SESSION VIII

RADIOIODINE REMOVAL

Wednesday, August 30, 1972
CHAIRMAN: G. Burley

CHAIRMAN'S OPENING REMARKS:

As we well know, radioiodine has considerable persistence, has been the topic of considerable discussion since the first conference, and promises to be around for quite a while longer. Specifically, iodine is of primary importance in determining the environmental impact of nuclear power plants, both because of its volatility and its biological hazards. Due to its volatility, it is released in appreciable quantities from defective fuel pins even during normal operations, and may be released nearly quantitatively during a major accident. It is specific to the thyroid and may be introduced either by inhalation or by ingestion, primarily via the milk cycle.

There has been a gradual evolution in the level of sophistication of research reported over the years. Early work dealt primarily with the identification of the different chemical forms of iodine present, and with a search for adequate removal mechanisms. Then came a period characterized by many quantitative measurements under a variety of conditions, mostly on a relatively small scale.

Several of the papers to be presented today are a continuation and a refinement of this trend, but new direction is beginning to emerge. This is represented here by a summary report on iodine removal by metal-substituted zeolites and by reports which cover experimental work on charcoal aging and the effect of radiation.

The session will also include a report on what promises to be a somewhat controversial subject during the next few years; namely, the effect of incident iodine concentration on overall removal effectiveness. With the current emphasis on "as low as practicable" releases, it is only now that iodine reduction of effluents previously released untreated is being proposed. The iodine concentration in such instances may be as low as 10^{-6} to 10^{-9} micrograms per cubic meter, and the linearity of commercially-available adsorbers when extended to such low concentrations remains to be proven.

EFFECT OF INTENSE GAMMA RADIATION ON RADIOIODINE RETENTION BY ACTIVATED CARBON*

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Abstract

Most nuclear reactor installations have activated carbon beds to confine radioactive halogens following a reactor accident. The intense radiation field resulting from adsorption of radiohalogens on these carbon beds can convert elemental halides to organic halides. The rates of formation and desorption of organic iodides are functions of radiation field intensity, relative humidity of the purge gas stream, type and service history of the carbon, and particle size distribution of the carbon. The principal formation mechanisms are probably free radical reactions; the necessary reaction components for these reactions are water, iodine, carbon, and an intense radiation field.

Desorption rates from several types of carbon and inorganic-base iodine adsorbers under various conditions are presented. Impregnated adsorbers (carbon and inorganic) retain iodine better under gamma radiation than unimpregnated carbons. New triethylenediamine-impregnated carbons have the best overall retention characteristics of the materials tested to date. Service aging characteristics are being determined. The type of carbon and method of impregnation may significantly affect iodine retention, particularly at higher temperatures (up to 180°C).

Introduction

The activity confinement system for each of the Savannah River production reactors was designed to collect halogens and particles that would be released in the unlikely event of a reactor accident(1). Continuing studies have been conducted at the Savannah River Laboratory to evaluate the performance characteristics of the confinement system under a variety of accident conditions and to enhance its reliability and efficiency(2-10). Elemental iodine retention characteristics of the activated carbon in the confinement system were studied extensively under a variety of simulated accident conditions (eg., temperature, velocity, humidity, carbon service, and iodine loading)(2-8).

Until recently, high intensity radiation sources were not readily accessible which would permit evaluation of performance characteristics under the severe radiation stress that would result from the accumulation and subsequent decay of radioiodine in the carbon beds. Two large ^{60}Co irradiation facilities have been constructed at the Savannah River Laboratory(10,11) where dose rates in excess of 10^7 rad/hr can be obtained in carbon test beds. These dose rates approach those which could be encountered in the SRP confinement system or in the carbon beds of many commercial power reactors following a major reactor accident.

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Formation of Penetrating Forms of Iodine in a Radiation Field

Confinement system studies at Savannah River have shown that elemental iodine retention on activated carbon is most strongly influenced by the operating temperature of the carbon beds, the moisture content of the air passing through the beds, and the length of time the carbon has been in service in the system. Extensions of the studies to include the effects of radiation on iodine retention revealed that organic iodides are formed when a system composed of elemental iodine, carbon, and moist air is exposed to an intense gamma radiation field. The extent to which the penetrating iodides are observed to be formed and desorbed from test carbon beds is a function of intensity and duration of irradiation, the carbon type and service history, the composition of the purge gas stream, and possibly the operating temperature of the carbon bed.

Radiation tests were first performed in a 500,000 curie ^{60}Co facility with two 6-inch-diameter access tubes as described in detail at the Eleventh Air Cleaning Conference(11). Subsequent tests have been conducted in a new 1.6 megacurie ^{60}Co facility with a 10-inch-diameter access tube which will be described in a later paper at this conference(12). The dose rate in the test carbon beds of the smaller facility was 1.5×10^7 rad/hr; that in the new facility was 3.0×10^7 rad/hr.

Tests performed in the older facility used 2-inch-diameter test beds in an apparatus described earlier(11). The newer facility was designed to accommodate a larger test apparatus with 3-inch-diameter test beds. The new apparatus can be assembled to provide individual components or the complete series of air cleaning components used in the confinement system (Figure 1). When used as a complete system, the apparatus consists of a moisture separator section (and condensate trap) containing moisture separator cloth, a particulate filter section containing HEPA filter medium and gasketing material, and a test bed section which can be packed with any desired iodine adsorber material.

Elemental iodine, tagged with ^{131}I, is volatilized into a humid air stream, passed through a test bed containing carbon or other iodine adsorbers, and then passed through a series of backup carbon beds before release to the atmosphere (Figure 2).

Reaction Components

Tests were first performed to demonstrate that the simultaneous presence of carbon, iodine, moisture, and radiation are required for formation of the penetrating iodides. The test carbon was an unimpregnated coconut base carbon. Test data are summarized in Table I.

Formation and desorption of penetrating iodine compounds continues for at least 100 hours when irradiation continues (Figure 3). Effect of carbon type and service history are also shown in Figure 3. Test conclusions are summarized below:

- Preirradiation of carbon caused no penetrating iodide formation.
- Irradiation of I_2-air-moisture mixture in absence of carbon caused no penetrating iodide formation.
- Desorption of penetrating iodides ceased when I_2-loaded carbon was removed from the radiation field.
- Desorption of iodine increases with increasing humidity in the purge gas stream.

- Desorption of iodine continues for at least 100 hours in a radiation field.

From this information, it can be concluded that the necessary components for the formation and desorption of penetrating iodine compounds are iodine, carbon, moisture, and an intense radiation field.

The radiation field strength affects the amount of iodine released as shown in Table II. Since all the dose rate tests were run for the same period of time (5 hours), the differentiation between the effects of total absorbed dose and dose rate cannot be made.

The rate of desorption of iodine in a radiation field as a function of time is shown in Figure 4. From these data, unimpregnated carbon has an initial desorption rate much higher than that of KI_3-impregnated carbon, but after about 15 hours the desorption rate is the same.

Reaction Products

Iodine compounds desorbed from the test carbon bed in the radiation field are passed through a series of backup carbon beds, which are located outside the gamma field. The backup beds are maintained at the same temperature or at higher temperatures than the test bed to prevent condensation of moisture in the backup beds and air lines. The first backup bed contains unimpregnated carbon; the next two backup beds contain KI_3-impregnated carbon.

The distribution of activity on the three backup beds varies with the operating temperature of the beds. When the system is maintained at about 80°C (the same temperature as the test carbon bed), the unimpregnated first backup bed retains 40 to 50% of the desorbed products, and the first impregnated carbon bed retains $\sim$99% of the activity passing through the first backup bed. Increasing the temperature of the air stream increases the fraction retained on the unimpregnated carbon. This behavior is consistent with that observed earlier(7) for methyl iodide, because increasing the temperature decreases the relative humidity of the air stream and increases the fraction retained on unimpregnated carbon.

Attempts to recover and analyze the activity trapped on the unimpregnated carbon backup beds have been only partially successful. Both inert gas purging and vacuum heating techniques have been attempted with a net removal of <20% of the activity on the bed. The gases removed from the beds are collected in liquid nitrogen cold traps and analyzed by gas chromatography.

Four organic iodides have been identified in the products collected from the backup beds: methyl iodide (CH_3I), methylene iodide (CH_2I_2), ethyl iodide (C_2H_5I), and vinyl iodide (C_2H_3I). Two noniodine compounds (methanol and nitromethane) are usually found, and as many as eight other as yet unidentified compounds are present in most samples. Other techniques for collection and identification of the desorption products are being investigated. The small sample size and large dilution factors make direct specific analysis difficult (<40 μg of iodine desorbed into $\sim$8 m^3 of air containing $\sim$1.5 kg of H_2O during a typical 4-hour desorption).

Reaction Mechanisms

The experiments to date have been scoping studies designed to define the nature and magnitude of the phenomenon, rather than to establish specific mechanisms or rate constants. The data are sufficient, however, to identify the critical components in the system and, thus, to infer some general reaction mechanisms.

Moisture is apparently one of the critical rate-controlling components in the system. Because the principal penetrating products appear to be organic iodides, the moisture content of the purge gas stream probably plays a dual role in iodine desorption:

- Radiolytic decomposition of water furnishes the hydrogen required to form stable alkyl iodides.
- The rate of desorption of organic iodides from the test bed is governed by the relative humidity of the purge gas stream.

In the highly energetic system existing in a radiation field of $\sim 10^7$ rads/hour, the reaction mechanisms are probably all free radical reactions. Of the numerous free radical pathways available to form organic iodides, the simplest (and most probable) is the radiation-induced iodination of organic side chains on the basic carbon structure followed by reaction with hydrogen and hydroxyl free radicals to form organic iodides. Thus, for methyl iodide, the reactions

$$I_2 + RCH_3 \longrightarrow RCH_2I + HI$$

$$H_2O + RCH_2I \longrightarrow R\text{-}OH + CH_3I$$

can be postulated. Similar equations can be written for methylene iodide, ethyl iodide, and vinyl iodide.

Sequential hydrogenation of unsubstituted carbon to form methylene free radicals ($\cdot CH_2 \cdot$) or methyl free radicals ($H_3C\cdot$) and subsequent reaction with sorbed or free radical iodine are also possible, but somewhat less probable because of the multiple reactions required.

Further evidence for the free radical mechanism postulate is provided by a series of tests in which nearly dry air, humid air, and humid N_2 were used as purge gases.

If the principal reaction mechanism for organic iodide formation is a free radical mechanism, oxygen in the purge gas stream should reduce the organic iodide yield by reacting with iodide precursors. The test results (Table III) show that more iodine is desorbed in N_2 gas than in air and indicate that the postulated free radical mechanism is correct.

Anhydrous air as a purge gas should inhibit organic iodide formation by restricting the supply of free hydrogen to complete the reaction. Equipment limitations prevented running an anhydrous test; however, reducing moisture with a dry air purge decreased iodine desorption more than a factor of ten. In the dry air test, approximately 70% iodine desorption occurred during the loading phase when air was being drawn through a glass frit containing moist iodine crystals.

Screening Tests for Alternative Iodine Adsorbers

The scoping studies previously discussed were designed to define the nature and extent of iodine penetration of activated carbon in the presence of an intense gamma radiation field. In the unlikely event of a major reactor accident, the radioiodine loading on the confinement system carbon could produce a radiation field of sufficient strength to desorb significant quantities of iodine. Consequently, a series of screening tests was undertaken to find alternative iodine adsorbers that are less sensitive to the radiation effects.

Three screening tests and a control test were designed to simulate a range of conditions to which carbon in the confinement system might be subjected in the unlikely event of a major reactor accident. The three conditions are: radiation exposure (as a result of adsorption and subsequent decay of radioiodine on the carbon); high temperature (180°C) exposure after iodine loading (assuming partial failure of emergency cooling); and artificial weathering using NO_2 to simulate service weathering of the carbon.

Test Conditions

In all tests, 2-inch-diameter by 1-inch-thick test beds were used. Air filtered by a 1-foot-thick carbon bed followed by an HEPA filter was used in all tests. The filtered air then passed through the test beds at a face velocity of 55 ft/min. Iodine loading was approximately 0.7 mg of I_2/g of carbon for carbon base adsorbers and approximately 0.35 mg of I_2/g of test material for inorganic adsorbers.

Control and Radiation Tests

The radiation screening tests were made in the old ^{60}Co facility (1.5×10^7 rads/hour absorbed dose rate in the carbon). Test conditions were limited by equipment design features of the test assembly (e.g., the absence of a condensate trap prevented running at high humidities). The control test was run under the same temperature and humidity conditions as the radiation test, but outside the ^{60}Co radiation field. Elemental iodine was loaded onto the carbon test bed over a 60-minute period in an air stream at 80°C and $\sim$75% relative humidity. Iodine was then desorbed for 4 hours at 80°C and $\sim$75% relative humidity. Iodine was loaded by vaporizing freshly precipitated $^{127}I_2$ tagged with ^{131}I into a prefiltered air stream.

High Temperature Test

Iodine was loaded onto the test carbon bed in 10 minutes in air at ambient conditions (23°C and $\sim$50% relative humidity) and desorbed for 4 hours with hot (180°C), dry air. The irradiation test apparatus was not designed to operate above 80°C; therefore the high temperature tests were run in the absence of the high-intensity gamma radiation field.

NO_2 Test

Samples of test carbon were artificially weathered in an NO_2-air stream as discussed in Reference 8. Total NO_2 exposure was 91.1 mg of NO_2/g of carbon or the equivalent of 36 months of weathering in the SRP confinement system. Elemental iodine was loaded onto the test bed as described in the high temperature tests. Iodine was desorbed for 4 hours with 80°C air saturated with moisture. As noted in Reference 8, the NO_2 weathering technique fails to simulate true service weathering when the test carbon bed is subjected to elevated temperature and airflow before iodine loading; therefore the NO_2 tests had to be run outside the radiation field.

Test Results

A total of 21 different iodine adsorbers were subjected to one or more of the screening tests. The primary objective of these tests was to select the best adsorbers for more detailed testing and eventual use in the confinement system. For this reason, some products that retained iodine poorly in one or more tests were not subjected to the complete series of screening tests.

All tests used new carbon as supplied by the vendors. Several conclusions are indicated by the test data shown in Table IV:

- The iodine retention efficiencies of coconut-base carbons impregnated with KI_3 varied widely from vendor to vendor, particularly in the high-temperature and NO_2 tests. In some cases the base carbon was the same, but different methods of impregnation were employed. Thus, the method of KI_3 impregnation appears to affect the performance of the product for nuclear applications.
- Petroleum-base carbons had consistently poorer iodine retention properties in the high-temperature test than most coconut-base carbons, regardless of the impregnant.
- Triethylenediamine (TEDA)-impregnated carbons were among the better adsorbers both in the radiation test and the NO_2 test. One adsorber, a TEDA-impregnated coconut-base carbon, gave consistently better test results than all other adsorbers. A similar carbon impregnated with TEDA and KI performed nearly as well as the carbon impregnated with only TEDA in most of the tests.
- The iodized carbons (KI_3, PbI_2, and I_2) are more sensitive to temperature and simulated weathering than either unimpregnated or TEDA-impregnated carbons (the exception being the TEDA-KI combination).
- Use of insoluble PbI_2 instead of highly soluble KI_3 appears to have no benefit for iodine retention under the conditions used in this test series.
- All the impregnated adsorbers performed better in the radiation test than the unimpregnated coconut-base carbons. This is consistent with earlier findings that the principal mechanism of iodine penetration in an intense radiation environment is formation and subsequent desorption of organic iodides.

The two TEDA-impregnated coconut carbons (TEDA and TEDA + KI) are being tested in the new irradiation facility under a wider variety of temperature and humidity conditions. Companion tests were also performed in the new facility on unimpregnated carbon with used (dust loaded) moisture separator cloth and HEPA filter medium. The later tests were performed because the dust accumulated on the confinement system components upstream of the carbon beds contains significant quantities of soot from diesel and coal burning power generators located near the reactor buildings. Because the soot provides a relatively large surface area and contains residual unburned hydrocarbons, significant quantities of iodine could be sorbed on the dust and subsequently converted to organic iodides. Unimpregnated carbon was used in the carbon test bed to maximize organic iodide penetration. The results (Table V) indicate that the dust loading has very little effect on iodine penetration, even in a radiation field.

Initial test data on unimpregnated carbon in the new test facility indicate that the relative humidity in the old apparatus (reported earlier(9-10) as 50%) was probably 70 to 80% as shown in Table VI. Entrained and condensed moisture could accumulate in the bottom of the old test apparatus (which had no condensate trap) and reevaporate into the airstream in the test assembly. The new apparatus has both a condensate trap and moisture separator immediately ahead of the HEPA filter so that humidity can be controlled more effectively.

Other data indicate a marked influence of the particle size distribution of the carbon on iodine retention efficiency under radiation stress. Two different lots of TEDA-impregnated carbon showed low iodine penetration in the screening test series in the old test apparatus (∿75% relative humidity). When a third lot was tested in the new apparatus at 100% relative humidity, the penetration was more than 50 times greater. Some increase in penetration was expected because of the increase in humidity, but the humidity effect was no more than a factor of three different in other carbons (impregnated and unimpregnated).

Several batches of carbon were sieved using the ASTM Procedure to determine the particle size distributions. The results are shown in Table VII. The third lot of TEDA carbon is considerably coarser than all the other carbons tested. When Lot 2 of the TEDA carbon was tested for iodine retention, the penetration was lower as shown in Table VIII.

All the radiation tests to date on impregnated carbons have been performed on new material. Confinement system beds containing TEDA-impregnated carbon and TEDA-KI impregnated carbon have been installed in two reactor buildings to obtain service aged carbon for further testing. Additional samples of carbon impregnated with TEDA, TEDA + KI, KI_3, and I_2 will be installed in a newly constructed weathering facility where the carbons are exposed to reactor building air at normal flow and twice normal flow. Iodine retention efficiencies as a function of service time will be made on all these carbons in a radiation environment.

Summary

Elemental iodine, carbon, and moisture combine in an intense gamma radiation field to form organic iodides. The rate of formation and subsequent desorption is a function of radiation field strength, carbon type, service history and particle size, and the moisture content of the purge gas stream. Unimpregnated carbons desorb the organic iodides more readily than impregnated carbons. Among new impregnated carbons, the coconut shell carbons impregnated with TEDA or TEDA and KI appear to offer the best overall retention characteristics. Weathered impregnated carbons will be tested in a radiation environment as samples become available.

References

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TABLE I

Effect of Radiation and Moisture on Iodine Penetration

Iodine Penetration (5 hr), %	Test Conditions
<0.01	Control test, no radiation
<0.01	Preirradiated carbon, no radiation during test
<0.01	Irradiation of I_2, air, and moisture, but not carbon
0.02	Dry air loading and desorption in radiation field
0.14	Moist air loading, dry air desorption radiation field
0.15	Moist air loading in radiation field, desorption outside radiation field
0.30	Moist air loading, ambient desorption, radiation field
0.43	Moist air loading and desorption, radiation field

TABLE II

Iodine Penetration as a Function of Dose Rate and Carbon Type

Carbon	Iodine Penetration, %[a] 1.5×10^7 rad/hr at 60°C	1.4×10^6 rad/hr at 60°C
Unimpregnated	0.318	0.0165
KI_3-Impregnated	0.0083	0.0003

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a. 1-hour loading and 4-hour desorption in 50% relative humidity.

TABLE III

Effect of Purge Gas Composition on Iodine Desorption

Radiation Field, rads/hr	Purge Gas	Relative Humidity, %	Iodine Penetration, %[a]
1.5×10^7	Air	∿75	0.283
1.5×10^7	N_2	∿75	0.474
1.5×10^7	Dry Air	<1	0.020

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a. 1-hour loading, 4-hour desorption, unimpregnated carbon.

TABLE IV

Screening Test Results

			Measured Iodine Penetration, %[a]			
Mfgr.	Adsorber	Impregnant	Control	Radiation	NO_2	High Temp
A	coconut	none	<0.001	0.283[b]	0.061[b]	0.004
B	coconut	none	<0.001	0.299	-	-
A	coconut	KI_3	<0.001	0.017[b]	0.229[b]	0.052
A	coconut	KI_3	0.002	0.132[b]	-	-
B	coconut	KI_3	<0.001	0.014[b]	0.029[b]	0.028[b]
B	coconut	KI_3	<0.001	0.029	0.074	0.056
C	coconut	KI_3	0.001	0.030[b]	0.364	18.08
D	coconut	KI_3	-	0.045	0.552	2.412
E	petroleum	KI_3	0.011	0.058[b]	2.049[b]	6.484[b]
B	coconut	I_2	<0.001	0.021	0.043	0.070
A	coconut	PbI_2	0.009	0.046	0.117	-
A	coconut	PbI_2	-	-	0.029	-
B	coal	PbI_2	0.002	0.015	1.877[b]	-
B	coconut	PbI_2	<0.001	0.160[b]	0.433	0.084
B	coconut	KI + TEDA	<0.001	0.037[b]	0.046[b]	0.006[b]
B	coconut	TEDA	<0.001	0.003[b]	0.018[b]	0.003[b]
E	petroleum	TEDA	-	0.008	0.080	12.03
E	petroleum	TEDA	-	0.014	0.028	4.556
B	inorganic	Ag	-	0.168	-	-
B	inorganic	Ag	0.008	0.195	-	-
F	inorganic	Ag	0.002	0.011	-	-

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[a] Test conditions are described in text.

[b] Average of replicate determinations.

TABLE V

Effects of Dust Loaded Moisture Separator and HEPA Media on Iodine Penetration

Unimpregnated carbon, 5 hours exposure at 3.0×10^7 rad/hr, 80°C, saturated air

	Iodine Penetration, %
New Moisture Separator, New HEPA Medium	0.37
New Moisture Separator, Dusty HEPA Filter	0.44
Dusty Moisture Separator, New HEPA Filter	0.44

TABLE VI

Effect of Relative Humidity on Iodine Penetration of Unimpregnated Carbon

5 hours test at 80°C in a radiation field of 1.5 to 3.0×10^7 rad/hr

Relative Humidity, %	Iodine Penetration, %
50	0.14
∿75	0.28[a]
100	0.37

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[a] Screening test results from Table IV.

TABLE VII

Particle Size Distributions of Selected Carbons

Impregnant	Lot No.	8-12 Mesh, %	12-16 Mesh, %
TEDA	1	19	80
	2	32	65
	3	58	34
TEDA + KI	1	56	40
	2	54	40
	3	40	50

TABLE VIII

Effect of Particle Size Distribution on Iodine Retention

Particle Size Distribution (U.S. Std. Sieves)	Iodine Penetration, % (5 hour @ 80°C & 100% relative humidity in gamma field of 3.0 x 10^7 rad/hr)
8-12 Mesh, 64.5% 12-16 Mesh, 35.5%	0.157
8-12 Mesh, 34.2% 12-16 Mesh, 65.8%	0.077

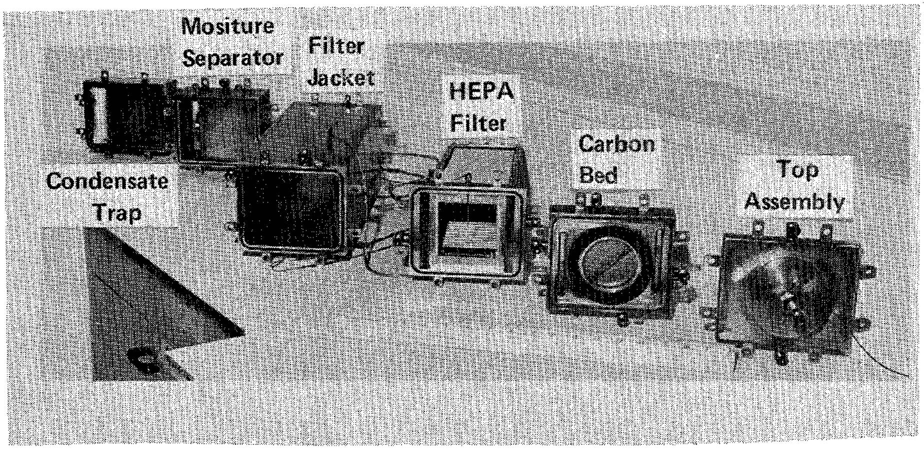

FIGURE 1. EXPLODED VIEW OF NEW TEST APPARATUS

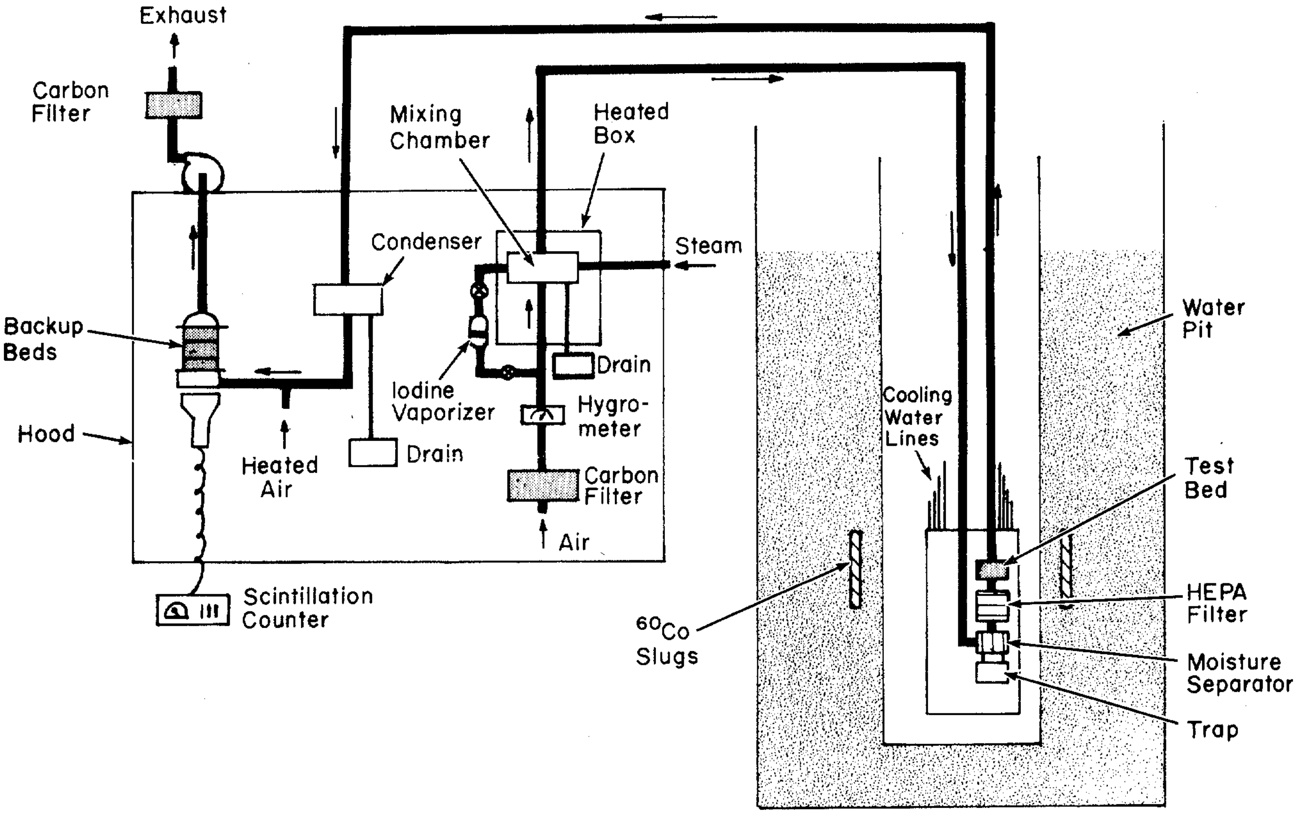

FIGURE 2. IODINE RADIOLYSIS FACILITY

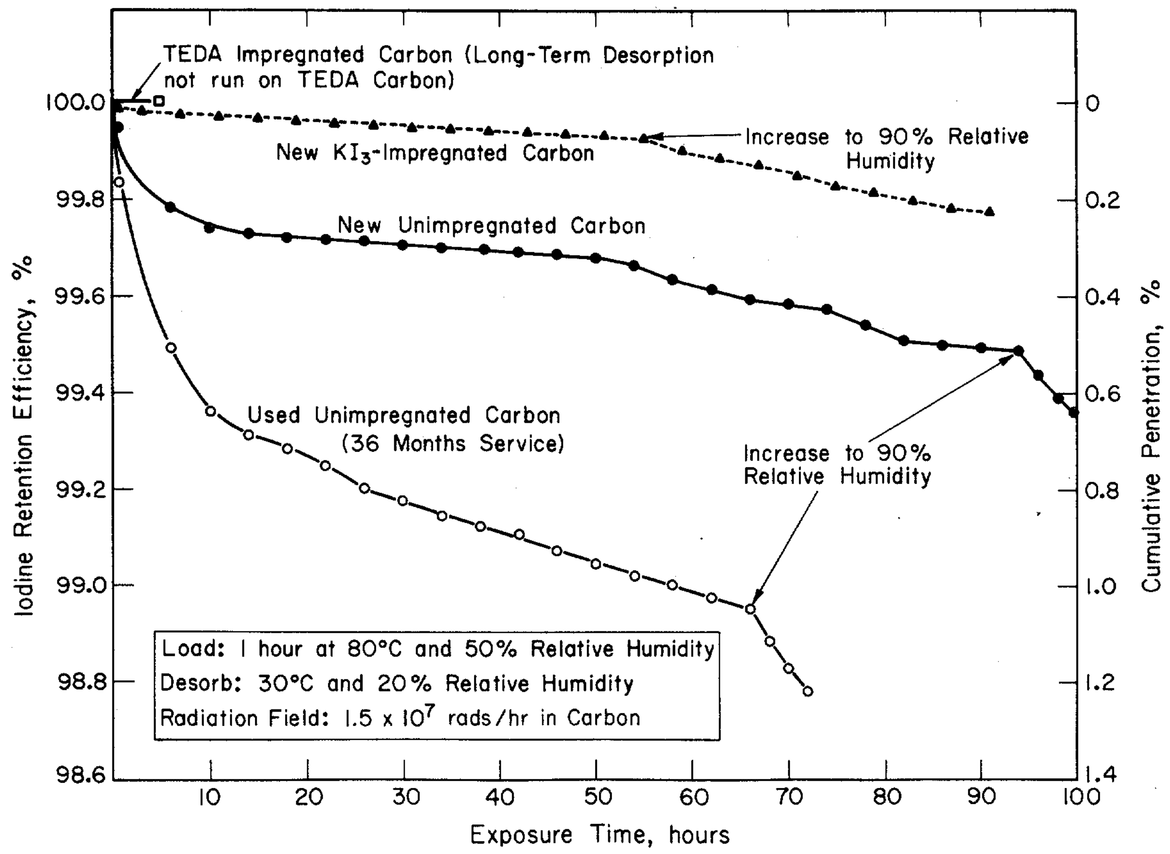

FIGURE 3. EFFECT OF RADIATION ON IODINE RETENTION

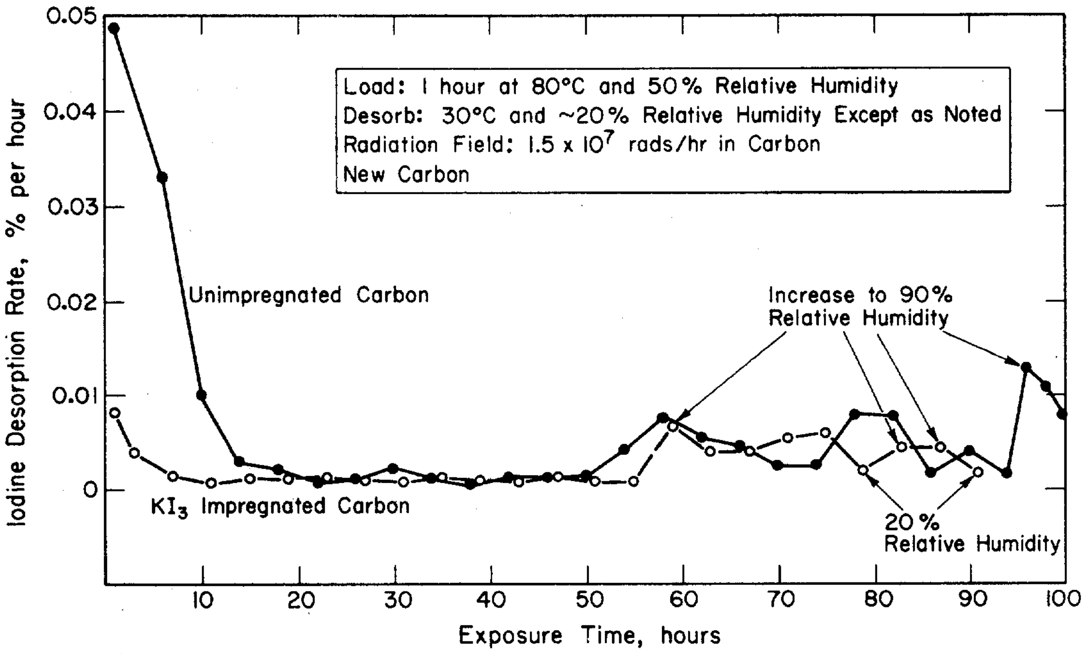

FIGURE 4. IODINE DESORPTION RATE OF NEW CARBONS

DISCUSSION

FIRST: Is it correct that the radiation experienced in an operating unit would be from the adsorbed iodine?

EVANS: That is correct.

FIRST: Would a solution to the problem be to put another unit in series, perhaps shielded from the first, since the amount of material that would pass through the first is relatively small, so that the radiation exposure of the second charcoal unit in series would be far less?

EVANS: That's one approach. A backup carbon bed remotely located with respect to the radiation; but in some power reactors I am not sure that it really would be practical. You might be able to remove the backup filter physically from the primary filter, but you may introduce another potential leak pathway in doing so since you have to put your iodine bed outside your containment dome. In a system like ours it might be possible to find a place to put a backup carbon bed (at some expense, of course) which would be shielded from the primary system.

WILHELM: On the last slide, you showed 0.37% penetration without dust and 0.44% with dust on the HEPA filter or moisture separator. What is the variation in your experiments? Can you get reliable numbers this close together?

EVANS: This is why we are saying that there is little apparent effect. Experimental variation can be that large.

WILHELM: Did you perform some re-runs so that you would have no doubt as to the variations?

EVANS: We were able to reproduce results fairly consistently, under the same test conditions. The runs with dusty demister and dusty HEPA filters are single runs, but we have run several tests with the uncontaminated media and are able to reproduce our data within 5 to 10 percent.

YARBRO: You noted in your remarks that you had included silver zeolite in some of your tests, but you didn't comment specifically about it. I wonder if you would elaborate a little more on zeolite.

EVANS: We evaluated silver zeolites in our radiation screening tests and it, like nearly everything else put in the system, is better than unimpregnated carbon. Initially, silver zeolite was not quite as good as TEDA impregnated carbon in terms of total penetration, but it was among the better adsorbers. For cost and for operational reasons we do not feel that the silver zeolites are practical at this time in our system. In other systems, silver zeolite may be quite satisfactory.

DEVELOPMENTS IN THE REMOVAL OF AIRBORNE IODINE SPECIES WITH METAL-SUBSTITUTED ZEOLITES*

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Abstract

A number of metal-exchanged zeolites have been investigated for possible use in airborne radioiodine removal. Although some show promise in dry atmospheres or heated adsorption bed applications, none compare with silver zeolite for overall adsorption efficiency for radioiodine. The radioiodine adsorption efficiencies and structural properties were examined in such adverse environmental conditions as high temperature steam atmospheres, high radiation fields, and high levels of various contaminant gases. A series of tests are described in which adsorption efficiencies of several adsorbent materials were examined as a function of airborne methyl iodide concentration. The results of these tests indicate that not enough is known about the adsorption performance of the commonly used radioiodine adsorbents to assure that the required DFs can be obtained to meet the specified radioiodine concentration levels with the present adsorbent systems.

Introduction

For the past several years, a program has been supported at the National Reactor Testing Station to evaluate the possible use of metal-exchanged zeolites for the removal of airborne radioiodine species. Although the original objectives of the program were directed toward the use of metal-exchanged zeolites in reactor emergency airborne radioiodine removal systems, more recently the emphasis of the investigations on the possible applications of these materials has been redirected to include ambient air, low level radioiodine species removal, and radioiodine removal from nuclear fuels reprocessing plant off-gas effluents.

In previous reports(1,2,3,4), the use of silver zeolites for the removal of airborne radioiodine species was shown to exhibit the following advantages when compared with other commonly used adsorbents: (1) nonflammability - samples containing adsorbed radioiodine have been heated to temperatures as high as 900°C before measurable amounts of radioiodine were liberated; (2) high temperature operability - efficient methyl iodide adsorption has been observed in investigations at temperatures as high as 400°C; (3) low explosion hazard when used in the presence of oxides of nitrogen - the oxides of nitrogen do not react with the basic zeolite structure; (4) silver zeolite has been shown to be the most efficient radioiodine species adsorbent of any tested in our laboratory under comparable conditions - even under such adverse conditions as 90 to 100 percent relative humidity; (5) resistant to poisoning - elemental iodine adsorption efficiencies of greater than 99 percent have been observed for silver zeolite in high concentrations of a variety of contaminant gases; and (6) the adsorbed radioiodine species form solid, insoluble products with silver zeolite which is desirable from a waste management standpoint.

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*Work performed under USAEC Contract (AT(10-1)1375)S-72-1

Only a summary of the various investigations we have conducted are reported here, but the details of test procedures and equipment used in the tests are available elsewhere(4). Unless otherwise specified, the adsorption tests were performed in 2.5-cm diameter by 5-cm deep adsorbent beds. Also, all the reported face velocities are actual or superficial velocities.

Metal-Cation Exchanged Zeolites Other Than Silver

A number of metal cation-exchanged zeolites in addition to silver have been examined for possible use as airborne iodine species adsorbents. These include: Cd, Cu, Hg, Pb, Tl, and some mixed rare earth cations. Although several of the exchanged materials show affinities for airborne elemental iodine, their adsorption efficiencies decrease appreciably with increasing relative humidity. This effect is shown in Table I for Cu- and Pb-exchanged X-type zeolite, CuX and PbX zeolites, respectively. Under dry conditions, both of these materials remove elemental iodine efficiently; however, in humid atmospheres near saturation, their adsorption properties rapidly deteriorate. Although the moisture content of saturated air increases considerably in going from 22 to 90°C, the adsorption efficiencies of both CuX and PbX increase. This strong temperature dependence indicates probable high iodine adsorption efficiencies for these materials in adsorption beds operated at elevated temperatures. Mercuric ion-exchanged Y-type zeolite*, $Hg^{2+}Y$, showed the best iodine adsorption efficiency of all the cation-exchanged zeolites tested other than silver. It exhibited an adsorption efficiency greater than 99.9 percent in a water-saturated atmosphere at 22°C and 23 cm/sec face velocity.

When methyl iodide was substituted for the airborne iodine species, the adsorption efficiencies of all the metal cation-exchanged zeolites other than silver decreased considerably. Of the various materials, only one showed an appreciable adsorption efficiency at high humidities; $Hg^{2+}Y$. At 125°C, 23 cm/sec and 90 percent relative humidity, an adsorption efficiency of 33.8 percent was found for $Hg^{2+}Y$. PbX shows some promise for methyl iodide adsorption when used in a heated adsorption bed(3).

Types, Shapes, and Sizes of Zeolites

Different types of zeolites have significantly different physical properties. An important property of zeolites is their Si/Aℓ ratio. The higher this ratio, the smaller the ion-exchange capacity, the harder the zeolite, and the more acid resistant the zeolite. Of the zeolites we have investigated, the X-type zeolite has the smallest Si/Aℓ ratio, ∿2.5; and the type we have designated as Z, which is a synthetic mordenite, has the highest ratio, 10. The X-type zeolite has an ion-exchange capacity about three times larger than that of the Z type. A comparison of the methyl iodide adsorption efficiencies of several different types and particle sizes of silver-exchanged zeolites is shown in Table II. Several other types of adsorbents are included for comparison purposes.

The effect of the degree of silver exchange in the zeolites is also shown in Table II. Only the silver ions near the surface of these materials are used in the adsorption process at face velocities near 25 cm/sec. The silver ions apparently tend to distribute themselves fairly uniformly in the particles during

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*Provided by the Molecular Sieve Department, Materials System Division, Union Carbide Corporation.

TABLE I

AIRBORNE ELEMENTAL IODINE ADSORPTION EFFICIENCIES OF METAL ZEOLITES

Material	Airborne Iodine Conc. (mg/m^3)	Temp. (°C)	Face Velocity (cm/sec)	Relative Humidity (percent)	Adsorption Eff. (percent)
PbX	5	22	23	98+	35.7
PbX	45	22	23	<5	99.9+
PbX	56	22	48	98+	5.2
PbX	25	90	46	98+	51.5
PbX	58	90	23	98+	67.2
PbX	69	90	23	<5	99.9+
CuX	5	22	23	98+	47.2
CuX	33	90	46	98+	54.0
CuX	75	90	23	98+	59.1
CuX	70	90	23	<5	99.1

the ion-exchange process. Satisfactory methods for surface silver exchanging the particles have not yet been devised.

The most often overlooked properties when comparing adsorption performance of different adsorbents are the particle size or size distribution and particle shape. Any increase to the exposed surface area will increase the adsorption efficiency; however, the extent of this increase is not always appreciated. Beads, extrudates, and pellets offer the smallest surface area and, thus, the smallest adsorption efficiencies. The granular materials, such as the ground zeolites and carbons, offer the greatest surface areas and, consequently, the highest efficiencies. The intra-particle surface area is, of course, also important but is generally a fixed property for a particular adsorbent. The methyl iodide adsorption efficiency for the AgX (14-18 Beads) compared with that for the AgX (12-14 Gran.) provides a good example of this phenomenon. Although the 14-18 mesh distribution beaded material is somewhat smaller than the 12-14 mesh granular material, the decontamination factors (DFs)* obtained with the 12-14 mesh granular silver zeolite were nearly 20 times greater. Other authors(5,6) have pointed out this effect, but it is still frequently not given sufficient consideration.

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*Decontamination Factor (DF) = $\frac{1}{\text{1-Adsorption Efficiency}}$

TABLE II

COMPARISON OF METHYL IODINE ADSORPTION EFFICIENCIES FOR SEVERAL TYPES AND SIZES OF ADSORBENTS

Conditions: 125°C, 25 cm/sec F.V., ∿ 0.1 $\mu g/m^3$ methyl iodide,

Material[a]	Degree of Silver Exchange (Percent)	Relative Humidity (Percent)	Adsorption Efficiency (Percent)	Decontamination Factor
AgX Zeolite (12-14 Gran.)[b]	>98	90	99.95	2000
Ag - AW300 (12-14 Gran.)[b]	∿60	91	79.00	4.8
Ag - AW500 (12-14 Gran.)[b]	∿90	90	94.81	19.2
AgZ Zeolite (12-14 Gran.)[c]	>98	90	91.83	12.2
AgX (10-20 Beads)[d]	>95	90	97.50	40.0
AgX (10-20 Beads)[d]	∿25	91	44.71	1.8
AgX (10-20 Beads)[d]	∿50	92	75.63	4.1
AgX (8-12 Beads)[d]	>95	90	92.97	14.2
AgX (10-16 Beads)[b]	>95	90	97.11	10.1
AgX (14-18 Beads)[d]	>95	90	99.04	104
AgX (12 Beads)[d]	>95	90	94.87	19.5
AgX (14 Beads)[d]	>95	91	95.14	20.6
AgX (16 Beads)[d]	>95	90	97.98	49.5
NACAR GX 135 (14-22 Gran.)[e]	-	90	96.39	27.5
KI-I_2 Imp. Carbon (8-16 Gran.)[f]	-	90	98.33	59.9
AgX (12-14 Gran.)[b]	>98	98+	99.90	1000
AgX (10-20 Beads)[d]	>95	98+	83.76	6.2
NACAR GX 135 (14-22 Gran.)[e]	-	98+	44.62	1.8
KI-I_2 Imp. Carbon (8-16 Gran.)[f]	-	98+	90.70	10.1

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[a] The indicated mesh size distribution refers to U.S. Standard Series.

[b] Products of Molecular Sieve Department, Union Carbide Corporation.

[c] Products of Norton Chemical Company.

[d] Products of Davison Chemical, W. R. Grace.

[e] Product of North American Carbon, a silver impregnated alumina-silicate base support material.

[f] MSA 85851, Mine Safety Appliance Company.

Environmental Effects

Prolonged Exposure to Steam Atmosphere

To evaluate the effects of prolonged exposure of silver zeolites to saturated steam atmospheres, a series of tests were conducted in which the methyl iodide adsorption efficiencies of several silver-exchanged zeolites were measured after their exposure to varying amounts of saturated steam. The results of these tests are presented in Table III. By raising the temperature of the preequilibration saturated-steam atmosphere to 139°C, the AgX zeolite (12-14 Gran.) lost about 0.4% to about 99.5 percent adsorption efficiency compared with about 99.9 percent in 98+ percent relative humidity atmospheres at 125°C and about the same face velocity. However, when the preequilibration time was extended to 5 hrs, the adsorption efficiency fell to about 66 percent. The KI-I_2 impregnated carbon faired even worse. Under the same conditions, its efficiency dropped to about 37 percent. It is unlikely that any solid radioiodine adsorbent with a high adsorption efficiency will be able to withstand these tests without considerable loss in adsorption efficiency.

Another purpose of this test was to determine any physical deterioration of the zeolite after prolonged exposure to saturated steam. After completion of the tests, an examination of the AgX zeolite adsorbent beds showed a slight "caking" after the 5-hr saturated steam exposure at 128°C, but the physical (crush) strength appeared to remain essentially the same as before the exposure. In a subsequent series of tests, the AgX zeolite (12-14 Gran.) was exposed to a 90 percent relative humidity atmosphere, 90°C, and at a 25 cm/sec face velocity for periods of 24 to 30 hrs without any apparent deleterious effects to adsorption efficiency or physical characteristics compared with one-hour exposed samples.

The X-type zeolite contains 15 to 20 percent inert clay binder. It has not yet been determined whether the observed caking effect was a result of the binder or zeolite crystal degradation. Some of the zeolites we have obtained contained binders which collapsed when exposed to water. However, the Ag-AW500 zeolite appeared similar to AgX zeolite after the 5-hr exposure. Although the binders in the X-type and AW500 zeolites are supposedly the same, the basic structure of the AW500 material is harder and more acid resistance than that of the X-type zeolite. The AgZ zeolite, a self-bonded zeolite, showed no apparent signs of caking.

TABLE III

ADSORPTION EFFICIENCIES FOR METHYL IODIDE FOR ADSORBENTS AFTER EXPOSURE TO HIGH TEMPERATURE SATURATED STEAM

Material	Preequilibration Time (hrs)	Purge Time (hrs)	Temp. (°C)	Face Velocity (cm/sec)	Adsorption Efficiency (percent)[a]
AgX Zeolite (12-14 Gran.)	1	0.25	139	26	99.49
AgZ Zeolite (12-14 Gran.)	1	0.25	139	26	86.44
Ag-AW500 Zeolite (12-14 Gran.)	1	0.25	140	25	88.58
AgX Zeolite (12-14 Gran.)	<1/6	3	128	28	92.01
AgX Zeolite (12-14 Gran.)	5	0.25	127	35	28.77
AgX Zeolite (12-14 Gran.)	5	0.25	128	23	66.22
KI-I_2 Carbon (8-16 Gran.)	5	0.25	128	26	36.59
AgX Zeolite (10-20 Beads)	5	0.25	127	23	24.29
Ag-AW500 Zeolite (12-14 Gran.)	5	0.25	127	23	20.43

(a) Adsorption efficiencies are given for 5-cm deep adsorption beds.

Radiation Exposure

Samples of three different types of silver zeolites were exposed to gamma radiation at a rate of about 10^6 Rad/hr for a total exposure of 10^8 Rads. The methyl iodide adsorption efficiencies of these materials were then tested at 125°C, 90 percent relative humidity, and 23 cm/sec face velocities. The results of these tests showed no measurable change in methyl iodide adsorption efficiencies for AgX, Ag-AW500, and AgZ zeolites after the irradiation.

Contaminant Gas Exposure

The methyl iodide adsorption efficiency of AgX zeolite (12-14 Gran.) was measured after its exposure to a number of possible contaminant gases. The results of these tests are given in Table IV. The procedure used during this series of tests was as follows: (1) the bed of AgX zeolite was preequilibrated for 1 hr at 90°C and 90 percent relative humidity air at the indicated volume percent of contaminant gas; (2) ^{131}I containing methyl iodide was added to the water vapor-air-contaminant gas mixture for another hour; (3) the methyl iodide and contaminant gas flows were stopped, and the water vapor-air mixture flow was continued for about 1 hr; and (4) the adsorbent, backup, and safety beds were cooled, disassembled and counted. Despite the unrealistically high levels of contaminant gases, only two had particularly serious effects on the adsorption efficiency of the AgX zeolite; H_2S and SO_2. In similar tests while evaluating the influence of contaminant gases on the elemental iodine adsorption efficiency of AgX zeolite, elemental iodine adsorption efficiencies of greater than 99.9 percent were obtained even in the presence of H_2S and SO_2. Ill effects caused by high concentrations of NO_2 and possibly propane are also indicated. Long-term tests at much lower concentration of several of these contaminant gases are clearly needed to properly evaluate their effects.

TABLE IV

THE EFFECTS OF CONTAMINANT GASES ON THE METHYL IODIDE ADSORPTION EFFICIENCY OF SILVER ZEOLITE

Conditions: 90°C, 90% R. H., 23 cm/sec F. V., and 0.1 $\mu g/m^3$ Methyl Iodide

Contaminant Gas	Contaminant Conc. (Vol. Percent)	Adsorption Efficiency (Percent)
O_2	10	99.94
CO_2	10	99.95
NO_2	10	99.79
H_2	1.9	99.97
H_2S	0.06	42.20
SO_2	1.9	31.48
Propane	10.0	99.89
Hexone	2.2	99.99
Kerosene	0.05	99.91

Laboratory Air Exposure

Laboratory ambient air was drawn through a 2.5-cm diameter by 5-cm long adsorbent bed of AgX zeolite (12-14 Gran.) for a period of about 6 months at a face velocity of approximately 125 cm/sec. The adsorbent bed sample and holder were transferred intact to the iodine species test apparatus. The adsorbent was preequilibrated at 90 percent relative humidity, 125°C, and 25 cm/sec face velocity before the addition of methyl iodide. At these conditions, the methyl iodide adsorption efficiency was determined to be 99.5 percent, about 0.4 percent lower than unexposed AgX zeolite (12-14 Gran.) at the same test conditions.

Concentration Effects

During the course of our investigations in the evaluation of AgX zeolite, the results of several of our experiments indicated that the adsorption efficiency of silver zeolite was a function of the airborne methyl iodide concentration at very low concentrations. More specifically, the methyl iodide adsorption efficiency of AgX zeolite appeared to fall rather significantly below a concentration level of about 10^{-6} µg/m^3 at 90°C, 90 percent relative humidity, and 25 cm/sec face velocity. A comparison with several other radioiodine species adsorbents indicated the same pattern.

The loss of adsorption efficiency per unit length of adsorbent material is a common observation. Kovach(6) observed this phenomenon and noted the length of the adsorption mass transfer zone is inversely proportional to the concentration of the adsorbate. Therefore, under similar conditions, deeper adsorption beds are required to remove adsorbates at lower concentrations at the same efficiencies than are required at the higher adsorbate concentrations. The data of many workers with several types of adsorbents illustrate this phenomenon; Adams and Browning(7) and Adams and Ackley(8) for elemental iodine and Collins et al(5), and Schuttelkopf and Wilhelm(10) for methyl iodide. However, the reverse situation is also frequently observed, particularly where the adsorbent bed has been poisoned by a contaminant gas. The data of Schuttelkopf and Wilhelm(10,11) illustrate this effect.

These observations raised the questions of (1) how capable are the commonly used radioiodine adsorbents in removing the various radioiodine species at low concentrations; (2) how are their efficiencies affected by contaminant gases, including water vapor, and at what concentration levels; and (3) how deep must the adsorbent bed be to obtain the required DF for a given set of conditions?

In view of the present low radioiodine airborne levels as established in 10 CFR 20, Appendix B, of 1 x 10^{-10} µci/cc or 8 x 10^{-10} µg/m^3 for soluble iodine ^{131}I species in an unrestricted area and the possibility that these values may be set even lower, a thorough understanding of the performance of radioiodine adsorbents is clearly needed.

Obviously, the number of variables involved in answering these questions is too large to allow collection of all of the answers at once. Our first choice was to restrict the initial investigations to the following conditions: (1) a single temperature - 90°C, (2) the intentional use of a single contaminant gas - water vapor, (3) one iodine species - methyl iodide, and (4) two face velocities - 25 and 50 cm/sec. There are several reasons for selecting methyl iodide for the low concentration studies. First, methyl iodide is generally easier to handle than elemental iodine because there is less plate-out and less chance of cross contamination. Second, Keller et al(12) indicate the predominant airborne iodine species below about 10^{-6} µg/m^3 is probably organic iodides. However, Kabat(13) and Keller et al(14) have observed that existence of airborne hypoiodous acid is possible under such conditions, and that its stability is greater than has previously been assumed. Also, Kabat(13) has observed the airborne hypoiodous acid is more difficult to remove than the other iodine species when conventional radioiodine adsorbents are used.

Experimental

To obtain more complete information from the adsorption tests, 5-cm diameter by 10-cm long adsorption beds were used in which four 2.5-cm sections were separated by stainless steel wire screens. A HEPA fiber glass filter was used on the down-flow side of the last 2.5-cm section. In some of the tests, about the last 20 percent, an equivalent amount of adsorbent was weighed each time the beds were filled to ensure uniform filling of each segment. Three different adsorbents were tested and some of these with a different particle shape and size distribution. These adsorbents were AgX zeolite, 12-14 mesh granular; AgX zeolite, 10-20 mesh beads; KI-I_2 impregnated carbon, 8-16 granular; and TEDA impregnated carbon, 8-16 mesh granular. Two different concentration ranges and two face velocities were used. The methyl iodide was prepared using essentially carrier free ^{131}I ($\sim$20 percent ^{131}I) and stored in a gas bomb with helium as a carrier gas.

Preequilibration times for all adsorbents were 18 to 20 hours, and loading times were from 1 to 6 hours depending on the concentration range being investigated. Purge times of about an hour were used in all tests. A heated 5-cm diameter by 10-cm long backup bed filled with KI-I_2 impregnated carbon followed the adsorption bed. Several condensers were used after the heated backup bed to cool the effluent to 25°C. Following the condensers was a 7.5-cm diameter by 5-cm long safety trap filled with TEDA impregnated carbon. The residence time of the effluent in the safety bed was on the order of 1 to 2 seconds. At the completion of a test, the contents of each 2.5-cm section of adsorbent bed were transferred to plastic vials for counting. The contents of the backup and safety beds were also transferred to plastic vials after being evenly split to ensure each vial contained about the same amount of material as the 2.5-cm sections. The contents of each of the vials were thoroughly mixed before being counted. Background counts were subtracted from the counts for each of the four adsorbent bed sections and the individual adsorption efficiencies calculated. After the appropriate background corrections, counts of each portion of the backup and safety beds were summed to get individual totals for both the backup and safety beds. A sodium iodide crystal detector, single channel analyzer, and associated equipment were used in the radioactivity measurements. A discriminator window setting of 60 Kev was used in the integration of the ^{131}I 364 Kev peak. The efficiencies of the analyzer and detector were periodically checked with fresh ^{131}I standards, and occasionally, samples were counted with a multichannel pulse height analyzer to watch for unexpected radioactive contaminants.

A calculation and error analysis scheme was written as a computer program which allows the calculation of the following data for each run: (1) the adsorption efficiency for each 2.5-cm section of the adsorbent bed, and the backup bed - the safety bed is assumed to be 100 percent efficient; (2) the error limits in the calculated adsorption efficiencies associated with the radioactive counting statistics; (3) the individual section DFs; (4) the cumulative adsorption bed efficiencies; and (5) the individual section and bed airborne iodine species inlet concentrations. The latter is determined by the radioactivity measured in the various sections with the appropriate corrections for radioactive decay.

Results and Conclusions

The results of this series of tests are presented for 25 and 50 cm/sec face velocities in Tables V and VI, respectively. A graphic display comparing the DFs of the various adsorbents at 25 cm/sec face velocity and initial iodine concentrations of about 1 μg/m^3 is presented in Figure 1. This figure shows AgX zeolite

TABLE V

DECONTAMINATION FACTORS FOR VARIOUS ADSORBENTS AS A FUNCTION OF METHYL IODIDE CONCENTRATION AND BED DEPTH

Conditions: 90°C, 90% R.H., 25 cm/sec F.V.

Material	Bed Depth (cm)	Individual Section DFs	Cumulative DFs	Calculated Total DF Based on First-Half DF
Initial Methyl Iodide Concentration - 0.1 to 10 $\mu g/m^3$				
AgX (10-20 Beads)	2.5	6.4	6.4	-
	5	6.6	42	-
	7.5	6.7	280	-
	10	6.8	$1.9x10^3$	$1.8x10^3$
KI-I$_2$ Impregnated Carbon (8-16)	2.5	7.3	7.3	-
	5	6.5	47	-
	7.5	6.8	320	-
	10	7.2	$2.3x10^3$	$2.2x10^3$
TEDA Impregnated Carbon (8-16)	2.5	17	17	-
	5	19	330	-
	7.5	19	$6.0x10^3$	-
	10	10	$6.0x10^4$	$1.1x10^5$
AgX (12-14 Gran.)	2.5	42	42	-
	5	39	$1.6x10^3$	-
	7.5	13	$2.3x10^4$	-
	10	5.1	$1.2x10^5$	$2.6x10^6$
Initial Methyl Iodide Concentration - 10^{-5} to 10^{-4} $\mu g/m^3$				
AgX (10-20 Beads)	2.5	9.7	9.7	-
	5	8.1	79	-
	7,5	3.0	245	-
	10	1.3	313	$6.2x10^3$
KI-I$_2$ Impregnated Carbon (8-16)	2.5	6.8	6.8	-
	5	6.6	45	-
	7.5	5.8	260	-
	10	3.7	960	$2.0x10^3$
TEDA Impregnated Carbon (8-16)	2.5	20	20	-
	5	22	450	-
	7.5	11	$4.8x10^3$	-
	10	2.6	$1.1x10^4$	$2.0x10^5$
AgX (12-14 Gran.)	2.5	37	37	-
	5	26	990	-
	7.5	3.2	$3.5x10^3$	-
	10	1.2	$4.1x10^3$	$9.8x10^5$

TABLE VI

DECONTAMINATION FACTORS FOR VARIOUS ADSORBENTS AS A FUNCTION OF METHYL IODIDE CONCENTRATION AND BED DEPTH

Conditions: 90°C, 90% R.H., 50 cm/sec F.V.

Material	Bed Depth (cm)	Individual Section DFs	Cumulative DFs	Calculated Total DF Based on First-Half DF
Initial Methyl Iodide Concentration - 0.1 to 10 $\mu g/m^3$				
AgX (10-20 Beads)	2.5	3.2	3.2	-
	5	3.4	11	-
	7.5	3.4	37	-
	10	3.2	120	120
$KI-I_2$ Impregnated Carbon (8-16)	2.5	2.6	2.6	-
	5	2.5	6.4	-
	7.5	2.8	18	-
	10	3.0	55	41
TEDA Impregnated Carbon (8-16)	2.5	4.7	4.7	-
	5	5.7	27	-
	7.5	5.3	140	-
	10	3.9	560	710
AgX (12-14 Gran.)	2.5	9.2	9.2	-
	5	9.1	83	-
	7.5	8.3	700	-
	10	6.6	4.6×10^3	7.0×10^3
Initial Methyl Iodide Concentration - 10^{-5} to 10^{-4} $\mu g/m^3$				
AgX (10-20 Beads)	2.5	3.3	3.3	-
	5	3.2	10	-
	7.5	3.1	32	-
	10	2.6	84	110
$KI-I_2$ Impregnated Carbon (8-16)	2.5	2.5	2.5	-
	5	2.6	6.4	-
	7.5	2.5	16	-
	10	2.1	34	42
TEDA Impregnated Carbon (8-16)	2.5	5.1	5.1	-
	5	6.4	33	-
	7.5	6.1	190	-
	10	3.6	690	1.0×10^3
AgX (12-14 Gran.)	2.5	8.0	8.0	-
	5	7.9	63	-
	7.5	7.5	470	-
	10	4.6	2.2×10^3	4.0×10^3

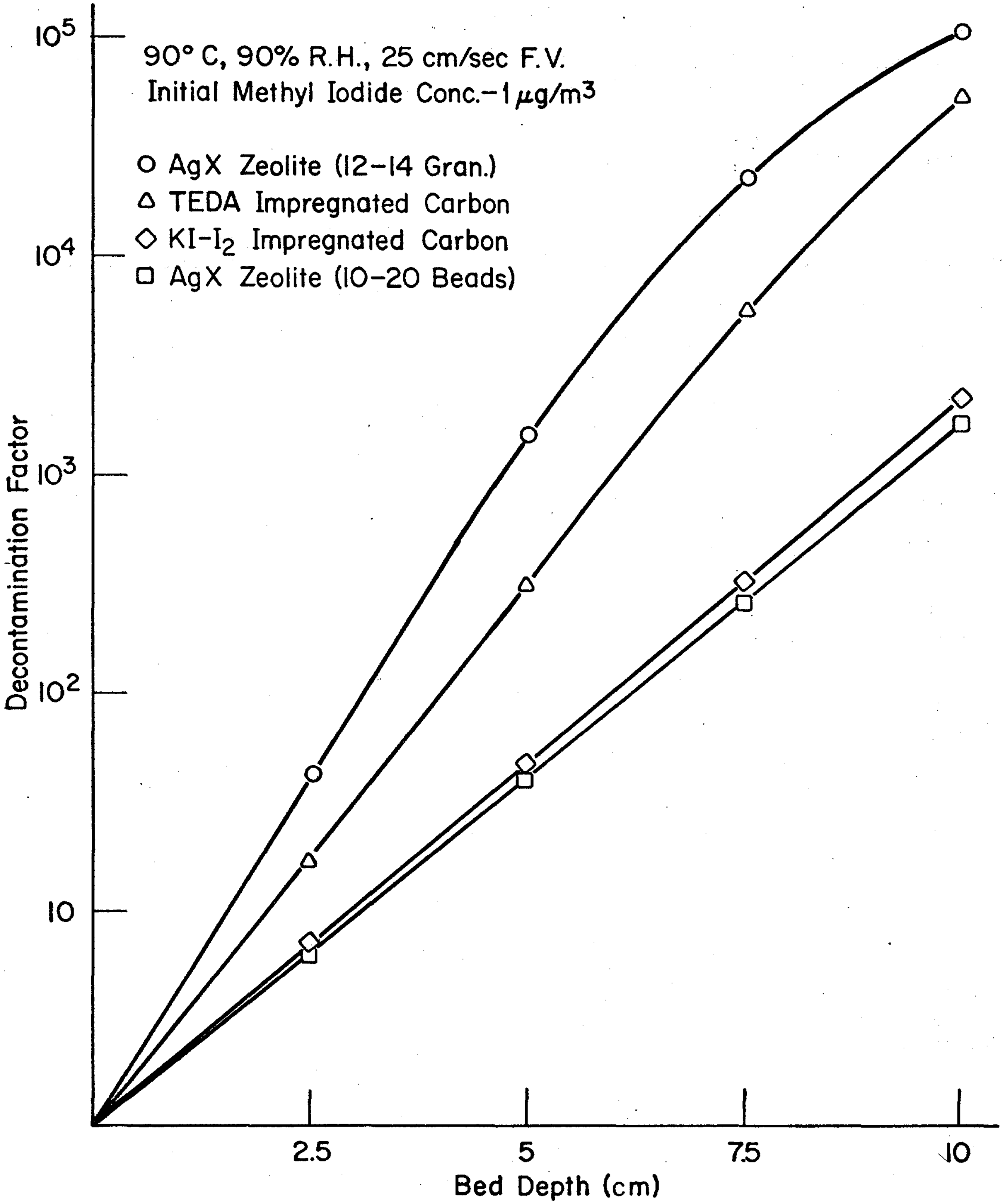

Figure 1. Methyl Iodide Decontamination Factors for Several Adsorbents as a Function of Adsorbent Bed Depth.

(12-14 Gran.) to be the most efficient of the adsorbents tested at the indicated conditions. The TEDA impregnated carbon was found to be nearly as efficient as the silver zeolite (12-14 Gran.), and the KI-I_2 impregnated carbon and the AgX zeolite (10-20 Beads) were nearly equal. The decrease in the DFs in the latter sections of the adsorbent bed prompted further studies at lower initial methyl iodide concentrations. The most pronounced effect was noted with AgX zeolite (12-14 Gran.) and is shown in Figure 2. When the initial methyl iodide concentration was in the range of 10^{-5} to 10^{-4} $\mu g/m^3$, the DFs in the second half of the 10-cm bed were reduced drastically at a face velocity of 25 cm/sec. The airborne methyl iodide concentration after the first 5-cm of adsorption bed is in the range 10^{-7} to 10^{-8} $\mu g/m^3$. The decrease in DFs along the length of adsorbents bed was much less at 50 cm/sec face velocity.

The apparent concentration dependency of the adsorbent bed efficiencies is noticeable in all of the adsorbents at the lower concentration range. However, in the higher concentration range, the concentration effect on the adsorption efficiencies of only the TEDA impregnated carbon and the AgX zeolite (12-14 Gran.) are apparent even at higher concentration levels than were expected from the results of the lower concentration tests. This is consistent with Kovach's(6) observation that the adsorbent efficiency per unit length of adsorbent bed is dependent on the adsorbate concentration. However, the DFs of the last sections of the adsorbent beds of the ~ 1 $\mu g/m^3$ concentration level tests were lower than the DFs of the first sections of the adsorbent beds at the 10^{-5} $\mu g/m^3$ concentration level tests even though the inlet concentrations of the last sections were higher than 10^{-5} $\mu g/m^3$.

One interesting comparison that can be made with the several types of adsorbents is related to the performance at different face velocities. The DF of a 10-cm adsorption bed of AgX zeolite (12-14 Gran.) at 50 cm/sec is nearly 100 times greater than a 5-cm bed of KI-I_2 impregnated carbon at 25 cm/sec and greater than 10 times that of a 5-cm bed of TEDA impregnated carbon. A similar comparison, but not quite as impressive, can be made with the AgX zeolite (10-20 Beads). The adsorption efficiencies of the zeolites are not as seriously affected by increased face velocities as are the impregnated carbons; however, the increased operating cost of added adsorbent bed pressure drop should be included for a more accurate comparison.

Before discussing the conclusions drawn from these experiments, several comments are in order regarding the reliability and reproducibility of the tests. Based on the counting error analysis, all data were rejected in which the error analysis scheme indicated errors larger than about ± 25 percent relative to the calculated values. There was one exception to this; the last segment of the AgX zeolite (12-14 Gran.) in which the calculated error limits were determined to be in the range of 50 to 100 percent relative. Based on the 25 percent maximum error, this places a lower concentration detection limit in the range of 10^{-7} to 10^{-8} $\mu g/m^3$ for methyl 131-iodide. The reproducibility of test conditions (relative humidity and air flow) are on the order of two percent, and the errors associated with adsorbent bed filling and uniform packing are probably slightly larger than two percent. All but one of the tests, the 10^{-5} $\mu g/m^3$ test with AgX zeolite (10-20 Beads), are averages of at least duplicate or greater tests. No attempts were made to remove the ambient airborne iodine species from the purge gas.

Several factors can be identified as contributors to the apparent loss of adsorption efficiency. Billard et al(15) have shown an elemental iodine

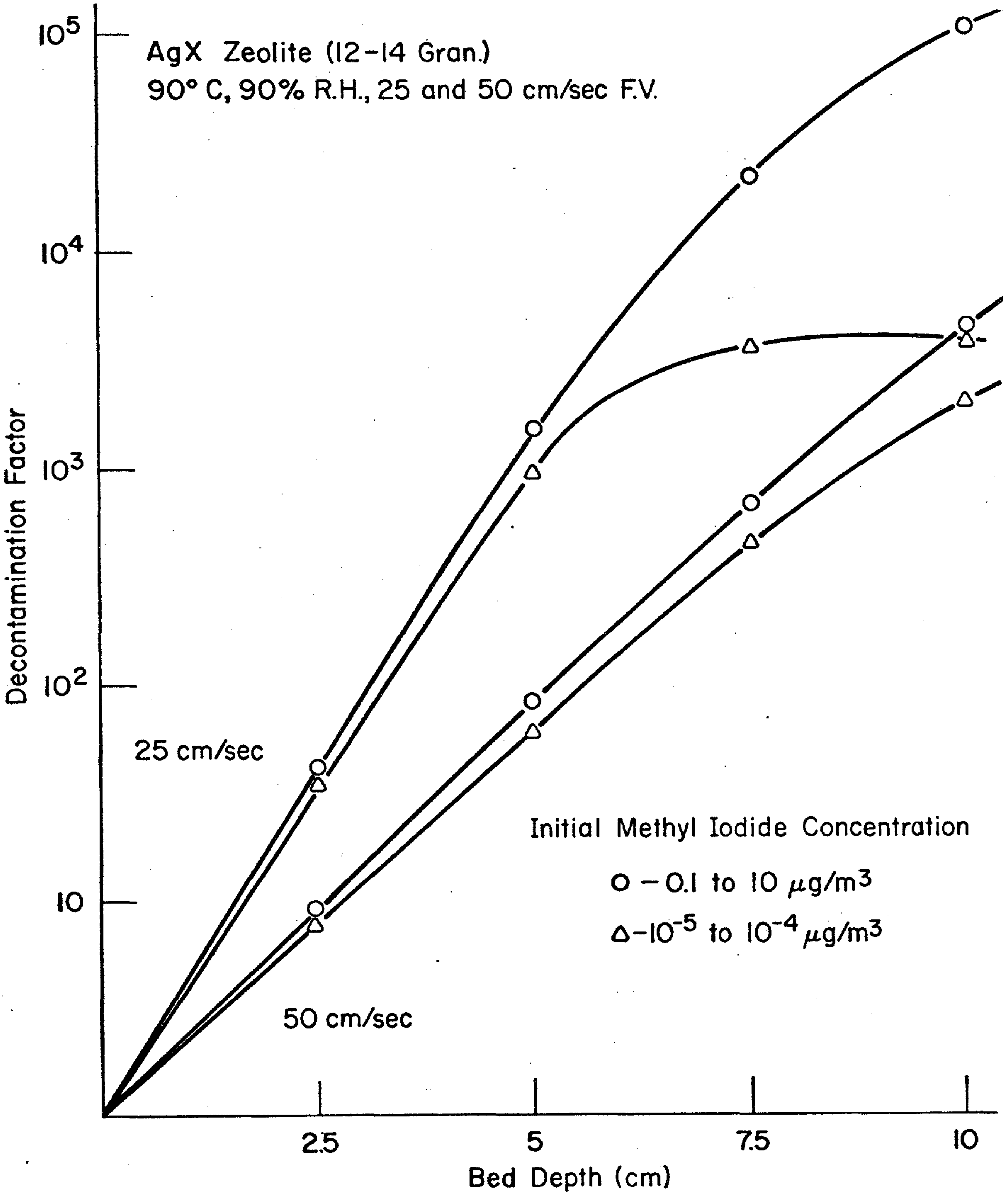

Figure 2. Methyl Iodide Decontamination Factors for Silver Zeolite as a Function of Adsorbent Bed Depth, Methyl Iodide Concentration, and Face Velocity.

concentration dependency by activated carbon in the presence of water vapor over the range of their studies ($\sim 10^{-5}$ to 100 $\mu g/m^3$). They attributed the loss in adsorption efficiency, a factor of about 10^3 in a 5-cm deep adsorption bed, to a probable change in iodine species. A change in iodine species to a form not as readily adsorbed by the adsorbents tested as methyl iodide is certainly a possible explanation for the observed effect reported here. Another possible explanation could be the result of trace impurities which are known to be present in the atmosphere at much higher concentration than the principal adsorbate being discussed. For this reason, an attempted explanation in terms of pure component adsorption isotherms would be fruitless. Especially when we know there are so many interacting variables which affect the adsorption isotherms, such as temperature, pressure, moisture content, impurity concentrations, species transformations, intra-particle diffusion rates, and others.

Based on the results of tests presented in Table V and VI and the above considerations, the following conclusions were made:

1. There is, at least, an apparent adsorbate concentration dependency of the adsorbent efficiency at airborne methyl iodide concentrations below about 1 $\mu g/m^3$.

2. This effect is more pronounced the more efficient the adsorbent material and under conditions that favor high adsorbent efficiencies.

3. The cause of the variable adsorption efficiency per unit length of adsorbent bed is not a simple relationship with one or two variables, but rather a complex one with many variables such as adsorbate concentration, moisture content, concentration of contaminant gases, adsorbent efficiency, face velocity, particle size and shape, temperature, chemical species of the adsorbate, and probably many more.

4. Regardless of the cause of the observed effect, its presence could have far reaching consequences on our theories of efficient adsorbent bed design and even in our philosophy on the extent of radioiodine removal from nuclear facility effluents.

When one considers the estimated background of natural iodine is on the order of 10^{-3} $\mu g/m^3$ for unpolluted air(16), the importance of removing the radioiodine from the most concentrated effluents possible becomes quite clear. The cost of removing radioiodines from ambient air in nuclear facilities to the levels required may be prohibitive. Therefore, it is imperative for us to understand the capabilities and limitations of the adsorbent systems over a wide range of possible operating conditions to ensure efficient removal before dilution. The shortcomings of shallow, 5-cm or less, adsorption beds are apparent. Even 5-cm adsorption beds with recirculation are probably inadequate for many operating conditions. New, more efficient adsorption bed designs are needed. Whatever these new designs may be, we feel that the high adsorption efficiencies, high resistance to poisoning, high temperature operability, and high loading capacities of metal-exchanged zeolites will contribute significantly in the development of improved radioiodine adsorption technology.

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DISCUSSION

KOVACH: Your slide showing particle size effect and particle shape effect points out something. At these velocities, it is external mass transfer that is rate controlling. This helps deeper beds and higher velocity beds, does it not?

PENCE: Yes.

KOVACH: When you showed your contaminant effects, were these in air or in nitrogen?

PENCE: Air.

KOVACH: With regard to your later comment on decontamination efficiencies, did you include your particulate counts or were they counted separately?

PENCE: We did not precede the adsorption bed with particulate filters. These were only at the end of the adsorption bed and included in the fourth bed.

WILHELM: When we only encounter this penetrating compound from artificially-made iodine (for example, from the reaction of dimethylsulfate and potassium iodide to generate methyl iodide or from the oxidation of potassium iodide), should we continue to be guided by these results? If we continue the present work with iodine from a real reactor, or from a reprocessing plant, we may run into problems because we don't use the right source, i.e., we may generate problems we don't have or overlook problems we do have.

PENCE: I don't think we can exclude the possibility that we may be producing artificial components in the preparation of our methyl iodide. However, I think that the results reported in Keller's paper and those reported by others on operating adsorbent beds are similar to what we see in the laboratory. Therefore, we must be generating articial components there, too. We have not observed any definite evidence that we are producing significant numbers of artificial compounds in our laboratory preparation of methyl iodide. The work that Kabat reported at the Health Physics Meeting in Las Vegas (Reference 13 in our paper) is a good example of mixed iodine species adsorption operational problems.

TESTING OF IODINE FILTER SYSTEMS UNDER NORMAL AND POST-ACCIDENT CONDITIONS

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Abstract

The method used in the German Federal Republic for testing iodine filters in nuclear installations includes testing of the adsorber material under simulated normal operating and post-accident conditions, and in-place tests of the whole filter system. The interval between in-place tests is extended by the use of by-pass adsorber beds fitted parallel to the original iodine adsorber bed to get information with respect to aging and poisoning of the adsorber material. Test results will be given for filter systems with small and large bed depths. The differential removal efficiency of the successive charcoal layers in deep bed adsorbers, including the effects of aging and poisoning as a function of bed depth and air-change, will be discussed.

A very recently built test facility will be desribed for testing of original off-gas filter components. The test facility is equipped to perform tests of demisters, HEPA-filters, iodine adsorbers and other components operating under simulated normal and post-accident conditions of a gas-cleaning system in water cooled reactors. The operational conditions which can be reached with this installation are: gas flow up to 2000 m^3/h, temperatures up to 200°C, and pressures up to 5 at ($\sim$75 psi). Tests can be performed with dry and wet air, air-steam mixtures and pure steam. The relative humidity can be controlled within ± 3 %. The effect of condensation and the removal of droplets by filter components can be measured by use of a water spray generator at temperatures up to 150°C. The generator is dimensioned for simulating condensation rates which correspond to a dew-point difference of up to 100°C between the air-steam mixture in the reactor containment and the off-gas upstream of the filter system.

I. Introduction

The types of iodine filters used in Germany for off-gas cleaning from reactor stations include pleated-bed adsorber cells (bed depth up to 5 cm) and container type filters with bed depths up to 50 cm. The pleated-bed adsorber cells are designed for low pressure drop together with a relatively high air flow capacity. The major points of view for the construction of container-type filters are: large bed depth and minor possibility of mechanical leaks by avoiding gaskets and seal pads.

It can be concluded from experience that the operating time of an iodine filter is normally not limited by the increasing amount of radioactivity in the adsorber material but in almost all cases by aging and poisoning effects. Aging experiments were performed over extended periods of time to get useful data for the dimensions of the charcoal beds of iodine filters.

II. Aging of Different Iodine Adsorber Materials in Air of an Industrial Environment

Aging rigs for adsorber materials were constructed, including a HEPA-filter upstream of the adsorber material, eight samplers in parallel, each sampler containing adsorber material in 6 successive test beds of 2.5 cm depth, and a blower downstream of the samplers. The airflow through each sampler is controlled by a flowmeter. These aging rigs were operated in the air of nuclear installations and at a place proposed as site of a reactor station. Because this site is located in an industrial area very near to several chemical factories, oil fired power plants, etc. we feel that the aging and poisoning of the adsorber material should be relatively serious and the data derived for the dimensions of the iodine adsorber beds should be on the conservative side. The samplers of the aging rigs were removed after various periods of operation and the remaining removal efficiencies for methyl iodine as the test medium were tested in well controlled laboratory experiments in an apparatus described earlier (1). In the following paragraphs the term "aging" includes "weathering and poisoning."

The standard test conditions for charcoal samples after aging were: wet air as the sweep gas, atmospheric pressure, 30°C, 100 % R.H. and a loading of appr. 75 μg CH_3I/g of charcoal (calculated for 10 cm bed depth); for zeolite and Ag-KTC samples (2) also air of 30°C was used as sweep gas, the relative humidity was 70 % and the loading 1.5 mg CH_3I/g of these inorganic adsorber materials.

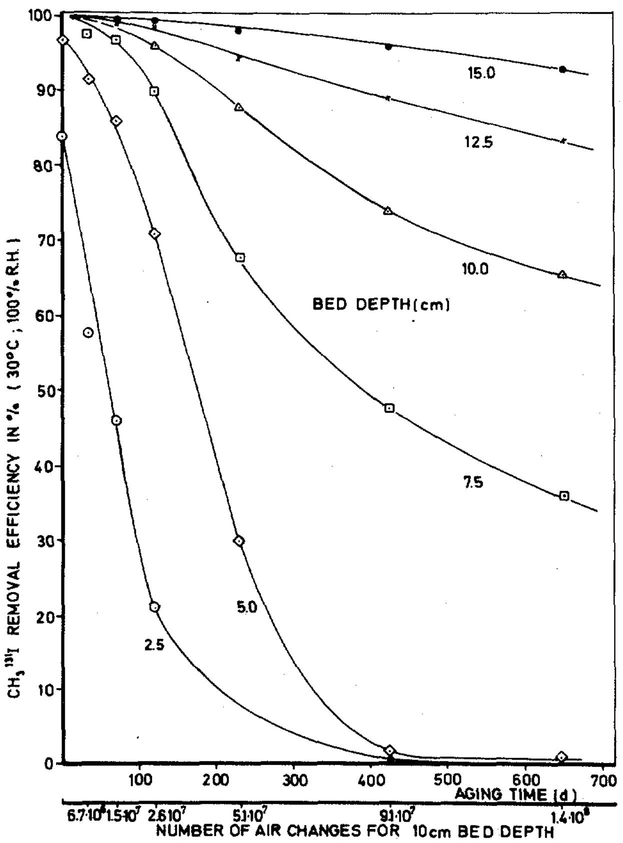

Fig.1 Aging of impregnated charcoal (NORIT RKI-1) in air from industrial environment

The data of the runs are given in Figs. 1 - 5. In Fig. 1 the remaining removal efficiencies for $CH_3{}^{131}I$ after aging are shown for a KI-impregnated charcoal of the type Norit RKI-1. This is an extruded charcoal with a pellet diam. of 1 mm. During aging the superficial velocity of the air was normally 25 cm/s. The plots in Fig. 1 show a relatively fast decrease of removal efficiency for low bed depths, but a much higher resistance against aging effects for larger bed depths.

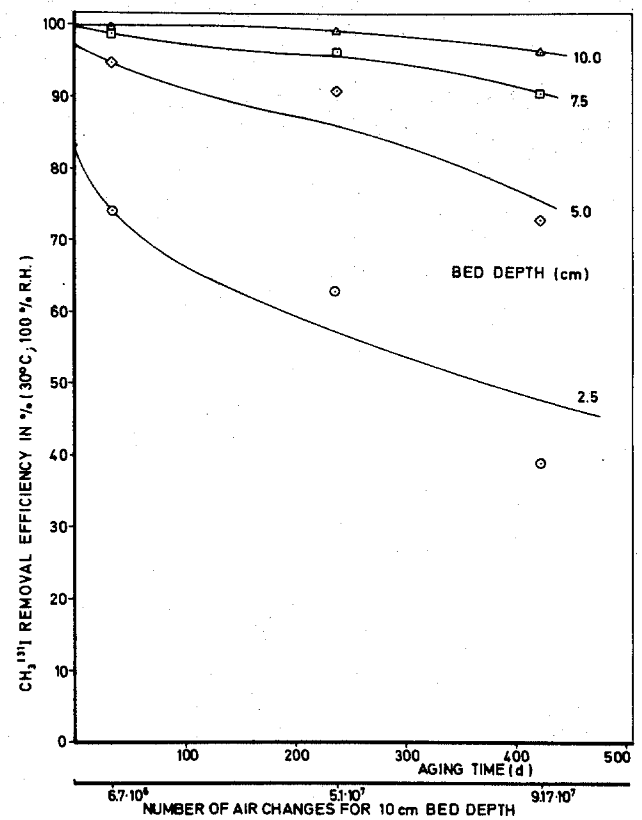

Fig. 2 Aging of impregnated charcoal (NORIT RKI-1) in prefiltered air

In Fig. 2 the removal efficiency of the same charcoal under identical conditions is given for charcoal from samplers which were fitted with two charcoal beds of unimpregnated charcoal of the type Norit RLX-1 upstream of the RKI-1 test beds. Comparison of Fig. 1 and Fig. 2 makes clearly visible the protecting effect of the unimpregnated charcoal beds.

Tab. I AGING OF KI-IMPREGNATED CHARCOAL IN AIR OF AN INDUSTRIAL ENVIRONMENT

Charcoal: Norit RKI-1 in 6 successive test beds of 2.5 cm depth

Aging medium: Air with impurities, filtered by a HEPA-filter, R.H. < 100 %, superficial air velocity ≈ 25 cm/s

Sweep gas (during testing in the laboratory): wet air, atmospheric pressure 30°C, 100 % R.H., superficial air velocity: 25 cm/s, stay time per test bed: 0.1 s

Duration of gas flow: Preconditioning ≥ 20 h, CH_3I-injection: 1 h, gas flow continued for several hours in addition.

Test medium: $CH_3{}^{131}I + CH_3{}^{127}I$

Number of air-changes per test bed	Aging time in d	$CH_3{}^{131}I$ Removal Efficiency (η differential) in %					
		bed 1	bed 2	bed 3	bed 4	bed 5	bed 6
0	0	83.2	84.4	84.8	83.4	-	-
$2.7 \cdot 10^7$	30	58.4	77.9	80.4	84.3	79.2	76.2
$6.0 \cdot 10^7$	70	46.6	76.5	81.6	82.4	81.5	68.0
$1.0 \cdot 10^8$	120	20.5	62.8	66.4	69.3	69.0	72.5
$2.0 \cdot 10^8$	240	0.5	29.2	54.2	61.3	60.8	58.6
$3.7 \cdot 10^8$	424	0.3	1.4	47.3	51.2	57.2	62.8
$5.6 \cdot 10^8$	649	0.2	0.9	35.3	45.8	52.3	57.2
Number of air-changes per 10 cm of bed depth	Aging time in d	$CH_3{}^{131}I$ Removal Efficiency (η integral) in %					
		Bed depth in cm					
		2.5	5.0	7.5	10.0	12.5	15.0
		Stay time in s					
		0.1	0.2	0.3	0.4	0.5	0.6
0	0	83.2	97.4	99.60	99.93	-	-
$6.7 \cdot 10^6$	30	58.4	90.8	98.2	99.72	99.94	99.986
$1.5 \cdot 10^7$	70	46.6	87.4	97.7	99.59	99.92	99.980
$2.6 \cdot 10^7$	120	20.5	70.4	90.1	97.0	99.05	99.74
$5.1 \cdot 10^7$	240	0.5	29.6	67.7	87.5	95.11	98.0
$9.1 \cdot 10^7$	424	0.3	1.6	48.2	74.7	89.2	96.0
$1.4 \cdot 10^8$	649	0.2	1.1	36.0	65.3	83.4	92.9

Tab. I indicates the exact data obtained from the experiments used for Fig. 1. Tab. I includes also the removal efficiencies for each of the 6 successive charcoal beds (differential removal efficiency, η differential). The decrease in the differential removal efficiencies can be correlated directly to the degree of aging depending on the bed depth. For the first and the second test beds there is a sharp decrease in removal efficiency as a function of the time of operation.

The time of test bed operation for an increase by a factor of 5 of penetration was 120 days for the first and 300 days for the second test bed. The third test bed, protected from test beds 1 and 2, showed an increase by a factor of 2 of penetration in 120 days and only reached a factor of 4 at the end of the test runs after 649 days.

From Fig. 1 and Tab. I it can be concluded that larger bed depth gives much more time of operation as can be expected from the increased amount of charcoal used. So the removal efficiency for CH_3I dropped down to 90 % after 30 days of operation, using 5.0 cm bed depth. For 10 cm of bed depth, the removal efficiency decreased to 90 % after 200 days of operation. This means ~7 times more time of operation for two times more bed depth under the conditions indicated. For larger bed depth, the relationship is still more favourable.

Figs. 3 and 4 show the aging behaviour of Ag-zeolite in the air of the same industrial environment.

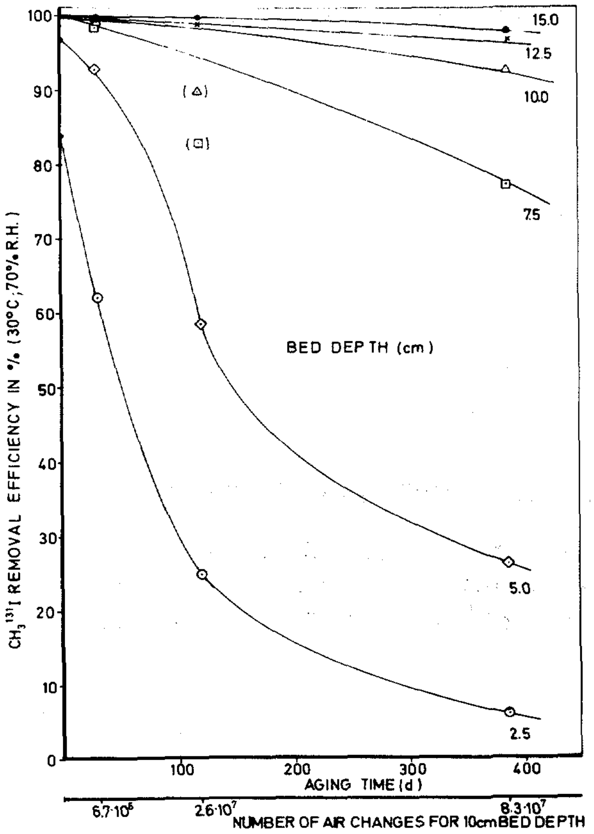

Fig. 3 Aging of zeolite Ag X in air from industrial environment

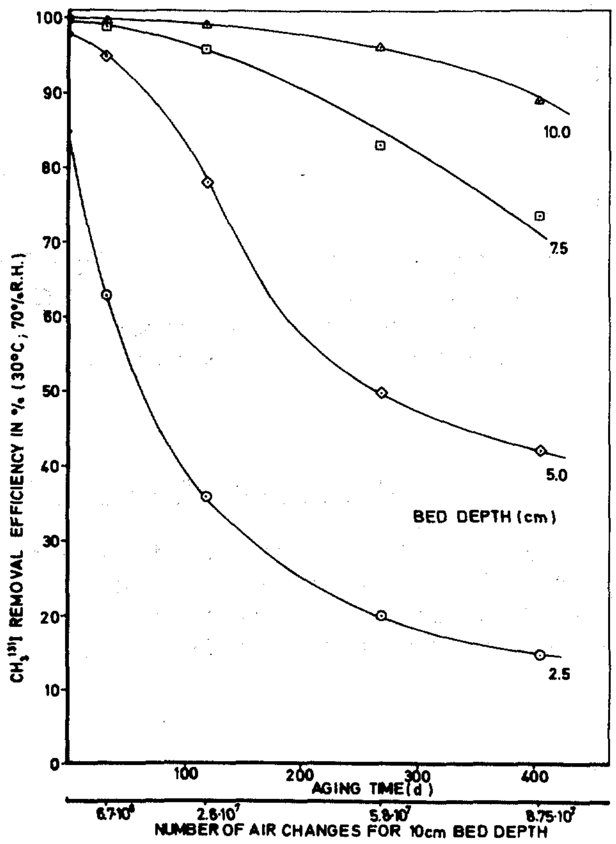

Fig.4 Aging of zeolit Ag X in prefiltered air

The Ag-zeolite test beds from which the data for Fig. 4 were derived were "protected" by two Na-zeolite beds of 2.5 cm depth. There is no important difference between the aging of the "unprotected" and the "protected" Ag-zeolite test beds; so the conclusion can be drawn that the Na-form of the zeolite does not adsorb much of the impurities which will poison the Ag-zeolite.

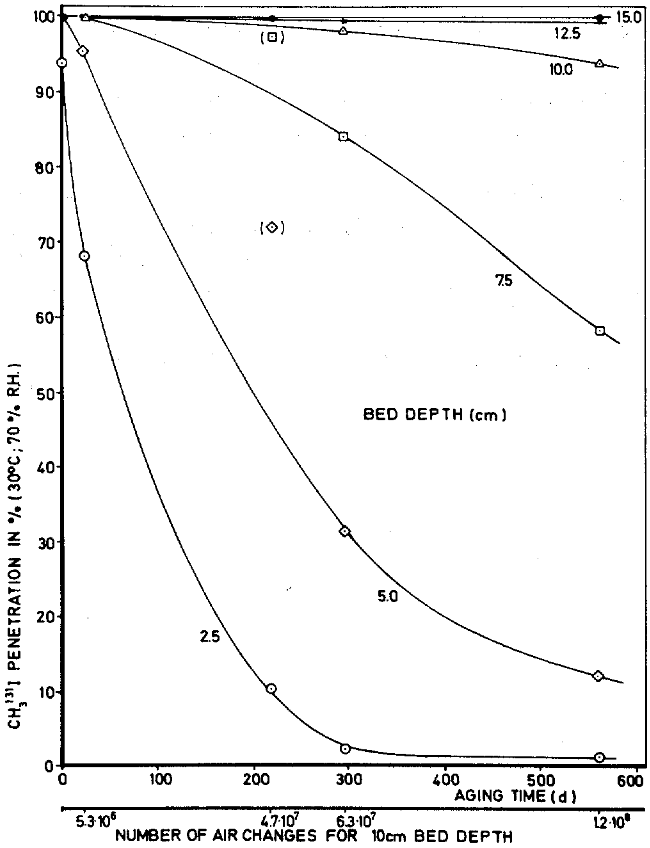

Fig.5 Aging of Ag-KTC in air from a reactor building

Fig. 5 shows the aging behaviour of Ag-KTC in the air of a reactor building. With respect to the data, the use of Ag-KTC in continuously operating iodine filters should be possible for times of operation at least equal to that of charcoal filters.

III. Aging of Iodine Filters under Continuous Operation

In-place tests were performed on continuously operated iodine filter systems, fitted with two successive banks of pleated-bed adsorber cells. The test medium was a mixture of $CH_3{}^{131}I$ and $CH_3{}^{127}I$. The test conditions and results are given in Tab. II.

Tab. II AGING OF A CONTINUOUSLY OPERATING IODINE FILTER, RESULTS OF IN-PLACE TESTING

Iodine filter: 2 successive filter banks with pleated-bed adsorber cells,
Charcoal: HSA 1565, 8 - 14 mesh (Tyler), bed depth: 5 cm (per adsorber cell).
Aging medium: air from reactor compartment, pressure ≤ 200 mm of water below atmospheric pressure.

Conditions during testing: temperature 14 - 28°C, R.H. 14 - 60 %, air flow 12,500 m^3/h, stay time: 0.33 s for the two successive filter banks.

Duration of in-place test: 6 - 10 h

Test medium: 150 - 200 mCi $CH_3{}^{131}I$ mixed with $CH_3{}^{127}I$.

Filterbank No.	Time of operation in month	$CH_3{}^{131}I$ removal efficiency in %
1	0	99.96
1	4	55.7
2	0	> 99.4 +)
2	4	99.90
2	10	92.4
1+2	0	≥ 99.9997 +)
1+2	4	99.96

+) activity of sampler after second filter bank near background.

The data show a very fast decrease within 4 month of removal efficiency in the first filter bank, dropping from 99.96 % to 55.7 % (bed depth: 5 cm, superficial air velocity 30 cm/s). The second filter bank of equal size showed a removal efficiency of 99.90 % after the same operating time. The effect of protection from the first filter bank is obviously. After an operating period of 10 months the second filter bank still had a removal efficiency of 92.4 %.

In-place test mostly can not be performed under standardized conditions, so the results depend to a certain extent on the special operating conditions prevailing during the test. To receive more information, samples of charcoal from the original filter elements or by-pass adsorbers were tested in the laboratory under standardized conditions. The results are given in Tab. III.

Tab. III AGING OF A CONTINUOUSLY OPERATING IODINE FILTER; RESULTS OF LABORATORY TESTS (UNDER SIMULATED MCA-CONDITIONS).

Iodine filter: same as in Tab. II

Samples: charcoal from the original adsorber cells or from by-pass samplers

Sweep gas (for laboratory test): air, atmospheric pressure, 43°C, 71 % R.H.

Stay time per 5 cm bed depth: 0.17 or 0.2 s (similar to the original iodine filter)

Test medium: $CH_3{}^{131}I + CH_3{}^{127}I$, specific loading: 40 - 160 µg CH_3I/g of charcoal
$^{127}I_2 + {}^{131}I$, specific loading: 280 - 320 µg I_2/g of charcoal

Duration of gas flow: Preconditioning ≥ 20 h
Injection of test medium: 1 h
Gas flow continued for ≥ 2 h in addition

Filter-bank No.	Type of charcoal	Period of operation in month	Removal Efficiency for 5 cm bed depth +) in %	
			^{131}I loaded as	
			methyl iodide	elemental iodine
1	HSA 1565	0	98.8	-
1	HSA 1565	6	26.0	-
1	RKI-1	0	98.1	99.99958
1	RKI-1	5	77.4	99.983
2	HSA 1565	0	98.7	-
2	HSA 1565	16	83.0	99.989

+) bed depth of one adsorber cell

Again the fast aging of the first filter bank can be seen, whereas the second filter bank had a removal efficiency of 83 % for $CH_3{}^{131}I$ and 99.989 % for ^{131}I in the form of elemental iodine, even after 16 months of operation. From the data given for the I_2-removal efficiency of the first filter bank a decrease can be seen from 99.99958 % down to 99.983 % within only 5 months.

The results of the in-place and laboratory tests again underline the value of larger bed depths for reasonable performance periods. For practical purpose it may be concluded that iodine filters with low bed depths should be protected by charcoal adsorber cells which could be manufactured to a lower standard and filled with low-priced activated charcoal to adsorb the bulk amount of poisoning materials upstream of the iodine adsorber cells. Since these pre-adsorbers are not taken in consideration for iodine filtering, there is no need of expensive in-place testing of the pre-adsorbers after the replacement. For the design of container-type iodine filters, the bed depth should be increased to compensate for the effects of aging. This can be done at a minimum of additional costs for material and labour.

IV. Comparison of In-Place Tests and Laboratory Tests for Container Type Iodine Filters

Since, under normal operating conditions the in-place tests may mostly not reflect the expected post-accident conditions for which the filters are constructed, additional laboratory experiments are always performed with the original charcoal under simulated MCA-conditions with respect to temperature, relative humidity, and also the loading. Bed depth and superficial air velocity is equal to the conditions in the original iodine filters. In Tab. IV the data for the removal efficiencies are compared for in-place tests of newly installed iodine filters of the container-type with the data received from these laboratory test of samples of the original charcoal batch. In all of these container-type filters, KI-impregnated charcoal of the type Norit CG II was used. In all cases the results of the in-place tests showed removal efficiencies greater than the values obtained in laboratory tests for charcoal. The leakage through the filters was very low and no significant mechanical leak was ever detected. In one case a by-pass adsorber failed.

Tab. IV COMPARISON OF IN-PLACE TESTS AND LABORATORY TESTS FOR CONTAINER-TYPE IODINE FILTERS

In-Place Tests								Laboratory Tests (simulated MCA-conditions)			
Test No.	Charcoal volume in l	Gas flow in m^3/h	Stay time in s	Test medium	R.H. in %	Temp. in °C	Removal efficiency in %	Test medium	R.H. in %	Temp. in °C	Removal efficiency in %
1	400	1000	1	CH_3I	<35	30-35	99.99997	CH_3I	100	65	99.97
2	400	1000	1	"	<35	30-35	99.99995	"	100	65	99.97
3	1025	3000	1	"	50	26	99.9996	"	100	31.2	99.86
4	400	500	2	"	60	26	99.982 +)	"	100	31.2	>99.86
5	400	500	2	"	60	26	99.9992	"	100	31.2	>99.86
6	1100	10000	0.4	"	48	22	98.4	"	70	36	97.2
7	1100	10000	0.4	I_2	28	24	99.93	10% CH_3I 90% I_2	70	36	99.73

+) the small leak was situated in a by-pass adsorber

In-place tests are relatively expensive compared to laboratory tests. To extend the interval between in-place tests of iodine filters and for testing of the aging of the impregnated charcoal, all the new iodine filters installed in German reactor stations are fitted with at least two by-pass adsorbers. These adsorbers are filled with charcoal of the original charge and will be removed after certain periods for tests in the laboratory under simulated MCA-conditions. The design must ensure isokinetic flow through the by-pass adsorber and the iodine filter; also any leakage through the by-pass has to be avoided by careful design. The charcoal in the adsorbers is divided in at least two portions for better detection of the degree of aging. There are precautions to avoid an unauthorized shutdown of the air flow through the by-pass adsorbers.

V. A New Test Installation for Filter Testing under Simulated Post-Accident Conditions

Today we are only able to perform in-place tests of the original iodine filter systems under conditions of normal operation. Only the adsorber material can be tested under simulated post-accident conditions expected for the atmosphere to be cleaned. These methods may be satisfactory as long as no additional effects on the filter performance are anticipated. But the removal efficiency may seriously decrease through these effects just when good filter performance is very urgently needed.

In PWR stations in Germany, the off-gas from the annulus between the pressure containment and the secondary containment is filtered by the use of so-called "MCA filter systems," including HEPA- and iodine-filters. They will be operated after an accident to provide a lower pressure (of some mm of water) in the annulus, compared to the environmental atmosphere. In case of an accident, the temperature in the off-gas from the annulus will increase, but considering a low leak rate of the pressurized containment, not much steam and activity will be transported to the annulus. In cases where once-through filters are used for exventing the post-accident atmosphere of the dry well of a BWR after a certain delay, there may be a large amount of steam and activity in the off-gas to be filtered. Internal recirculating post-accident filter systems in a pressure containment of a PWR or in the dry well and secondary containment (reactor building), respectively, of a BWR could be loaded with highly radioactive fission products; also the atmosphere to be filtered will include steam and steam-air mixtures at higher temperatures and mostly at elevated pressure.

The various types of filter systems cannot be discussed exhaustively here. The system used and the components of the filters required as well as the post-accident conditions in the atmosphere to be filtered depend on the reactor type and containment design. But the conclusion can be drawn that one should be able to test whole filter systems under simulated post-accident conditions which may be extremely different from that of normal filter operation.

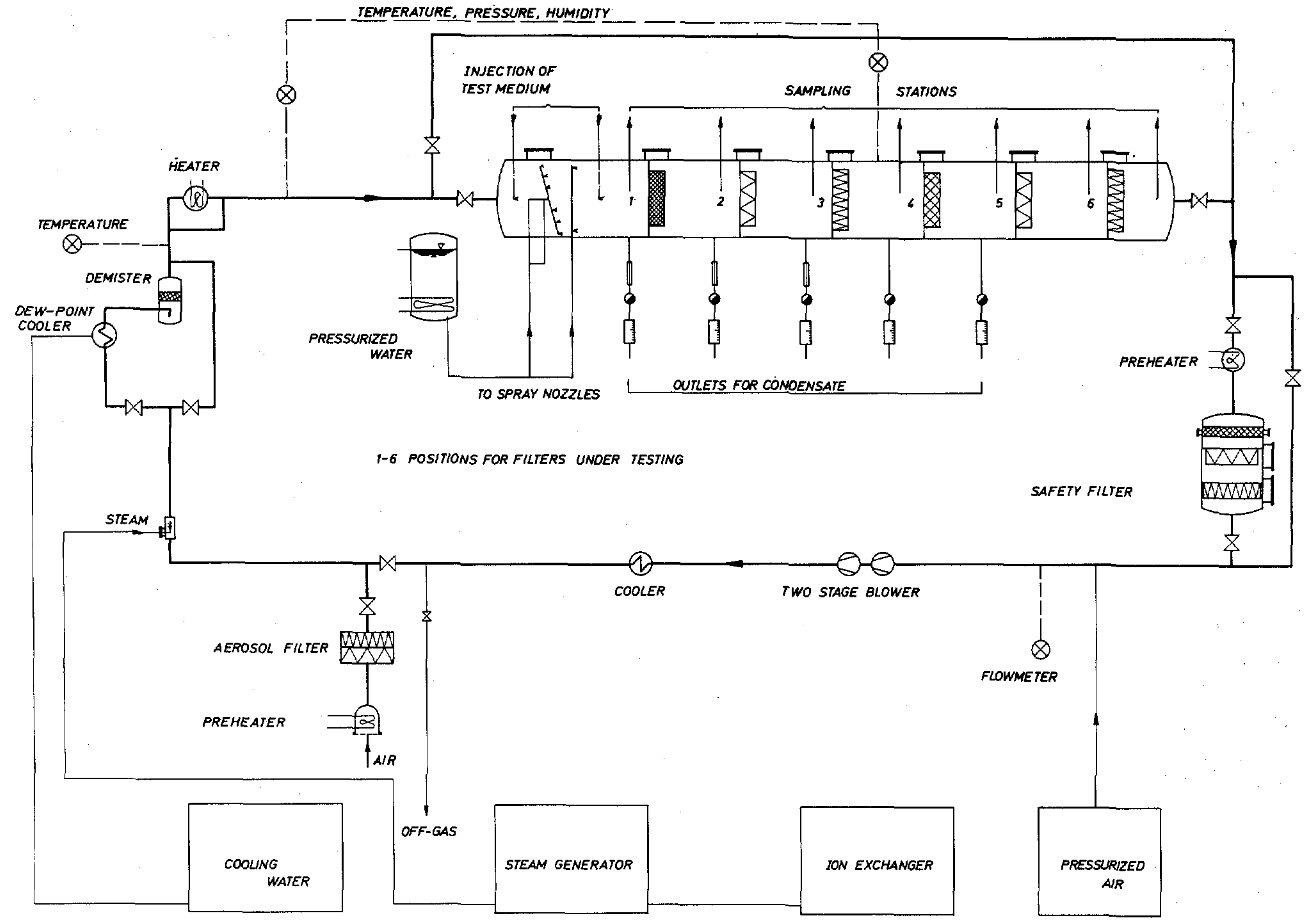

Fig. 6 INSTALLALATION FOR FILTER TESTING UNDER SIMULATED POST-ACCIDENT CONDITIONS

In Fig. 6 the flowsheet is given of a very recently built installation for testing filter systems under all post-accident conditions to be expected in reactor containments. Two exceptions are of course the specific activity of the containment atmosphere and the radiation level. The size of the installations allows to test HEPA filters and charcoal adsorber cells up to the standard size of 610 x 610 x 292 mm (24 x 24 x 11.5 inch). Moreover, container-type filters can be tested in the by-pass to the test duct for the cell-type filters. In addition to the use for testing filters of present day design, the installation will be used for the development of new internal filters of the recirculating type for post-accident clean-up.

The filter test installation is constructed for a gas flow between 400 and 2000 m^3/h. Test positions for six successive components of filter systems may be used simultaneously. With a once-through gas flow, mixtures of air and steam in the test duct can be handled at atmospheric pressure, temperatures between 25 and 50°C and relative humidities between 30 and 100 %. In addition, water-air aerosols may be generated. By use of a recirculated gas flow, air-steam mixtures with a dew-point $\leq$ 151°C can be handled at temperatures up to 200°C. The upper temperature limit for saturated steam is 151°C.

An aerosol generator for aerosols with a original particle size of 60 - 70 μ is provided, converting pretemperated water with a flow rate up to 9 m^3 of water/h into aerosol for short periods of time. For unlimited time periods, pretemperated water at a flow rate up to 120 l of water/h can be converted into aerosol. With the use of this water-aerosol generator, all conditions can be simulated which are expected from cooling of steam-air mixtures upstream of filter systems.

The characteristic curve of the two-stage blower allows a pressure drop of up to 760 mm of water over the components under test at atmospheric pressure, and more than 760 mm at elevated pressure. All components of the installation exposed to the air-steam mixture are made of stainless steel and are designed to withstand an internal pressure of 5 at.

It is proposed to use as test medium CH_3I, I_2 and different aerosols containing tracer amounts of radioactive isotopes.

The temperature and pressure in the air-steam mixture will be controlled to such an extent that unintended variations of the relative humidity should be limited to ± 3 %. The data for the relative humidity will be derived from the measurement of the temperature and the steam concentration by means of two specifically designed infrared-spectrometers.

The filter test installation will be operated from a control room where all important variables are indicated and registered. After start up, the operation of the test installation will be by automatic control up to periods of one week.

REFERENCES

(1) J.G. WILHELM, Testing of Iodine Filters for Nuclear Installations, IAEA Proceedings Series; TREATMENT OF AIRBORNE RADIOACTIVE WASTES, VIENNA 1968.

(2) J.G. WILHELM and H. SCHUETTELKOPF, Inorganic Adsorber Materials for Trapping of Fission Product Iodine; PROCEEDINGS of the ELEVENTH AEC AIR CLEANING CONFERENCE, CONF 700816, Dec. 1970, p. 568 - 578.

DISCUSSION

FISH, J: You mentioned that the tests were run in the reactor building. Are the organics within the building the source of the poisoning compound or is it brought in from outside of those buildings, do you think?

WILHELM: For the tests with KTB, they were run inside the building and we didn't add anything to the atmospheres. All other tests were performed outside a building on the proposed reactor site. The only additional thing we did was to add HEPA filtering of the incoming air.