 | 18.6 | 9.9 | 9.9 | 9.9 | 9.9 |
| | 70 | 28.6 | 28.5 | 28.6 | 28.6 | 9.0 | 9.5 | 9.6 | 9.6 |
| | 90 | 29.8 | 30.0 | 29.7 | 29.9 | 9.5 | 9.5 | 9.4 | 8.8 |
| MSA 463563 | 50 | 23.2 | 21.5 | 20.7 | 20.1 | 8.2 | 8.3 | 8.3 | 8.3 |
| | 70 | 35.9 | 36.1 | 36.5 | 36.1 | 8.1 | 8.1 | 8.1 | 8.1 |
| | 90 | 38.4 | 38.9 | 39.9 | 38.7 | 8.3 | 8.3 | 8.3 | 8.2 |
| S&S (5% TEDA) | 50 | 16.2 | 15.4 | 15.2 | 14.8 | 8.4 | 8.4 | 8.4 | 8.4 |
| | 70 | 26.4 | 26.8 | 27.2 | 26.5 | 8.3 | 8.3 | 8.4 | 8.4 |
| | 90 | 31.7 | 31.7 | 31.9 | 32.1 | 8.6 | 8.7 | 8.7 | 8.7 |
| AAF 2701 | 50 | 21.3 | 19.2 | 18.1 | 17.0 | 9.0 | 9.0 | 9.1 | 9.1 |
| | 70 | 44.1 | 44.2 | 43.3 | 43.0 | 8.7 | 8.5 | 8.6 | 8.6 |
| | 90 | 51.0 | 51.3 | 51.5 | 52.2 | 8.7 | 8.7 | 8.7 | 8.7 |
| G 617 | 50 | 22.7 | 20.5 | 19.6 | 18.6 | 9.4 | 9.4 | 9.4 | 9.5 |
| | 70 | 58.2 | 58.3 | 55.9 | 57.0 | 9.2 | 9.2 | 9.2 | 9.2 |
| | 90 | 61.9 | 60.6 | 63.0 | 60.3 | 9.6 | 9.6 | 9.6 | 9.6 |
| KITEG | 50 | 19.5 | 18.8 | 18.3 | 17.8 | 7.6 | 7.6 | 7.7 | 7.7 |
| | 70 | 28.6 | 28.3 | 29.7 | 29.8 | 7.7 | 7.6 | 7.7 | 7.7 |
| | 90 | 38.8 | 39.6 | 40.5 | 41.3 | 7.8 | 7.7 | 7.7 | 7.7 |

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Appendix 7: ASTM Suggested Performance Requirements of New
Nuclear Grade Carbons (Draft 2, 7 August 1978)

| Test | ASTM Test Method | Specification |
|--|------------------|-----------------------|
| 1. Methyl iodide penetration at 30°C, 95% RH ⁽¹⁾ | D | 3.0 percent, maximum |
| 2. Methyl iodide penetration at 80°C, 95% RH | D | 1.0 percent, maximum |
| 3. Methyl iodide penetration at 130°C, 95% RH ⁽²⁾ | D | 2.0 percent, maximum |
| 4. Elemental iodine penetration @30°C, 95% RH ⁽¹⁾ | D | 0.1 percent, maximum |
| 5. Elemental iodine retention @180°C | D | 99.5 percent, minimum |

Physical Properties

| Test | ASTM Test Method | Specification |
|---|------------------|-----------------------|
| 1. Apparent density | D 2854 | 0.38 g/ml, minimum |
| 2. Particle size distribution, ASTM E-11 Sieves: | D 2862 | |
| Retained on No. 6 | | 0.1 percent, maximum |
| Retained on No. 8 | | 5.0 percent, maximum |
| Through No. 8, Retained on No. 12 | | 60.0 percent, maximum |
| Through No. 12, Retained on No. 16 | | 40.0 percent, minimum |
| Through No. 16 | | 5.0 percent, maximum |
| Through No. 18 | | 1.0 percent, maximum |
| 3. Ash content (3) | D 2866 | State value |
| 4. Moisture content | D 2867 | State value |
| 5. Ignition temperature | D 3466 | 330°C, minimum |
| 6. CCl ₄ activity (3) | D 3467 | 60 percent, minimum |
| 7. Ball-pan hardness | D | 92 percent, minimum |
| 8. pH | D | State value |

(1) - Methyl iodide and elemental iodine tests at 30°C and 95% RH to be performed only for qualification purposes.

(2) - Methyl iodide test at 130°C and 95% RH to be performed only for qualification purposes on activated carbon to be installed in primary containment clean-up systems.

(3) - These tests to be performed on the base carbon prior to impregnation.

Appendix 8: Relative Humidity % and Dew Points (°F)

Observations at 3-hour Intervals During the 48 Hours
Before Charcoal Sampling

| Date | Hour | % RH | d.p.-°F | Date | Hour | % RH | d.p.-°F |
|----------|------|------|---------|--------|------|------|---------|
| 2 May | 13 | 28 | 29 | 4 Feb | 13 | 36 | 6 |
| | 10 | 37 | 28 | | 10 | 44 | 5 |
| | 7 | 48 | 27 | | 7 | 57 | 6 |
| | 4 | 51 | 26 | | 4 | 55 | 8 |
| | 1 | 44 | 25 | | 1 | 47 | 9 |
| 1 May | 22 | 32 | 23 | 3 Feb | 22 | 47 | 10 |
| | 19 | 23 | 19 | | 19 | 47 | 11 |
| | 16 | 20 | 19 | | 16 | 39 | 10 |
| | 13 | 23 | 21 | | 13 | 41 | 10 |
| | 10 | 24 | 18 | | 10 | 47 | 11 |
| | 7 | 30 | 18 | | 7 | 62 | 11 |
| | 4 | 32 | 19 | | 4 | 63 | 13 |
| 1 | 23 | 17 | 1 | 69 | 16 | | |
| 30 April | 22 | 23 | 20 | 2 Feb | 22 | 63 | 17 |
| | 19 | 26 | 29 | | 19 | 63 | 18 |
| | 16 | 31 | 40 | | 16 | 67 | 22 |
| 1 June | 13 | 40 | 61 | 10 Aug | 13 | 59 | 70 |
| | 10 | 51 | 61 | | 10 | 69 | 71 |
| | 7 | 62 | 60 | | 7 | 93 | 71 |
| | 4 | 71 | 60 | | 4 | 93 | 71 |
| | 1 | 84 | 65 | | 1 | 90 | 70 |
| 31 May | 22 | 76 | 65 | 9 Aug | 22 | 87 | 70 |
| | 19 | 67 | 65 | | 19 | 83 | 71 |
| | 16 | 65 | 70 | | 16 | 55 | 69 |
| | 13 | 79 | 70 | | 13 | 52 | 69 |
| | 10 | 76 | 67 | | 10 | 61 | 70 |
| | 7 | 79 | 66 | | 7 | 85 | 74 |
| | 4 | 87 | 65 | | 4 | 91 | 74 |
| | 1 | 79 | 65 | | 1 | 85 | 74 |
| 30 May | 22 | 69 | 63 | 8 Aug | 22 | 72 | 73 |
| | 19 | 65 | 67 | | 19 | 68 | 74 |
| | 16 | 50 | 65 | | 16 | 63 | 73 |

Appendix 9: Dew Points, °F (Monthly Average) at
the Chicago O'Hare International Airport

| | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 | 1978 |
|-----------|------|------|------|------|------|------|------|------|------|
| January | | 9 | 11 | 21 | 18 | 21 | 13 | 1 | 9 |
| February | | 20 | 14 | 22 | 19 | 20 | 25 | 17 | 10 |
| March | | 25 | 23 | 35 | 29 | 25 | 31 | 32 | 24 |
| April | | 32 | 35 | 38 | 39 | 33 | 37 | 38 | 35 |
| May | | 41 | 48 | 44 | 47 | 50 | 43 | 50 | 47 |
| June | | 60 | 53 | 59 | 55 | 61 | 56 | 53 | 56 |
| July | | 58 | 62 | 64 | 61 | 61 | 60 | 63 | 63 |
| August | | 59 | 65 | 65 | 61 | 64 | 57 | 60 | 62 |
| September | | 58 | 57 | 57 | 49 | 50 | 49 | 57 | 58 |
| October | | 51 | 41 | 50 | 41 | 43 | 36 | 43 | 41 |
| November | | 30 | 32 | 34 | 33 | 39 | 20 | 33 | 33 |
| December | | 28 | 20 | 23 | 25 | 25 | 11 | 18 | 20 |

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