HYPOIODOUS ACID: AN AIRBORNE INORGANIC IODINE SPECIES IN STEAM-AIR MIXTURES

J. H. Keller, F. A. Duce, D. T. Pence, and W. J. Maeck

Idaho Nuclear Corporation
Idaho Falls, Idaho

ABSTRACT

Hypoiodous acid was first postulated by this laboratory (in early 1968) to exist as an airborne species of iodine. It has an airborne half-time on the order of a day, is the major airborne inorganic iodine species after the initial washout of elemental iodine from a steam-air atmosphere, and is not easily removed by sprays. Airborne hypoiodous acid is generated by the injection of elemental iodine into a steam-air atmosphere or by purging a dilute aqueous solution of iodine in water with air or other gases. We have prepared hypoiodous acid in solution by the well known reactions ($I_2 + H_2O + HgO \rightarrow 2HOI + HgI_2$), confirmed its presence by a specific chemical reaction, then purged the heated solution with air into a cold trap where hypoiodous acid was again detected by the specific chemical reaction. Further, chemical tests for elemental iodine and species with oxidation states higher than hypoiodous acid were negative for the volatile fraction. The equilibria concerned with the hydrolysis of iodine are discussed to show that hypoiodous acid is a major species in solution. Relationships are given for the ratio of hypoiodous acid to total iodine in solution as a function of pH and temperature. In a water-cooled power reactor, the accident-released fission products will contact a heated water solution at a pH of 7 to 10 and then will transport to a steam-air atmosphere. These conditions seem ideal for the formation and stable existence of hypoiodous acid in the vapor state. Thus, it, rather than methyl iodide, could well be the hazardous species from the biological standpoint. Hypoiodous acid, like methyl iodide, penetrates various adsorbents including silver surfaces commonly used in atmospheric samplers and thus may explain the abnormally high organic fractions reported by other investigators. Hypoiodous acid is important to the spray technology program because its removal rate differs from that of elemental iodine and methyl iodide.

Introduction

The existence of airborne hypoiodous acid (HOI) in a steam-air atmosphere was first postulated in this laboratory in 1968(1). A volatile iodine species with air airborne half-time of at least one-half day, which was neither elemental nor organic iodine, has been identified in laboratory tests and in the Contamination-Decontamination Experiment (CDE). In the CDE, iodine was transported into a steam-air atmosphere, and the natural response observed. Identification of hypoiodous acid was made using selective inorganic adsorbents and gas chromatographic analyses to confirm the organic iodides.

Numerous other investigators(2,3,4) have also observed an iodine species in humid atmospheres which was neither elemental nor organic iodine. The slow acceptance of hypoiodous acid as this airborne species results from earlier reports that hypoiodous acid is unstable(5) and nonvolatile(6). However, Styrikovich et al(7) state that it is the principle airborne iodine species in high pressure, high alkaline, boiling water systems. Most, if not all of the earlier work on hypoiodous acid has been concerned with the aqueous chemistry of this species. Eggleton(8) has discussed the hydrolysis reactions of iodine and their consequence in iodine-steam-air atmospheres. He concluded, in light of the various equilibria involved in the iodine hydrolysis reactions and kinetic considerations, it is doubtful that hypoiodous acid would exist at appreciable concentration in the liquid phase at equilibrium, and its gas phase concentration would be negligible even if hypoiodous acid were found to be volatile.

The existence of an inorganic iodine species that forms under PWR-accident conditions and remains airborne for days is of great concern to the reactor safety program. If such a species were to constitute a significant fraction of the total iodine remaining in the containment atmosphere after the initial washout of the elemental iodine, it, rather than methyl iodide, could govern both the final removal rates of iodine and the design of gas cleaning systems. Information concerning it would be vitally important in extrapolating the models for fission product release, transport, and diffusion in LOFT-ECCS to full-scale PWR system. This species could well be the "unidentified iodine species" reported by other investigators that penetrates various adsorbents including silver metal surfaces. Its property of penetrating adsorbents is similar to that of the organic iodide species and thus may explain the abnormally high organic iodide fractions reported by various investigators who did not measure organic iodides by direct techniques such as gas chromatography. A species like this also is important to the spray technology program because its washout rate should be different than that of elemental iodine and methyl iodide.

Experiments are described in this report which show that hypoiodous acid can be volatilized from aqueous solutions and has an apparent airborne stability. The various equilibria involved in the iodine hydrolysis reactions are discussed; and from these equilibria, relationships have been established which represent conditions favorable for a high ratio of hypoiodous acid to total iodine in solution as a function of total iodine concentration, pH, and temperature.

Identification of Hypoiodous Acid in the Vapor State

Two experiments have been conduted that show that hypoiodous acid is volatilized from aqueous media as a stable airborne species. In the first, hypoiodous acid was identified directly by a specific chemical reaction. In the second, it was implied from reactions observed on various adsorbent materials.

In the first experiment, hypoiodous acid was generated in solution by the well known reaction of elemental iodine with excess mercuric oxide(9):

$$2HgO + 2I_2 + H_2O \rightarrow 2HOI + HgO \cdot HgI_2$$

The solution was filtered to remove the mixed mercuric iodide-mercuric oxide residue, and the clear filtrate was placed in a distillation flask except for a small portion that was set aside for an analysis for hypoiodous acid. A slow air purge of approximately 100 cc/min was passed through the filtrate as it was heated to boiling. The vapor was passed through a water trap maintained just above freezing until droplets of water were observed in the distillate. Then a second trap was substituted which collected 5cc of the distillate. Aliquots from each trap and the small portion of the initial clear filtrate that had been set aside were tested for elemental iodine and for hypoiodous acid.

Thiodene, which forms a highly sensitive colored product in the presence of elemental iodine, was added and no elemental iodine was present in any of the three solutions. The test for hypoiodous acid was based on the generation of elemental iodine and its reaction with Thiodene after iodide and dilute sulfuric acid were added to the sample under two conditions--(a) with phenol added prior to the iodide and sulfuric acid, (b) with no phenol added. With no phenol present, any positively charged iodine species oxidized iodide to iodine. With phenol present, only iodine species with oxidation states higher than hypoiodous acid oxidize iodide to iodine. This is because hypoiodous acid is the sole iodine species that iodinates phenols(10); and therefore, it should be removed by the phenol. In all three test solutions, no iodine was produced when the phenol was present, only when it was absent. This confirms that the hypoiodous acid that had been generated by the reaction of elemental iodine and mercuric oxide was volatilized as a relatively stable species on heating an aqueous solution.

The second type of experiment, the reaction of airborne iodine species with various adsorbent materials, provides indirect evidence for the existence of hypoiodous acid as a stable airborne species. We first postulated that airborne hypoiodous acid can be formed when air is passed through a heated solution of elemental iodine in water. This postulation was based on experimental evidence that a significant fraction of the airborne iodine was neither elemental nor methyl iodide. This fraction penetrated adsorbents that retain elemental iodine, including various silver metal surfaces, hydrous zirconium oxide in the iodide form, and cadmium iodide dispersed on Chromosorb-P[a]. Gas chromatrographic analyses showed that it was not methyl iodide.

[a] Product of John Mansville, Inc.

Since the original postulation, many laboratory experiments have been performed with hydrous zirconium oxide-iodide and cadmium iodide elemental iodine adsorbents to ensure that the observed effect was not caused by some property of the adsorbents themselves. Although several conditions were noted in which the adsorbent did not completely retain the elemental iodine, such as at very high flow rates and/or in a condensing system, no evidence was found to indicate the species passing the elemental iodine adsorbent bed was a product of these adsorbents.

Many experiments were performed in which air at a slow flow rate was passed through a heated aqueous solution of elemental iodine tagged with I-131, then through one of the adsorbent test beds which was maintained at a temperature higher than the stream temperature so that condensation did not occur. Longitudinal scanning of the test beds with a scintillation counter showed that the adsorbed activity was concentrated in a sharp band at the entrance of the adsorbent beds. However, a significant fraction of the I-131 activity passed through the test beds that was not methyl iodide or other alkyl iodides as determined by gas chromatrographic analyses. We concluded that the sharp band was adsorbed elemental iodine and that an inorganic iodide species, namely, hypoiodous acid, passed through the test beds.

Airborne Stability of Hypoiodous Acid Atmospheres

Laboratory studies have been made with the glass apparatus, shown in Figure 1, in which atmospheres of predominately hypoiodous acid have been produced.

The apparatus consists of a glass steam generator, a 22-liter glass containment vessel, and a gas sampling oven. This system provides the capabilities for: (a) varying the ratio of steam to air in the containment vessel, (b) injecting various iodine species, (c) introducing atmospheric contaminants, (d) continuously monitoring the pressure and temperature of the containment vessel, (e) drawing gas-phase samples and measuring the sample flow through the samplers, and (f) collecting condensate samples.

Typically, a test consists of reducing the pressure in the containment vessel to about 10 mm Hg, adding steam and air from the boiler, and injecting the iodine species either into the boiler liquid or into the steam transport line. Vessel atmosphere samples can be taken as a function of time as can condensate samples. The temperature and pressure of the vessel atmosphere can be maintained by adding steam and air, or the temperature and pressure can be allowed to decay as samples are taken.

Optimum conditions for the production of hypoiodous acid atmospheres in the vessel are: initial concentration of iodine in the boiler liquid at about 10^{-6} $\underline{M}$, initial boiler pH of about 10 and a boiler temperature of $90^{\circ}C$. Analyses of gas samples using the Particulate-

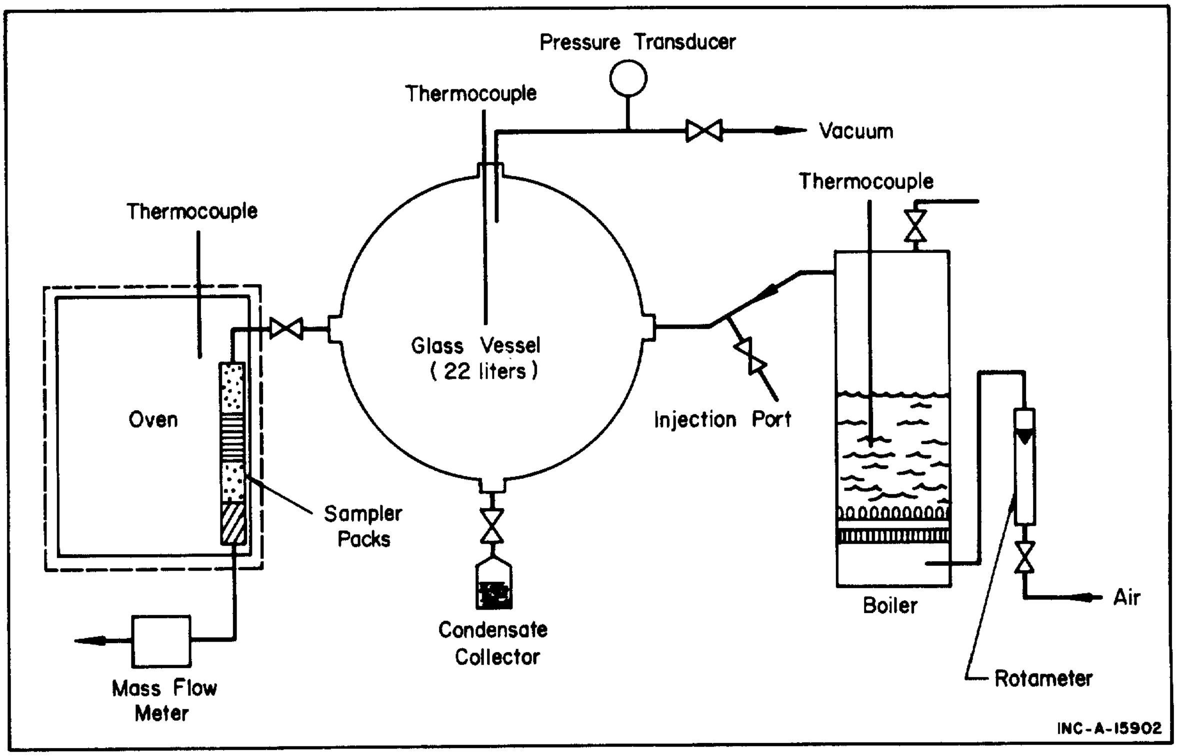


Fig. 1 Laboratory Iodine Behavior System

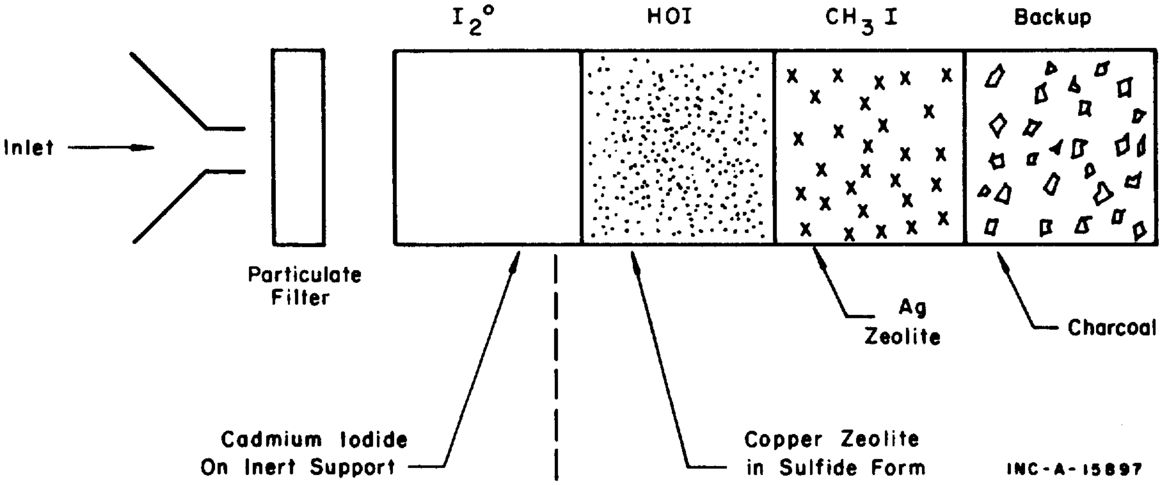


Fig. 2 Particulate Iodine Sampler

Iodine sampler, shown in Figure 2, indicate that atmospheres can be produced which contain 90 percent hypoiodous acid if the optimum conditions are used. Usually, the fraction of iodine transported from the boiler to the vessel is about 5-10 percent of the total, and the remainder is retained in the boiler solution.

The majority of the laboratory tests were conducted under transient conditions. The hypoiodous acid formed was purged into the glass vessel by the steam generated in the boiler. The injected steam raised the temperature and pressure in the glass vessel. After the pressure had reached one atmosphere and the temperature was the maximum for the particular run, 80°C, the boiler containing the iodine species was replaced by a boiler which contained only water. The temperature and, hence, the pressure of the glass vessel was allowed to decrease to ambient conditions. During the temperature transient, water-saturated air was pulled into the vessel by the vacuum produced by the decreased temperature, thereby maintaining a 100 percent relative humidity atmosphere.

Gas samples were taken at various times during the temperature transient and at several times over an extended period after the temperature had reached ambient conditions. Analyses of samples taken with the P-I samplers showed that the hypoiodous acid concentration decreased with the temperature, but remained essentially constant for 20 hours after the temperature reached ambient conditions.

In CDE tests where elemental iodine with a small fraction of methyl iodide impurity was injected into the steam-air atmosphere, the P-I sampler results indicated that hypoiodous acid had an airborne half-time of approximately one-half day. The exact half-time was difficult to determine because of the relatively short duration of the test compared with the half-time. The results of a typical CDE test are shown in Figure 3.

These experiments showed that hypoiodous acid can be produced in steam-air atmospheres, and that it will remain airborne for long periods of time.

Partition Coefficient

Provisions were made for taking condensate samples in the laboratory test system. If the concentration of hypoiodous acid in the vapor state and the concentration of the iodine in the condensate are known at a particular time, a partition coefficient can be calculated for that time. The partition coefficient is defined as the ratio of the mass per unit volume of the species in the condensate to the mass per unit volume of airborne species.

The concentration of airborne hypoiodous acid can be obtained from the P-I sampler data, however, the condensate concentration is not directly obtainable. If it is assumed that optimum conditions exist and only hypoiodous acid is volatilized from the boiler, it will be the only species in the glass vessel; and the total iodine activity in the condensate represents the hypoiodous acid concentration. If this assumption is valid, the calculated partition coefficient for hypoiodous acid at 21°C is about 300. This value is in reasonable agreement with one, 30 at 80°C, obtained by Coleman(11) for a nonelemental iodine species which we believe to be hypoiodous acid.

Equilibria Involved with the Hydrolysis of Iodine

The major equilibria controlling the hydrolysis of iodine in solution are:

		25°C	100°C
(1)	$I_2 + I^- \rightleftarrows I_3^-$	768	305
(2)	$I_2 + H_2O \rightleftarrows H^+ + I^- + HOI$	5.4×10^{-13}	1.6×10^{-10}
(3)	$I_2 + H_2O \rightleftarrows H\,OI^+ + I^-$	1.2×10^{-11}	3.9×10^{-11}
(4)	$3I_2 + 3H_2O \rightleftarrows IO_3^- + 5I^- + 6H^+$	4×10^{-48}	not reported

Only the first three reactions are known to attain equilibrium rapidly and will be discussed independently of reaction (4). Using these three equilibria and a mass balance relationship for iodine, algebraic expressions were derived for the equilibrium concentration of the five iodine species I_2, I^-, I_3^-, HOI, and H_2OI^+. Over the acidity range of 10^{-1} to 10^{-10} N and an initial elemental iodine range of 10^{-4} to 10^{-8} M, equilibrium (2) is governing and accounts for over 90 percent of the hydrolysis both at 25 and 100°C. The fraction of hypoiodous acid, expressed as the mole ratio with respect to total initial iodine, as a function of hydrogen ion concentration and initial total iodine is shown in Figure 4 for 25°C and in Figure 5 for 100°C. It is evident that hypoiodous acid is a dominant species at these low iodine concentration levels, and that the relative amount increases with decreasing total iodine concentration, decreasing hydrogen ion concentration, and increasing temperature. Care must be emphasized when extrapolating data or conclusions beyond the range limits of the variables. This especially applies to highly alkaline solutions where other reactions become important.

Equilibrium (4) will now be considered for its effect on the existence of hypoiodous acid in solution. At equilibrium, calculations show that the formation of iodate becomes essentially complete at pH $\geq$ 7 and at elemental iodine concentrations $\leq 10^{-6}$ molar. Because our experiments show that hypoiodous acid is volatilized from solutions with pH values as high as 10, the kinetics of equilibrium must be considered.

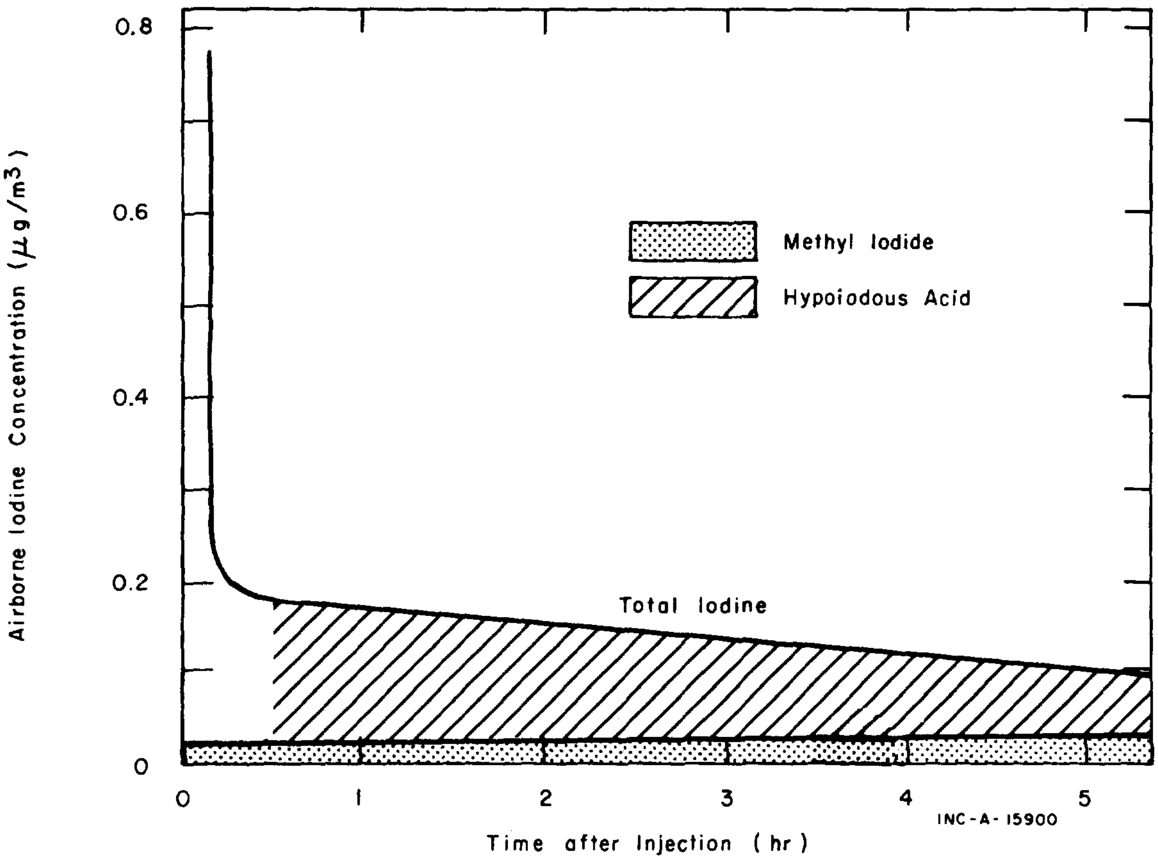


Fig. 3 Airborne Iodine Behavior in Contamination-Decontamination Experiment

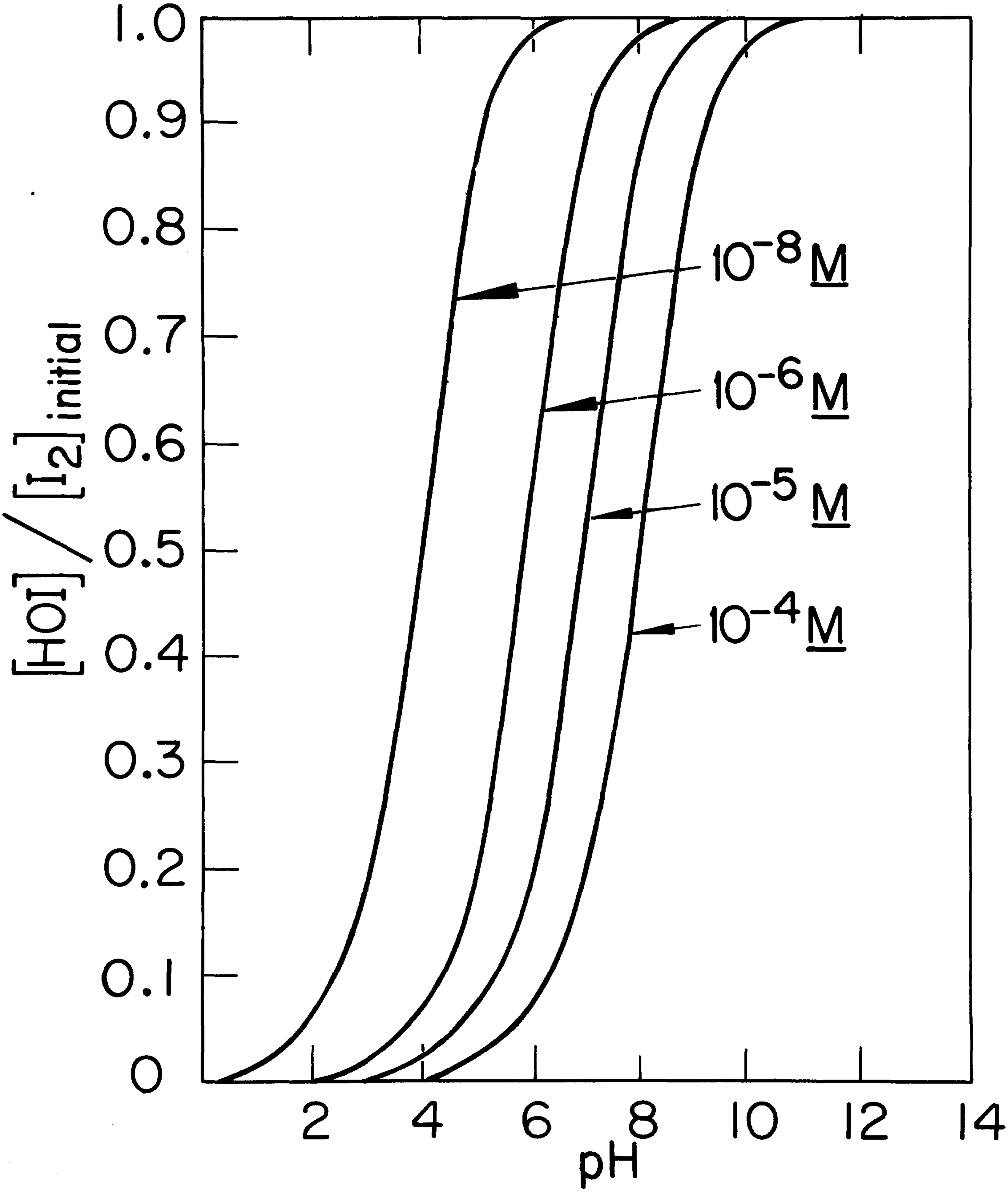


Fig. 4 Mole ratio of $(HOI)/(I_2)_{initial}$ as a Function of pH and Initial Molarity of Elemental Iodine at 25°C

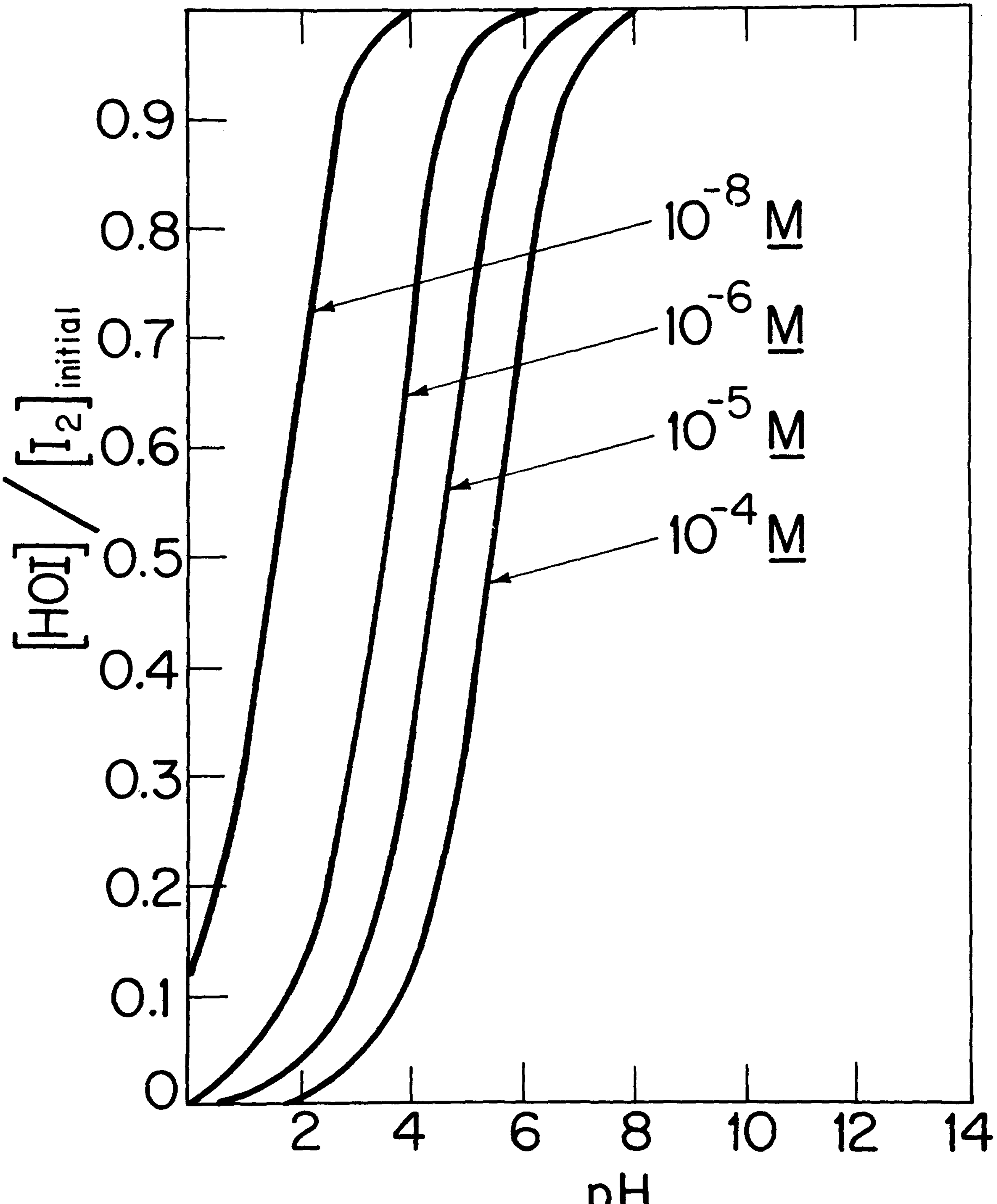


Fig. 5 Mole Ratio of $(HOI)/(I_2)_{initial}$ as a Function of pH and Initial Molarity of Elemental Iodine at 100°C

The reaction rate that apparently governs the disappearance of iodate in equilibrium (4) at low concentrations of total iodine has been given (12) as:

$$(5) \quad -\frac{d(IO_3^-)}{dt} = k\,(IO_3^-)(I^-)(H^+)^2 \quad l^3 \ mole^{-3}\ sec^{-1}$$

The experimental data for this rate were obtained with acidic solutions. Eggleton and investigators before him assumed that the rate constant for the reverse direction, the hydrolysis of elemental iodine to form iodate and iodide, was the same value. This seems highly unlikely for such a complicated reaction which involves a series of intermediate reactions with multiple electrons transfers. From the standpoint of considering the competitive effect of this hydrolysis reaction with the hydrolysis reaction that produces hypoiodous acid, a more pertinent consideration is that the rate of hydrolysis reaction (4) is different for strongly alkaline solution than it is for acidic media(13). Therefore, in the intermediate pH range of about 4 to 10 where the rate for the hydrolysis reaction is not known, one cannot calculate the relative amounts of hypoiodous acid, iodate, and other hydrolysis products at nonequilibrium conditions.

Discussion and Conclusions

Because hypoiodous acid apparently exists in the vapor state only at low concentrations,it has not been identified by conventional analytical techniques. Attempts to identify it using mass spectroscopy yielded inconclusive results. It does not possess a sufficiently strong molar adsorptivity in the infrared or ultraviolet spectral regions to be readily identified with most commercially available spectrometers. To date, the existence of hypoiodous acid has been determined only by indirect methods, and it wasn't until a selective adsorbent sampler was developed that quantitative data became available. This helps explain why hypoiodous acid in the vapor state has not been reported before.

Although an airborne iodine species that has a relatively long half-time has been identified as hypoiodous acid, the fact that it is a stable airborne species has not been determined. Neither laboratory experiments nor the results from the CDE tests proved what fraction of the hypoiodous acid was generated from a gas-phase reaction and what fraction was a result of the volatilization of hydrolyzed iodine in the condensate. The latter method of formation is easily demonstrated in laboratory experiments and is probably the dominant mechanism of formation.

Regardless of the mechanism of formation, the existence of hypoiodous acid as a relatively long airborne long half-time species has serious implications to the reactor safety program. In a water-cooled power reactor, the accident-released fission products will contact a heated water solution at a pH of 7 to 10 and transport to a steam-air atmosphere. These conditions seem ideal for the formation of hypoiodous acid and its airborne persistency. Presently, our experiments indicate that approximately 5 percent of the iodine in a solution of 10^{-6} to 10^{-8} M initial iodine, pH 10, and 90°C is transported to the vapor phase by an air purge. The ratio of hypoiodous acid to elemental iodine in this vapor phase is about 20 to 1. We also find that hypoiodous acid at an initial level of approximately 1 $\mu g/M^3$ remains airborne in a water-saturated atmosphere for several days, even when the temperature becomes ambient.

References

(1) F. O. Cartan, H. R. Beard, F. A. Duce, and J. H. Keller, "Evidence for the Existence of Hypoiodous Acid as a Volatile Iodine Species Produced in Water-Air Mixtures," Proceding of the 10th AEC Air Cleaning Conference, CONF-680821 December 1968.

(2) W. E. Browning, R. E. Adams, and J. Wilhelm, "Investigation of Occurrence and Behavior of Volatile Compounds of Iodine," Nuclear Safety Program Semiannual Progress Report for Period Ending June 30, 1964, ORNL-3691, November 1964, p. 68.

(3) A. C. Chamberlain, A. E. J. Eggleton, W. J. Megaw, and J. B. Morris, "Physical Chemistry of Iodine and Removal of Iodine from Gas Streams," J. of Nuclear Engr., Parts A/B, 17, pp 519-550 (1963).

(4) I. E. Nakhutin, N. M. Smirnova, G. A. Laushkina, and G. A. Loshakov, "Adsorption of Radioactive Iodine Vapors from Air," At. Energy (USSR), 26, 390-391 (1969).

(5) N. V. Sidgwick, The Chemical Elements and Their Compounds, Vol. II, Oxford University Press, London, p. 1225, (1951).

(6) J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II, Longmans, Green & Co., New York, p. 250 (1946).

(7) M. A. Styvikovich, et al, "Transfer of Iodine from Aqueous Solutions to Saturated Vapor," Atomnaya Energiya, 17 #1, pp. 45-49 (1964).

(8) A. E. J. Eggleton, "A Theoretical Examination of Iodine-Water Partition Coefficient," AERE-R-4887, 1967.

(9) J. R. Partington, Textbook of Inorganic Chemistry, 6th Ed., McMillan, New York, p. 333, (1957).

(10) V. Cofman, J. Chem. Soc., 115, 1040-1049, (1919).

(11) L. F. Coleman, "Iodine Gas-Liquid Partition," Nuclear Safety Quarterly Report, Nov., Dec., 1969, Jan. 1970, BNWL-1315-1, March 1970, p. 2.21.

(12) E. Abel and K. Helferling, Z. Physikal Chem., 136, p. 186 (1928).

(13) O. Haimowich and A. Treinin, J. Phys. Chem., 71, p. 1941 (1967).

Work performed under Contract AT(10-1)-1230 U. S. Atomic Energy Commission, Idaho Operations Office.

DISCUSSION

CLOUGH: Could I ask you first of all about the behavior of the iodine compound on ordinary charcoal filters? And could I ask you whether you have tried the techniques which were used to identify methyl iodide in the early work that is gas chromatography and the effusion method for measuring the molecular weight?

KELLER: To answer your first question. Apparently impregnated charcoal is an efficient adsorbent for hypoiodous acid. In answer to your second question, we have attempted to use mass spectrometry for this application, and apparently whenever we put hypoiodous acid in a high vacuum, it decomposes. We have also been unable to find a suitable chromatographic column. We have the feeling that once you dry this species out it decomposes or goes back to elemental iodine or something else. There is a problem. We do not have an unequivocable direct identification for this species. The identification is indirect.

CLOUGH: I think that the effusion technique which was used for methyl iodide is a useful approach because it gives you the molecular weight and if hypoiodous acid is stable on being condensed, the method should work. It is necessary to condense the specimen in the cell before the effusion takes place. If it's stable to that stage then you can probably measure the molecular weight in the same way as was done with methyl iodide.

KELLER: We have talked about this, but have not got around to doing it yet.

BEATTIE: I am leaving the chemistry to Mr. Clough. I couldn't compete with him on the chemistry, but, Mr. Chairman, you did ask me last night what I would think of this new thing that has been thought of. Well, I was very glad to hear the speaker, Mr. Keller, say that it was stopped by impregnated carbon. I would like to close with just a little dig at Westinghouse. I'm taking on the giants today, really. I remember last November at the Conference in Paris, the Westinghouse man standing up and saying their fuel elements never fail. And yesterday we had Mr. Shaver who said that his containment was 100% perfect. So this is no problem with Westinghouse anyway, if you will excuse my saying so.

FIRST: Could you tell me how you made certain that you were not getting droplet carry over to your flask.

KELLER: Yes, we have used HEPA filters in the stream. Whether or not this is a perfect guarantee, I couldn't tell you. But we seem to see this particular behavior in almost all the systems that we have looked at.

FIRST: The filter does not show in the figure you flashed on the screen.

KELLER: Yes, that's right. This is an older diagram, and we have placed HEPA filters in this stream.

YARBRO: Most of the data that you presented was on the basic side of the acid base spectrum. Do you have data on the volatility in the slightly acid or very acid solutions?

KELLER: In very acid solutions we have always volatilized predominately elemental iodine. And as we go from more acid to more basic media, we get a higher percentage of the hypoiodous acid.

YARBRO: My interest here is in the volatility of iodine from acid solution for the purpose of iodine removal from solution by volatilization.

KELLER: The only thing that we have is at the low pH we volatilize predominately elemental iodine. As we go from the lower pH to the higher pH the composition of the volatile species changes from iodine rich to hypoiodous acid rich mixture. And the overall yield also drops; you get less out of the high pH.

CHARCOAL TESTING WITH METHYL IODIDE USING A PYROLYZER-MICROCOULOMB DETECTOR*

Donald R. McFee
Ralph R. Bechtold

Argonne National Laboratory
Argonne, Illinois

ABSTRACT

A pyrolyzer and a following (in series) Microcoulomb Detector were evaluated as a direct reading instrumental system for in-place testing of charcoal adsorbent bed filters, using normal methyl iodide as the test penetrant. Sensitivity was found to be about 2 parts per billion (ppb) by volume. The system can be used for scanning the face of a charcoal filter with a movable sampling probe to locate leaks, to make direct evaluations of the charcoal itself, and to make penetration tests of a total system.

The alkyl iodides, especially methyl iodide, are some of the main radioiodine-containing contaminants that charcoal filters remove from off-gas systems for nuclear fuels. Charcoals showing a high efficiency for removal of methyl iodide can be expected to show a high efficiency for trapping other compounds of iodine. Thus, the high efficiency of a charcoal filter, an absence of leaks, and the over-all uniform integrity of a system can be verified through in-place testing with methyl iodide. If, on the other hand, the efficiency for methyl iodide is found to be low, the filter still may prove efficient for other iodine compounds and must be judged on the basis of the compounds it is supposed to remove from the air stream, which may or may not be organic iodides.

Tests conducted on the impregnated charcoal filters in the containment clean-up system for Argonne's CP-5 Research Reactor (5 megawatt) showed methyl iodide penetrations of 0.1 to 0.2%. Tests in the laboratory on fresh charcoal from the same lot showed penetrations of less than 0.01% until breakthrough occurred.

Tests on other charcoal systems containing old, nonimpregnated charcoal showed penetrations ranging from a few percentage points to greater than 20%.

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

INTRODUCTION

In-place testing of charcoal adsorbent bed filters is a necessity if their reliability is to be assured. Favorable laboratory results do not give assurance of good performance by the installed system. There are too many unknowns. Furthermore, system integrity can be violated by faulty construction, poor maintenance, or abusive use. Periodic in-place testing is, therefore, necessary and is now quite common. As procedures are simplified, it will become even more common.

In-place testing does not replace laboratory tests, under which the media can be subjected to a full range of potential environmental conditions for qualification. In-place testing, at its best, is primarily a nondestructive test indicative of performance at ambient or at other than ambient conditions that can be simulated in a practical manner.

Several types of in-place tests have been developed over the years. Initially, inorganic forms of iodine-131 were used as the test penetrant because extremely low levels of detection could be achieved and because iodine-131 was the principal radioactive material which charcoal filters were to remove. Later, it became apparent that a significant portion of the material that penetrated charcoal filters was not inorganic iodine, but an organic iodide, of which the greatest percentage was methyl iodide. Methyl iodide tagged with iodine-131 then became the penetrant of interest.

Each of the test procedures required the use of radioactive iodine with all its attendant problems. Procedures were simplified somewhat with the introduction of Freons-12 and -113 as penetrants. Using these as penetrants and employing a gas chromatograph, very low levels of penetration (in the ppb range) could be detected without resorting to the use of radioactivity. Further sensitivity was reported by Viles and Silverman in 1967[1] using copper beads for collection and a cerium sulfate-arsenious acid reaction for the analytical determination. None of these methods has been suitable for use with direct-reading instrumentation which could be used to scan the face of a filter, as is done in particulate testing of high-efficiency particulate air filters.

The Ninth AEC Air Cleaning Conference[2], which convened in 1966, produced several reports of methods for in-place testing of charcoal filters. Among these was a report by Thomson and Grossman[3] on the use of the electronic detector-recorder for measurement of gaseous iodine. This device was the Mast Ozone Meter, also referred to as a Microcoulomb Detector and as an oxidant meter. In these tests, iodine was generated and injected upstream, and the concentration of iodine penetrating the filter was measured and recorded with this electronic detector. The lower limit of sensitivity was 1 ppb. The method described herein is simply another innovation permitting the use of this equipment for measuring levels of methyl iodide in the air.

In establishing a charcoal filter in-place test procedure for facilities at Argonne National Laboratory, certain considerations were of importance. One of the systems to be tested was the containment air clean-up system for Argonne's CP-5 Research Reactor. This system is a circulating type that returns its effluent into the container shell. The use of a nonradioactive and nontoxic penetrant for testing was desirable. A somewhat predictive test also was desired, whereby the condition or potential life of a filter might be evaluated rather than simply stop short at a "go" or "no-go" indication as constituting the sum total result of the test. This required more detailed information on the characteristics of each individual filter. Scanning the charcoal filter face with a sampling probe coupled to direct reading instrumentation would provide some of the desired data.

As for the penetrants, methyl iodide seemed to be the most suitable material. Most charcoals are highly efficient for the removal of inorganic forms of iodine from nuclear fuels, but are not as effective for the removal of organic compounds containing iodine. A certain fraction of iodine-131 present in a nuclear fuel's "off" gases is apt to be an organic iodide and should be removed. Removal of the organic forms of iodine is one of the principal problems in reactor effluent air cleaning. Of these organic compounds, methyl iodide is quite predominant, and it is one of the principal compounds to be removed by the charcoal. Also, methyl iodide is the lowest in the homologous series of organic iodides. It has a high vapor pressure, and, from a physical-chemical standpoint, should be one of the most difficult of the organic iodides to remove from an air stream.

A charcoal showing a high efficiency for methyl iodide also should show a high efficiency for other compounds of iodine. A low efficiency for methyl iodide, on the other hand, does not necessarily mean a low efficiency for the other forms of iodine because the physical-chemical characteristics of other iodine compounds are such that they are more apt to be adsorbed than methyl iodide. If the efficiency for methyl iodide is found to be low, the filter still may be efficient for other iodine compounds, and must be judged on the basis of the specific compounds it is supposed to remove from the air stream, compounds which may or may not be organic iodides. If the penetration data show leaks, weak areas in the charcoal, or excessive penetration, and if the history of usage of the system indicates a high potential for deteriorating conditions that may negate the usefulness of the charcoal for other iodine compounds, then even the efficiency for the other compounds would be questionable and replacement should be made without further evaluation.

Iodide impregnated charcoals, such as potassium iodide impregnated charcoal, which accomplish their function through the mechanism of isotopic exchange, can be tested with methyl iodide, especially with respect to leaks and uniform system integrity. These charcoals have a very high adsorptive capacity for methyl iodide. That portion of efficiency related to isotopic exchange, however, cannot be tested with methyl iodide.

After considering diverse factors, it was decided to utilize methyl iodide as the primary test penetrant.

The concentration of penetrant also was taken into account. A test procedure that provided a 1 ppb level of detection, with an upstream concentration in the one- to ten-parts per million range, was considered satisfactory for several reasons. The amount of adsorption that takes place on the surface of a particle is proportional to the concentration of adsorbate and the number of sites available for adsorption. Penetration values calculated from data in which upstream concentrations of penetrant were several orders of magnitude below the parts per billion range were not deemed necessarily valid indications of penetration for filter systems handling concentrations in the parts per million range and above.

A review of potential levels of airborne iodine compounds from nuclear fuels showed that concentrations of iodine compounds, to which a charcoal filter may be subjected, may extend well into the parts per million range if calculated on the basis of air flow rates commonly employed with present-day charcoal filters. Furthermore, the allowable rate of penetration and release will be fixed at some acceptable low level. The proportion of iodine-131 that must be removed then is dependent on the upstream concentration. The required decontamination factor may be decreased as the upstream concentration is lowered. Also, many impregnated charcoal beds have an efficiency of 99.99% or greater for methyl iodide. A test procedure with a 1 ppb level of sensitivity on the downstream side and a 10 ppm level on the upstream side could show a decontamination factor of 10^4. Higher decontamination factors could be measured by increasing the upstream concentration to higher levels. Thus, there was no significant justification for utilizing a technique which employed lower upstream concentrations.

A 2 ppb level of detection for gaseous iodine is available from the Microcoulomb Detector. Methyl iodide and other organic iodides decompose with pyrolysis to form gaseous iodine.[4] Methyl iodide can be measured by drawing the sample through a pyrolyzer to form gaseous iodine, and then through the Microcoulomb Detector for direct readout of the concentration of iodine on the recorder.

Direct-reading instrumentation permits the use of a movable sampling probe. This makes it practical to scan the downstream face of filters, thereby locating leaks and higher-than-average penetrations from less efficient areas of the charcoal. Also, low levels of penetrant, which may be diluted by several orders of magnitude below detectable levels farther downstream, can be detected easily at the downstream face. To preclude the missing of leaks and to prevent overloading the detector, sampling can be started well downstream where levels are the most diluted, and then moved toward the face in a predetermined pattern.

PYROLYZER

The pyrolyzer consisted of a one-foot long, 6 mm internal diameter quartz glass tube, with about 8 inches of its length wrapped with three layers of asbestos tape and several coils of No. 20 gauge Nichrome wire, having a spacing of 1/2 cm apart. This was covered with 3/8 inch of asbestos and two coats of Saurereisen Insa-lute Adhesive Cement No. 1 paste, then air-dried for 24 hours, then baked slowly until dry. A thermocouple was inserted against the glass approximately 3-3/4 inches from the downstream end of the pyrolyzer, and then was cemented in place with the Saurereisen paste. An 8 ampere fuse was connected into one of the leads. A rheostat was used to control the temperature.

The entire pyrolyzer-Microcoulomb Detector system is shown in Figure 1. Figure 2 is a schematic of the system. The system was tested against

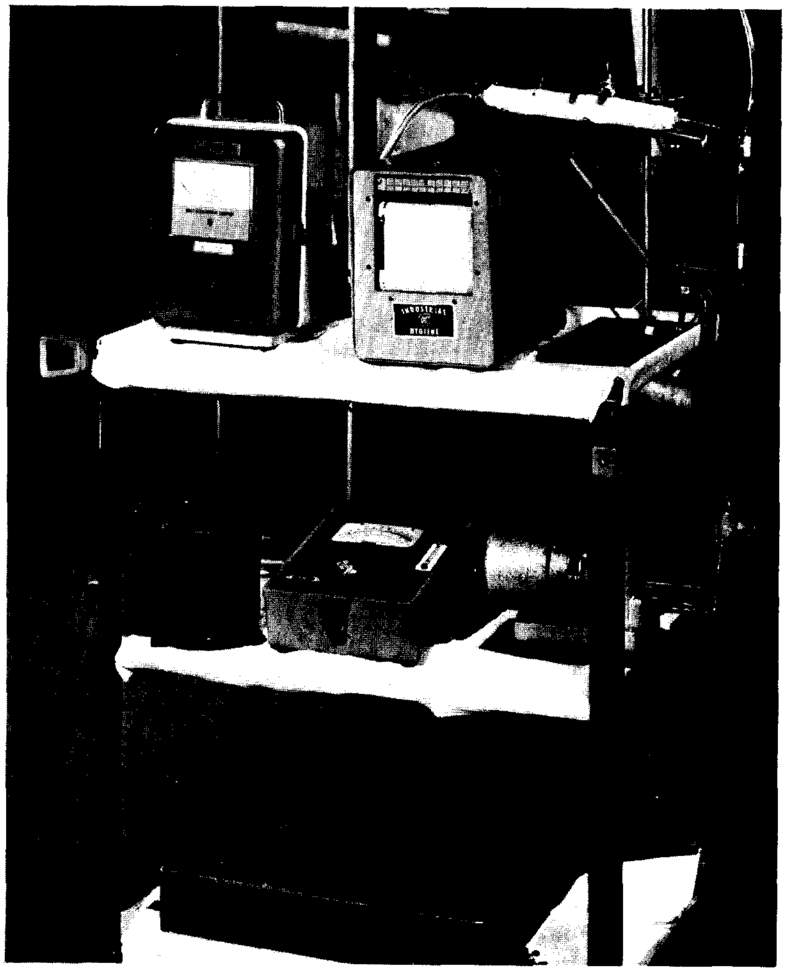


FIG. 1. PYROLYZER-MICROCOULOMB DETECTOR SYSTEM

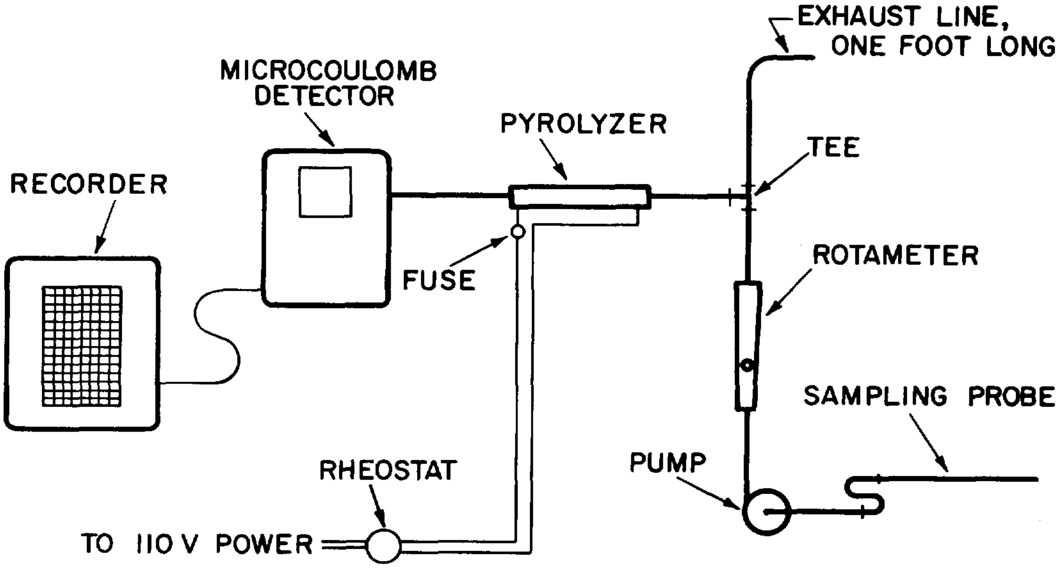


FIG. 2. PYROLYZER-MICROCOULOMB DETECTOR SYSTEM SCHEMATIC

known concentrations of methyl iodide in air, and calibration was completed at the maximum temperature which showed the greatest sensitivity. The system was then used to measure the methyl iodide penetrations of charcoal bed filters both in the laboratory and in the field.

TEST PROCEDURES

Any bubbler of suitable size may be used to feed the vapor into the ventilation system sufficiently far upstream of the filter to give uniform distribution for test purposes. An Air Technology, Incorporated, smoke generator, model TDA-4A, containing methyl iodide, was used to generate vapor for testing the 2,800 cfm CP-5 Reactor's containment clean-up system. A 500 ml fritted glass bubbler was used for the smaller systems. A HEPA filter was used after the generators to remove any mist and to assure that the methyl iodide was in the form of a vapor.

A Davis Flame Ionization Meter was used to monitor the concentrations of methyl iodide upstream of the charcoal bed. The Pyrolyzer-Microcoulomb Detector, with readout traced on the recorder, monitored penetration on the downstream side. Both monitors were sensitive to pressure differentials in excess of about 1 inch of water. Therefore, small pumps were used, when required, to draw the sample streams of 2 liters per minute each from the ventilation system and deliver them to the instrument inlets for analysis. Instrument inlets were connected perpendicular to the direction of flow, taking only that sample volume required for operation. The balance of each sample stream was exhausted.

The tests were conducted by first allowing the upstream and downstream sets of instrumentation to stabilize and record background levels. The methyl iodide generator then was turned on and adjusted as required to maintain the desired concentration of methyl iodide upstream, viz., 20 to 50 parts per million in these tests. The concentrations upstream and downstream were recorded while the sampling probes were moved to scan the face of the filter and seals and to check concentrations at selected locations. The over-all downstream penetration was determined by moving the downstream sampling probe to a location in the ventilation system as far downstream of the filters as necessary to have a uniform distribution of penetrant. Figure 3 is a picture of a typical setup for testing a single filter system.

RESULTS

Figure 4 is a typical recording of the upstream concentrations as monitored by the Flame Ionization Meter. Figure 5 is a typical recording of the downstream concentrations as determined by the pyrolyzer-Microcoulomb Detector System. The percentage penetration may be determined for any point of sampling. The amount of penetration across the face of some filters was quite variable and was dependent upon the age of the filter, the quantity of the organic materials that had passed through the filter, and the pattern of air flow across the face of the filter. As an example, the percentage penetration found on one filter ranged from less

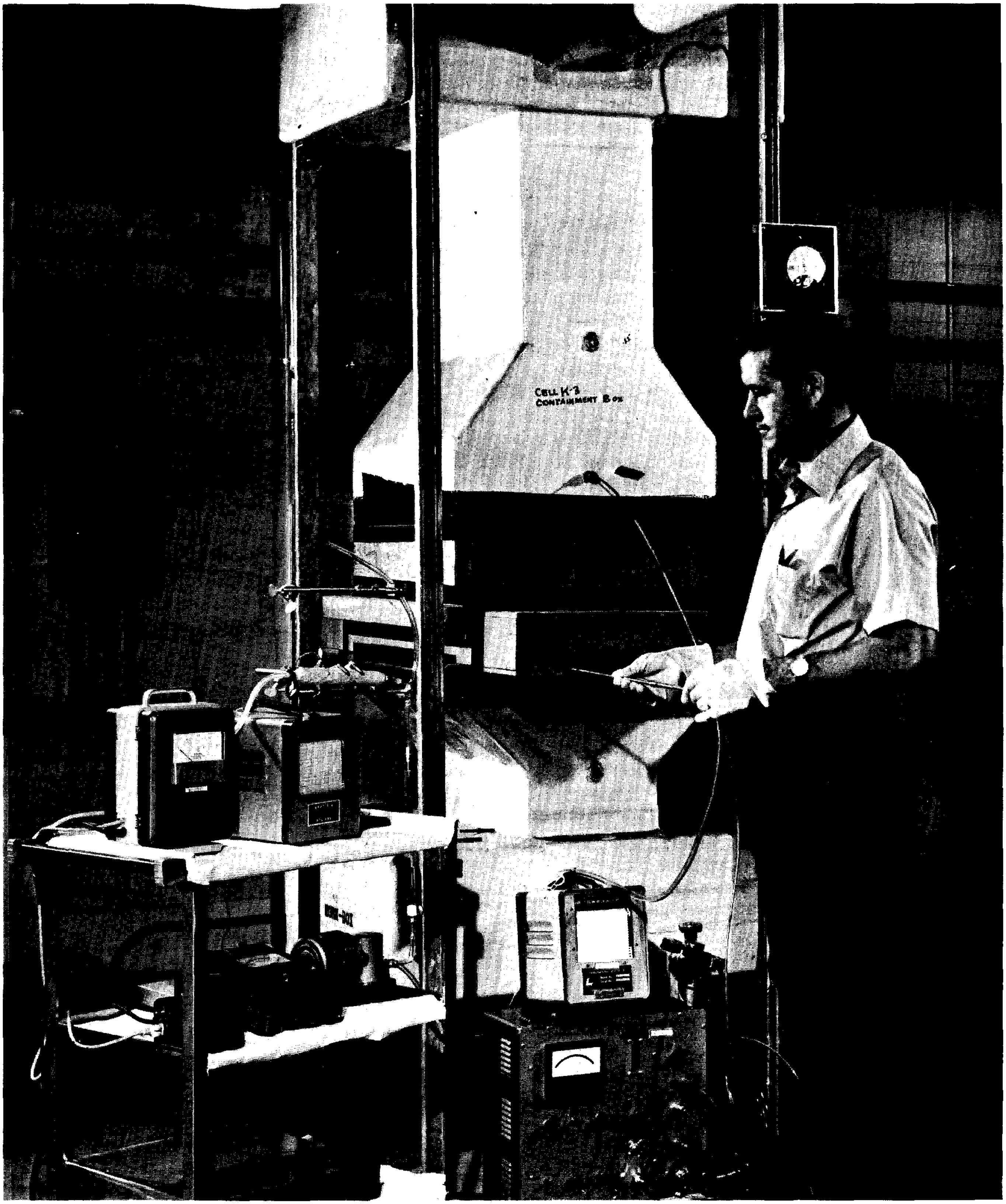


FIG. 3. IN-PLACE TESTING CHARCOAL FILTER USING PYROLYZER-MICROCOULOMB DETECTOR DOWNSTREAM AND FLAME IONIZATION METER UPSTREAM

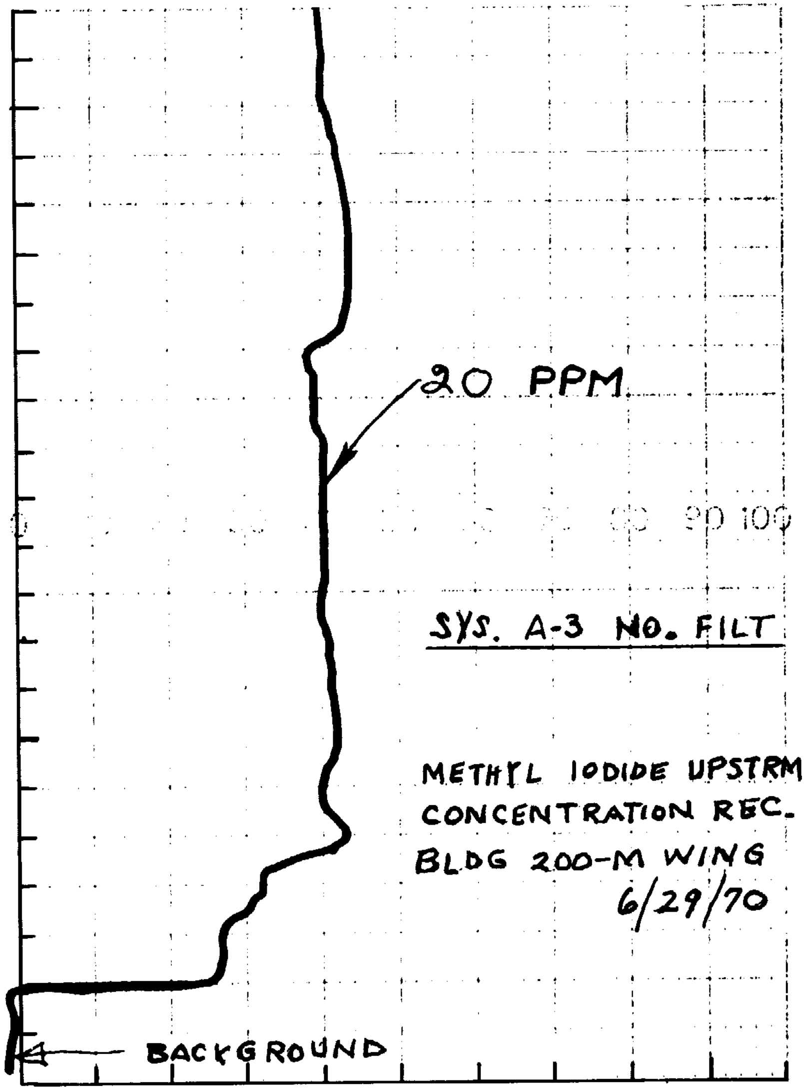


FIG. 4. FLAME IONIZATION METER RECORDER TRACE

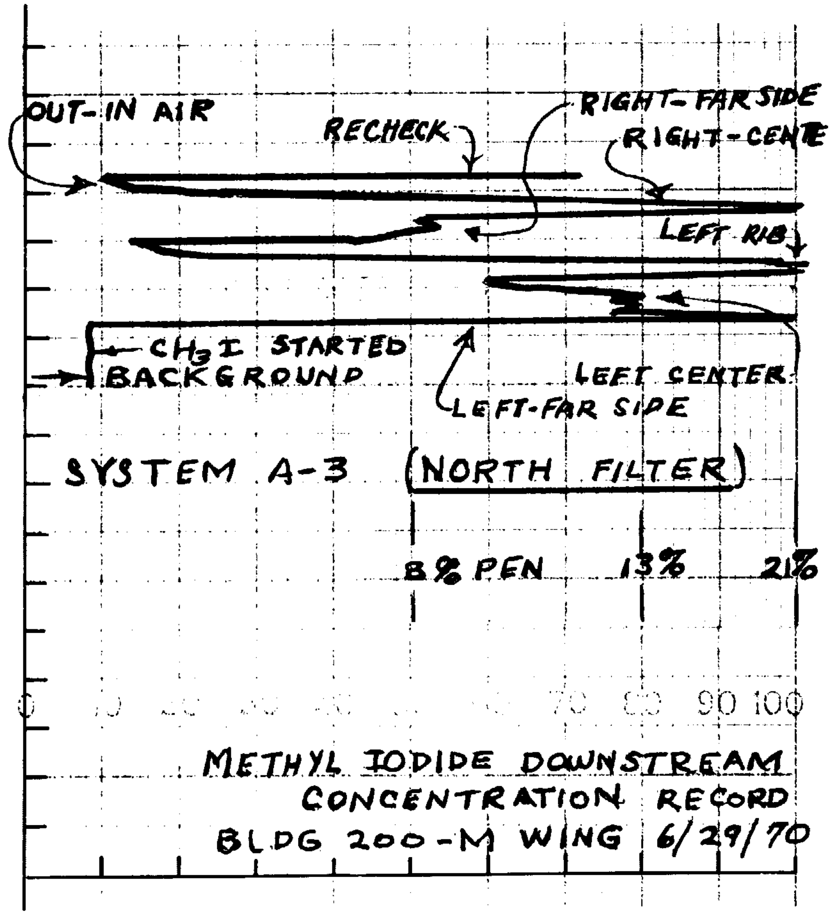


FIG. 5. MICROCOULOMB DETECTOR RECORDER TRACE

than 2% to greater than 20%, depending upon the location of the sampling probe. The filter was scanned with the Flame Ionization Meter, and relatively high levels of hydrocarbons were found to be desorbing from those areas of the filter showing high levels of penetration by the methyl iodide. These areas also were the same as those where the air stream was apt to deposit loadings of organic contaminants. It was assumed that the contaminants were solvents and other organic materials used in the cell which the system exhausted. Such findings should be sufficient reason for replacement of the charcoal in the filter. In this case, replacement would have been cheaper than further testing. All of the single filter charcoal beds that were tested, contained straight activated charcoal.

Charcoal beds in the CP-5 Research Reactor contained Barnebey Cheney #727, a charcoal impregnated with potassium iodide. Laboratory tests on fresh samples of this charcoal, using the pyrolyzer-Microcoulomb Detector system, showed a penetration of less than 0.01% until breakthrough occurred. This same charcoal in the field, about nine months after installation, showed a penetration of 0.1 to 0.2% in areas of the charcoal face that were well away from points of leakage. Leaks around the sealing gaskets were quite apparent in that they produced discrete peaks on the recorder trace. These peaks ranged up to several percentage points of penetration.

DISCUSSION

The results indicated that methyl iodide can be a useful penetrant, and that the pyrolyzer-Microcoulomb Detector system can be a suitable detector for in-place testing of charcoal filters.

Other organic iodides of higher molecular weight, e.g., ethyl and propyl iodides, also would be useful. They also decompose to give free iodine,[4] and, therefore, should be equally adaptable for detection and measurement with the pyrolyzer-Microcoulomb Detector system. These higher molecular-weight iodides should be useful for leak testing charcoals in which methyl iodide breaks through too quickly.

As noted in the Introduction of this text, penetration values from tests utilizing organic iodides are directly applicable towards predicting releases from charcoal filters that are used to remove radioiodine because it is the organic radioiodides that are often the penetrants of concern. Any charcoal showing a high efficiency for methyl iodide also should have a relatively high efficiency for all other iodides. But, if the efficiency for methyl iodide is low, the charcoal still may be efficient for inorganic iodides and free iodine. For this reason, methyl iodide will be useful primarily as a screening and leak test penetrant on some systems, e.g., on systems in which the probability of the presence of organic iodides is negligible. Unless overall penetration through the charcoal is exceptionally high leaks will be easily detected by scanning the downstream face. Concentrations in the air streams at points of leakage are not reduced significantly, and the leaks should show as high peaks on the recorder chart.

Some charcoals, e.g., charcoals impregnated with potassium iodide, supposedly, accomplish their function partially by isotopic exchange, i.e., radioiodine in the air stream is exchanged for nonradioactive iodine in the filter. It would seem that test procedures must be able to differentiate between the two forms. However, results show that charcoal has a sufficiently high retention of normal methyl iodide, that methyl iodide can be used for in-place leak testing of these systems, at least with respect to the times, levels, and concentrations employed in these tests. That aspect of iodine retention related to isotopic exchange, however, was not measured.

CONCLUSIONS

The pyrolyzer-Microcoulomb Detector system answers the need for a versatile, direct-reading, instrumented means of in-place testing of charcoal filter systems. There are several disadvantages but they are outweighed by the advantages. Both are summarized as follows:

Disadvantages

1. Frequent and close calibrations of the entire system are required.
2. Response is a little slower than desired, e.g., there is almost a full minute of delay before readout of very low concentrations.
3. Inorganic iodine may contaminate the system and may require heating and lengthy purging to obtain sufficiently low background readings.
4. Halogenated hydrocarbons or compounds other than methyl iodide, which previously may have been adsorbed onto the charcoal and then begin to slowly release, can interfere by producing a high background reading on the downstream recorder trace.

Advantages

1. A nonradioactive form of the principal contaminant of concern is utilized.
2. Analysis, readout, and recording of data are all automatic at the time of sampling.
3. The system is a continuously monitoring type, practical for scanning the face of the filter and, thus, one giving more detailed information than is obtainable by discrete samples analyzed after completion of sample collection.
4. Can be operated by one person.
5. Lightweight and portable with respect to all individual components. Proper packaging could make this unit into a lightweight highly portable two- to three-component system.
6. Either methyl iodide or elemental iodine concentrations can be measured.

REFERENCES

1. Viles, F. J. Jr. and L. Silverman: In-Place Iodine Removal Efficiency Test, Proceedings of the Ninth AEC Air Cleaning Conference held in Boston, Massachusetts, 13-16 September 1966, Vol. 2, CONF-660904 (January, 1967), p. 1108.

2. Morgan, J. M., Jr. and M. W. First, Eds.: Proceedings of the Ninth AEC Air Cleaning Conference held in Boston, Massachusetts, 13-16 September 1966, CONF-660904 (January, 1967), 1202 pages.

3. Thomson, W. G. and R. E. Grossman: In-Place Testing for Iodine Removal Efficiency Using an Electronic Detector, op. cit., p. 1134.

4. Benson, S. W.: Kinetics of the Pyrolysis of Organic Iodides, J. of Chem. Phys. 38:8 (April 15, 1963), pp. 1945-51.

DISCUSSION

SCHINDLER: Do you have any figures on how effective your pyrolyzer is? That is, what fraction of the organics get through without the pyrolyzer?

McFEE: No, it really doesn't make too much difference as long as the system is calibrated. One of the disadvantages is that it (the calibration) is sensitive to changes in any part of the system. So you have to take the complete system, test it, and use it in the way you have it set up. If you use it identically the same way each time, you can get highly reproducible results. We don't know what fraction is not decomposed.

MURROW: Regarding your Davis unit when you take the upstream sample, do you find that the instrument is reasonably stable, or do you have to calibrate it each time you set it up?

McFEE: No, we find that the Davis Flame Ionization Meter is very stable. Once it's calibrated it will last for several months without too much tuning. With respect to the slide that I showed, all the variation there is definitely due to the variation in the vaporization rig. The Flame Ionization Meter will give nearly a straight line if you have a steady concentration.

SCHWENDIMAN: My question is much along the same line as the last one. Is the Detector completely reproducible for the very low levels of methyl iodide? Aren't line losses significant? I think it would be interesting to see just how much iodine for each microgram of methyl iodide actually reach the micro-coulometric detector. Apparently you found the instrument was stable even with very low concentrations, and the conversion of I^- to I_2 was reproducibly constant.

McFEE: It is stable, if you maintain a constant temperature. I mentioned that we did calibrate it at the point of maximum sensitivity. We find that there is a definite change with temperature, but you do reach a maximum point or plateau where over 30 - 40° you can get a rather stable reading from it.

SCHWENDIMAN: Was this glass all the way right up to the detector in the Microcoulomb Detector unit?

McFEE: No. The Microcoulomb Detector has a teflon probe, about 8 to 12 inches long. It was placed right at the exhaust end of the pyrolyzer. This will make a difference.

KOVACH: Would you explain in more quantitative terms what the advantages are in your method over the conventional Freon method? And the second question I have, do you expect any efficiency measurements other than leak tests on the system, at least based on the information that you gave us in your paper.

McFEE: I will take your first question first. This system is a little more sensitive than the instrumentation normally used with Freon, except when you use a very sensitive gas chromatagraph. The pyrolyzer-Microcoulomb Detection system is cheaper than a gas chromatagraph. It's lighter, and it is easier to handle. It can be packed in smaller units. In that sense, it is an advantage. Primarily its advantage is the fact that you are testing with a penetrant that you want the filter to remove. Furthermore, you have immediate and direct readout which allows you to scan the face of a filter. Whereas with a gas chromatagraph, unless you have a highly sophisticated one that would give you rapidly repeated and continuous sampling readout, it would be very difficult to scan the face of a filter and get much information.

Now with respect to your second question on testing the efficiency of the charcoal, as I previously pointed out, with impregnated charcoal you can not measure that portion of efficiency that's related to isotopic exchange. Except for this one aspect, it is this other question of charcoal efficiency versus leakage that you can measure with a Detector System such as this. When you measure the methyl iodide going in and the methyl iodide coming out, you are measuring penetration, whether it is due to leakage, channeling, or nonadsorption. Which one depends on the location of your sampling probe at the downstream face, or further downstream. The results from efficiency tests that we have run in the laboratory correspond favorably to what we find in the field at the downstream face of filters well away from points of leakage. However, when trying to measure filter efficiency in the field, I think that most of the time you are measuring penetrations through leaks rather than efficiency of the charcoal.

KOVACH: I'm not sure if I got the answer for my question, but I accept it, thank you.

McFEE: I will repeat it if you would like it and I will try to be more specific.

IN-PLACE TEST RESULTS OF THE N REACTOR CHARCOAL CONFINEMENT FILTER SYSTEM USING IODINE TAGGED WITH IODINE-131 TRACER.

JE MECCA
NUCLEAR SAFETY TECHNOLOGY
DOUGLAS UNITED NUCLEAR, INC.
RICHLAND, WASHINGTON

and

JD LUDWICK
BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON

ABSTRACT

This document describes the in-place test developed to measure the iodine removal capability of the Hanford N-Reactor exhaust gas system prior to the release of the gases to the atmosphere.

Reported herein are the system descriptions, the experimental techniques, equipment developed, final test procedures used, and the test results obtained in the initial tests conducted on May 15th and 16th, 1969 at the N-Reactor. Information is also presented on recently conducted tests of new replacement charcoal filters presently installed.

INTRODUCTION

The operating reactors (KE and N) at Hanford are equipped with a confinement facility and associated equipment designed to control and entrap the radioactive materials which would be present in the exhaust system in the event of a reactor incident. These facilities include the fog spray system, exhaust fans, associated ductwork, monitoring devices for automatic activation of the systems and a series of filter banks. The primary purpose of this facility is to provide protection by ensuring the filtration of all exhaust air prior to its release to the atmosphere. One of the primary release considerations is the removal of radioiodine.

In order to achieve a high degree of reliability and to ensure proper maintenance of the systems which provide for iodine removal (confinement system charcoal filters) a reliable inspection, testing and maintenance program is essential.

The program developed for the Hanford production reactors can be described in four steps:

1. All new filters or adsorbers as some prefer to call them are

tested prior to installation to insure that no production failures have occurred and no voids are present due to charcoal settling. Only if all filter units in a system are judged within specification can the system as a whole be considered trustworthy.

2. On a quarterly basis, one confinement cell at each reactor is isolated and visually inspected for plugging due to corrosion or other effects. Voids, mechanical damage and other obvious flaws are also corrected at this time.
3. At the time of visual inspection, charcoal samples are obtained and tested under a variety of conditions to insure that the pollutant materials present in the exhaust air stream have not severely deteriorated their iodine adsorption efficiency.(1)
4. In-place testing is conducted on the system to indicate that the designed capability is present and that there are no gasket leaks, installation errors, or other failures that have taken place since individual filter testing. Annual in-place testing will be conducted to insure the continued high efficiency of the gas confinement system.

This report is concerned with implementation of the fourth step at the N-Reactor and includes a description of the equipment, procedures and results obtained in testing of the charcoal filter confinement systems at the N-Reactor initially and subsequently to the present time.

Previous tests on the C, KE and KW Single Pass Production reactors were conducted earlier. The results of the tests can be found in DUN-SA-105.(2)

GENERAL DESCRIPTION OF THE N REACTOR CONFINEMENT SYSTEM

A. Confinement System

The intent of the confinement system is to ensure that all ventillation air be confined to a definite flow path and exhausted from specific confinement zones through the filters before release to the atmosphere. These zones are defined as areas within the reactor building where airborne radioactive materials will be found in the event of a reactor incident.

There are five major zones and three flow paths at N-Reactor to accommodate the critical locations within the reactor building.

The two zones of prime importance are those which are kept negative with respect to atmosphere and are exhausted through the filter banks and stack. These two zones are Zone I (Primary Zone) which exhausts all air immediately adjacent to the reactor graphite stack and Zone II (Secondary Zone) which handles all exhaust air immediately adjacent to Zone I areas. For a further description of the Zones consult reference three.(3)

The general flow pattern and system layout is shown in Figures I and II for the N-Reactor system.

In order to ensure a workable system, it is required that all confinement zones at N-Reactor be maintained at a pressure slightly less than atmospheric. Also, the exhausting equipment must provide a maximum degree of reliability as well as being capable of handling quantities of flow, involving air, steam, and fission products which will be present in a reactor incident.

B. Filter Building

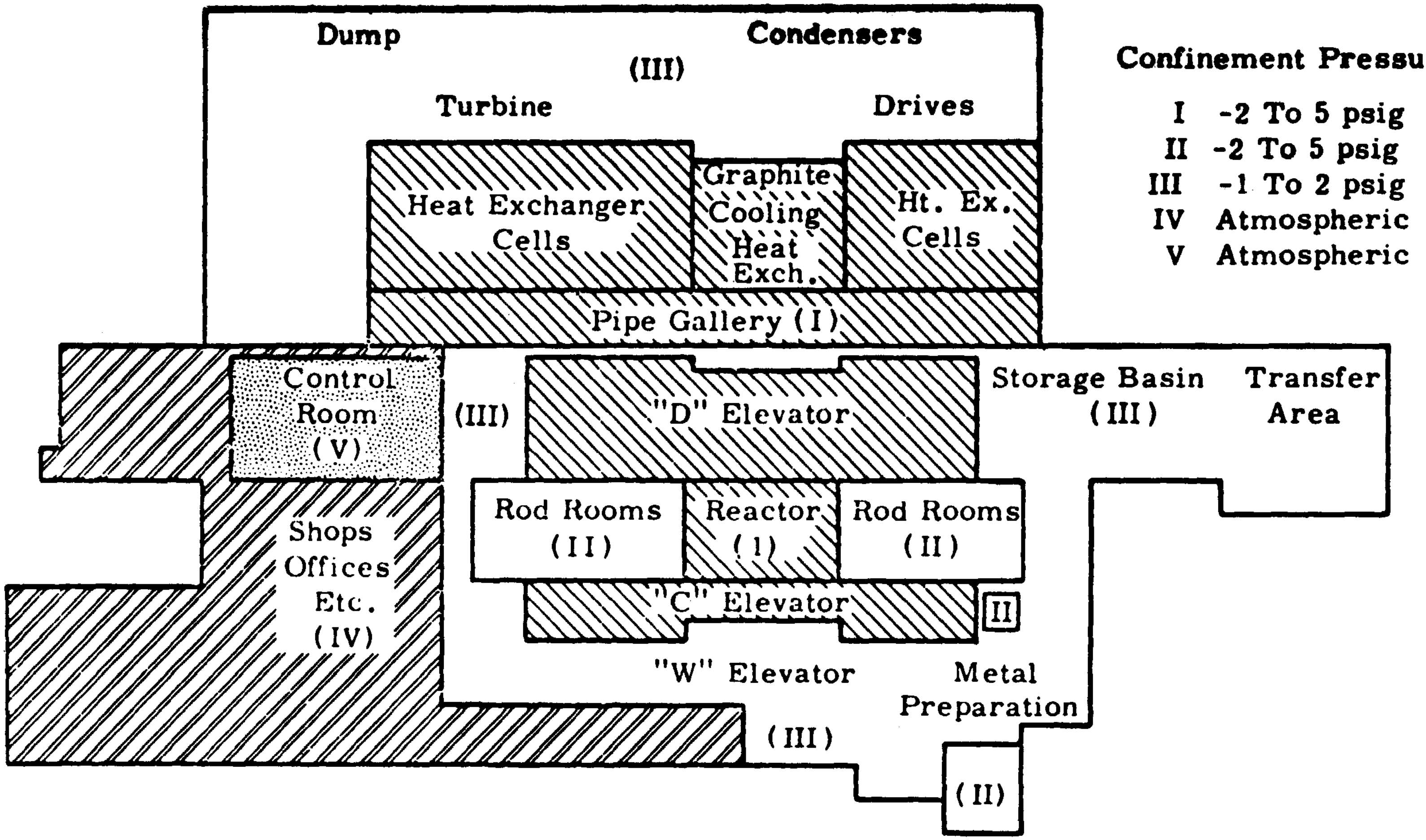
The filter or 117 Building is of reinforced concrete and is approximately 75 percent below grade with a designed capacity of about 340,000 cfm for the N-Reactor. The exhaust air leaves the building and passes through concrete ducts to the filter building where it is filtered and then exhausted out the stack. The filter building layotu is shown in Figures III and IV for the N-Reactor.

The filter building at N-Reactor consists of four identical cells: A and B cells are located on the east side of the building; C and D cells are on the west side of the building as shown in Figure III. Each cell is made up of three seperate stages which consist of two aluminum filter frames for each stage. Stage 1 consists of two frames of 10 moisture seperators each for a total of 20 per stage and are designed to remove moisture in the 1 to 10 micron range. The second and third stages consist of 40 filter units for each frame for a total of 80 per stage and differ only as to type and function of the filters. The second stage is loaded with absolute or HEPA filters for particulate removal, while the third stage contains charcoal filters for halogen removal. See Figure V for the general arrangement of the filters in each frame.

TEST EQUIPMENT AND LOCATION

A. Sample Line Location

The sample lines are constructed of 3/4 inch schedule 80 FLUOROFLEX (VF-2) KYNAR pipe, permanently installed on the upstream and downstream side of each cell. This material is manufactured by Resistoflex Corporation and consists of a crystalline homopolymer of vinylidene fluoride.



Confinement Pressures

I	-2 To 5 psig
II	-2 To 5 psig
III	-1 To 2 psig
IV	Atmospheric
V	Atmospheric

Figure I 105-109-N CONFINEMENT ZONES

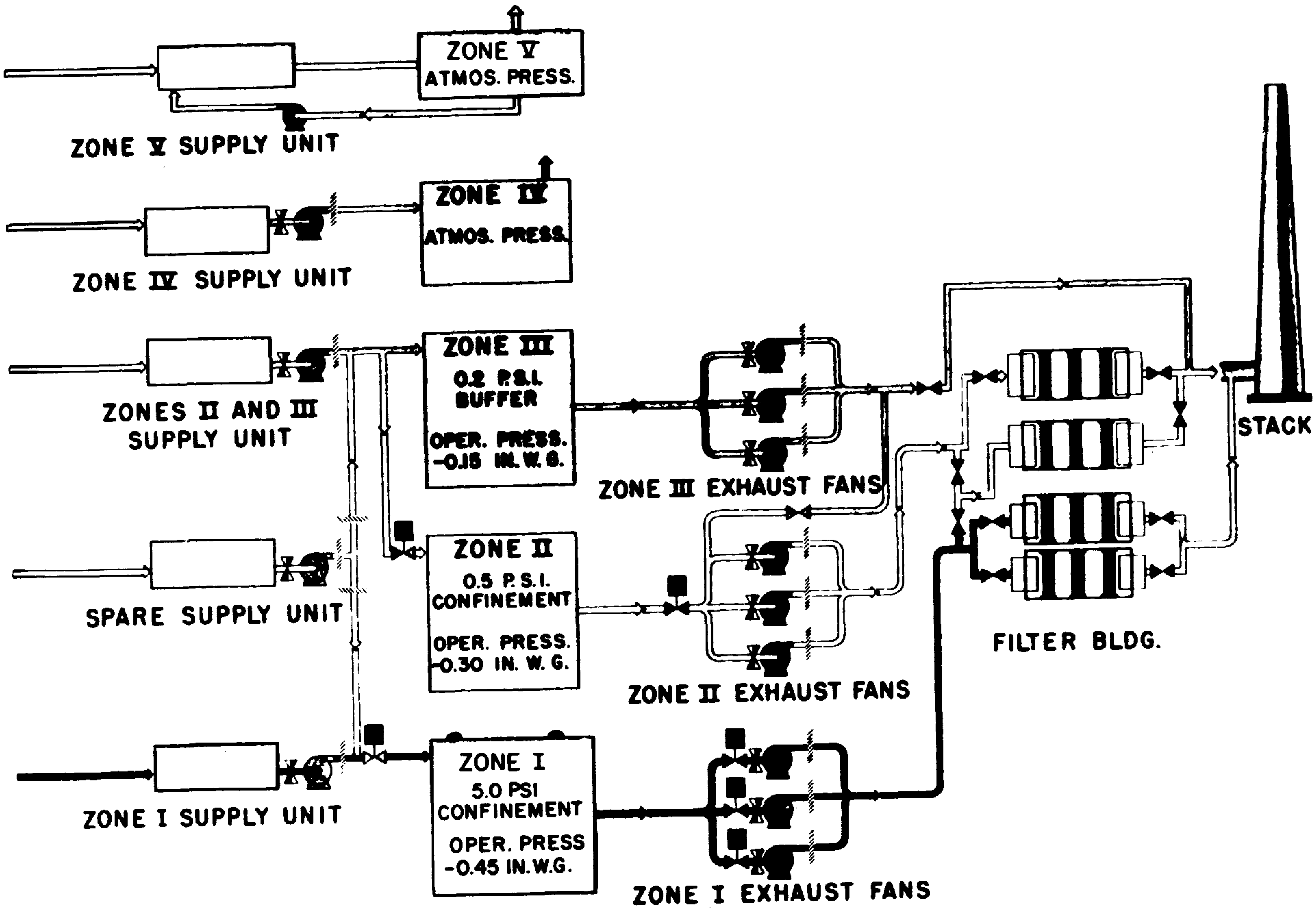


Figure II 105-N VENTILLATION AND FILTER SYSTEM

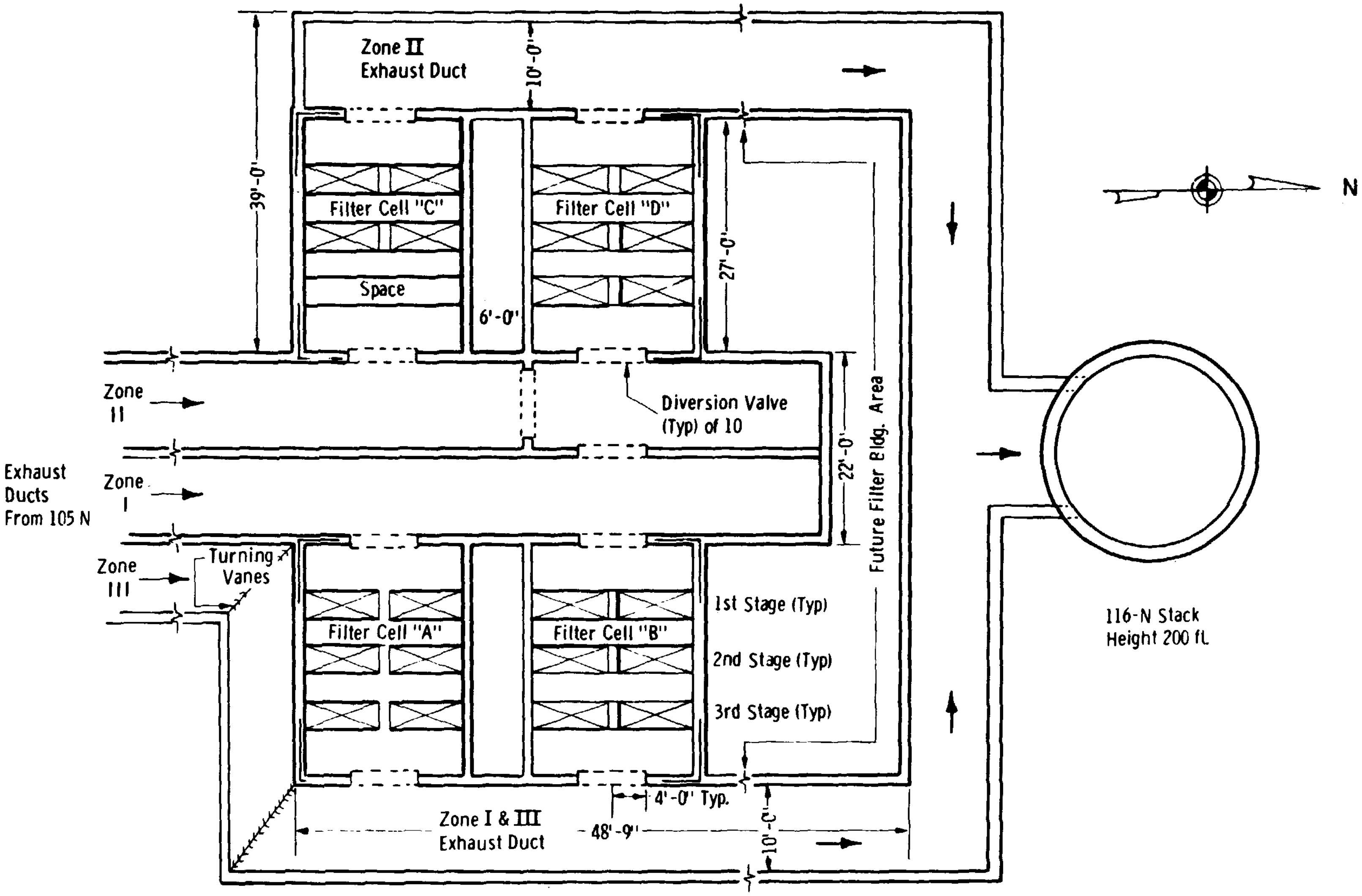


Figure III 117-N - EXHAUST FILTER AND DIVERSION SYSTEM

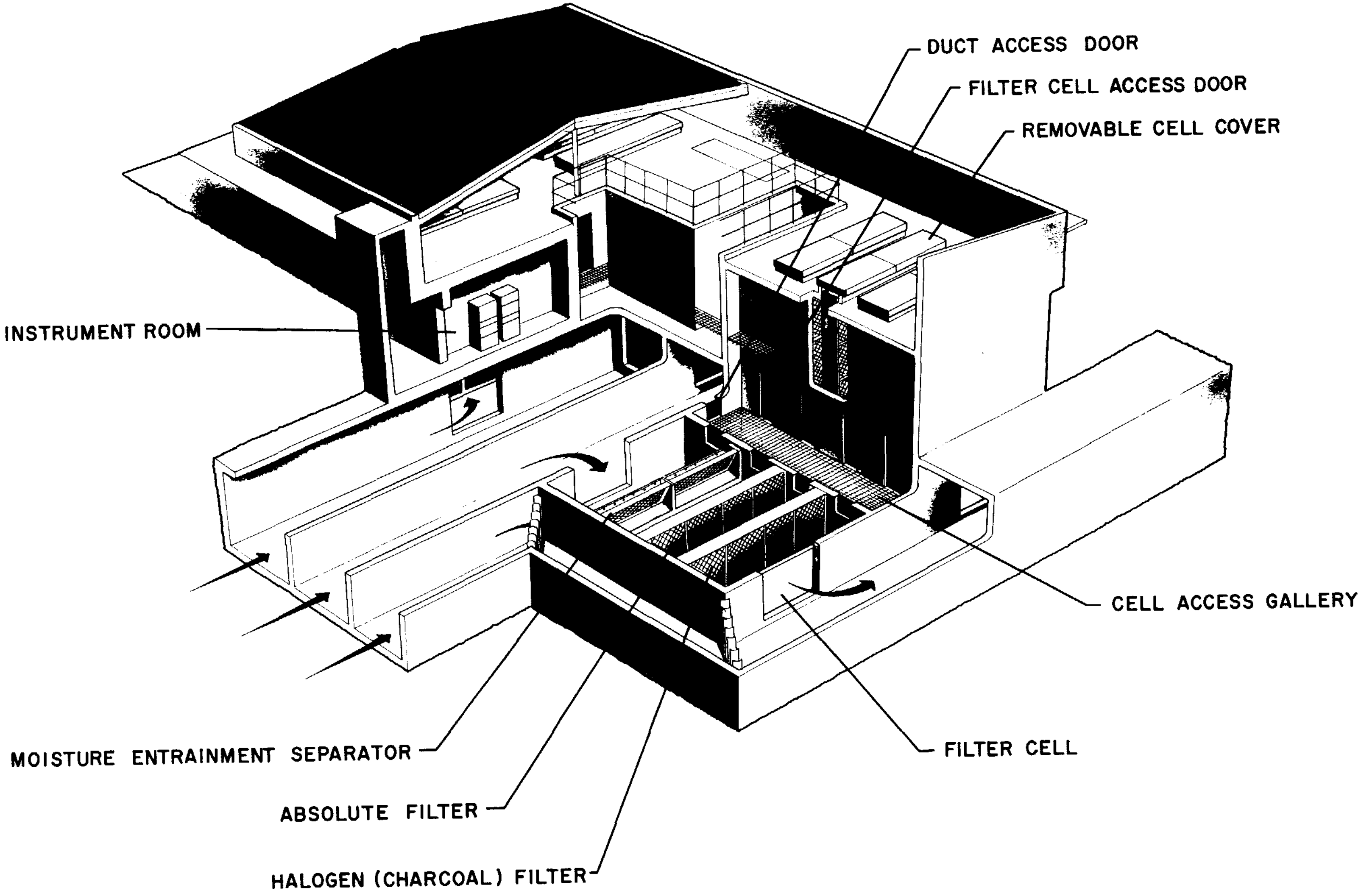
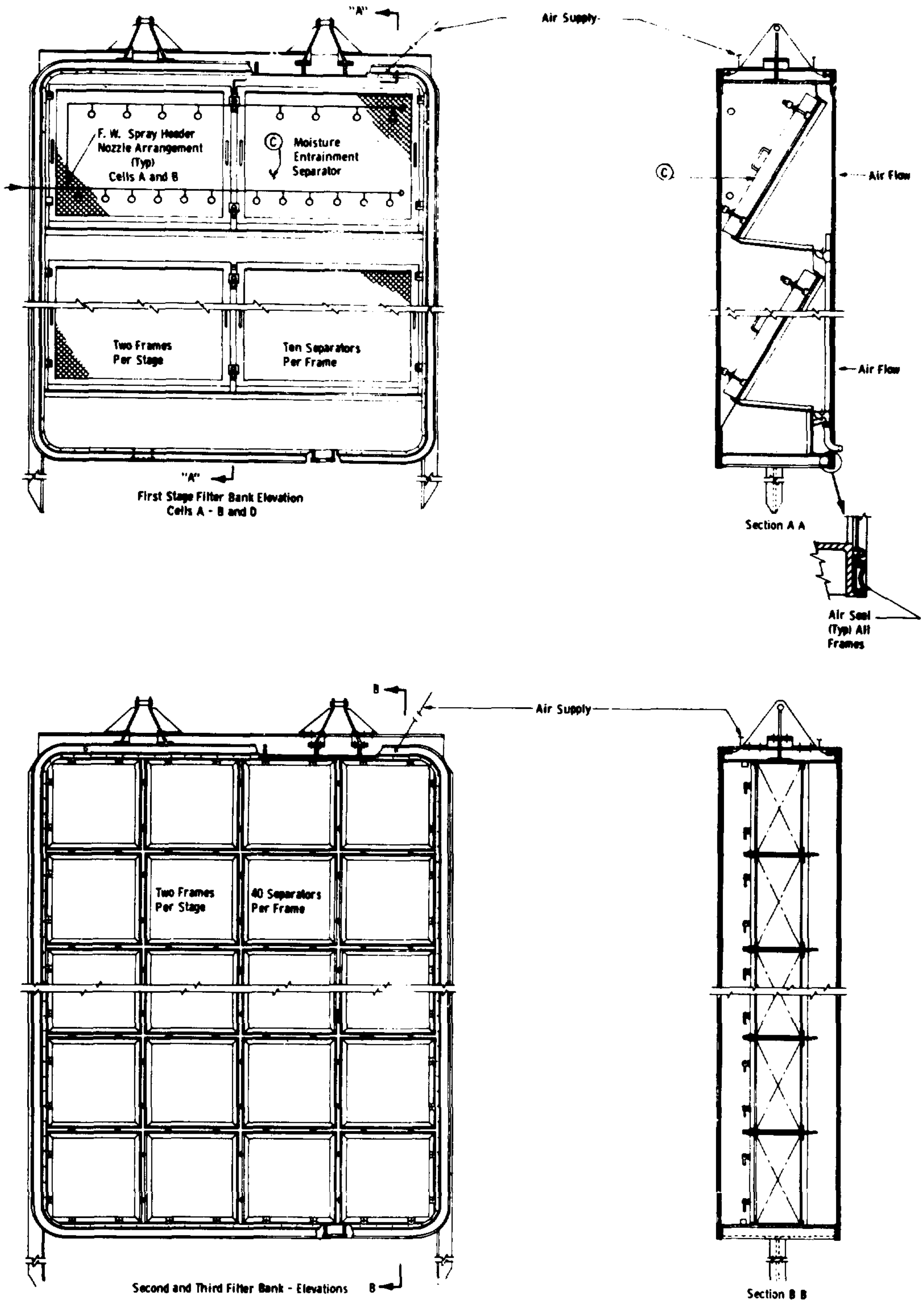

DUCT ACCESS DOOR
FILTER CELL ACCESS DOOR
REMOVABLE CELL COVER
INSTRUMENT ROOM
CELL ACCESS GALLERY
FILTER CELL
MOISTURE ENTRAINMENT SEPARATOR
ABSOLUTE FILTER
HALOGEN (CHARCOAL) FILTER

Figure IV



Moisture Separator and Filter Bank Assembly

Figure V 117-N FILTERS

Several small holes (0.055 inch ID) are drilled in each sample line, seperated 12 inches apart to serve as sampling ports and are designed to insure a representative sample of the gas to be measured. At N-Reactor the sample lines are 12 feet long and located within a foot of the confinement gates inside of the cells. The sampling ports on all installed lines are oriented towards the direction of the air flow. The sample lines extend through the wall of each cell and into the operating gallery as shown in Figure VI. The end of the sample lines are fitted with Hanson Quick Connect ST (Straight Through) stainless steel couplings which allow no impedance to flow. These couplings are mounted on the wall just inside the operating gallery. To these couplings are fitted the samplers, which in turn are connected to vacuum pumps with a flexible sample line equipped with Hanson Quick Connect couplers. The vacuum pumps are permanently mounted at each end of the operating gallery and service two cells, one for both upstream samplers and one for the two downstream samplers. The position and general configuration of the vacuum pumps and sampler locations are shown in Figure VII.

B. Test Samplers

In order to simulate linear flow rates of 65 to 70 ft./min., which are typical of those utilized in reactor filter banks, a 1½ inch ID sampler was chosen. This sampler is constructed of stainless steel and provided with a orifice which will regulate the air flow through the filter sections at a velocity of 1cfm when a vacuum of at least 15 inches of Hg. is maintained.

The sampler was designed to differentiate by selective entrapment,(1) molecular iodine and other organic forms such as methyl iodide. The sampler, as designed, when properly utilized will provide information not only on iodine removal efficiency of a system but also on the general cleanliness of the associated ducts, cells, filter systems and possible plate-out information. The materials found most satisfactory to accomplish the above were a series of sections made up of charcoal impregnated filter paper backed by a (5u) silver membrane for the molecular iodine species and four inches of KI impregnated charcoal for the organic species.

Figure VIII shows in detail the sampler by sections and the materials utilized.

C. Iodine Generator and Injection Location

The assembled iodine generator can be seen in Figure IX and the locations upstream of the filter building in the Reactor Building proper were as noted on Figure X.

Solutions for molecular iodine generation were individually prepared and contain the desired iodine quantity and excess stoichiometric amounts of other reactant materials. The generator flask was loaded with 400 ml of 4.5N H_2SO_4 prior to positioning the end into the reactor exhaust duct. The center separatory flask was loaded with NaI solution containing a small quantity of Na_2SO_3 to prevent pre-oxidation. Then the iodine-131 tracer activity was transferred into this flask by means of a pipette and mixed completely. The radioiodine was obtained in the form of iodide to facilitate the tagging operation. The other separatory flask which was built with a drawn down exit tip, contained excess $NaNO_2$ solution.

Molecular iodine generation was initiated when the NaI solution was emptied into the main generator flask and the second separatory flask stopcock was opened. The restricted tip allowed the unattended dropwise addition of nitrite solution to the generator flask. This produced molecular iodine at a steady precalculated rate for 20 minutes. The heating mantle maintained the temperature of the generator flask at about 210°C while the tube furnace was set at about 550°C to further heat the evolving iodine and prevent immediate plateout. Nitrogen gas, introduced on the rear side of the flask, was used to agitate the solution and sweep the iodine into the duct system. A positive nitrogen flow was continuously maintained into the duct during the entire experiment. The rate of iodine generation was measured by radiation monitoring equipment. A more extensive stepwise procedure for iodine generation can be found in references two and three.(2)(3)

TEST RESULTS

A. Method of Sampler Analysis

It is understood that prior to any operational test, the full complement of samplers must be installed and functioning. The samplers should be allowed to remain in place and be operational for at least one-half hour before generation and for four subsequent hours to ensure that iodine, which may have been adsorbed on the ducts, particulate filters and fan blades, has had ample time to desorb. In all tests, background samples were also obtained for a period of at least two hours prior to testing. After sampling for the length of time indicated the vacuum pumps were stopped and the samplers removed.

The samplers were now moved to the Radiation Monitoring Room in 105 Reactor Building where they were carefully disassembled. Each sampler section was transferred to a previously marked plastic bottle. The sampler sections as shown in Figure VIII consisted of two charcoal impregnated filter papers backed by a (5u) silver membrane, G and H in Figure VIII. The next two additional sections contained one-inch deep charcoal beds, as seen in Figure VIII and labeled C and E. The fourth and final section was a two-inch deep backup charcoal bed, labeled A in Figure VIII. All charcoal used in the tests was KI impregnated. The marked sample bottles were counted in a gamma-ray spectrometer which utilized a 9-inch NaI(Tl) well-type crystal to determine the amount of iodine-131 present.

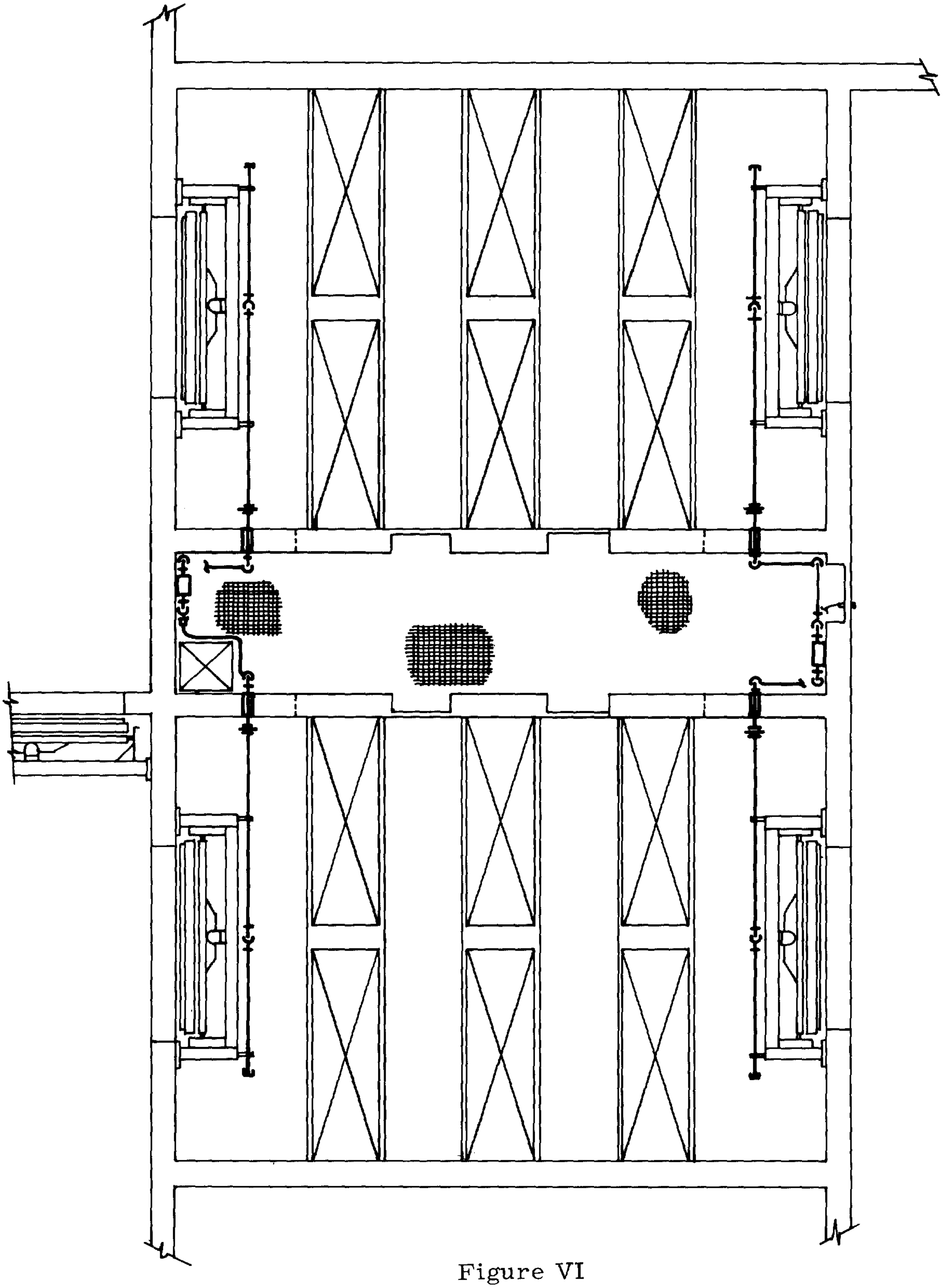


Figure VI

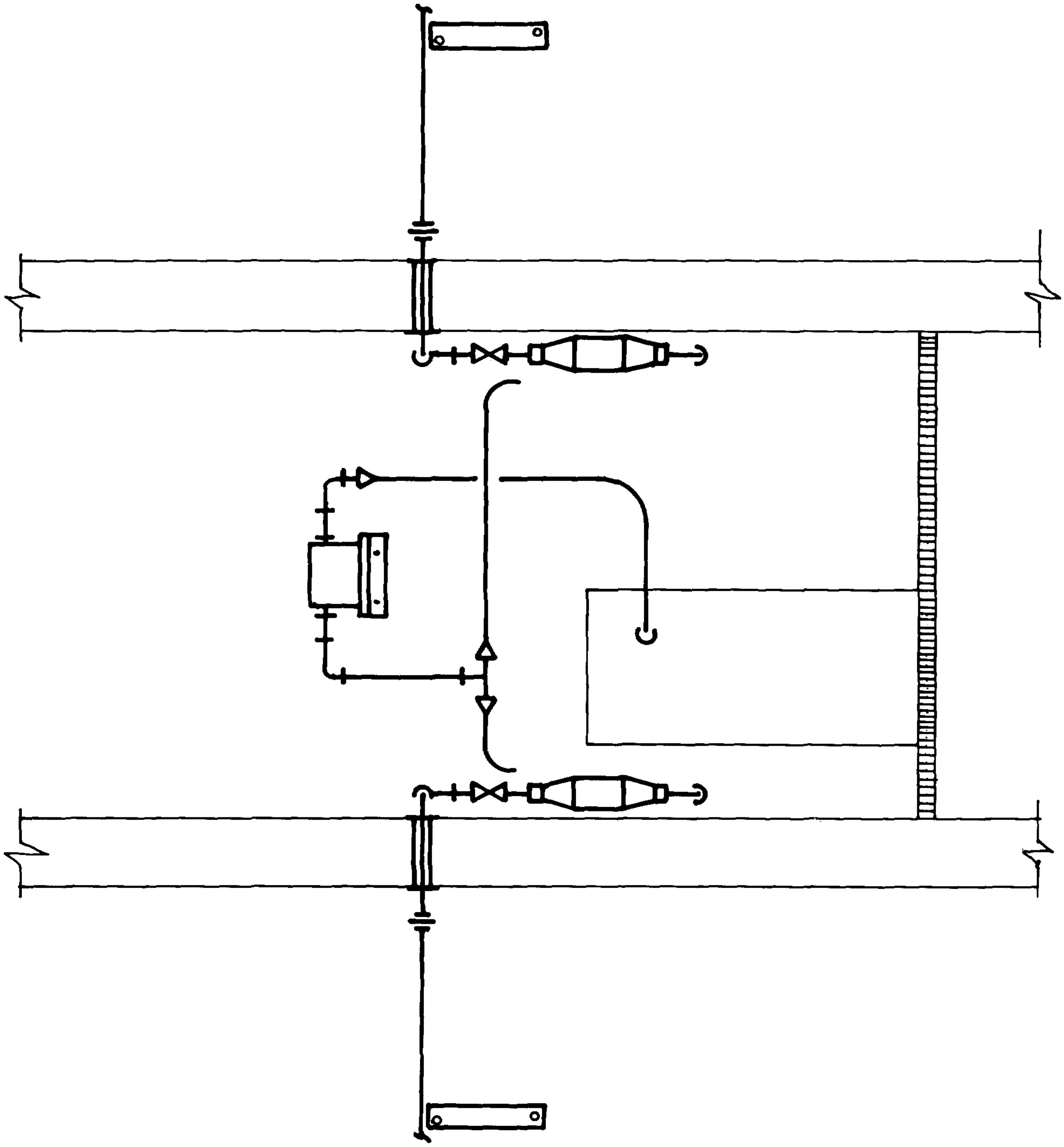


Figure VII

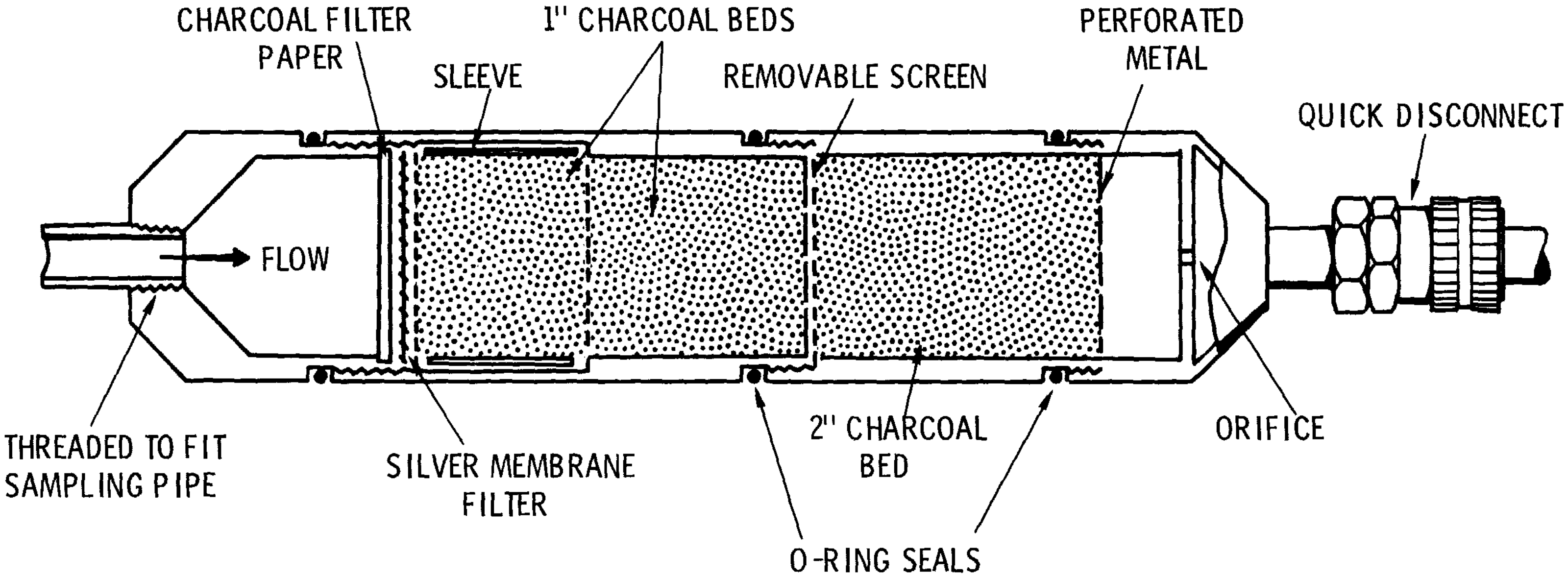


Figure VIII STAINLESS STEEL IODINE SAMPLER amounts of other reactant materials. The generator flask was loaded with 400 ml of 4.5N H_2SO_4 prior to positioning the end into the reactor exhaust duct. The center separatory flask was loaded with NaI solution containing a small quantity of Na_2SO_3 to prevent pre-oxidation. Then the iodine-131 tracer activity was transferred into this flask by means of a pipette and mixed completely. The radio-iodine was obtained in the form of iodide to facilitate the tagging operation. The other separatory flask which was built with a drawn down exit tip, contained excess $NaNO_2$ solution.

Molecular iodine generation was initiated when the NaI solution was emptied into the main generator flask and the second separatory flask stopcock was opened. The restricted tip allowed the unattended dropwise addition of nitrite solution to the generator flask. This produced molecular iodine at a steady precalculated rate for 20 minutes. The heating mantle maintained the temperature of the generator flask at about 210°C while the tube furnace was set at about 550°C to further heat the evolving iodine and prevent immediate plateout. Nitrogen gas, introduced on the rear side of the flask, was used to agitate the solution and sweep the iodine into the duct system. A positive nitrogen flow was continuously maintained into the duct during the entire experiment. The rate of iodine generation was measured by radiation monitoring equipment. A more extensive stepwise procedure for iodine generation can be found in references two and three.(2)(3)

TEST RESULTS

A. Method of Sampler Analysis

It is understood that prior to any operational test, the full complement of samplers must be installed and functioning. The samplers should be allowed to remain in place and be operational for at least one-half hour before generation and for four subsequent hours to ensure that iodine, which may have been adsorbed on the ducts, particulate filters and fan blades, has had ample time to desorb. In all tests, background samples were also obtained for a period of at least two hours prior to testing. After sampling for the length of time indicated the vacuum pumps were stopped and the samplers removed.

The samplers were now moved to the Radiation Monitoring Room in 105 Reactor Building where they were carefully disassembled. Each sampler section was transferred to a previously marked plastic bottle. The sampler sections as shown in Figure VIII consisted of two charcoal impregnated filter papers backed by a (5u) silver membrane, G and H in Figure VIII. The next two additional sections contained one-inch deep charcoal beds, as seen in Figure VIII and labeled C and E. The fourth and final section was a two-inch deep backup charcoal bed, labeled A in Figure VIII. All charcoal used in the tests was KI impregnated. The marked sample bottles were counted in a gamma-ray spectrometer which utilized a 9-inch NaI(Tl) well-type crystal to determine the amount of iodine-131 present.

Figure IX

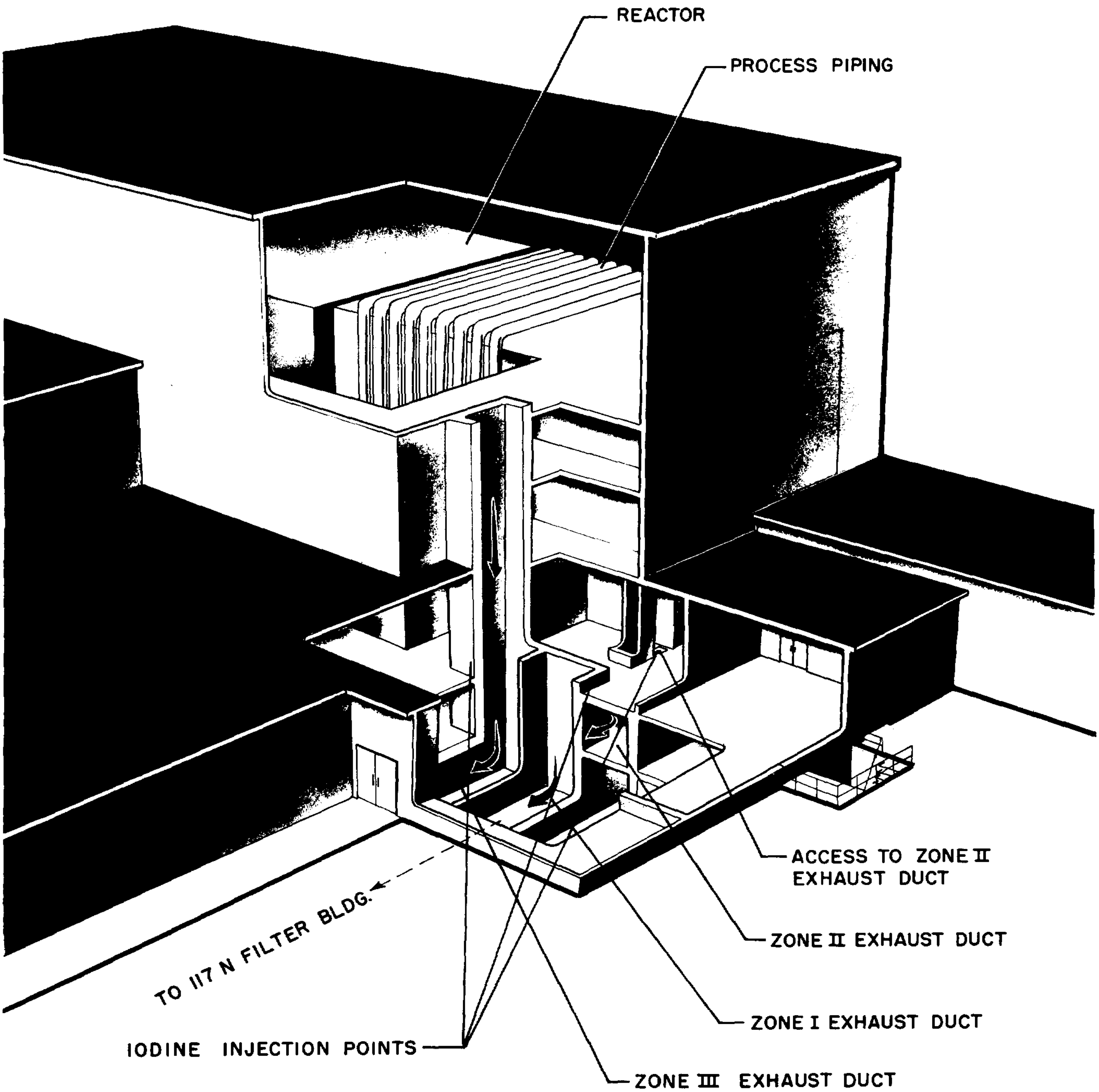

REACTOR
PROCESS PIPING
ACCESS TO ZONE II EXHAUST DUCT
ZONE II EXHAUST DUCT
ZONE I EXHAUST DUCT
ZONE III EXHAUST DUCT
TO 117 N FILTER BLDG.
IODINE INJECTION POINTS

Figure X

The bottles were marked F-1 for the filter papers and silver membrane and C-1, C-2, and C-3 respectively, for the charcoal segments mentioned above. From the amount of indroduced and recovered radioiodine and a knowledge of the samplers' performance, as defined in Reference 2, the fraction and form of iodine present at positions downstream were measured.

B. Initial Test Results

In early May of 1969, four activated charcoal filter units were removed from the main air flow stream at N-Reactor. The filter units were immediately opened and one-pound samples were retrieved and hermetically sealed for the laboratory. Tests were conducted on the sampled charcoal at ambient conditions (30°C, 50% RH) and at high temperature (100°C, 100% RH) to determine the iodine retention capability of the activated charcoal and efficiency in a one-inch bed depth configuration. The air flow velocity was 67 fpm and the amount of iodine fed to the test bed in a 30-minute period was about 25 ug of I_2 per gram of charcoal. The results of the tests conducted can be seen in Table I. All samples were pre-equilibrated for three hours at the desired test conditions, fed the iodine for one-half hour and eluded for another two hours. The complete test procedure and laboratory description can be found in References 2 and 3.

The basis for the quantity of iodine fed to the samples in the laboratory was that it closely represents the quantity that might be present in a major accident situation and, second, it is similar to the amount of iodine to be used for the in-place test.

TABLE I

N-REACTOR ACTIVATED CHARCOAL SAMPLE TEST RESULTS, MAY, 1969

Cell	Date Sampled	Ambient Test Efficiency	100°C, 100% RH Test Efficiency
A	5/15/69	99.9%	98.8%
B	5/15/69	99.9%	98.8%
C	5/15/69	94.6%	81.3%
D	5/15/69	99.9%	99.9%

During the week of May 15, 1969, the filter cells at N-Reactor were in-place tested. Since the reactor was in an outage condition, the air temperatures and humidity were 28°C and 50% RH. Flow rate per cell was at 80,000 SCFM. Table II indicates the results of the in-place test performed.

TABLE II
IN-PLACE TEST RESULTS N-REACTOR WEEK OF MAY 15, 1969

Cell	In-Place Ambient Test Result	Ambient Sample Test Table I	Percent Leak
A	92.5%	99.9%	7.4%
B	92.5%	99.9%	7.4%
C	72.0%	94.6%	22.6%
D	98.8%	99.9%	1.1%

The in-place tests conducted and previously described in other documents(2,3) utilized 25 grams of molecular iodine, generated over a 30-minute period for each cell tested. Each filter cell contains approximately 4,000 pounds of activated charcoal.

As can be noted in Table II, the in-place test efficiency numbers are compared to the ambient sample tests of the laboratory. This can be done since flow rates, temperatures and all other conditions are held as close to the in-place test conditions as possible. The result of the comparison is the percent leak value which, with rare exception to be discussed later, is due principally to mechanical degradation as voids in the activated charcoal filter beds, gasket bypass and filter frame seal failure.

An interesting projection of efficiency can be made, exhibited by Table III, if it is assumed that the percent leak attributed to the various causes stays constant and the system is subjected to the condition of 100°C and 100% RH (steam). By subtracting the leak value of Table II from the laboratory charcoal results of 100°C, 100% RH of Table I, the extrapolated cell efficiencies under accident conditions are observed in Table III.

TABLE III
EXTRAPOLATED EFFICIENCIES IF 100°C, 100% RH CONDITIONS WERE TO PREVAIL, WITH AMBIENT LEAK VALUE

Cell	High Temperature Test Result Table I	Leak Value Table II, Precent	Extrapolated Efficiency
A	98.8%	7.4%	91.4%
B	98.8%	7.4%	91.4%
C	81.3%	22.6%	59.7%
D	99.9%	1.1%	98.8%

C. Discussion of Initial Test Results and Action Taken

As can be expected, the Zone I sister cells, A and B, looked to be very similar in test results. An inspection of the two cells utilizing floodlights on one side and inspectors on the other was begun immediately. It was noted that the individual N-Reactor activated charcoal filter units or adsorber canisters measured 22 x 22 inches squre and that to position and seat them properly in the frame, 3/8-inch pads were welded to the bottom of each canister case. This was necessary since the frames were built to accommodate 24 x 24 inch square units and had the smaller version installed. The sum total effect of this installation situation means that even when installed properly, only 1/4-inch of filter unit face gasket was available to seal the units against the filter frame. Floodlight inspection showed many canisters to be mispositioned due mainly to loose hold-down devices that had evidently loosened with air flow vibration. All units were repositioned and tightened. Charcoal void areas were minimal and frame seals were found to be sound.

The high efficiency of D-cell can be attributed to the fact that it is a standby Zone I backup cell and used only very sparingly. It, therefore, did not see the charcoal poisoning effects nor experience the wear attributed to the air-flow vibration of A and B-cells. A leaking upstream frame seal was noted and repaired and could have been responsible for the 1.1% leak value.

An investigation into the C-cell low efficiency exhibited all the problems seen in Cells A and B. In addition, it was noted that the upstream side of the cell was covered with a rather heavy concentration of oil. The oil covering all walls, the ceiling, being thick on the floor and saturating the particulate filters (HEPA) obviously had an effect. Further investigation showed that a leaking and eventually a broken hydraulic line associated with the upstream cell confinement gate was the fault for the condition observed. The cell was ordered scrubbed and steam cleaned and all particulate units (HEPA) were replaced.

In reviewing data associated with the impregnated activated charcoal backup beds both in the charcoal sample test facility and in the in-place test samplers, it was obvious that the charcoal was poisoned. High concentration of iodine was observed in the backup sampler beds indicating the iodine had indeed changed form. The differences in numbers 94.6 percent for the test facility and 72.0 percent for the in-place test can be attributed to the fact that in performance of the in-place test the iodine had much more exposure to oily surfaces and converted to a higher degree, while the charcoal sample test facility number shows only the degree of charcoal poisoning due to pollutant uptake by the charcoal itself.

As previously described in Reference 2, the samplers designed for in-place testing when used correctly are capable of separating elemental molecular iodines from its organic forms to a relatively high degree. Elemental iodine in the amount of 99.25 percent is usually trapped on the charcoal impregnate filter papers and silver membrane and only 0.75 percent passed on to the first backup bed section. This was the first in-place cell test indicating other difficulty besides that of mechanical degradation.

Since no iodine removal credit is claimed for the Zone II filter cell, it was decided only to reposition and clean the C-cell as well as possible. Also, delivery of new replacement stainless steel activated charcoal filter units(5) were expected to arrive shortly and would allow replacement in the near future.

D. Subsequent Testing Results

Table IV is a listing of all subsequent activated charcoal tests performed in the laboratory. Special note should be made of the table footnotes which will be discussed in greater depth in the next section.

TABLE IV

FOLLOW-UP ACTIVATED CHARCOAL SAMPLE TESTS N-REACTOR

Cell	Date Sampled	Ambient Test Efficiency	100°C, 100% RH Test Efficiency
*(a) A	11/7/69	98.8%	92.3%
B	1/4/70	99.1%	91.7%
*(a) A	1/7/70	99.9%	99.9%
A	1/30/70	99.9%	99.9%
B	1/30/70	99.9%	99.9%
C	1/30/70	99.9%	99.9%
*(b) D	3/20/70	99.9%	98.1%

*(a) Upon checking the quarterly sample of 11/7/69, the cell was isolated and D-cell, the standby, was placed on the line leaving Zone I with B and D cells operational.

The filter units from A-cell were removed and eighty 24 x 24 inch units removed from the deactivated reactor facilities were repacked with a North American Carbon Charcoal, G-602.(4)

By mid-January, installation was complete and B-cell was isolated leaving A and D cells on the line.

Upon repacking A-cell, it was returned to service and a new in-place test was performed on the Zone I charcoal confinement filter units. The results of this test are reflected in Table V.

TABLE V
N-REACTOR IN-PLACE TEST RESULTS CONDUCTED ON JANUARY 23, 1970

Cell	In-Place Ambient Test Result	Ambient Sample Test Table IV	Percent Leak Value
A	99.7%	99.9%	0.2%
B	97.9%	99.1%	1.2%

From looking at the in-place test result of B-cell, Table V, it was concluded that the tightening and repositioning of the units previously discussed had definitely improved the percent leak value situation. Using the new leak values and sample test results of Tables IV and V respectively, a new extrapolated efficiency value was calculated as seen in Table VI.

TABLE VI
EXTRAPOLATED EFFICIENCIES IF 100°C, 100 PERCENT R.H. CONDITIONS WERE TO PREVAIL, WITH AMBIENT LEAK VALUES, 1/23/70

Cell	High Temperature Test Result Table IV	Leak Value Table V, Percent	Extrapolated Efficiency
A	99.9%	0.2%	99.7%
B	91.7%	1.2%	90.5%

Note: The extrapolated efficiency (accident condition) averages 95.1 percent for the two cells.

In substantiating the poor condition of the B-cell charcoal filter units, it was isolated and the D-cell once more placed in service with the A-cell to handle the Zone I exhaust. In mid-February of 1970, the new stainless steel activated charcoal filter units (5) on order for over a year began to arrive, B-cell was the first cell to receive the new units and together with D-cell was placed into service in Zone I with A-cell in standby. At this time, new units were also installed in C-cell, Zone II. Table VII indicates the condition prevailing on March 15, 1970 and includes the extrapolated 100°C, 100 percent R.H. efficiency.

TABLE VII
N-REACTOR IN-PLACE TEST RESULTS AS OF MARCH 15, 1970

Cell	In-Place Ambient Test Results	Ambient Sample Test Table IV	Percent Leak Value	100°C., 100% RH Sample Test Table IV	100°C, 100% RH Extrapolated Efficiency
B	99.6%	99.9%	0.3%	99.9%	99.6%
D	99.7%	99.9%	0.2%	98.1%	97.9%
C	99.9%	99.9%	0.0%	99.9%	99.9%

E. Discussion of Subsequent Test Results

As seen in Table IV late in the year of 1969 and early 1970, the charcoal filter system was seen to degradate badly. Unlike the initial conditions previously discussed, the situation was one of charcoal poisoning rather than mechanical deficiency. This condition can only be attributed to a rather high leak rate from the reactor cooling system into the confinement filter system. Temperatures during operation were noted to hover at about 160°F with the air being in a 100 percent R.H. or saturated steam condition.

As noted in footnote (a) of Table V, the charcoal efficiency problem was recognized and 8,000 pounds of North American, G-602 Activated Coconut Shell Charcoal was ordered. Because of the difficulty of proper seating of the 22 x 22 inch N-Reactor charcoal canister units and because of the highly corroded state of the canisters, the relatively good looking 24 x 24 inch canisters from the deactivated reactor areas were scavenged, repacked, and installed in A-cell, an operation which had been performed previously for the K production reactors.(4)

With the arrival of the new stainless steel canisters as exhibited in Figure XI, B and C cells were completely replaced. D-cell, although degradating now due to use in the system because of the conditions in either A or B cell over the past months, was not replaced since the efficiency values were considered within operating specifications.

Before use of the newly shipped canisters and charcoal for the repacking of A-cell, a most thorough seriea of iodine loading curves were obtained for each charcoal lot number. The composite results of these tests conducted at ambient and 100°C, 100 percent R.H. are shown in curve form on Figure XII. The charcoal was tested and loaded in independent test steps with concentrations ranging from about 1 ug of I_2 per gram of charcoal up to 1 mg of I_2 per gram of charcoal. Rather flat curves at 99.99 percent retention were seen in all cases.

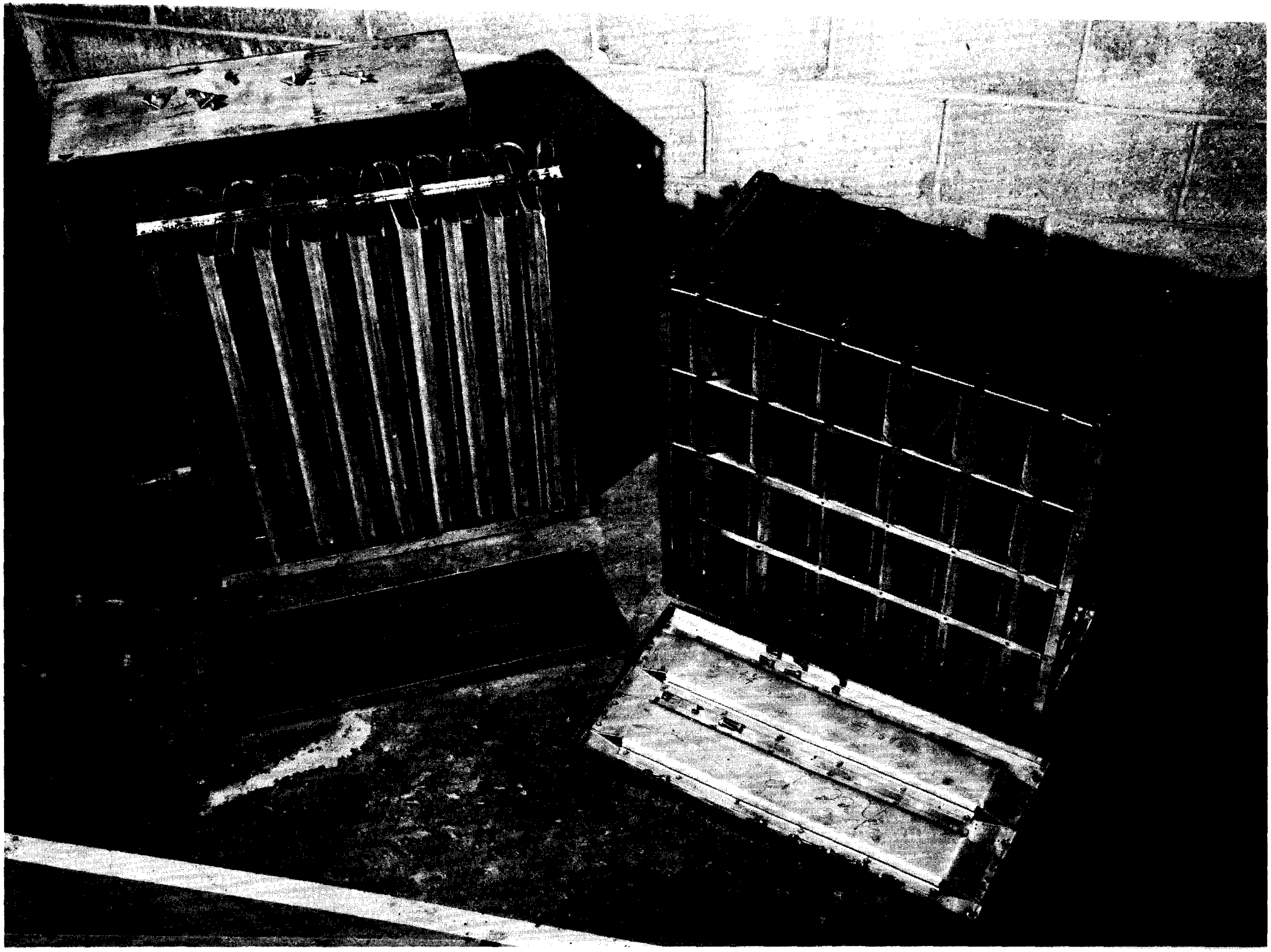
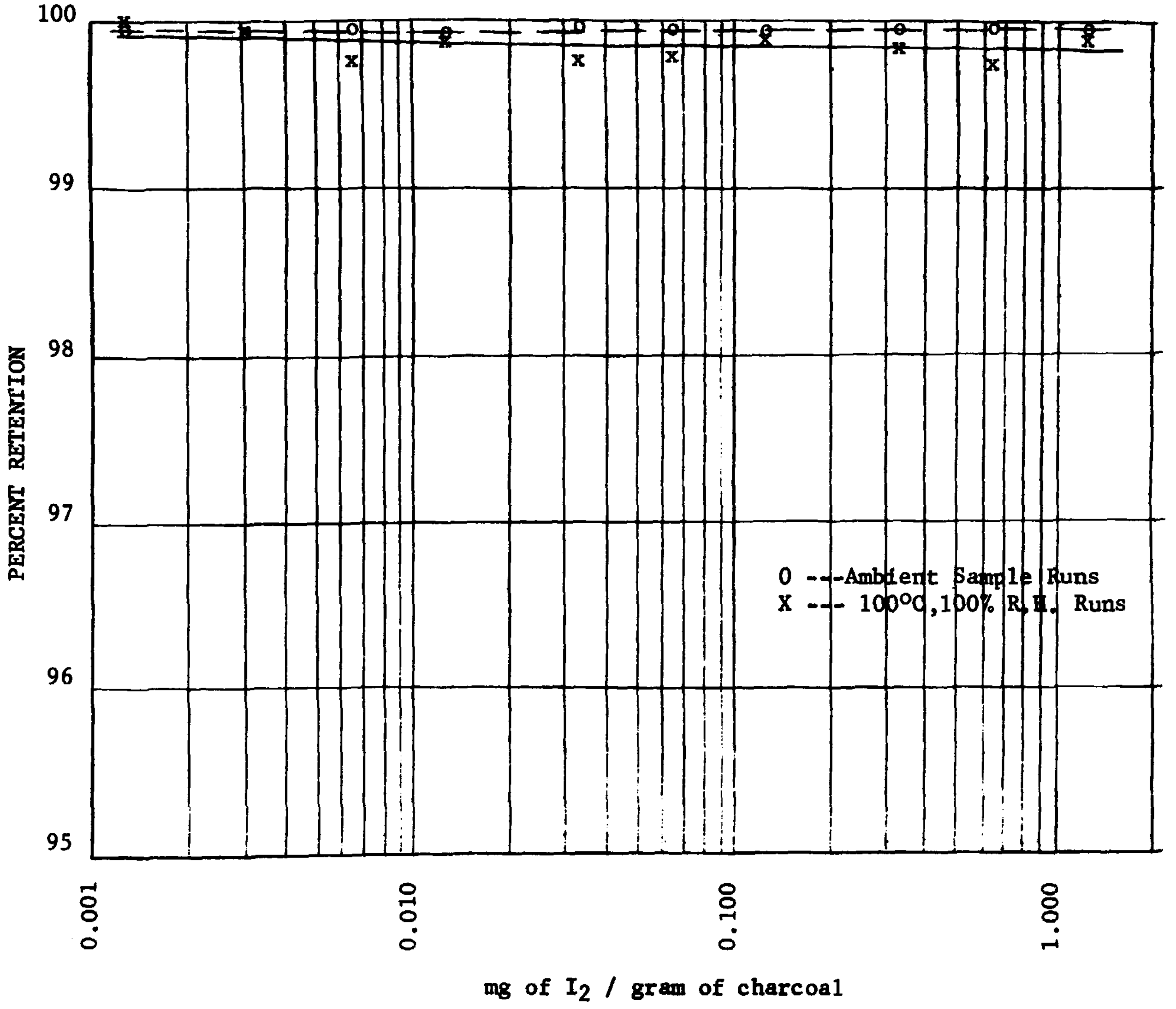


Figure XI Old single pass charcoal canister vs the new stainless steel

FIGURE XII

Iodine loading curves for NACAR G-602 activated coconut shell charcoal installed at the N and KE reactors in March of 1970



All new charcoal adsorbers of filter unit canisters were freon tested by the vendor before shipment to the Hanford installation and spot tested by Douglas United Nuclear, Inc. Figure XIII depicts the in-house freon test facility. No rejections were found and all units tested indicated an efficiency of 99.99 percent +. At least two canisters per pallet were tested or about 20 percent of the total shipment.

From the unloading and testing area, the units were carefully loaded into their respective frames for installation into the reactor 117 Filter Buildings. Figure XIV shows one of the frames in the process of being loaded. All old hold-down, cam-lock type of clamps were discarded and a new stainless steel spring-loaded bolt type of clamp was provided for a more positive clamping arrangement. A rather pictorial display of how the frames are handled, transported and installed can be found in Reference 6.

SUMMARY

At the March 1970 testing date, all systems were functioning properly and were within specified limits even when extrapolated to the 100°C, 100 percent R.H. condition. The newly installed, permanent sampling systems greatly expedited the testing procedures.

The test method of utilizing iodine with a tracer although not performed under reactor operating conditions is considered quite accurate in describing the overall general condition of the systems tested.

Iodine generation as close to the graphite stack as possible and therefore as far upstream as practical, the sampling technique used, and the laboratory comparison testing of samples have provided information on system plateout and cleanliness of ductwork, fan blades, duct turning vanes, etc. Average tests have indicated plateout to be less than ten percent for the quantity of iodine fed the systems in any one test. Normally, the systems have been quite clean and free of pollutants as hydrocarbons that may be the cause of conversion of iodine to other more difficult forms. The exception was that observed and discussed earlier where a hydraulic line break caused an iodine conversion problem in the C-cell of Zone II.

The comparison of laboratory sample tests to in-place tests has allowed system analysis into the causes of poor efficiencies and assisted to a great extent in making judgments on the extent of mechanical degradation and degree of charcoal poisoning present.

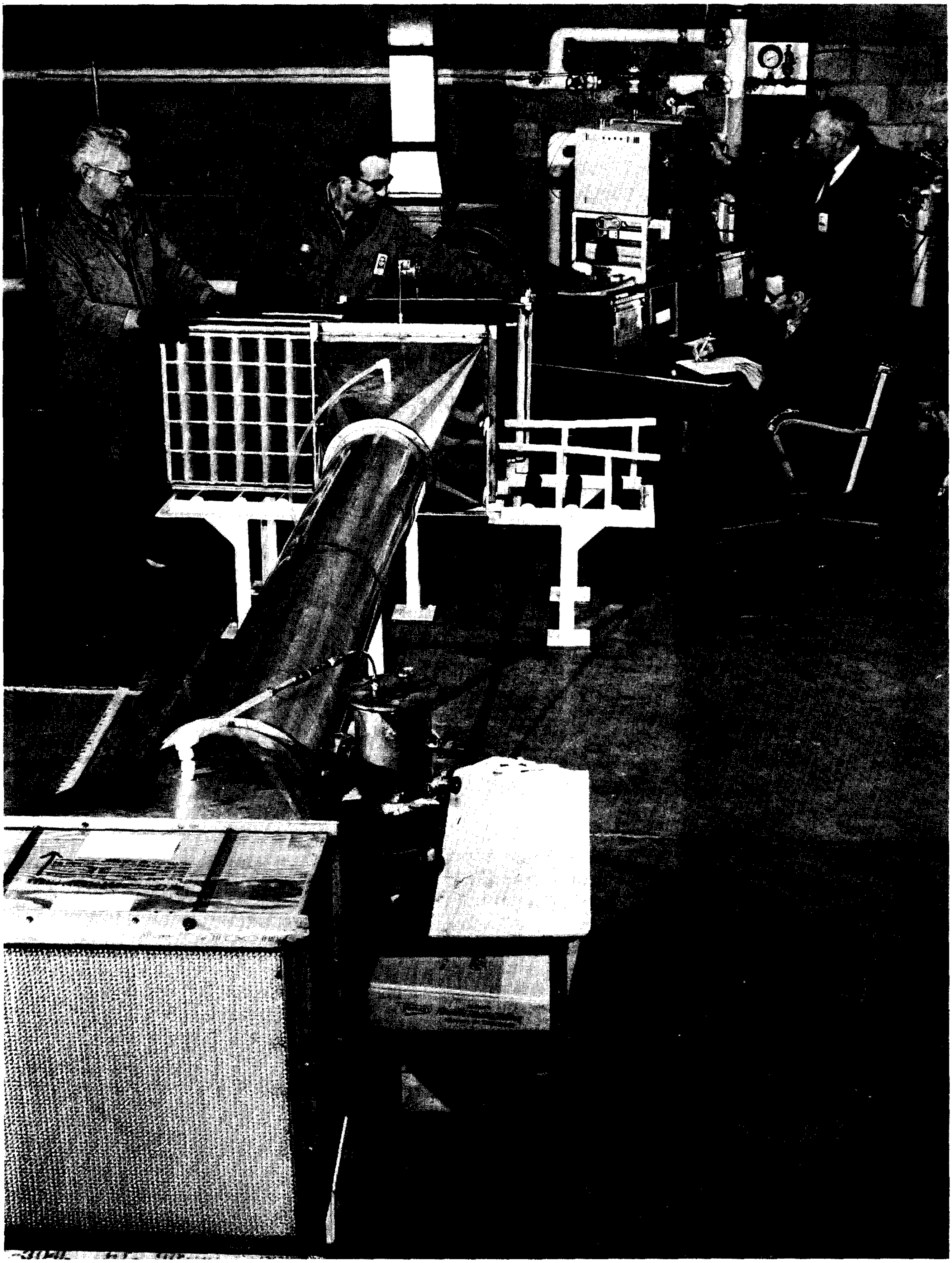


Figure XIII DUN Freon Test Facility

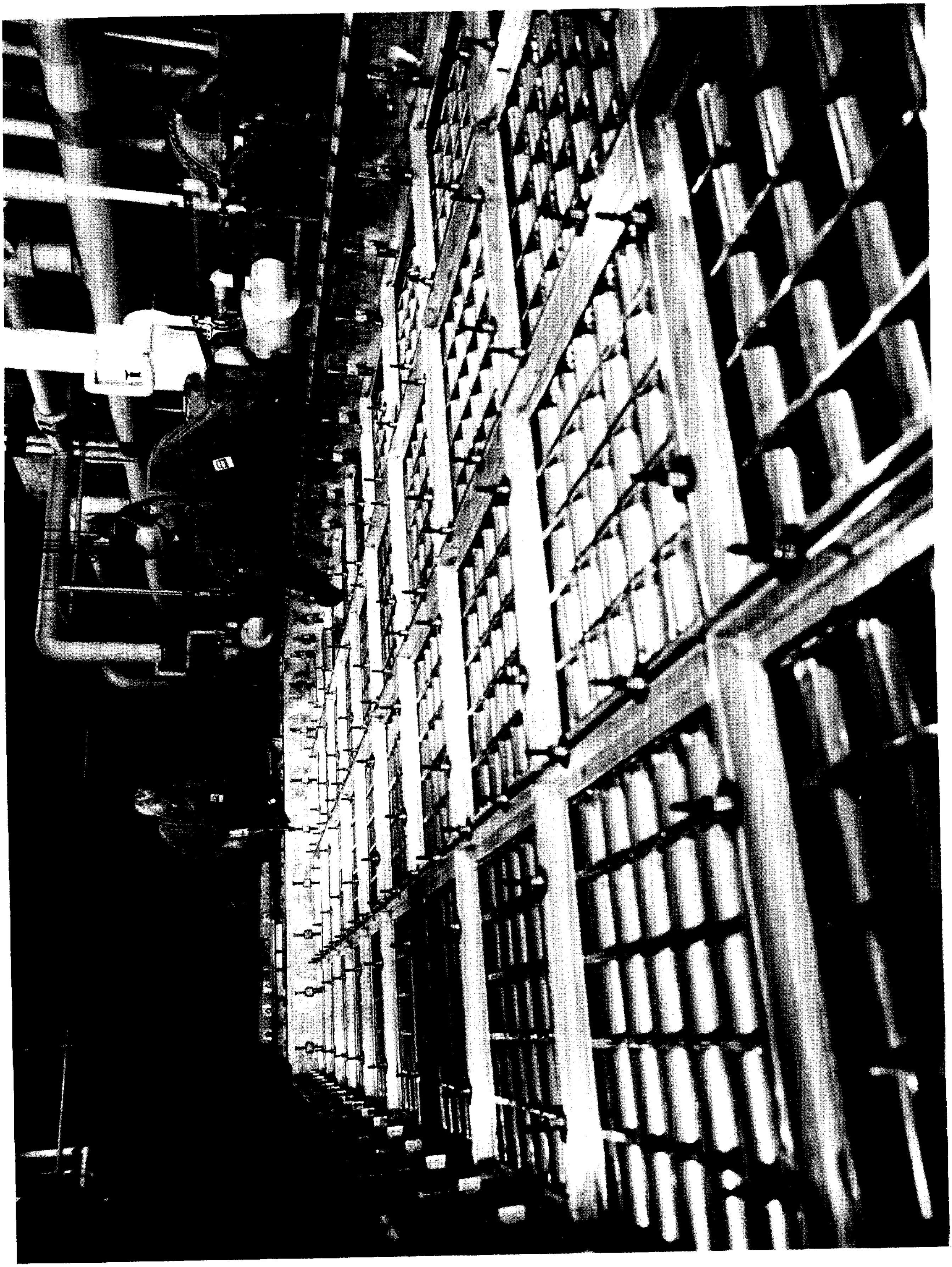


Figure XIV Typical Filter frame being loaded for N Reactor

Laboratory sample testing at high temperature and with steam has enabled the investigators to make educated guesstimates as to the possible performance of the system under the accident condition and has given insight into when charcoal replacement should begin to be considered.

Other test methods, such as freon, would require that the moisture content per gram of charcoal be reduced to 20 percent before accurate results can be obtained. Even then, the system efficiency must be at least 99 percent or the test will simply indicate a leaking system. Individual charcoal tests would still be necessary to determine the reason for the leakage. Should these tests affirm the integrity of the charcoal, the true magnitude of the leak would still be unknown using the freon test method.

The N-Reactor confinement system is a large, underground, moisture-laden system. Substantial engineering problems would be encountered if testing required even small operational changes. Efficiency for the N-Reactor charcoal filter system is currently set at a minimum of 95 percent and, therefore, does allow some fluctuation. Douglas United Nuclear's practice at the current time is to replace charcoal adsorber units when the 95 percent removal value for iodine has been reached for the extrapolated high-temperature, steam condition.

Currently, enough spare charcoal filter adsorbing units are on hand for a complete changeout of all operating reactors. In addition, 8,000 pounds of activated, high temperature, coconut shell charcoal is available for one additional reactor confinement system.

Present reactor operation dictates that all filter cells be tested on a semi-annual rather than an annual basis and watched more closely than normal. This is being done as can be noted from the test frequency. Current operation indicates that the activated charcoal system will be ready for replacement in about three year's time.

ACKNOWLEDGMENT

The authors wish to thank all those individuals who from time to time over the past three years have contributed their time, effort and ideas to this program. In particular, we wish to express our graditude to Mr. D.L. Hirschel who has always unselfishly devoted his utmost to this program and without whom this document and the ones preceding might never have been written.

REFERENCES

1. BNWL-SA-2458, Iodine Collection Efficiency of Activated Charcoal From Hanford Reactor Confinement Systems: Methyl Iodide Retention by Activated Charcoal, J.D. Ludwick, October, 1969.

2. DUN-SA-105, In-Place Testing of the Hanford Reactor Charcoal Confinement Filter Systems Using Iodine Tagged with Iodine-131 Tracer, J.E. Mecca and J.D. Ludwick, June, 1969.

3. DUN-5870, In-Place Test Procedure for Confinement Charcoal Filters, D.L. Hirschel, September, 1969.

4. DUN-SA-116, Activated Charcoal Filter History of the Hanford Single-Pass Production Reactors From March 1968 to the Present Time, J.E. Mecca, October, 1969.

5. HWS-8730, Douglas United Nuclear, Inc., Specifications for Confinement System Charcoal Filters, J.E. Mecca and E.L. Etheridge, February, 1969.

6. ORNL-NSIC-65, Design, Construction, and Testing of High-Efficiency Air Filtration Systems for Nuclear Application, C.A. Burchsted and A.B. Fuller, January, 1970.

DISCUSSION

WILHELM: Did I understand you right that you introduced roughly 50 millicuries of iodine?

MECCA: For a particular test run we tag about 50 grams of iodine with 50 millicuries.

WILHELM: By using 50 millicuries of iodine in that equipment you showed to us for in-place filter testing don't you get problems without any shielding or anything?

MECCA: No, not really. Have never had any real problem.

WILHELM: Well, did you measure the dose rate here on the place where you had the glass equipment?

MECCA: Oh, yes. At the moment, we are going to transfer the Iodine-131, which is delivered in a lead cask, to the generator our own health physics and radiation monitors are available. There is a period of time when the sodium iodide spike must be loaded into the proper separatory flask, and this is done under the auspices of radiation monitoring. Either myself or Dr. Ludwick would perform the transfer. The spiked sodium iodide is very quickly run into the generator with an automatic pipette, and the whole solution mixed. I also mentioned that we have a necked-down separatory flask section for the sodium nitrite. The reason for this type of separatory is that we don't want to pour the nitrite solution directly into the generator. If you do solid iodine will form which you can't get rid of easily. The reason for the necked-down separatory section is to allow the sodium nitrite to drip into the generator at a predetermined rate and so that we could remove ourselves from the generator location. I hope that answers your question. Once we get the generator functioning we remove ourselves. We are not even near the generator anymore.

WILHELM: But, it is right that you don't have any shielding then?

MECCA: No.

WILHELM: Do you have some numbers for the dose rates?

LUDWICK: First of all we are dealing with something closer to 30 millicuries because we order in terms of 50. Actually when the transfer of iodine spike is made the dose to your hand is 0.5 R for approximately 5 seconds. Once it gets into the flask the surface dose of the flask is 100 mr. And as you walk about 5 feet away you are down to about 5 mr. This is no problem at all. We constantly check temperatures, which require moving very close to the flask. You increase your dose from 5 mr while you are standing around the room to something like 50 mr as you take a look at it just momentarily.

WILHELM: You don't expect some break in your glassware on your equipment?

LUDWICK: No, however, if there is a break, all the air flow is in the direction of ducts and you simply clear the area.

WILHELM: Well, I ask you because we have problems. We perform a test like this and we have our iodine in a U-tube which is in a steel container which itself is shielded with lead. But the U-tube for testing with elemental iodine is made of glass. And we have lots of trouble to convince the health physics people that we can work that way with equipment like that. Finally, I wouldn't do without that because I wouldn't be sure to have no contamination in the air.

LUDWICK: Excuse me, contamination of what?

WILHELM: Of the air. If we open our protection iodine container we will get some iodine in the air. It's mostly a question of how good you can measure the activity release to the air, whether you see some of the iodine or you don't.

EFFECT OF GAMMA RADIATION ON ADSORPTION OF IODINE AND METHYL IODIDE ON ACTIVATED CARBON*

by

L. R. Jones

Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, South Carolina 29801

ABSTRACT

The effect of gamma radiation on the adsorption of iodine and methyl iodide on activated carbon exposed to flowing mixtures of steam and air is being measured at the Savannah River Laboratory. The steam-air-iodine mixtures are exposed to a radiation field of ∿1.7 x 10^7 rads/hr while flowing through a bed of test carbon. Test conditions simulate a postulated loss-of-coolant accident where adsorption of radioiodine on carbon beds would produce an intense gamma radiation field.

This paper describes the test facilities and results of tests that are under way to define the effects on carbon adsorption efficiency of variables such as face velocity, relative humidity, temperature, type of carbon, carbon service age, iodine and methyl iodide concentration in the steam-air mixture, and loading on the carbon.

INTRODUCTION

Radioactive iodine must be confined following an unlikely reactor accident because of the potential hazard to the surroundings if released to the atmosphere. Under accident conditions radioiodine may exist in several forms, primarily elemental iodine and hydrogen iodide. A small fraction of the radioiodine may also exist as methyl iodide.

Elemental iodine and hydrogen iodide are very reactive and are adsorbed and retaine from air by activated carbon, under a wide variety of adverse conditions, with efficienci >99.9%; however, methyl iodide is not as efficiently adsorbed.[1] Atkins and Eggleton[2] identified methyl iodide as the most penetrating form of iodine that could be released during a reactor accident. Collins, Taylor, and Taylor[3] found that retention of methyl iodide by activated carbon was especially poor when the relative humidity of the gas carrying the methyl iodide was >80%.

---

* The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

Under reactor accident conditions, methyl iodide would be exposed to an intense gamma radiation field generated by fission products adsorbed on the carbon beds. Decomposition of methyl iodide by radiolysis was investigated by Tang and Castleman.[4,5] Mixtures of methyl iodide and dry air were placed in sealed bulbs and irradiated under static conditions. Additional tests were also run with mixtures of methyl iodide and moist air. Decomposition was dependent on total radiation dose and independent of dose rate. Results from tests with methyl iodide and moist air showed that water vapor inhibits the decomposition of methyl iodide by radiolysis.

Results of preliminary tests, in which only relative humidity and face velocity were varied, were reported at the 10th AEC Air Cleaning Conference.[6] This report presents results of continued tests to determine the effects of: face velocity, relative humidity, methyl iodide loading on the carbon, and methyl iodide concentration.

The effect of gamma radiation on the adsorption of iodine and methyl iodide on activated carbon is being measured at the Savannah River Laboratory (SRL) as part of a continuing program,[7] in support of the reactor confinement facilities at the Savannah River Plant (SRP).

APPARATUS AND TECHNIQUES

The methyl iodide radiolysis apparatus is shown in Figure 1. A mixture of ambient air, elemental iodine, methyl iodide tagged with ^{131}I, and steam was passed through a test bed of carbon positioned in the gamma field and then through three backup carbon beds. Each backup carbon bed was one inch thick and contained impregnated carbon especially treated to retain methyl iodide.

A gamma detector was mounted three inches from the backup beds and connected to a scaler. Methyl iodide penetration of the test bed as a function of time during each test was measured by taking a one-minute count every two minutes during the methyl iodide loading and every 10 minutes during the remainder of the test.

The gas stream was prepared by mixing ambient air at ∿25°C with saturated steam at 100°C. A volumetric ratio of air to steam of 2.28:1 produces a slightly supersaturated steam-air mixture temperature of 65°C.[8] The steam-air-iodine mixture flowed to and from the test carbon bed through tubing insulated with a jacket through which water flowed at 70°C. Dry air at 100°C was added to the steam-air-iodine mixture immediately upstream of the backup carbon beds to reduce relative humidity to <10%. Elemental iodine was injected into the gas stream by passing ambient air at constant velocity through a glass frit containing solid iodine.

Liquid methyl iodide tagged with ^{131}I was placed in a short length of tubing valved off at both ends. After warming the liquid to room temperature, the methyl iodide vapors were flushed into a large reservoir tank which was then pressurized to 15 in. of mercury with compressed air. Initial flow of methyl iodide-air mixture out of the reservoir tank was set so that the pressure in the reservoir tank was reduced to atmospheric pressure in 60 minutes. One-third of the original methyl iodide sample was injected into the system in an exponentially decreasing concentration

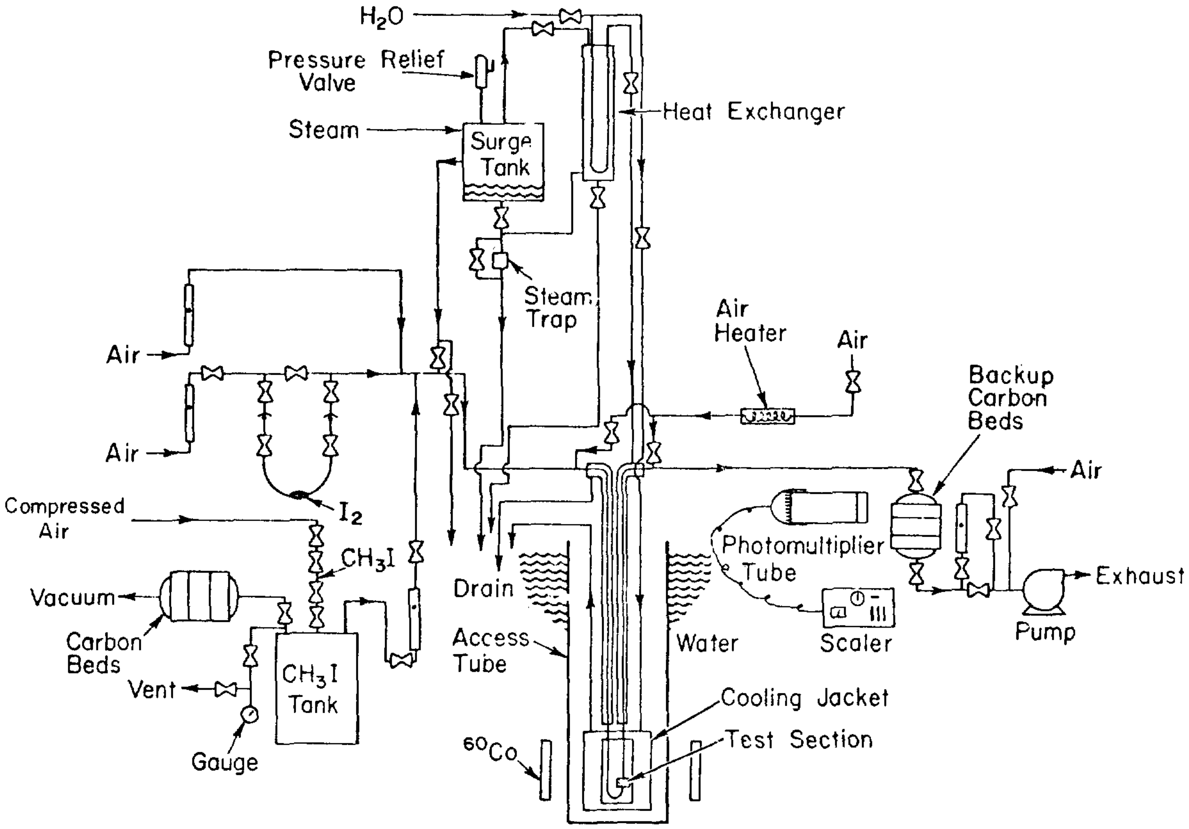


FIG. 1 METHYL IODINE RADIOLYSIS APPARATUS

FIG. 2 ALUMINUM TUBES LEADING TO ^{60}Co SOURCE

assuming that the methyl iodide completely mixed with the air in the tank. The remaining two-thirds of the sample was discarded. Therefore, material balance calculations were based on one-third of the original methyl iodide sample.

*Teflon** tubing was used in the apparatus, and all stainless steel pieces except for the test carbon bed assembly were *Teflon* coated to minimize iodine deposition. The test carbon bed assembly was not coated with *Teflon* because it decomposes in an intense gamma radiation field.

Samples of particulate filter media and other materials used in filter construction were irradiated in the test carbon bed assembly during some tests in the radiation field. Physical properties of these materials before and after irradiation are being determined at the Naval Research Laboratory in Washington, D. C.

The test carbon bed assembly and jacketed tubing were inserted into one of the two six-inch-diameter air-filled aluminum tubes leading to the ^{60}Co source (Figure 2). The source (Figure 3) consists of ∿750,000 curies of ^{60}Co in 44 slugs (22 slugs surrounding the base of each of the two tubes). Shielding is provided by 24 feet of water.

In tests run in the gamma radiation field, the temperature of test carbon bed assembly was controlled by flowing water through a jacket surrounding the assembly to remove heat generated by gamma absorption. In tests run out of the gamma radiation field, the test bed assembly was heated by flowing hot air through the jacket.

Each test ran three hours. The system was preheated with dry air flow at 65°C for 30 minutes. Then the system was pre-equilibrated with steam-air flow at 65°C for 30 minutes. When pre-equilibration was complete, 17% of the air flow was diverted through the elemental iodine source holder to begin elemental iodine sample injection. Five minutes later methyl iodide sample injection was started and continued for 60 minutes. After the 60 minutes of loading, both sample holders and the steam were valved off. Ambient air flow was continued through the system for 60 minutes with the test carbon bed temperature reduced to ∿40°C.

After each test, major parts of the apparatus were disassembled. The test carbon bed, particulate filter support (perforated metal cylinder), particulate filter container, and cooling water jacket are shown in Figure 4. The amount of ^{131}I tracer on each piece was determined by counting in a gamma detector. A computer program converts these counts to mass of CH_3I and calculates penetration of the test carbon bed, material balance, methyl iodide loading on the test carbon bed, and methyl iodide adsorption on other pieces of the apparatus.

---

* Du Pont Trademark

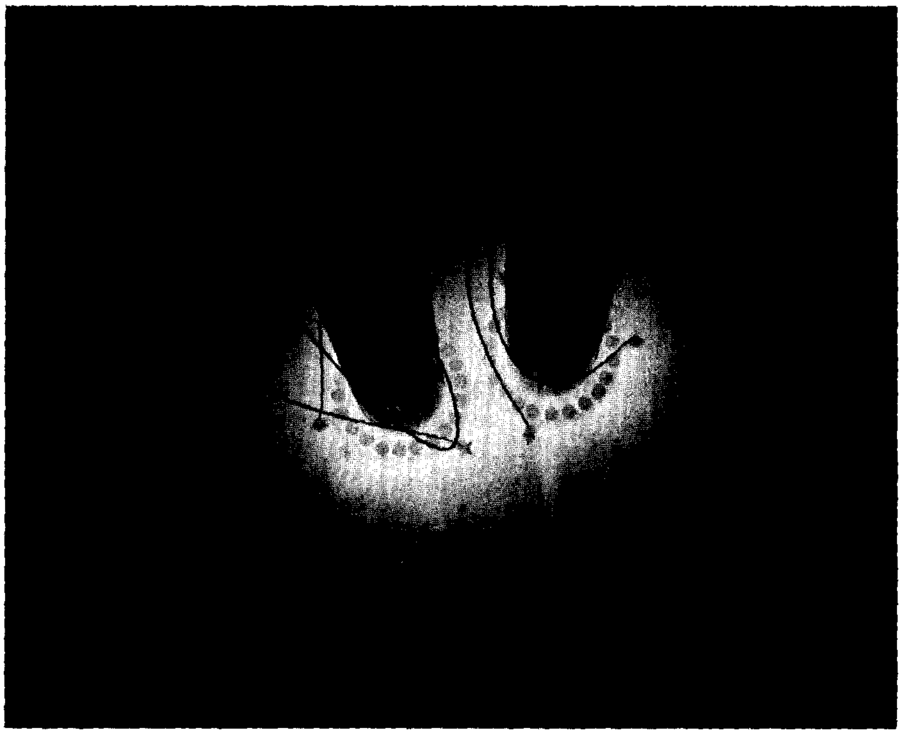


FIG. 3 ^{60}Co SOURCE

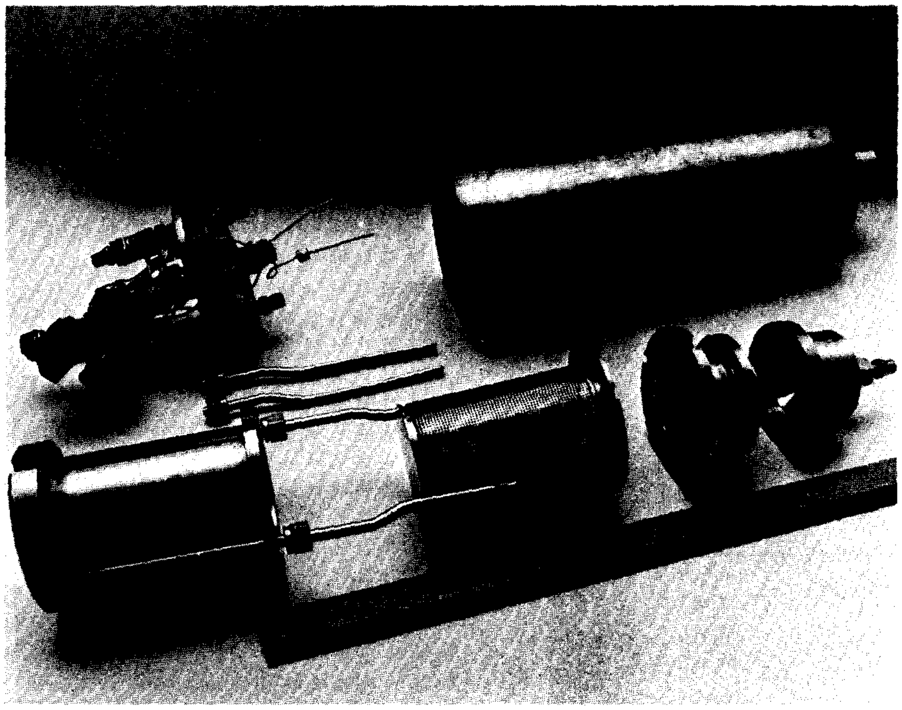


FIG. 4 TEST CARBON BED ASSEMBLY AND WATER COOLING JACKET

Comparison of Previous and Present Test Conditions

Methods used in previous tests for cooling the test bed container while in the gamma field caused relative humidity gradients across the test carbon bed of up to 55%. Data were correlated with average humidity even though the downstream portion of the test bed was at a relative humidity up to 22% higher than average.

The gamma field in the ^{60}Co source used in the preliminary tests was reported as ∿2 x 10^7 rads/hr. More accurate dosemetry has since determined the source field to be ∿1 x 10^7 rads/hr. Methyl iodide loading on the carbon averaged about 0.01 mg/g carbon.

Subsequent tests reported in this paper were run in a new larger ^{60}Co irradiation facility with larger access tubes. A jacket was added to the test carbon bed container, and the apparatus cooled with water by forced convection. Relative humidity gradients across the test bed averaged less than 8%.

The new ^{60}Co source produced a gamma field of ∿1.7 x 10^7 rads/hr inside the test carbon bed container (dosimetry by methods described in reference 9). This dose rate approximates that which would be expected in the air cleaning system of a large modern reactor shortly after a full core meltdown. Methyl iodide loading was increased to an average of 0.10 mg/g carbon because of the difficulty in holding carbon loading constant with the minute sample quantities required to produce carbon loadings near 0.01 mg/g carbon.

RESULTS

Effect of Relative Humidity

Tests were run with and without the gamma field for Type 416 carbon* at constant iodine loading and injection rate. Relative humidity and face velocity were the test variables. Test results are shown in Figure 5. Methyl iodide penetration of the test carbon bed decreased as relative humidity was decreased. Penetration decreased from 19.5% with no radiation field to 9.8% in the radiation field at 55 ft/min face velocity and 27% relative humidity.

Tests at <5% relative humidity at both velocities resulted in penetrations which indicated no effect of the radiation field. More data is needed at 10 to 30% relative humidity to adequately predict penetration as a function of relative humidity at both velocities. Average methyl iodide loading on the carbon was ∿0.10 mg/g carbon. The test carbon was Type 416 unimpregnated carbon.

---

* Product of Barnebey-Cheney Company, Columbus, Ohio.

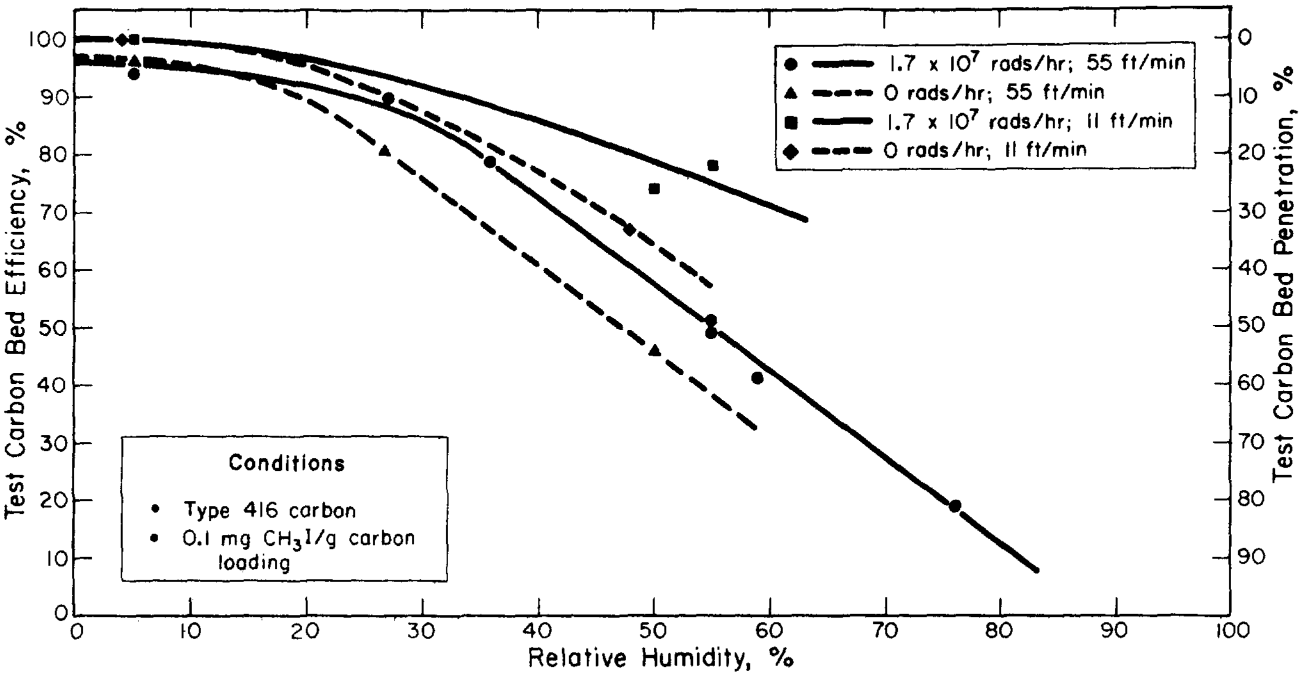


FIG. 5 EFFECT OF RELATIVE HUMIDITY ON EFFICIENCY OF TEST CARBON BED

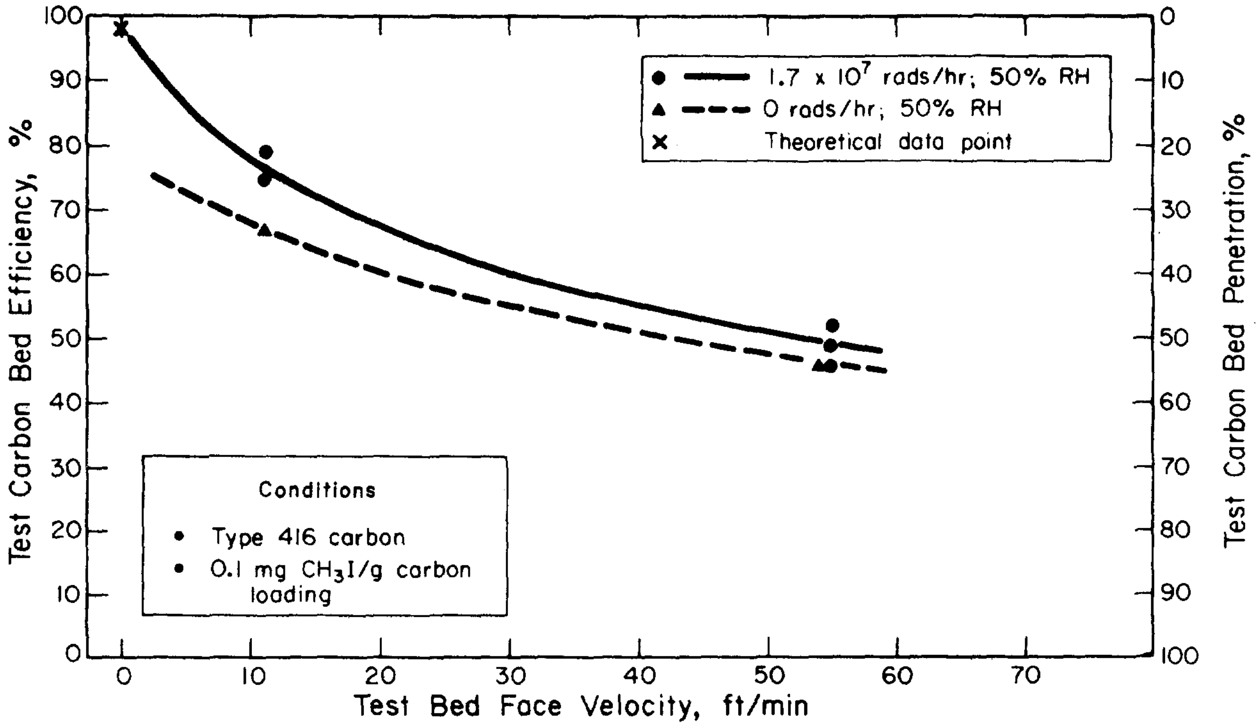


FIG. 6 EFFECT OF FACE VELOCITY ON EFFICIENCY OF TEST CARBON BED

Effect of Face Velocity

Tests were run with and without the gamma field holding carbon type and test conditions constant with face velocity as the test variable. Results are shown in Figure 6. The radiation field reduced penetration by ∿5% at 55 ft/min velocity and by ∿27% at 11 ft/min velocity. The reduction in penetration became larger as face velocity was reduced probably because of increased methyl iodide residence time in the gamma field at the lower velocity.

Based on the assumption that the reduced penetration in the radiation field was the result of radiolytic decomposition of the methyl iodide, a theoretical point was placed at zero velocity. At zero velocity, residence time and radiation dose to the methyl iodide would be infinite. Concentrations of air, steam, elemental iodine, and methyl iodide ($\sim 10^3$ μg/M^3) would strongly favor greater than 99% decomposition of the methyl iodide. Data reported by Tang and Castleman[4,5] indicate that an absorbed dose of less than 10^6 rads would produce greater than 99% decomposition. Thus, a penetration of less than 1% would be expected at zero velocity.

Typical data on penetration versus time during tests at 55 ft/min velocity and at 11 ft/min velocity are shown as the lower curves in Figures 7 and 8, respectively. The upper curves show percent of the methyl iodide sample which has been injected into the system as a function of time during the test. The percent of the total methyl iodide sample adsorbed on the test carbon bed at any time during the test is the difference of the two curves at that time.

Residence time in the radiation field was determined at both velocities by subtracting calculated residence time in tubing carrying the sample to and from the radiation field from the measured delay in arrival of initial penetration at the backup beds. Residence times are shown in Figures 7 and 8.

Effect of Methyl Iodide Loading on Carbon

Tests were run holding carbon type and test conditions constant with methyl iodide loading on the carbon as the test variable. Results are shown in Figure 9. The percentage reduction in penetration caused by the gamma field varied from approximately zero at loadings greater than 0.12 mg of CH_3I/g of carbon to 34% at a loading of 0.02 mg of CH_3I/g. Penetration became smaller with decreasing methyl iodide loading on the carbon in tests in the radiation field and with no radiation field.

Effect of Methyl Iodide Concentration

Tests were run in which the methyl iodide loading time in steam-air was reduced from 60 minutes to 15 and 5 minutes. The methyl iodide concentration in the steam-air mixture was 2.4×10^3 μg/M^3 for loading in 60 minutes, 9.6×10^3 μg/M^3 for loading in 15 minutes, and 28.8×10^3 μg/M^3 for loading in 5 minutes. Loadings were approximately the same in all cases. Results, shown in Figure 10, indicate little sensitivity to methyl iodide concentration over the range investigated.

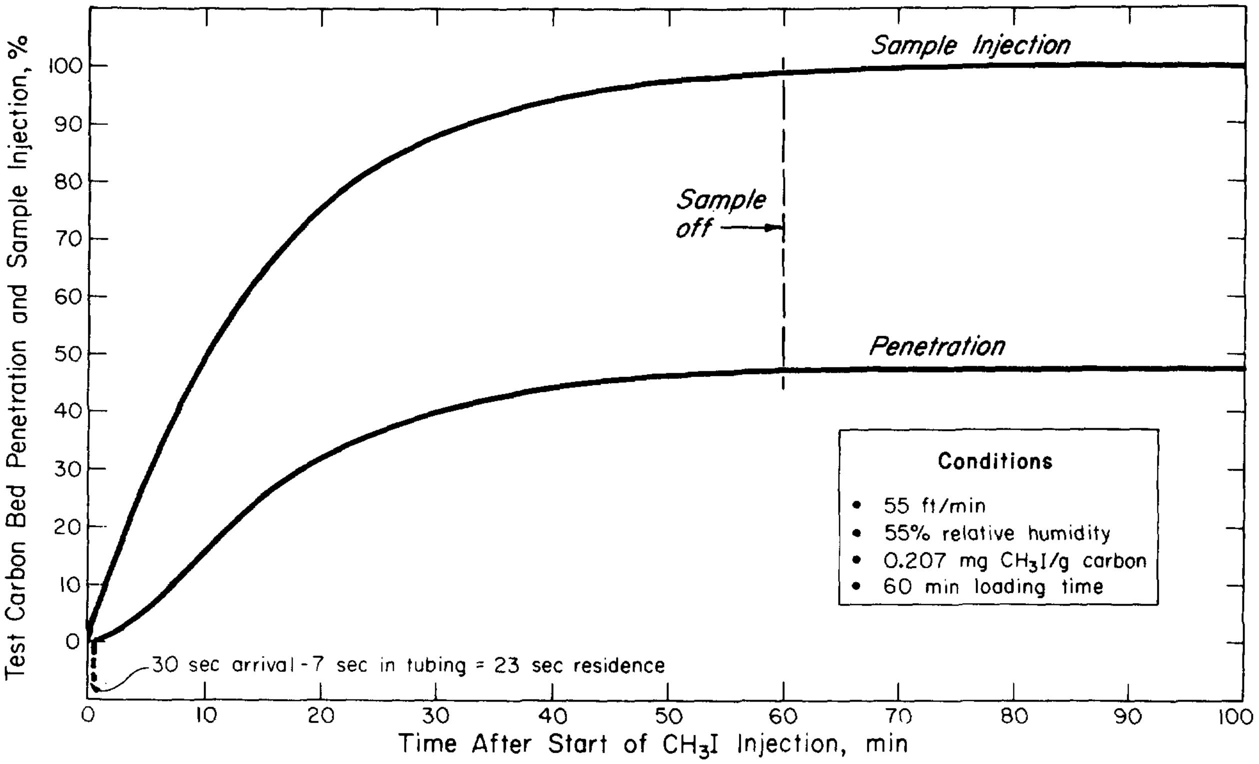


FIG. 7 PENETRATION OF METHYL IODIDE VERSUS TIME (Face Velocity, 55 ft/min)

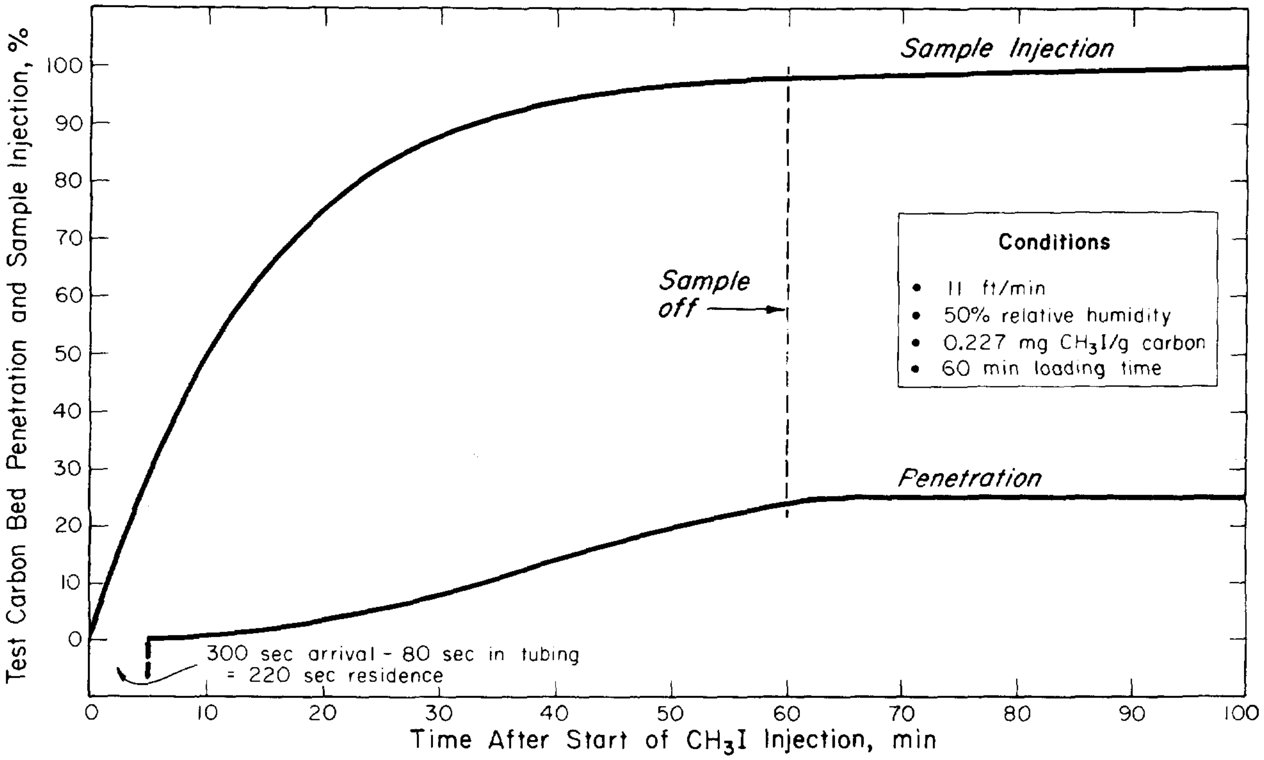


FIG. 8 PENETRATION OF METHYL IODIDE VERSUS TIME (Face Velocity, 11 ft/min)

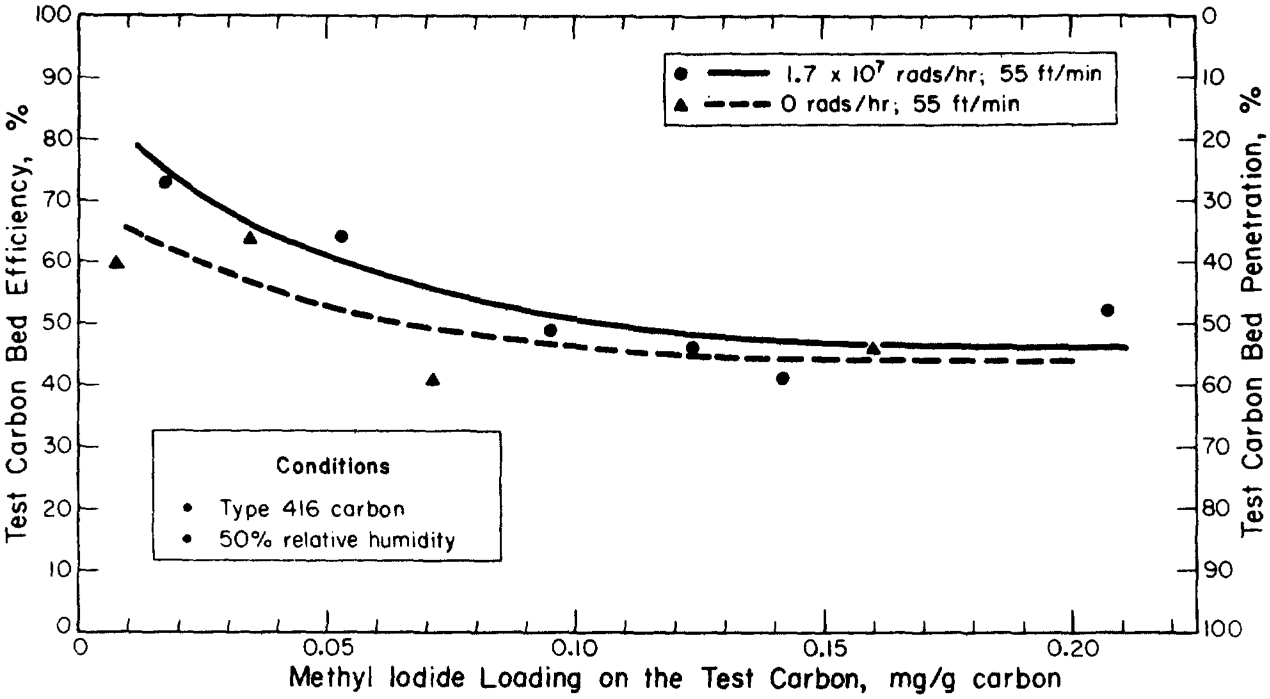


FIG. 9 EFFECT OF METHYL IODIDE LOADING ON CARBON BED EFFICIENCY

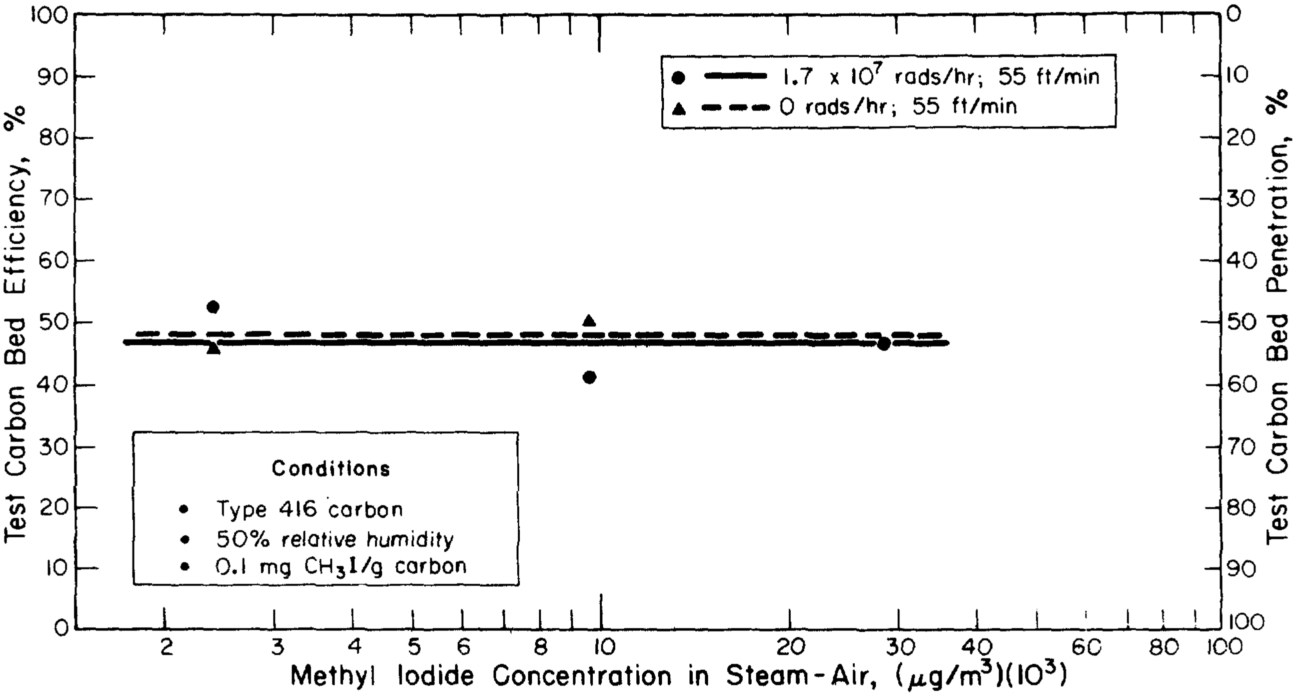


FIG. 10 EFFECT OF METHYL IODIDE CONCENTRATION ON CARBON BED EFFICIENCY

Radiolytic Decomposition of Methyl Iodide

Based on the assumption that radiolytic decomposition of the methyl iodide into non-penetrating forms of iodine was the only factor causing the reduced penetration measured in the gamma field, decomposition was calculated and compared with published data. Tests at 27% relative humidity and 55 ft/min face velocity (23 second residence time, Figure 7) indicate 50% decomposition. Data by Tang and Castleman[4,5] indicate that 50% decomposition should be expected at a residence time of slightly less than 30 seconds in a 1.7×10^7 rad/hr field.

Tests at 11 ft/min velocity and 50% relative humidity (220-second residence time, Figure 8) indicate ∿38% decomposition. Data by Tang and Castleman[4,5] indicate that >99% decomposition should be expected at a residence time greater than 120 seconds.

The carbon may inhibit the radiolytic decomposition of methyl iodide by two mechanisms. The addition of carbon to a gas system containing methyl iodide greatly reduces the mass concentration of methyl iodide and the probability of direct gamma absorption by a methyl iodide molecule. During most of the residence time in the gamma field the methyl iodide must be temporarily adsorbed on the surface of the test carbon. If a methyl iodide molecule is decomposed, the ions formed are not in the free gaseous state where they are likely to collide and react with other ions or molecules; they are in a partially immobilized adsorbed state where they are most likely to recombine because of their proximity. Thus, decomposition is inhibited.

In a discussion of data on radiolysis of methyl iodide adsorbed on silica gel reported by Sagert, Reid, and Robinson,[10] the authors attribute the observed long lifetime of CH_3I^- to a back reaction accelerated by caging effects of narrow pores in the silica gel. The authors postulate that this caging keeps methyl radicals and negative iodide ions close together after decomposition favoring recombination to form CH_3I^-.

Immobilization of methyl iodide molecules by adsorption on the carbon surface must greatly increase at low relative humidities (<10%) as evidenced by very low penetration. Failure of data at <5% relative humidity to indicate any decomposition might be attributed to this reduced freedom of the ions to react with other molecules or ions to form stable non-penetrating species.

PROGRAM

Additional tests on the effects of low relative humidity, velocities less than 11 ft/min, and various concentrations of methyl iodide in steam-air are planned. Tests to determine the effects of lower steam-air mixture temperature and tests on impregnated carbon and carbon with service in a Savannah River reactor confinement system are also planned. Tests will be run with elemental iodine and methane to determine the effect of radiation on formation of methyl iodide.

SUMMARY

Methyl iodide penetration of Type 416 unimpregnated carbon was reduced by up to 50% for mixtures of methyl iodide, elemental iodine, steam, and air at >20% relative humidity flowing through a one-inch-thick test carbon bed and exposed to a gamma radiation field of $\sim 1.7 \times 10^7$ rads/hr. Tests at less than 5% relative humidity showed no effect of the radiation.

The presence of carbon significantly inhibits the radiolytic decomposition of methyl iodide into non-penetrating forms of iodine by reducing the mobility of methyl radicals and iodide ions. The radiation field is most beneficial at high relative humidity where methyl iodide adsorption efficiency is low, and least beneficial at low relative humidity where efficiency is high. Therefore, the radiation field does not significantly extend the effectiveness of carbon for methyl iodide adsorption.

REFERENCES

1. W. S. Durant, R. C. Milham, D. R. Muhlbaier, and A. H. Peters, *Activity Confinement System of the Savannah River Plant Reactors*, USAEC Report DP-1071, Savannah River Laboratory, August 1966.

2. D. H. F. Atkins and A. E. J. Eggleton, *Iodine Compounds Formed on Release of Carrier-Free Iodine-131*, British Report AERE M-1 211, May 1963.

3. D. A. Collins, R. Taylor, and L. R. Taylor, "The Removal of Methyl Iodide from Reactor Effluent Gases," in *International Symposium on Fission Product Release and Transport Under Accident Conditions*, Oak Ridge, Tennessee, USAEC Report CONF - 650407, Vol. 2, pp. 853-868, 1965.

4. I. N. Tang and A. W. Castleman, Jr., "Radiation Induced Decomposition of Methyl Iodide in Air," *Trans. Amer. Nucl. Soc., 11:* 76 (1968).

5. I. N. Tang and A. W. Castleman, Jr., Brookhaven National Laboratory, personal communication, 1968.

6. Proceedings of the Tenth AEC Air Cleaning Conference, New York, New York, August 1968. USAEC Report CONF - 680821.

7. A. G. Evans, *Effect of Service on Retention of Iodine by Activated Carbon, Eleventh AEC Air Cleaning Conference*, Richland, Washington, September 1970.

8. A. H. Peters, *Application of Moisture Separators and Particulate Filters in Reactor Containment*, USAEC Report DP-812, Savannah River Laboratory, 1962.

9. N. W. Holm and K. Sehested, *Advances in Chemistry Series, No. 81*, American Chemical Society, Washington, D. C. 1968, p. 568.

10. N. H. Sagert, R. A. Reid, and R. W. Robinson, *Radiolysis in the Adsorbed State, III. Methyl Iodide Adsorbed on Silica Gel*, AECL No. 3484, Physical Chemistry Branch, Chalk River Nuclear Laboratories, Atomic Energy of Canada Limited, Chalk River, Ontario; *Can. J. Chem., 48:* 17 (1970).

PDW:sce

EFFECT OF SERVICE ON RETENTION OF IODINE BY ACTIVATED CARBON*

A. G. Evans

Savannah River Laboratory
E. I. du Pont de Nemours and Company
Aiken, South Carolina 29801

ABSTRACT

Activated carbon is installed in many reactor confinement systems to remove radioiodine from effluent gases in the unlikely event of a nuclear accident. For on-line confinement systems in which reactor building ventilation air and vent gases continuously pass through carbon beds, iodine retention and effective surface area of the carbon both decrease with increasing service time.

Coconut shell carbon used in the confinement systems at the Savannah River Plant was found to contain increasing amounts of trace gaseous pollutants (CO_2, NO, CO, H_2, and ethylene) with increasing service. The most significant pollutant was NO_2, which was formed in the air around the reactor tank. The NO_2 reacts with the carbon in the confinement system forming CO and NO, which destroy or occupy three active carbon sites for each NO_2 molecule reaching the carbon bed; thus, the iodine removal efficiency of the carbon is decreased.

Used carbons can be partially regenerated by treatment with hot flowing air or vacuum heating, but complete regeneration was not accomplished even at temperatures up to 300°C. New or partially regenerated carbons can be artificially aged by passing NO_2-air mixtures through the carbon beds. Increasing NO_2 concentrations accelerate the aging process.

Tests have been designed to simulate the temperature and humidity conditions calculated to occur in the Savannah River reactor confinement systems in the unlikely event of a reactor accident. These tests show that the carbon performance under accident conditions would become marginal after the carbon has been in service in the confinement system for about four years of normal reactor operation.

INTRODUCTION

Activated carbon is used in some reactor confinement systems to remove radioactive iodine that might be released in the unlikely event of a nuclear accident. At the Savannah River Plant (SRP), about 4-1/2 tons of activated carbon is used in the confinement system of each reactor. The carbon is placed in five compartments located on the roof of the reactor building. Each compartment contains three banks of

---

* The information contained in this article was developed during the source of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

7/23/70

filters in series as shown in Figure 1. The first bank has 20 moisture separators, the second has 32 particulate filters, and the third has 32 activated carbon beds. The moisture separators (*Demisters**) remove about 99% of 1- to 5-μ entrained water particles to prevent water repellent particulate filters from rupturing. The particulate filters remove >99% of all particles of 0.3-μ diameter or larger. The activated carbon beds remove >99.9% of the elemental iodine vapor that might be released from a reactor in the event of a nuclear accident.[1,2]

Because of the reaction kinetics,[3,4] iodine would be expected to be desorbed from carbon at elevated temperatures. Oak Ridge National Laboratory has reported[5] that activated carbons impregnated with elemental iodine were quite stable at 150°C, but at 200°C and higher, significant amounts of iodine (up to 50% in 4 hours) were evolved and swept out of the carbon by flowing air. Above 200°C, the compound between iodine and the carbon began to decompose.

In the unlikely event of a nuclear accident, carbon in the confinement system may become overheated from the decay of adsorbed iodine or from radioactive debris, and some of the adsorbed iodine might be desorbed and cause an unacceptable release of iodine. Normal cool air flow (about 70 ft/min) will remove heat from the carbon beds so rapidly that iodine release would be insignificant. However, at low air flow (<10 ft/min) or elevated air temperature (>100°C), the temperature of the carbon would increase, and excessive amounts of iodine would be released.

The iodine removal and retention efficiencies of activated carbon deteriorate with service in the confinement system. A test program is conducted at the Savannah River Laboratory (SRL) to assure that carbon in the system meets the minimum retention specification of 99.85%. Research programs are also conducted at SRL to develop test procedures, define mechanisms of deterioration of carbon in service, and to evaluate new types of activated carbon for service in the confinement system.[6-10] Results of these research programs are summarized in this paper.

EXPERIMENTAL METHOD

Type 416 activated carbon**, both unused and with up to 4.7 years service in the SRP confinement system, was evaluated. This activated carbon is made from coconut shell and is tailored to confinement systems.[11] Coconut shell carbon has a high adsorption efficiency for iodine (99.99+%), a narrow mesh range (10-14 Tyler size) for dense packing, and hardness (97%) that minimizes dusting during continuous on-line service.

A desorption apparatus (Figure 2) was constructed to measure the sorption and retention of iodine on activated carbon under varying conditions of air temperature, velocity, relative humidity, iodine loading, and carbon service history. Sections of the apparatus through which iodine

---

* Registered trademark of Otto H. York Co. Commercial names are used for identification only, and their use does not necessarily constitute endorsement by the author.

** Product of the Barnebey-Cheney Company, Columbus, Ohio.

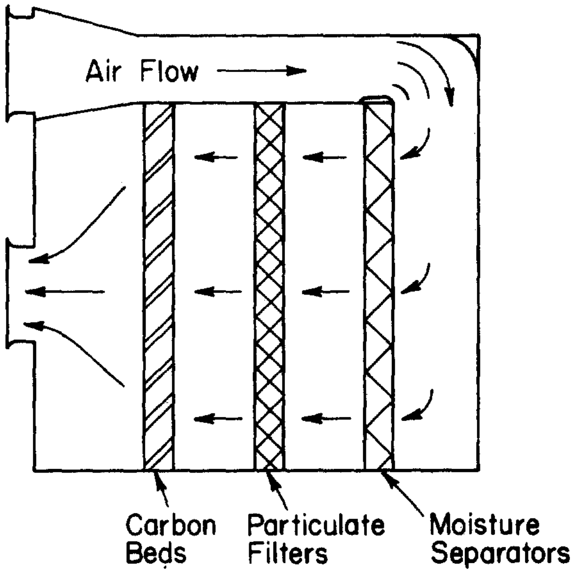


FIG. 1 FILTER COMPARTMENT (ELEVATION CROSS SECTION)

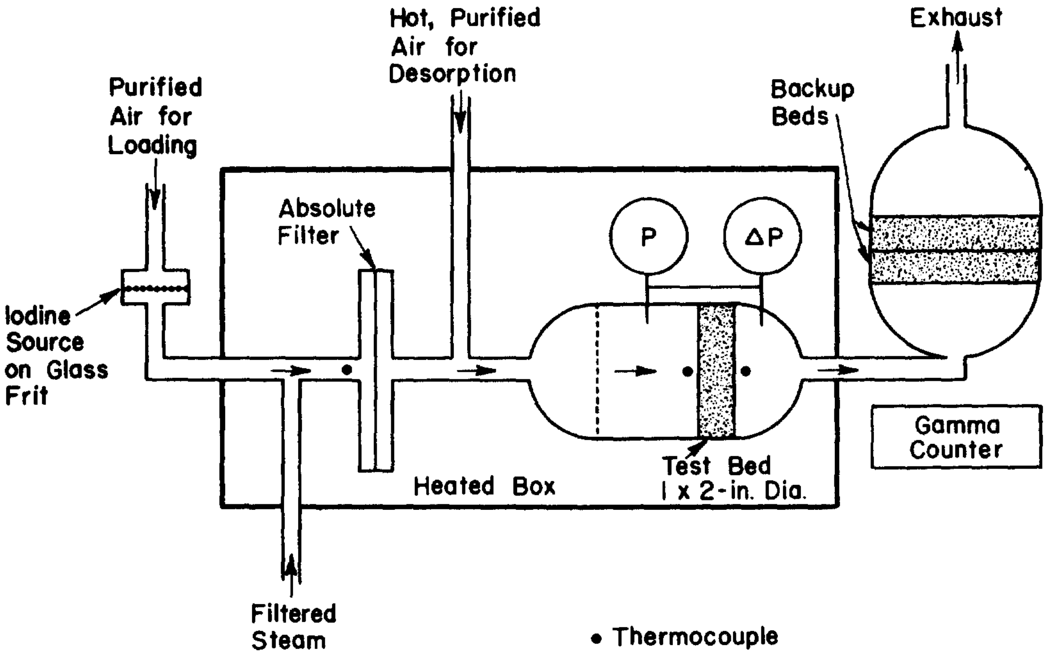


FIG. 2 DESORPTION APPARATUS

pass were built of glass and *Teflon**-coated stainless steel to minimize the deposition of iodine on surfaces. Operating temperatures are limited to about 220°C to avoid decomposition of *Teflon*.

Freshly precipitated ^{127}I (usually 50 mg) tagged with 1 mCi of ^{131}I is vaporized from a glass frit into the test assembly during a 10-minute loading phase. Iodine vapors are mixed with prefiltered air or steam-air, filtered to remove moisture and entrained particulates and passed to the test bed. Backup beds are provided to retain any iodine that penetrates the test bed.

Temperatures at selected points in the apparatus are measured with thermocouples and charted on a multipoint recorder. Upstream pressure and pressure drop across the test bed are also measured.

Backup beds (2 in series) are situated inside a shielded gamma counter to monitor the activity collected during all phases of the loading and desorption steps.

For safety, the apparatus is in a hood and operated at negative pressure. Spent test gases are vented into the building off-gas exhaust system where they are filtered, monitored, and discharged to the atmosphere.

After testing, the desorption apparatus is disassembled and individual pieces of the assembly counted separately to obtain a complete inventory of ^{131}I added to the system. Counting data are summarized in a standard format on an IBM 360 computer.

Detailed safety analyses of the operation of the SRP reactors are used to determine the conditions that might exist in the confinement system in the unlikely event of an accident. Carbon samples were subjected to two tests, the loss of coolant test and the power surge test to simulate these conditions.

In the loss of coolant test it is assumed that all coolant is lost, the emergency core cooling system fails to operate promptly, and a core meltdown occurs with the resulting release of radioiodine. Emergency cooling water is then assumed to quench the molten core materials resulting in evolution of steam for a short period of time. Carbon in the confinement systems would then be subjected to an extended exposure to warm humid air. The test is conducted by loading the iodine on the test bed in ambient air (10 minutes), heating the apparatus as quickly as possible to 80°C (∿10 minutes), passing 80°C steam-air through the bed (5 minutes), then passing 80% relative humidity, 40°C air through the bed for 20 minutes to several hours.

In the power surge test, partial core meltdown in the presence of moderator is assumed (steam-air-iodine loading of the carbon). This is followed by an extended period of warm humid air exposure for the confinement system. The test is conducted by preheating the test apparatus to

---

* Du Pont's trademark for its fluorocarbon resin.

80°C, passing 80°C steam-air through the carbon (5 minutes), loading the iodine in a steam-air mixture (10 minutes), and then following with 20 minutes to several hours of 40°C, 80% relative humidity air exposure.

High temperature desorption tests were conducted by loading a preheated test bed in a steam-air environment, followed by desorption for 1 to 3 hours with hot dry air (usually 200°C).

RESULTS AND DISCUSSION

Effect of Service

The retention of iodine by activated carbon decreases with increasing carbon service time for all tests performed. As determined in the loss of coolant and power surge tests, the useful life of carbon is slightly less than 4 years in the SRP confinement systems (Figure 3).

Nitrogen dioxide is the principal contaminant in reactor building air which ages confinement system carbon. Low concentrations of NO_2 (≤ 0.03 ppm) formed by irradiation of air around the reactor tank slowly age the carbon by destroying or occupying adsorption sites. Each NO_2 molecule adsorbed destroys one active site, and occupies two others when the reaction products NO and CO are adsorbed.

Iodine retention curves similar in shape to those shown in Figure 3 have been obtained in laboratory tests by exposing new carbon to NO_2-air mixtures. The decrease in retention is a direct function of NO_2 concentration (constant exposure time) or exposure time (constant concentration). Aging curves for the SRP confinement system can be duplicated by exposing new carbon to approximately 30 mg of NO_2 per gram of carbon per year of service as shown in Figure 4.

Other impurities may block active adsorption sites also, but their contribution to aging of SRP confinement system carbon is probably negligible, based on their relatively low concentration as shown in Figure 5.

Total effective surface area of carbon granules decreases with increasing service time as well (as shown in Figure 6). Some correlation exists between desorption and surface area; however, the correlation is not sufficiently precise to be useful. Samples from the upstream and downstream half of the bed were measured and showed that the surface area of the upstream samples was smaller than that of the downstream samples. This difference is caused by the greater concentration of impurities in the upstream half of the bed.

Effect of Temperature

Temperature also has a great influence on iodine desorption. As shown in Figure 7, desorption is insignificant (<0.03%) at 65°C from partially regenerated carbon with 4.7 years service. However, desorption

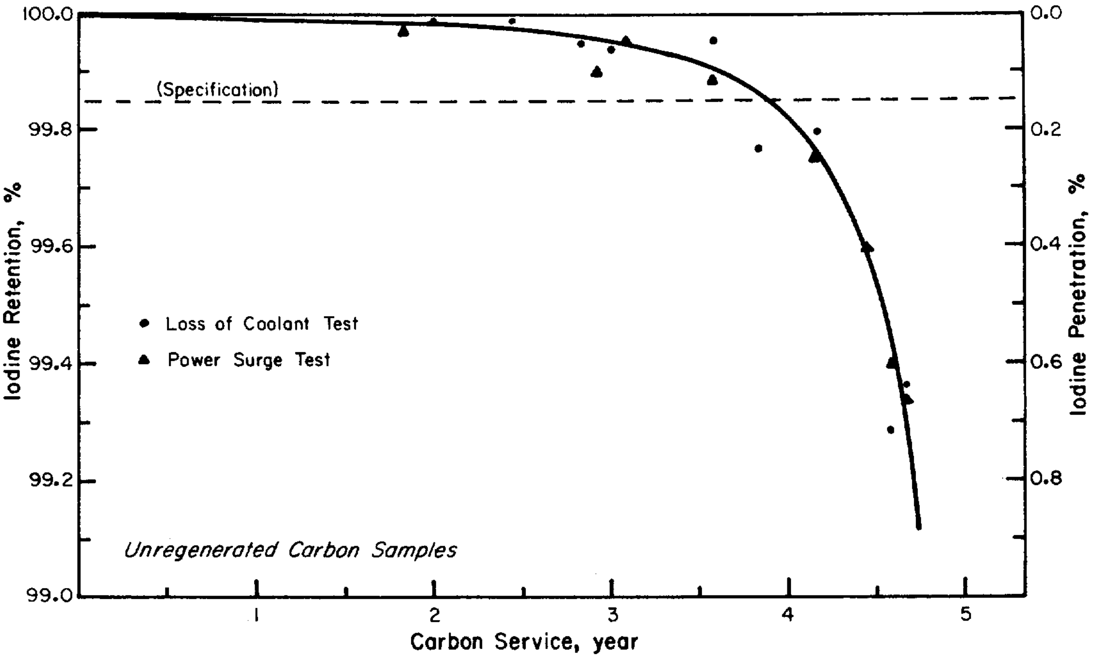


FIG. 3 EFFECT OF SERVICE ON CARBON

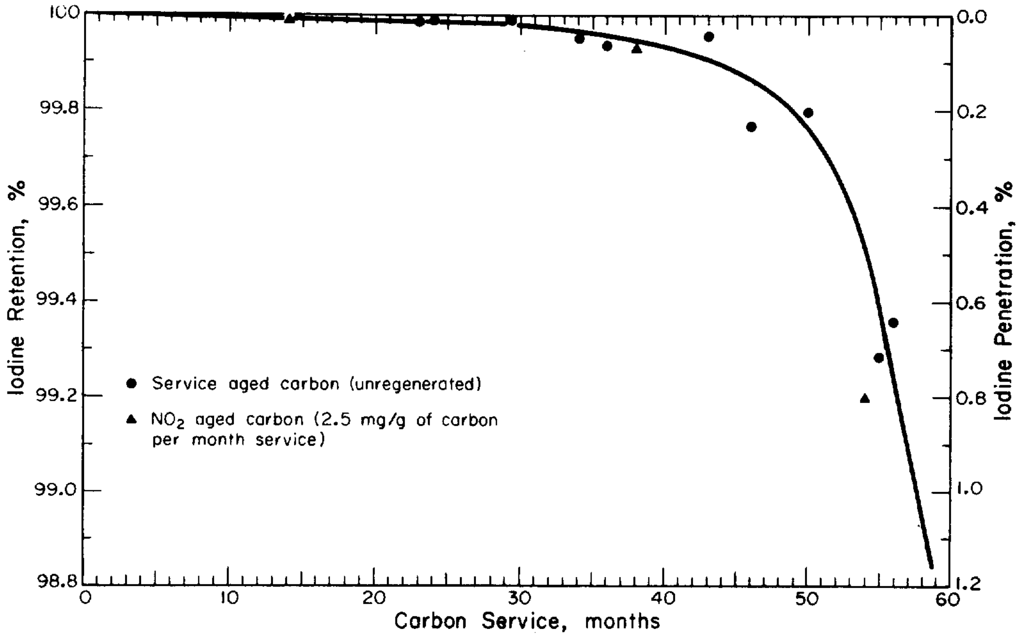


FIG. 4 COMPARISON OF SERVICE AGED AND NO_2 AGED CARBON

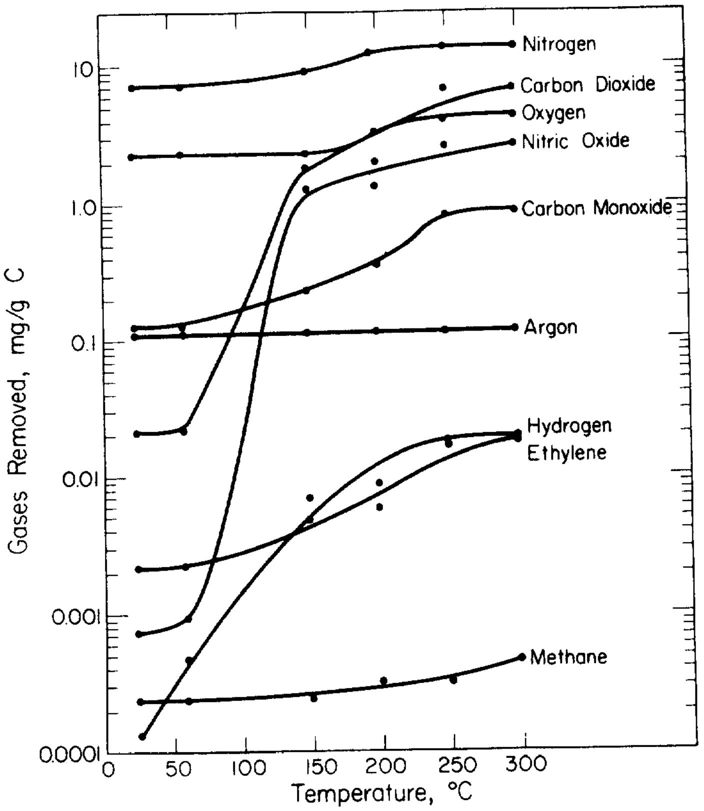


FIG. 5 DESORPTION OF GASES FROM UNREGENERATED CARBON AFTER 2-1/2 YEARS SERVICE

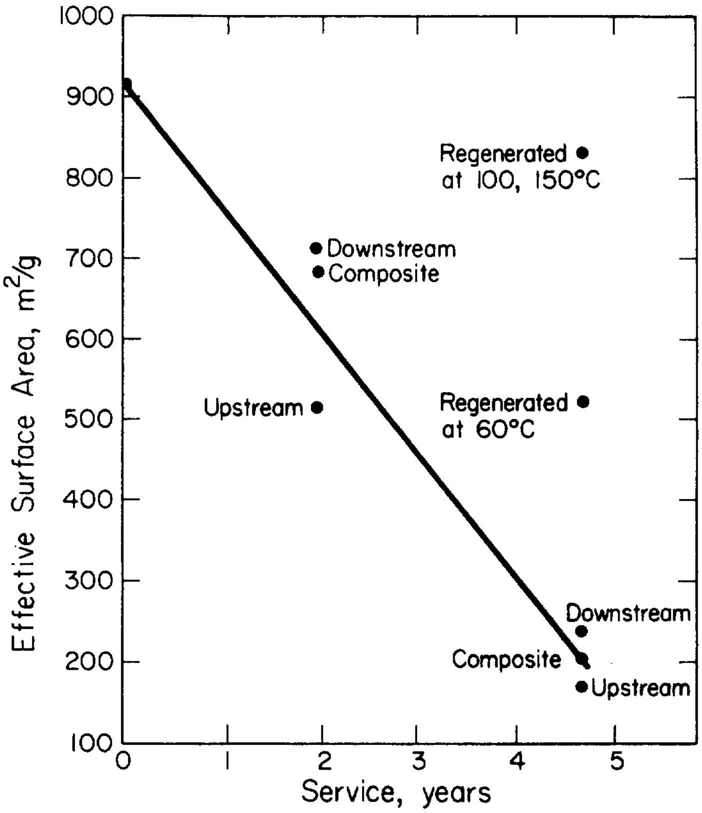


FIG. 6 EFFECT OF SERVICE ON SURFACE AREA

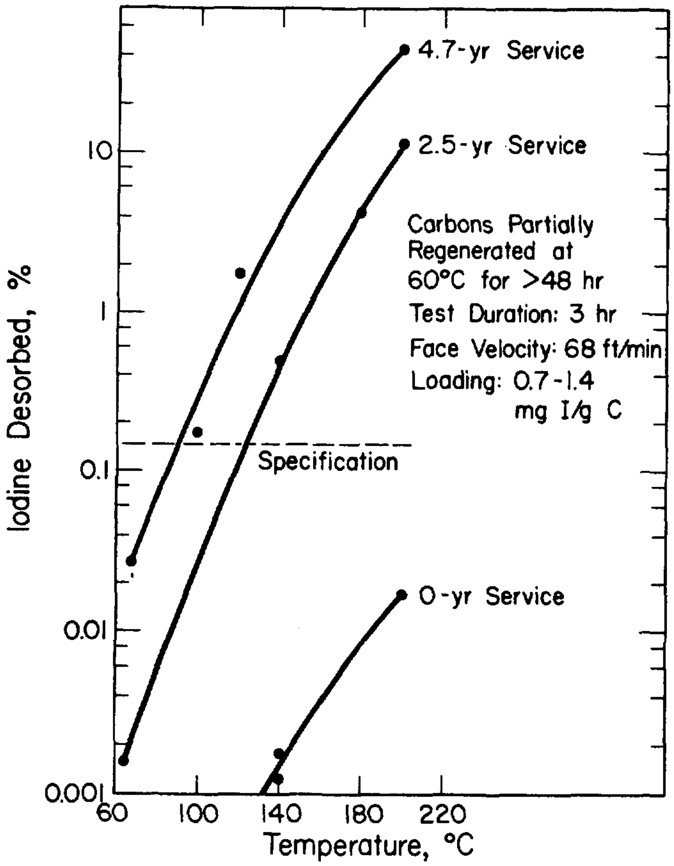


FIG. 7 EFFECT OF TEMPERATURE AND SERVICE ON DESORPTION

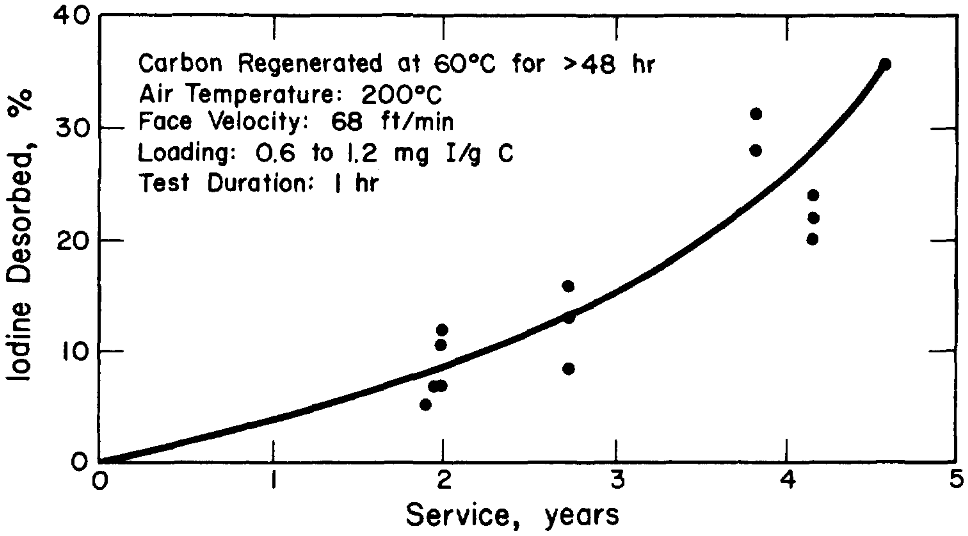


FIG. 8 EFFECT OF SERVICE ON DESORPTION

becomes unacceptably large above 100°C for carbons with about 4 years service. Similarly, desorption becomes unacceptably large above 120°C for carbons with 2.5 years service. Carbon with no service time can withstand temperatures above 200°C without significant desorption.

Desorption of iodine at 200°C from used carbons is unacceptably high as shown in Figure 8. These results show that heat must be removed from the confinement system to avoid excessive iodine releases caused by decay heat from molten fuel debris or from sorbed iodine.

Effect of Moisture

New carbon will adsorb and retain 99.99% of the iodine in an 80°C steam-air mixture. Retention consistently decreases with increasing carbon service. The moisture effect is temperature dependent however, as shown in Figure 9. Steam-air at 80°C desorbs significant iodine from 4-year old carbon, but saturated air at 40°C results in no further desorption.

Regeneration of Used Carbon

Carbon can be partially regenerated by heating. As indicated in Figure 6, the surface area of carbon with 56-months service is more than doubled by passing dry 60°C air through the bed for 48 hours. Regeneration at 100°C further increased the surface area, but no increase was noted between 100 and 150°C.

Removal of nitric oxide (one of the reaction products of NO_2 with carbon) is shown in Figure 10 as a function of temperature for carbon with 2.5 years service. Continued removal of NO at temperatures up to 500°C (not shown in the figure) indicates that complete regeneration is not accomplished at 300°C.

Partial regeneration of carbon at 60°C during the annual *Freon** leak tests of the confinement system[12] may extend the life of carbon. Carbons regenerated at various temperatures will be evaluated by NO_2 aging techniques to determine if treatment of used carbons is practicable.

SUMMARY

The ability of activated carbon to retain adsorbed iodine:

1. Decreases as on-line service life increases.
2. Decreases as carbon temperature increases.
3. Can be partially restored by regeneration techniques.

---

* Du Pont's trademark for its fluorinated hydrocarbons.

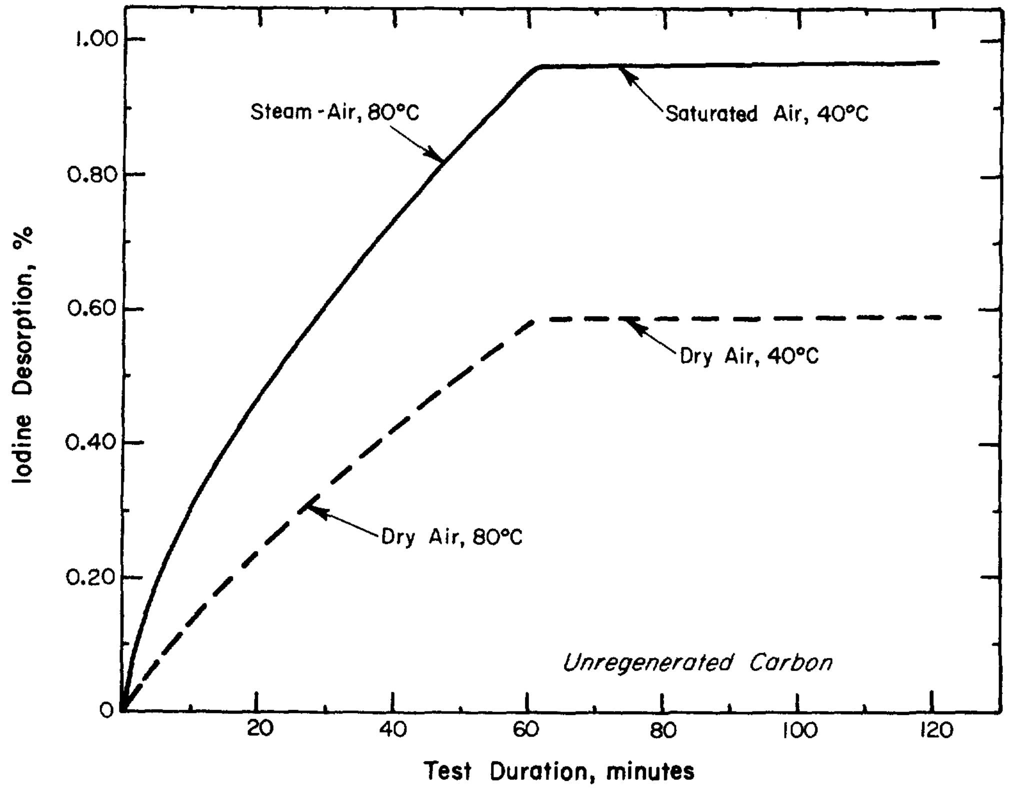


FIG. 9 EFFECT OF MOISTURE AND TEMPERATURE ON 4.2 YEAR CARBON

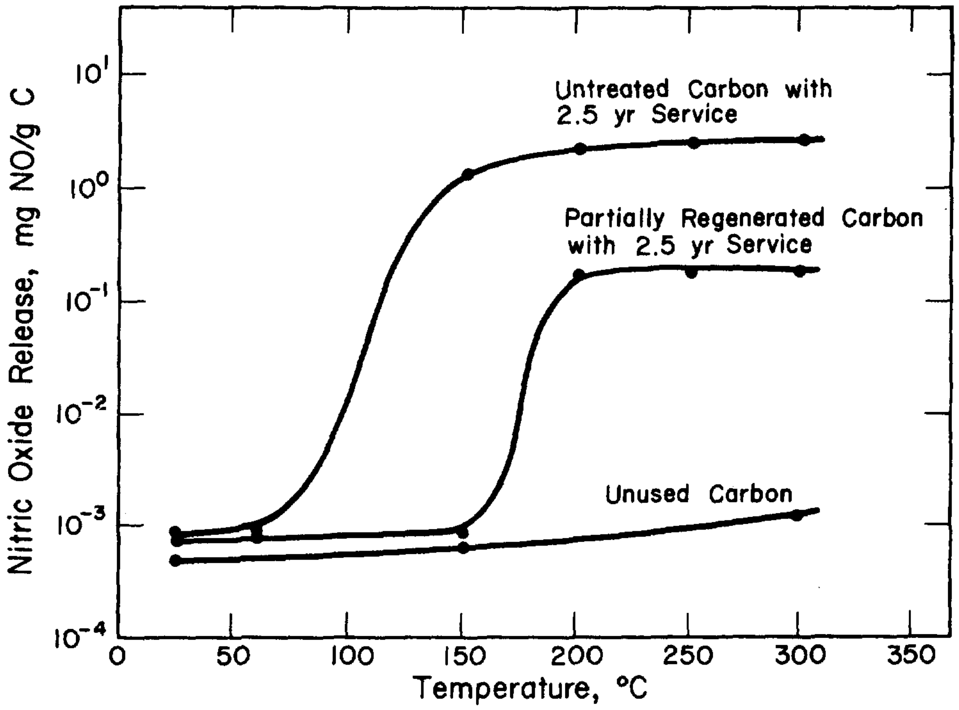


FIG. 10 RELEASE OF NITRIC OXIDE FROM CARBON

Carbon beds in reactor confinement systems must therefore be tested periodically, under simulated accident conditions, to ensure that they provide the required protection against release of radioiodine. In addition, on-line carbon beds must be designed to remain cool under accident conditions.

One of the key impurities that degrades the quality of carbon is nitrogen dioxide, which is produced by the intense gamma irradiation of air around reactors. The exclusion of air from the immediate vicinity of the reactor should be considered as a means to extend the useful life of on-line carbon beds.

Regeneration techniques are being investigated that could extend the useful life of carbon.

REFERENCES

1. G. H. Prigge. *Application of Activated Carbon in Reactor Containment.* USAEC Report DP-778, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1962).

2. W. S. Durant. *Performance of Activated Carbon Beds in SRP Reactor Confinement Facilities - Progress Report: September 1962 - September 1965.* USAEC Report DP-1028, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1966).

3. J. W. Hassler. *Active Carbon.* Chemical Publishing Co., Inc., Brooklyn, New York (1951).

4. C. L. Mantell. *Industrial Carbon.* D. Van Nostrand Co., Inc., New York, N. Y. (1946).

5. R. E. Adams, R. D. Ackley, and Zell Combs. *Nuclear Safety Program Annual Progress Report for Period Ending December 31, 1967.* USAEC Report ORNL-4228, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1968).

6. R. C. Milham. "High Temperature Properties of Activated Carbon: Part I. Desorption of Iodine, Part II. Standard Method for Ignition Temperature Measurement." *Proceedings IAEA Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes.* New York, August 26-30, 1968, pp. 417-37, IAEA (1968).

7. R. C. Milham. "Charcoal Post Treatment; Heat Degradation and Service Life." *Proceedings of the Tenth AEC Air Cleaning Conference.* New York, August 28, 1968, USAEC Report CONF-680821, pp. 167-69 (1968).

8. R. C. Milham and L. R. Jones. *Iodine and Noble Gas Retention Studies - Progress Report: October 1966 - December 1968.* USAEC Report DP-1209, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1969).

9. R. C. Milham and L. R. Jones. *Iodine Retention Studies - Progress Report: January 1969 - June 1969.* USAEC Report DP-1213, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1969).

10. R. C. Milham and L. R. Jones. *Iodine Retention Studies - Progress Report: July 1969 - December 1969.* USAEC Report DP-1234, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1970).

11. W. S. Durant, R. C. Milham, D. R. Muhlbaier, and A. H. Peters. *Activity Confinement System of the Savannah River Plant Reactors.* USAEC Report DP-1071, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1966).

12. D. R. Muhlbaier. *Standardized Nondestructive Test of Carbon Beds for Reactor Confinement Applications - Final Progress Report: February 1966 - June 1966.* USAEC Report DP-1082, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1967).