IODINE BEHAVIOR AND CONTROL IN PROCESSING PLANTS FOR FAST REACTOR FUELS*

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ABSTRACT

One of the major problems confronting the development of a reprocessing system for fast reactor fuels is the removal of radioiodine from plant effluents. The plutonium content and resulting high specific value of fast reactor fuels make it economically desirable to process after as little as 30 days' decay. This reduced decay time requires plant retention factors for iodine approaching 10^8, and will place demands on the iodine removal equipment four to five orders of magnitude greater than proven technology can guarantee. Development work at ORNL is directed toward a better understanding of basic iodine behavior and the development of iodine removal systems capable of meeting these demands. A number of experimental systems including both aqueous scrubbers and dry adsorbers have demonstrated decontamination capabilities in excess of 10^4. Small-scale, short-term engineering demonstrations using an actual dissolver off-gas stream as feed have produced overall decontamination efficiencies in excess of 10^6, and have indicated that the individual component efficiencies are not significantly reduced when several components are operated in series. Work is continuing on the many remaining uncertainties both in understanding basic iodine behavior and in demonstrating long-term dependability of attractive removal systems.

Introduction

A significant factor in the continuing development of the Liquid Metal Fast Breeder Reactor (LMFBR) is the availability of an economical fuel reprocessing technology. Fuel from early demonstration LMFBR's can be reprocessed in existing reprocessing plants, with minimal modifications, after long (> 200 days) decay times. For long-term application, an economic incentive exists for reducing the inventory charges on the high-value plutonium content of LMFBR fuels by reducing fuel decay times, prior to reprocessing, to as little as 30 days. Among the more challenging problems to be solved in developing short decay processing capability is the acquisition of basic data on iodine behavior in the reprocessing plant,

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and the development and demonstration of systems for very efficient removal of iodine from plant effluent streams.

Requirements for Iodine Control

The magnitude of the problem of containing iodine in a reprocessing plant for 30-day decayed LMFBR fuel is illustrated in Table 1. The iodine content and required decontamination factor for a 1-metric ton/day plant reprocessing LMFBR fuel decayed 30 or 60 days is compared with a typical plant processing 150-day decayed LWR fuel. The 150,000 curie/day ^{131}I input to the reprocessing plant handling 30-day decayed LMFBR fuel requires a plant retention factor for ^{131}I in excess of 10^7, which is four to five orders of magnitude greater than that available in existing LWR reprocessing plants. The 1.7 million curie inventory of ^{131}I in the waste system of the short-decay processing plant is quite significant, as it puts rather severe demands on the storage and handling of the major iodine containing waste streams. The ^{129}I content of the LMFBR fuels will require permanent storage of the primary iodine waste after sufficient time is allowed for decay of the ^{131}I components.

In order to attain the very high iodine retention required for plants reprocessing short-decayed LMFBR fuel, greater attention must be given to improved containment and to the reduction of the volume of both gaseous and liquid effluents from the plant. All cell as well as equipment off-gas will require extensive treatment for iodine removal, as minute leakage into a process cell atmosphere can carry many times the total allowed daily release of iodine to the environment. One approach to the control of iodine in a short-decay reprocessing plant is depicted in flowsheet form in Fig. 1. The approach taken in this example is to drive most of the iodine away from the fuel in the early processing steps, into a relatively small off-gas volume, from which the bulk of the iodine can be effectively removed for permanent disposal. This approach simplifies the primary removal equipment by reducing the gas volume to be treated, but, more important, it prevents the bulk of the iodine from contacting organics in the solvent extraction equipment and forming organic iodide species, which are very difficult to subsequently remove from off-gas.

It is desirable to remove ~99.9% of the 1.5×10^5 curie/day iodine input in the head-end and dissolution steps to reduce the iodine reaching the solvent extraction portion of the plant to a few hundred curies. The primary iodine removal equipment on the dissolver off-gas should provide decontamination capabilities in excess of 10^3, so that iodine remaining in the effluent is no greater than that evolved from downstream equipment. The effluent from the primary system is combined with the off-gas from the remainder of the process equipment, and the off-gas from the high-level analytical cells, and passes through a secondary iodine removal system with a DF capability in excess of 10^3. The effluent from the secondary system is combined with the cell off-gas and is passed through a final iodine removal system where a normal DF of ~10 is required. This final system should have a capability of removing iodine by a factor approaching 10^4, however, to protect against abnormal conditions such as temporary malfunction of one of the preceding systems or a significant release of iodine to the cell atmosphere.

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Table 1. Iodine Content of LWR and LMFBR Fuels

	1 METRIC TON/DAY LWR FUEL DECAYED 150 DAYS	1 METRIC TON/DAY LMFBR FUEL	
		DECAYED 60 DAYS	DECAYED 30 DAYS
^{131}I INPUT, CURIES/DAY	2	1.1×10^4	1.5×10^5
^{131}I DECONTAMINATION REQUIRED	200	1.1×10^6	1.5×10^7
^{131}I INVENTORY IN PLANT WASTE, CURIES	23	1.3×10^5	1.7×10^6
TOTAL IODINE INPUT, GRAMS/DAY	270	520	515
^{129}I INPUT, CURIES/DAY	0.03	0.06	0.06

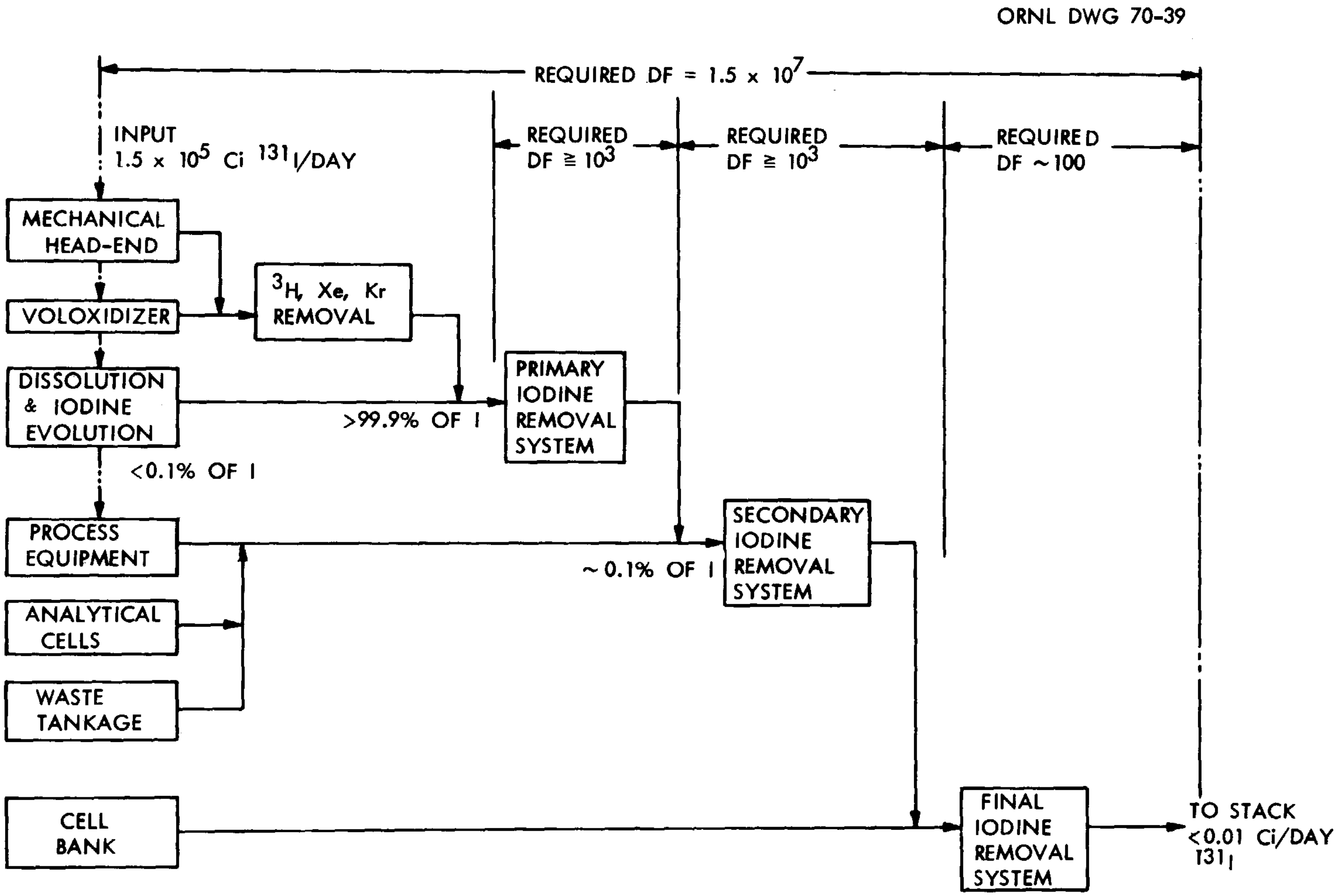

Fig. 1. Iodine Treatment Flowsheet - LMFBR Fuel Processing Plant.

Research and Development

An understanding of iodine chemistry and behavior at all points in the fuel reprocessing system is required in order to control the routing of iodine through the system, and to develop engineering equipment to efficiently and dependably remove iodine from plant effluent streams. Basic research and small-scale engineering development are being conducted to define iodine behavior in both gaseous and liquid systems and to study the interaction between iodine and various liquid and solid sorbents. The current status of this research is summarized in relation to its application to the example flowsheet presented in Fig. 1. Much of the experimental information could be applied in many combinations in an actual plant, and the approach taken here is to present the data and relate it to typical process applications.

Voloxidation

Voloxidation is a process in which chopped LMFBR fuel (UO_2-PuO_2) is heated to 450° to 750°C in an oxygen atmosphere to drive off volatile fission products and convert the UO_2 in the fuel to U_3O_8. In limited experiments to date[1] evolution of tritium has been essentially complete, evolution of noble gases ~50% complete, and iodine evolution has ranged from 40 to 80%. The UO_2 in the fuel rod can be effectively converted to U^3O_8. Potential advantages to be gained from voloxidation, directly applicable to the control of iodine in subsequent process steps, include the following.

1. If significant evolution of iodine (>90%) can be obtained by voloxidation, the bulk of the iodine input to a plant can be relatively simple to remove from the voloxidizer off-gas stream.

2. Conversion of the UO_2 to U_3O_8 reduces the evolution of nitrous oxide in the dissolution step by a factor of three, thus simplifying the pretreatment of the dissolver off-gas prior to the primary iodine removal system.

Other advantages gained from the voloxidation step, not directly related to iodine control, include improved dissolution rates and the evolution of essentially all of the tritium where it can be effectively removed before it contacts and exchanges with plant aqueous streams. Although not essential to subsequent control of iodine in downstream process steps, voloxidation has many desirable features and may be required in future plants.

Evolution of Iodine from Solution

The removal of iodine from the dissolver depends on the volatilization of iodine from the dissolver solution into a vapor stream, either gas or steam. Experiments with macro ($\sim 10^{-3}$ molar) iodine concentrations produced the relationship shown in Fig. 2 between the concentration ratio

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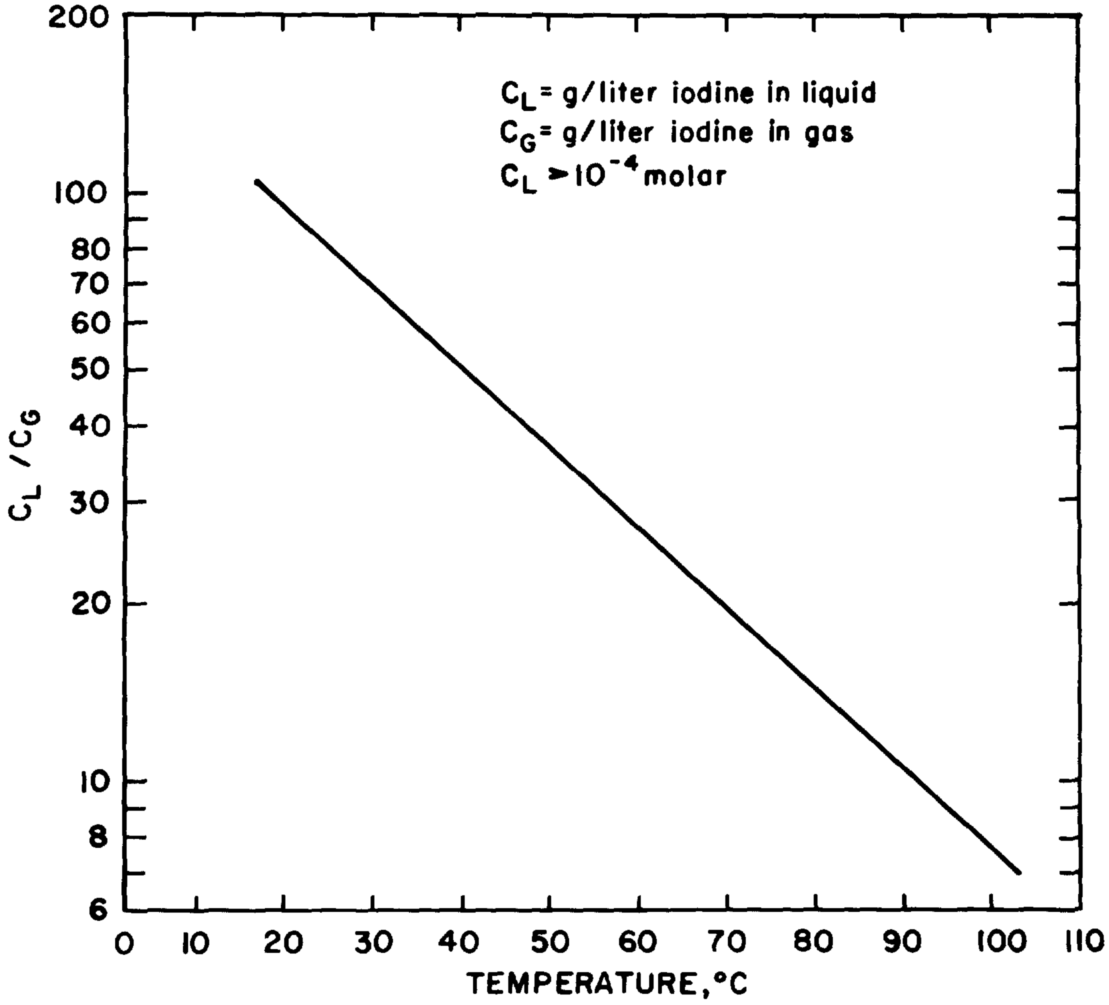

Fig. 2. Iodine Vapor Liquid Equilibrium Variation With Temperature.

of iodine in the liquid-to-gas stream and the liquid phase temperature. As these data predict, ~95% of the elemental iodine can be readily volatilized from a solution initially at 10^{-3} molar iodine, by air sparging or by evaporating a few percent of the solution. At this point (~10^{-5} molar), however, the iodine volatility decreases rapidly to a value 10-100 times less than predicted by Fig. 2, as the aqueous phase concentration is reduced to 10^{-6} molar. The residual iodine activity remaining in solution after such a volatilization experiment will not significantly exchange with stable iodine added to bring the total iodine concentration back to 10^{-3} molar, even on long standing, and a number of valence adjustments between iodide and iodate. Extensive studies are underway to identify the non-volatile species and to develop practical techniques that will produce exchange between the residual activity and subsequently added carrier.

Two specific techniques have so far been found that produce essentially complete exchange. Addition of carrier to the acid solution containing the residual activity, followed by the adding of sodium hydroxide to 1.5 molar basic solution, and then re-acidification to 2 molar acid, produced essentially complete exchange between the volatile and non-volatile forms. This procedure has little practical application, but gives some insight into the nature of the species.

The second successful experiment which yielded exchange between the residual activity and carrier consisted of autoclaving the solution at 250°C after addition of carrier. The tests to date have been in a batch autoclave that has a 24-hr heat-up and cool-down cycle time, and little information is available on the effects of temperature and residence time on effective exchange. If residence times can be reduced to a few minutes, autoclaving becomes a practical method of achieving exchange of the non-volatile species with additional carriers, and makes >99.9% removal of iodine from dissolver solution a possibility. With straight volatilization without subsequent treatment to obtain exchange for further volatilization, iodine evolution from the dissolver solution may be limited to 97-99%.

Data obtained on the volatility and behavior of iodine in water or acid solutions have numerous potential applications other than evolution from the dissolver solution. A primary iodine removal system on the dissolver off-gas stream might include a dilute acid scrubber to remove >99% of the iodine from the off-gas followed by a steam fractionating tower to concentrate the iodine into a small volume for storage. Removal of low concentrations of iodine from the low-level aqueous discharge from a plant presents a formidable problem. If simple techniques can be developed to render iodine at low concentrations volatile, this problem could be solved by a simple distillation step.

Solid Sorbents

Charcoal has long been used to effectively remove both elemental and methyl iodide from clean dry gas streams. Decontamination factors approaching 10^4 have routinely been demonstrated in laboratory tests. Applications of charcoal beds for removal of iodine from actual plant off-gas streams have often proven ineffective due to the sensitivity of charcoal to poisoning by trace organic vapors and other contaminants in the off-gas. The efficiency and useful life of charcoal beds for removing iodine in the off-gas can be greatly improved by preceding the charcoal by a catalytic oxidation step to convert all iodine to the more effectively adsorbed elemental form and to completely oxidize all organic vapors in the gas stream. Thus, with the addition of the oxidation step prior to the charcoal bed, charcoal continues to rate high in effectiveness, particularly for removal of the last trace quantities of iodine from the larger off-gas streams encountered in the final iodine removal steps.

Most of the work on an oxidation system to remove organics and convert iodine to the elemental form has centered around Hopcalite, a proprietary material marketed by Mine Safety Appliances. A Hopcalite bed operating at 350°C with gas residence times of ~1 second can effectively (>99.9% oxidation) destroy organics in the inlet air stream.[2] Methane is the most difficult to oxidize, with oxidation efficiency increasing with increased complexity of the organic molecule. Operating temperatures of the catalyst bed are fairly critical, as efficiency drops off rapidly as temperature is decreased below 350°C, and there is significant bed degradation at 350°C, which increases to an intolerable degree at 450°C. If a destruction efficiency in excess of 99.9% is required, bed-life may be limited to a few months or residence time of a few seconds may be required.

Other solid sorbents for elemental and organic iodine compounds have been investigated and one of the more attractive developments is Linde 13X Molecular Sieve, in which the normal sodium zeolite matrix has been converted to silver zeolite. This material has removal capability equal to, and possibly better than, charcoal for most iodine forms, with the additional advantages that it is non-combustible and appears to be much less effected by organic contaminants in the off-gas stream. Methyl iodide decontamination factors in excess of 10^4 are routinely obtained at gas velocities of 20-50 ft/min for 2-in.-thick beds of silver zeolite. The most favorable operating temperature for silver zeolite beds is in the range of 150 to 200°C.

The efficiency of silver zeolite for removing iodine compounds is adversely effected by the presence of organic vapors in the gas stream, and long-term exposure to organic contaminants has a poisoning effect on the bed. This effect, although much less than for charcoal, is quite significant when the very high removal efficiencies are required. Also, the basic cost of silver zeolite is 3 to 10 times the cost of charcoal, and extension of the life expectancy by preceding the zeolite by an oxidation step is economically desirable.

Numerous other solid sorbent systems have been, or are being, looked at for removal of iodine from off-gas streams, and the systems described above are the ones that have recently shown the most promise in our recent work. Application of a solid sorbent system to a short-decay processing plant off-gas is limited primarily to the latter stages of iodine removal, and in particular the final removal system where mass iodine concentration and heat generation rates are very low. Solid sorbent systems can be economically applied to large gas flowrates due to the short residence times and relatively low pressure drops required, and thus are particularly applicable on the larger gas flows.

Aqueous Scrubbers

Caustic scrubbers have been used in many applications in the past for removing iodine from off-gas streams and are quite effective in the sorption of elemental iodine. Decontamination factors obtained in actual plant applications have often been disappointingly low, in the range of 100 or less. This low removal efficiency is attributable to a few percent of the iodine being in the form of organic iodides which are not effectively removed by caustic.

An aqueous scrubbing medium,[3] made up of mercuric nitrate in nitric acid, is effective in removing organic iodide compounds from gas streams if sufficient contact time is allowed for the relatively slow, but irreversible, reaction between the absorbed organic iodide and the mercury ion. Decontamination factors obtained by dispersing an air stream containing iodine through a medium frit at the bottom of a column containing mercuric nitrate-nitric acid solution are summarized in Table 2. Decontamination factors for methyl iodide and iodine in excess of 10^4 were obtained by passing finely dispersed gas through a 32-in. depth of scrubber solution. The pressure drop across the scrubber was ~1.5 psi.

Removal efficiency decreases with increased gas flow, and the 2-in.-diam column becomes inoperable at gas flows of 40 $\mathrm{lb/hr \cdot ft^2}$. Increasing mercury concentration has a marked effect on removal efficiency of all species. Methyl iodide removal efficiency is not significantly affected by nitric acid concentration, but acid concentrations up to 5 molar are required for effective removal of long-chain alkyl iodides.

A scrubbing system based on finely dispersed air into the bottom of a liquid-filled scrubber has limited application in a large-scale plant because of the high pressure drops and large gas flows encountered. Such a system could be used as the last step in the primary iodine system, or possibly in the secondary iodine removal system where gas flows are relatively low.

The removal efficiency for methyl iodide in a gas-phase continuous column was studied using three types of packing including ordinary Berl saddles, a special porous saddle and cellulose sponge cut into 1/4-in. cubes. Typical data from such experiments are summarized in Table 3. Solution holdup in the column was 5 to 6 times as large with the porous saddles, and 11 times as large with the sponge, as with regular Berl saddles. As indicated in Table 3, methyl iodide removal efficiencies are poor for conventional packing, even at very low gas flowrates. Significant improvement was gained in going to the sponge packing, although such a system would have limited application in a large reprocessing plant.

Table 2. Removal Efficiencies of Iodine Forms in Liquid-Phase-Continuous Scrubbers

Iodine Form	$HgNO_3$ (Molar)	HNO_3 (Molar)	Gas Flow $\left(\frac{lb/hr}{ft^2}\right)$	Solution Depth (in.)	Iodide Concentration in Inlet Gas (mg/liter)	DF
CH_3I	0.1	0.1	4[a]	6	15	20
CH_3I	0.1	0.1	4[a]	14	15	700
CH_3I	0.1	0.1	14[b]	32	0.05	1.2×10^4
CH_3I	0.1	0.1	21[b]	32	0.05	7×10^3
CH_3I	0.3	0.1	21[b]	32	0.05	6.7×10^4
I_2	0.1	0.1	4[a]	6	1	1.9×10^3
I_2	0.1	0.1	4[a]	37.5	1	2.8×10^4
	0.1	0.1	14[b]	32	0.05	800

[a] 1-in.-diam columns.

[b] 2-in.-diam columns.

Table 3. Decontamination Factors for CH_3I in Gas-Phase-Continuous Scrubbers

(2-in.-diam column, 3-ft packing depth)

Type of Packing	$HgNO_3$ (Molar)	Air Flow (lb/hr ft^2)	Liquid Flow (lb/hr ft^2)	Iodine DF	Relative Solution Holdup
Berl Saddles	0.2	14	580	1.8	1.0
Berl Saddles	0.2	3.5	580	18	1.0
Berl Saddles	0.2	3.5	1700	44	1.3
Porous Saddles	0.4	14	290	6	5.9
Porous Saddles	0.4	3.5	580	640	6.8
Sponge[a]	0.2	14	86	430	6.8
Sponge[a]	0.4	14	86	1.4×10^4	6.8
Sponge[a]	0.4	35	86	96	6.8

[a] 1/4 in. cellulose sponge cubes.

A brief engineering study into the application of mercuric scrubbers on a large off-gas stream indicated that some type of bubble plate or nozzle plate scrubber might be best suited to provide the required solution hold-up volume at a reasonable pressure drop and gas throughput. Although the mercuric nitrate-nitric acid scrubbing system has potential for providing very efficient removal of most organic iodide species, considerable engineering development is required before a practical system is available for plant application on large off-gas rates.

Hot-Cell Engineering Demonstrations

After a system has been proven feasible in laboratory and tracer-level experiments, the next logical step is to evaluate the system under conditions approximating those encountered in an actual plant. The Transuranium Processing Plant (TRU) at ORNL provides an ideal location to carry out such engineering demonstrations on our more promising systems. A typical TRU target campaign will last about 2 or 3 weeks and will handle fuel containing 200-800 curies of ^{131}I. Two or three runs are made each year.

The first experiment[4] installed on the TRU evaporator off-gas system was designed to test a Hopcalite bed - charcoal bed system for removal of iodine from a 3-4 cfm stream containing relatively high organic loadings. A charcoal bed previously operated on this gas stream was totally ineffective in trapping iodine due to rapid poisoning by organic vapors. The Hopcalite bed was operated at ~650°F, and the charcoal bed at 100 to 150°F.

The iodine DF across the Hopcalite bed - charcoal bed system averaged 10^3 for a 4-week period following the start of the run. Iodine decontamination factors in excess of 10^4 were demonstrated where iodine concentrations were significant and organic content of the inlet gas streams was relatively low. The average iodine release rate through the charcoal bed for the 4-week period was 0.1 mc/day, with the maximum release rate being 0.25 mc/day. Organic concentrations were at least an order of magnitude higher than would be expected in most applications of such a system and presented temperature control problems in the Hopcalite bed due to the high heat evolution from the oxidizing organics.

Based on results from the above experiment and further laboratory development of both solid sorbents and liquid scrubbers, the system shown in Fig. 3 was installed on the TRU dissolver off-gas in August 1969 and operated during the subsequent three processing campaigns. Iodine was evolved from the nitric acid dissolver solution to the extent of 97-99%, either by air sparging for 8-10 hours or by evaporating ~15% of the solution volume from the dissolver over a 2-hr period. This evolution of iodine is consistent with that predicted by laboratory experiments on iodine volatility.

The combination of iodine removal components used for this experiment is not one likely to be used on an actual plant dissolver off-gas, but was intended to demonstrate the effectiveness of the various components and to verify that the previously demonstrated

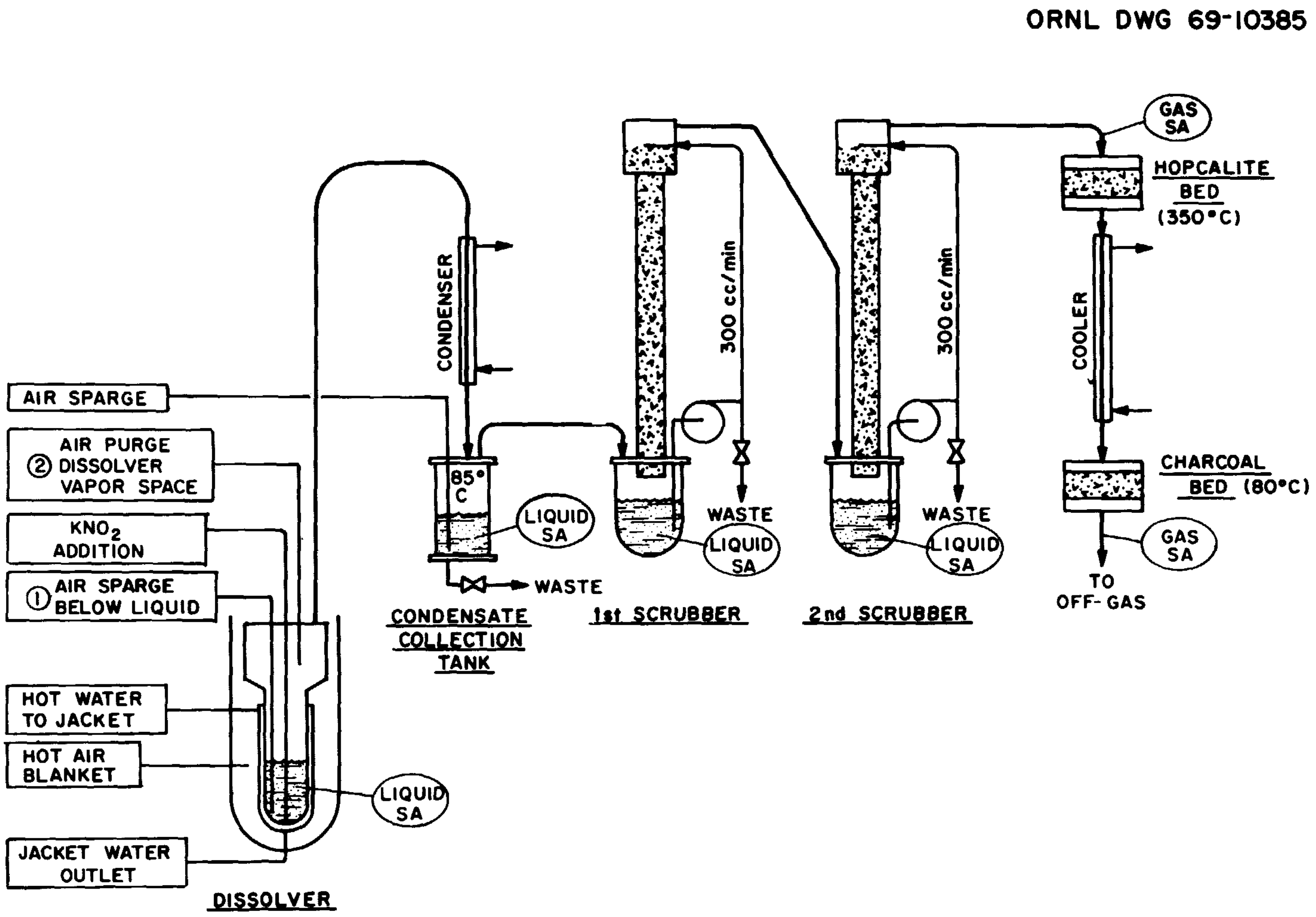

Fig. 3. Dissolver Off-Gas Iodine Removal Experiment Flowsheet.

removal efficiency (of $>10^4$) of the Hopcalite bed - charcoal bed system would not be adversely affected by preceding it with other iodine removal systems.

Data from the eight experiments carried out with this equipment are summarized in Table 4. Decontamination factors of 20-100 were observed across the mercuric nitrate scrubber when operating with 0.1M $HgNO_3$, and 500-1000 when the concentration was increased to 0.4 M in the final series of runs. These results are in general agreement with laboratory studies for this type of scrubber. The variations in scrubbing efficiency are normal and caused by changes in the iodine species fed to the scrubber and minor change in flowrates. The second scrubber, operating on 0.1 M NaOH demonstrated decontamination factors ranging from 1 to 10 depending on the efficiency of the preceding scrubber. The primary purpose of the second scrubber was to protect downstream equipment from acid vapors, and little iodine removal was expected. In one instance (Run 13-DS-3) where the first scrubber was operated on 0.1 M NaOH, a DF of 160 was demonstrated which is typical of a caustic scrubber operating on a primary iodine source.

In the early runs the decontamination factors across the catalytic oxidation (Hopcalite) bed and charcoal bed were in excess of 10^4, which agreed with earlier experiments. As indicated by Table 4, the effectiveness of the charcoal bed decreased with time to a value of ~10 for the last two runs, indicating serious degradation of either or both the Hopcalite and charcoal beds. The overall system DF of $3\text{-}4 \times 10^6$ in the early runs is encouraging and approaches the 10^7-10^8 total DF required for a short-decay processing plant. The loss in effectiveness of the charcoal bed points up the need for an understanding of long-ranged factors affecting the life of solid sorbent beds. Samples of both the charcoal and Hopcalite from this experimental system have been obtained, and tests will be run to determine their efficiencies and, hopefully, indicate the cause of their failure.

Additional valuable information in the area of life expectancy of iodine removal systems based on solid sorbents will be gained during the coming year with the installation of a Hopcalite-charcoal system on the total vessel and cubicle off-gas (400 cfm) from the TRU system. Although this system is the primary iodine removal system for the TRU facility and not experimental in nature, much information can be gained on factors which influence DF and bed life, and it will be possible to make long-term tests on a number of sorbent materials.

Conclusions

Recent advances in better understanding iodine behavior and in further developments of both old and new concepts of iodine removal from off-gases indicate that the very high (~10^8) containment efficiencies required for plants processing short-decayed fuel are attainable.

Table 4. Summary of Data from TRU Iodine Experiments

Run	Date	Iodine Passing Through Charcoal Bed (mc)	I-131 DF			
			First Scrubber	Second Scrubber[a]	Charcoal Bed	Overall
13-DS-1	9/4/69	0.01	18[b]	9	2×10^4	3×10^6
13-DS-2	9/6/69	0.02	29[b]	13	1×10^4	4×10^6
13-DS-3	9/9/69	0.85	160[a]	2	270[d]	1×10^5
16-DS-1	1/27/70	0.01	209[b]	2.5	1.3×10^4	6.6×10^6
16-DS-2	1/30/70	0.48	116[b]	6	186	1.4×10^5
19-DS-1	4/8/70	0.033	1100[c]	1.2	1.7×10^3	3.0×10^6
19-DS-2	4/11/70	5.0	960[c]	3.2	8	2.7×10^4
19-DS-3	4/12/70	3.0	443[c]	4.6	14	3.3×10^4

[a] 0.1 M NaOH.

[b] 0.1 M $HgNO_3$ + 0.1 M HNO_3.

[c] 0.4 M $HgNO_3$ + 0.2 M HNO_3.

[d] Charcoal bed saturated with water from high humidity in off-gas.

Techniques have been developed to the early engineering demonstration stage, which are applicable to each of the iodine removal systems previously discussed and which, at least on short term tests, provide the required decontamination. Areas where continuing development is required to provide information for design of an adequate system for iodine control on a short-decay reprocessing are as follows:

1. Continued basic research into iodine chemistry so as to better understand the function, and malfunction, of various iodine control systems.

2. Continued engineering demonstrations of attractive systems for iodine removal with special emphasis on life expectancy and factors leading to the degradation of removal efficiencies with time and use.

3. Engineering studies to determine the best relationship between the various applicable iodine control systems as well as their relation and effect on plant design and operating parameters.

Future work is planned to provide additional data in these areas and hopefully to provide the basis for a working system when the day of the short-decay reprocessing plant arrives.

References

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DISCUSSION

YARBRO: I will entertain one question if someone insists.

PARKER: Since you are real accommodating, I'll ask a question myself. I think it might be worthwhile if Mr. Yarbro would comment on the fact that there have been some observations at Oak Ridge of strange forms of iodine particularly from alkaline solutions. Could you say just a word or two?

YARBRO: Yes, we have seen strange forms of iodine that have been batted around as being HOI and other things. It would be real interesting to apply some of the techniques that we have seen here today in identifying these forms. We have not been able to identify them specifically as HOI. We have found a species that is volatile from basic solution when elemental iodine is added to caustic. Its volatility decreases from about 30% volatility immediately after addition to a very low volatility after a period 24 to 48 hours. I mentioned in a comment before also we are interested in the 2% of the iodine that is not volatile or only slightly volatile from the acid solution. It is suspected that this may be either HOI or some complex of HOI with contaminants in the solution.

INORGANIC ADSORBER MATERIALS FOR TRAPPING OF FISSION PRODUCT IODINE

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ABSTRACT

For the removal of fission product iodine at elevated temperatures and in oxidizing gases, inorganic, nonflammable adsorber materials should be used instead of charcoal. Experimental work is performed to evaluate the usefulness of inorganic adsorber materials for iodine filtering devices. Special interest was concentrated on materials for off-gas cleaning in fuel reprocessing plants and gas cleaning inside the reactor containment under MCA conditions.

Considering the high price of silver and the sensitivity of molecular sieves for acids, new inorganic adsorber materials are developed with relatively low silver loadings and high removal efficiencies for methyl iodide and iodine.

Experimental data are given for the removal efficiencies of new inorganic adsorber materials in wet air and superheated steam; besides, experiments are reported to evaluate the effect of nitrogen oxides on the performance of the adsorber materials. The efficiencies and the prices of the new materials are compared with those of silver impregnated molecular sieves.

Introduction

Relatively low desorption temperatures and flammability limit the use of impregnated, activated carbon for the removal of fission product iodine. The silver form of Zeolites (molecular sieves) showed good removal efficiencies in dry and wet air up to high relative humidities and high temperatures (1, 2). In the range of a few mg per g Zeolite AgX and for 70 % R.H. there was no significant influence of loading on the removal efficiency. For higher loadings, an exponential relationship between loading and removal efficiency could be shown (3).

For good removal efficiencies of the Zeolites, nearly all of the Na^+ of the Zeolite NaX have to be exchanged with Ag^+. The total amount of silver is then in the range of 50 - 57 g Ag per 100 g Zeolite (as delivered). The price of this material is high. Zeolites do not withstand steam of high temperature and pressure; also, they will be destroyed by acids.

Search was continued for an inorganic adsorber material with good removal efficiencies at a low silver content and a high resistance to acids.

Among the materials tested, different Bayer catalyst carriers, impregnated with $AgNO_3$ in our laboratory, showed good CH_3I removal efficiencies. These catalyst carriers are built of amorphous silicic acid, some with a small amount of aluminum oxide. They have a very broad spectrum of pores and a porosity above 50 %. The specific surface is around 110 m^2/g and larger for some of the experimental products. The results of three different types of catalyst carriers tested will be reported.

The catalyst carriers KTB, KTC and KTD are experimental products of the Bayer factory. Besides $AgNO_3$-impregnation, also KI as an impregnant was tested on those materials. With KI removal efficiencies < 1 % were measured for CH_3I (10 cm bed depth, 0.4 sec stay time and 70 % R.H.). If not otherwise indicated, the KT-material used for the experiments reported was in the form of beads with a diam. between 1 and 2 mm. The pressure drop of this material is around 60 mm of water for 10 cm bed depth and a superficial air velocity of 25 cm/sec (air of 25°C, 1 atm.). $AgNO_3$-impregnation was made by soaking the KT-material with aqueous solutions of $AgNO_3$ under vacuum and subsequent boiling for 2 h. Then the material was dried. The total volume of the $AgNO_3$-solution was little more than the bulk volume of the beads.

Experimental Technique

The method and the apparatus used for most of the experiments are reported in detail elsewhere (4). To measure the removal efficiency for methyl iodide and elementary iodine, they were mixed with ^{131}I in form of tracer amounts of $CH_3{}^{131}I$ and elemental radioiodine, respectively. The radioactively labeled material was introduced into a sweep gas stream and sucked through successive test beds of the inorganic adsorber material. The methyl iodide or elementary iodine which penetrated the test beds was trapped downstream in 9 successive beds (safety beds). These were made out of KI-impregnated charcoal in the experiments without nitrogen oxide, otherwise out of Zeolite AgX and / or $AgNO_3$-impregnated KT-material. In some experiments, an additional HEPA-filter was used between test beds and safety beds. Complete removal in the safety beds was assured by a stay time of 0.9 sec and a decreased relative humidity of the sweep gas by heating of the safety beds. After penetration of the safety beds, the wet sweep gas was cooled to a temperature of 6 - 9°C and the condensate also measured for radioactivity.

After the run, the ^{131}I activity in the test beds and in the safety beds was measured by γ-spectroscopy. The removal efficiency was calculated from the ^{131}I-activity in the test beds compared with the total activity in the test and safety beds. The data calculated by the use of a program are: 1. the integral removal efficiencies for the successive test beds; 2. the differential removal efficiency for each single test bed; 3., 4. the integral and differential penetrations; 5., 6. the integral and differential indices of performance. In this paper, mostly the integral removal efficiencies are given for the successive test beds.

Experimental Results

Table I shows the standard conditions for the experiments. In Table II, the removal efficiencies of some Zeolites (silver form) and $AgNO_3$-impregnated catalyst carriers are compared. For KTC-material some runs are reported with different silver loadings. As was to be expected, there is a steep increase in the removal efficiency with an increasing amount of silver. Compared to Type X and Y Zeolites, the necessary amount of silver for a certain removal efficiency is much lower. For filtering purposes it should be taken into account that the pressure drop in the KT beds with beads of 1 - 2 mm diam. is roughly 3 times higher than in the Zeolite AgX beds of the same bed depth, made of pellets of 1.6 mm diam. With respect to equal pressure drop a KT bed (1 - 2 mm beads) of 2.5 cm bed depth should be compared with a Zeolite AgX bed of 7.5 cm bed depth. With an impregnation of 18 g Ag per 100 g of KTC beads (as delivered), for both test beds of different lengths the removal efficiency was measured to $\eta = 98.6$ % under standard conditions (Table II). On this basis (same pressure drop and removal efficiency) the total amount of silver used for the KTC bed is 10 times lower than for the Zeolite AgX bed. The great influence of the bead diameter on the removal efficiency can be seen by comparison of the results for KTC 1 - 2 mm beads and KTC 3 - 6 mm beads. Type Y Zeolite was tested because it has a slightly higher resistance to acids (acid degradation below pH 3) than a Type X Zeolite (acid degradation below pH 5) and for the better hydrolytic and thermal stability of the Type Y Zeolite.

Table I EXPERIMENTAL STANDARD CONDITIONS FOR TESTING OF INORGANIC ADSORBER MATERIALS WITH METHYL IODIDE

Sweep gas: Wet air, filtered by HEPA-filter, atmospheric pressure, temperature: 30°C, R.H.: 70 %, superficial air velocity: 15 m/min.

Duration of air flow: pre-humidification: $\geq$ 20 h, CH_3I-injection: 1 h, air flow continued for $\geq$ 20 h. Variations of injection time on the order of $\pm$ a few minutes in some experiments due to correction for loading.

Loading: 1.5 ± 0.5 mg $CH_3{}^{127}I$ + 3 - 30 μCi $CH_3{}^{131}I$ per g inorganic adsorber material (calculated for 10 cm bed depth). Within the given limits, the activity used in a single experiment depends on the expected removal efficiency.

Concentration: 100 ± 30 mg CH_3I per m^3.

Table II CH$_3$^{131}I REMOVAL EFFICIENCY OF DIFFERENT INORGANIC ADSORBER MATERIALS UNDER STANDARD CONDITIONS

Material		CH$_3$^{131}I Removal Efficiency (%)				
Adsorber Type	Ag impreg. (g/100 g)+)	Bed depth (cm)	2.5	5.0	7.5	10.0
		Stay time (sec)	0.1	0.2	0.3	0.4
Zeolite AgX ++)	54.0		74.1	94.2	98.7	99.67
Zeolite AgY	45.0		74.8	94.3	98.7	99.69
KTB	14.0		96.8	99.928	99.9982	99.9995
KTD	6.8		89.5	98.4	99.86	99.986
KTC	1.8		27.4	47.5	63.8	74.4
KTC	3.2		68.4	91.5	98.0	99.32
KTC	7.8		90.8	99.45	99.970	99.9944
KTC	18.0		98.6	99.985	99.9994	(99.9997)
KTC	18.0		98.6	99.985	99.9996	99.9997
KTC +++)	3.0		18.7	33.5	44.5	54.5
KTC +++)	28.6		63.5	85.8	95.6	98.7

+) g silver per 100 g adsorber material (as delivered),

++) pellets, diam. 1.6 mm, average values of 3 experiments,

+++) beads, diam. 3 - 6 mm (all other materials in the form of beads, diam. 1 - 2 mm),

( ) activity of test bed near background.

Table III shows experiments with air of 100 % R.H. and 30°C as the sweep gas. On 100 % R.H. the removal efficiency of $AgNO_3$-impregnated KT-material for $CH_3{}^{131}I$ is low. After some hours of pre-humidification, the KT-material had a wet appearance. The total amount of adsorbed water was between 50 and 100 % of the impregnated and then dried KT-material. This uptake of water was measured after the experiments were finished. With respect to the given data, $AgNO_3$-impregnated KT-material cannot be used in a sweep gas of 100 % R.H. To avoid these conditions, it will be necessary to heat off-gases with extremly high relative humidities. In these cases, the difference between off-gas temperature and the dewpoint temperature should be at least 10°C.

Table III $CH_3{}^{131}I$ REMOVAL EFFICIENCY OF DIFFERENT INORGANIC ADSORBER MATERIALS IN AIR OF 100 % R.H. +)

Material		$CH_3{}^{131}I$ Removal Efficiency (%)				
Adsorber Type	Ag-impreg. (g/100 g) ++)	Bed depth (cm)	2.5	5.0	7.5	10.0
		Stay time (sec)	0.1	0.2	0.3	0.4
Zeolite AgX +++)	54		17.8	34.4	48.8	62.1
KTC	3.2		1.6	3.6	5.7	8.3
KTC	7.8		2.9	9.5	18.0	27.0
KTB	13.0		3.3	8.9	17.9	-

+) all other conditions are the same as given in Table I,

++) g silver per 100 g adsorber material (as delivered),

+++) pellets, diam. 1.6 mm.

Some experiments were performed to test the $CH_3{}^{131}I$ removal efficiency in superheated steam of 110°C and 150°C. No air was added to the steam. The removal efficiency in all those experiments was relatively high ($\eta > 99.998$ %, see Table IV). From the small amount of ^{131}I activity on SS-screens and springs at the front end of the test beds it can be concluded that only an unimportant part of the CH_3I was changed to a more reactive form like I_2.

For the steam-experiments loading was 0.8 - 1.6 mg CH_3I per g of adsorber material (calculated for 10 cm bed depth). Time of pre-conditioning with superheated steam was 18 - 24 h and CH_3I-injection time 0.75 - 1.5 h; the steam flow was continued for an additional 16 - 22 h.

Table IV $CH_3{}^{131}I$ REMOVAL EFFICIENCY OF DIFFERENT INORGANIC ADSORBER MATERIALS IN SUPERHEATED STEAM

Material		$CH_3{}^{131}I$ Removal Efficiency (%)				
Adsorber Type	Ag impreg. (g/100 g) +)	Bed depth (cm)	2.5	5.0	7.0	10.0
		Stay time (sec)	0.1	0.2	0.3	0.4
Zeolite AgX ++)	54	150°C	99.36	99.944	99.9985	(99.9987)
KTC	3.2	150°C	57.7	96.4	99.88	99.9986
KTC	7.8	150°C	75.6	99.62	99.9972	99.9990
KTC	10.7	110°C	71.2	99.84	99.9982	(99.9984)

+) g silver per 100 g adsorber material (as delivered),

++) pellets, diam. 1.6 mm,

( ) activity of test bed near background.

Because the $AgNO_3$-impregnated KT-material may be used in iodine filters for reprocessing plants, further experiments were performed with sweep gas containing NO_2 (mostly 10 vol. %). With a sweep gas of 70 % R.H. and 5 vol. % nitrogen oxides, the adsorbed total amount of nitrogen oxides, water and acids built up from both was 90 - 140 wt. % of the unused KTC-material. The adsorber beds were soaked and practically no removal efficiency was measured for CH_3I under otherwise standard conditions. A series of additional experiments were performed with a temperature of 80°C in the sweep gas and adsorber bed. The dewpoint of the sweep gas was 30°C. The impregnated KTC-material used in one experiment was aged above fuming HNO_3 for 1.5 month and, unfortunately, a small amount was soaked with HNO_3 prior to pre-conditioning. The total weight gain on aging and soaking was 63 %. Table V shows the results of those experiments.

TEST CONDITIONS :

WET AIR, 30° C, 70% R.H.
PRE-HUMIDIFICATION ≥ 20 h
CH_3I - LOADING 1-2 mg/g
(calculated for 10 cm bed depth)
CH_3I - INJECTION : 1 h
AIR FLOW CONTINUED FOR AN
ADDITIONAL 20 - 24 h

○ = 2,5 cm BED DEPTH (KTC)
× = 5,0 cm BED DEPTH (KTC)
□ = 7,5 cm BED DEPTH (KTC)
▽ = 10,0 cm BED DEPTH (KTC)
● = 10,0 cm BED DEPTH (ZEOLITE)

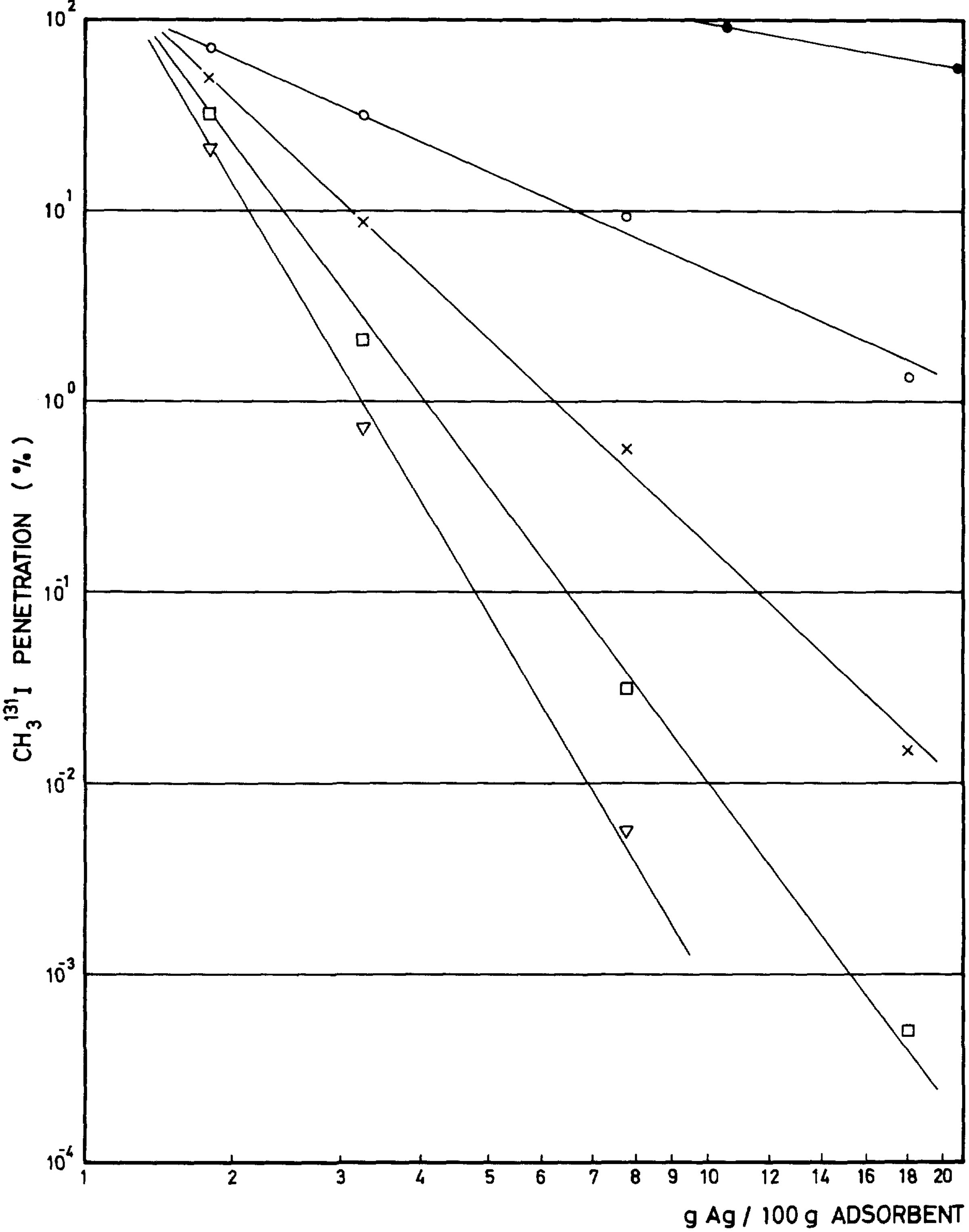

FIG. 1 $CH_3{}^{131}I$ PENETRATION OF Ag - IMPREGNATED ADSORBENTS AS A FUNCTION OF THE Ag - IMPREGNATION

In the CH_3I-experiments the concentration of the CH_3I in the sweep gas is constant over the injection time. A mixture of gaseous CH_3I and air is injected over a flowmeter from a storage tank. The I_2 is injected by a heated air stream flowing directly through the U-tube with solid elementary iodine. Temperature and gas flow are controlled, but the evaporation depends on the surface area of the I_2 crystals. The decrease of radioactivity in the U-tube is measured continuously and the concentration is calculated for the injection time of the main amount of I_2.

Table V $CH_3{}^{131}I$ AND ELEMENTAL RADIOIODINE REMOVAL EFFICIENCY OF KTC-MATERIAL WITH AN AIR-NO_2 MIXTURE AS THE SWEEP GAS

Experimental Conditions				Removal Efficiency				
Ag impreg. (g/100 g)+)	NO_2 vol.%	Loading (mg/g)++)	Concentration mg/m^3	Bed depth (cm)	2.5	5.0	7.5	10.0
				Stay time (sec)	0.1	0.2	0.3	0.4
8.0	8	1.6(CH_3I)	60		89.8	98.7	99.66	99.960
8.0	10	1.6(CH_3I), KTC aged	60		90.8	98.7	99.43	99.77
7.8	10	7.2 (I_2)	230		58.4	91.2	99.55	99.87
7.8	10	27.7 (I_2)	440		47.8	82.1	97.1	99.88
10.4	10	4.5 (I_2)	150		83.1	96.8	98.9	-
10.4	10	9.9 (I_2)	150		61.0	92.8	98.4	99.44

+) g silver per 100 g adsorber material (as delivered),

++) mg CH_3I or I_2 per g of impregnated adsorber material, calculated for 10 cm bed depth.

Three experiments are performed with I_2 in air of 30°C and 70 % R.H. Pre-humidification was $\geq$ 20 h. Loading and concentration were changed within a range of about 1 : 10. After loading, gas flow was continued for an additional 16 - 20 h. The conditions and the results are given in Table VI. Because the integral removal efficiencies (η integral) for larger bed depth are much smaller than expected, the removal efficiency for each single test bed (differential removal efficiency, η differential) is also given. From these data it can be concluded that an additional iodine compound is present. For this compound the KTC-material has a very low removal efficiency, much lower than for $CH_3{}^{131}I$. Analytical work is in progress with respect to the chemical nature of this compound.

Fig. 2 shows the penetration of the KTC test beds versus bed depth for two of the I_2 experiments. Each print represents one of the successive test beds. One run with $CH_3{}^{131}I$ is also included in the drawing. As demonstrated, $CH_3{}^{131}I$ is not the penetrating compound in the I_2 runs.

Table VI REMOVAL EFFICIENCY OF KTC FOR ELEMENTAL RADIOIODINE

Experimental Conditions			^{131}I Removal Efficiency (%)				
Ag impreg. (g/100g)+)	Loading (mg/g)++)	I_2 concentr. mg/m^3	Bed depth (cm)	2.5	5.0	7.5	10.0
			Stay time (sec)	0.1	0.2	0.3	0.4
7.8	1.3	20	η integral	99.959	99.984	99.989	99.991
			η differ.	99.959	61.6	29.4	17.9
7.8	2.6	150	η integral	99.83	99.984	99.988	99.990
			η differ.	99.83	90.8	23.9	18.7
7.8	9.4	250	η integral	97.6	99.975	99.983	99.986
			η differ.	97.6	98.98	30.1	19.9

+) g silver per 100 g adsorber material (as delivered),

++) mg I_2 per g of impregnated adsorber material, calculated for 10 cm bed depth.

Conclusion

In air of 70 % R.H. and in superheated steam of 110 and 150°C $AgNO_3$-impregnated KT-material showed very high removal efficiencies for CH_3I. Good removal efficiencies could also be measured for CH_3I and I_2 in air-NO_2 mixtures. For I_2 in wet air (70 % R.H.) the removal efficiency is also good, but under these conditions an unknown iodine compound was detected which is more penetrating than CH_3I. Under extremely high relative humidity (100 % R.H.), the $AgNO_3$-impregnated KT-material has low removal efficiencies and heating of the sweep gas is neccessary for good results.

So, $AgNO_3$-impregnated KT-material could be a useful adsorber material for fission product iodine with special suitability for off-gas cleaning in reprocessing plants. Due to the small amount of silver needed for the impregnation of the KT-material, the price will be relatively low. It is supposed to be about 3 times higher than the price of a good iodine-impregnated charcoal and about 1/10 of the price of Zeolite AgX.

TEST CONDITIONS:

WET AIR, 30° C, 70% R.H.
PRE - HUMIDIFICATION ≥ 24h
AFTER ^{131}I - INJECTION
AIR FLOW WAS CONTIN-
UED FOR AN ADDITIONAL
20 - 24 h

○ = LOADING : 25 mg I_2 /g
CONCENTRATION : 150 mg I_2 /m^3
△ = LOADING : 9 mg I_2 /g
CONCENTRATION : 250 mg I_2 /m^3
□ = LOADING : 1.2 mg CH_3J/g
CONCENTRATION : 60 mg CH_3J/m^3

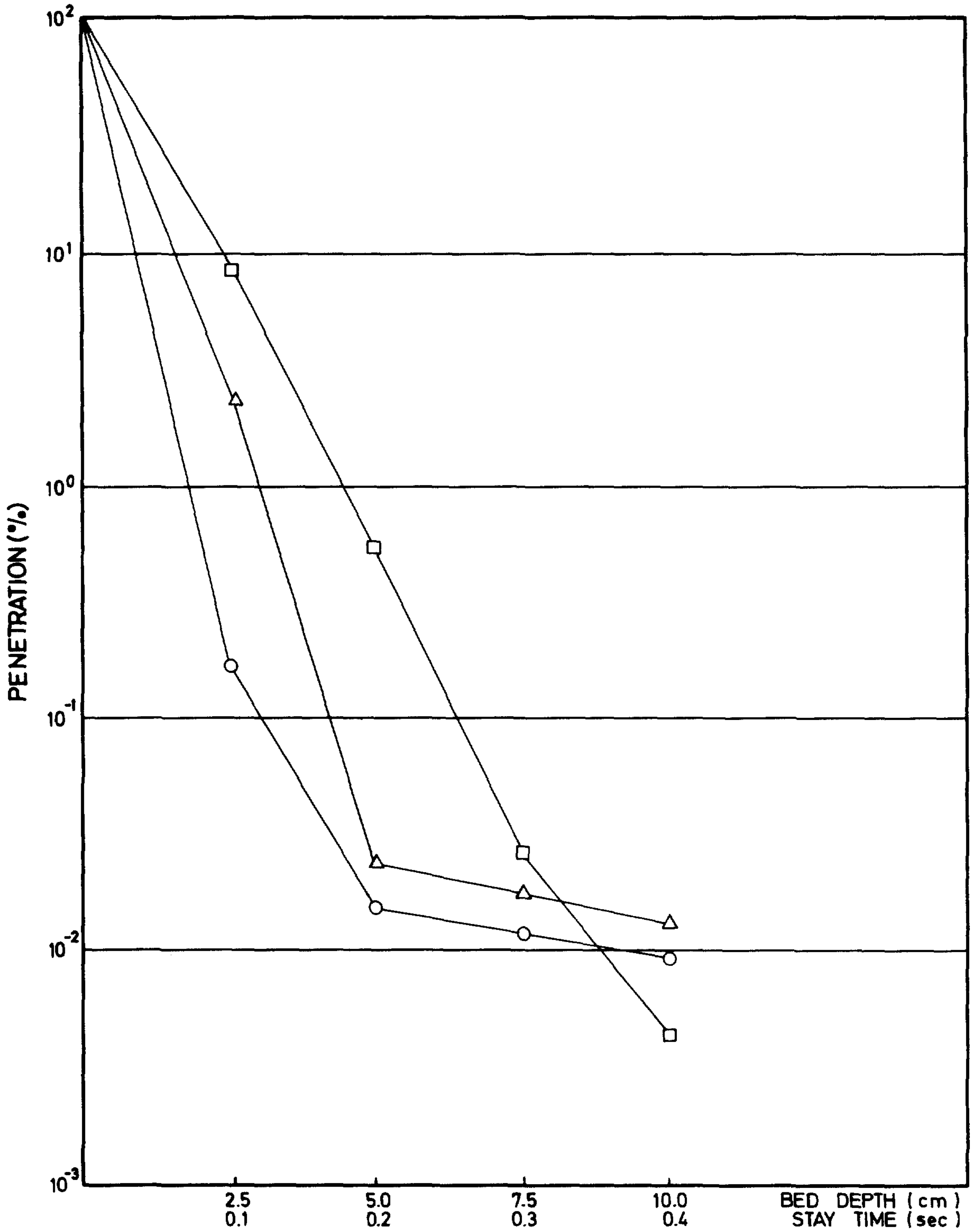

FIG. 2 PENETRATION OF ^{131}I IN FORM OF CH_3I AND I_2 THROUGH Ag - IMPREGNATED KTC - MATERIAL.

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DISCUSSION

YARBRO: I am very interested in your new approach to the application of silver and would like to comment rather than question. We have investigated silver zeolites with silver loadings down to as little as 10% of stoichiometric silver loading which is about 5% silver by weight. When operated at 200°C where silver zeolite is most effective and at iodine loadings less than 10 milligrams/cc this low silver zeolite is equally effective on the high silver materials, ~ 99% removal per inch of bed. This does get the cost down, maybe not quite as low as your reported costs, but to something approaching it for the silver zeolites.

WILHELM: We tested several silver zeolites and we tested the removal efficiency of silver zeolites against the amount of silver in the zeolite under high humidity conditions and it turned out the best thing to do is to have as much silver in the zeolites as possible. It is really the problem to get all of the silver in the zeolites that we like to get in. For relatively low relative humidity, like the conditions you mentioned, there is no problem at all because there is a broad variety of materials you could use. We are looking for two things. One thing is the adsorber material for a recirculating filter in the containment shell. And you won't have that low relative humidity in that case. The other thing is the off-gas stream of our reprocessing plant. And there we wouldn't like to keep the temperature that high.

YARBRO: We agree with your results. You get the good efficiency on a zeolite only at relatively low humidity and the higher temperatures.

WILHELM: Zeolites are very sensitive to humidity. We just learned that in our own experiment.

KOVACH: I would like to confirm your results, as you are aware that we have similar aluminum silver nitrate materials which were used on the sampling systems for a long time on short cooled fuel reprocessing. We found good efficiencies even at the very high humidity ranges and not only for methyl iodide but even for some of the higher organic iodides, which occur in the reprocessing plant sampling. Efficiency similar to the one obtained by you.

WILHELM: I really couldn't get your data; I think it's not possible at the moment. But I know you used aluminum oxide and we mostly used amorphous silicia acid. I think a very important part of the business is the porous structure of the material.

KOVACH: Yes, we used aluminum-silicate.

WILHELM: I don't know anything about the surface area and pore structure of your material.

KOVACH: We have about twice the surface area of your material.

WILHELM: In that paper I indicated only the lower numbers. I didn't give all the numbers for the different materials.

A STUDY OF THE ADSORPTION PROPERTIES OF METAL ZEOLITES FOR AIRBORNE IODINE SPECIES

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ABSTRACT

Silver zeolite as an adsorbent for various species of airborne radioiodine was first discussed at the Tenth AEC Air Cleaning Conference. Because of the promising nature of this material, a more detailed investigation of the properties and characteristics of both silver zeolite and other materials for the adsorption of various airborne iodine species is being conducted. The objectives of this program are to thoroughly investigate the adsorption properties of silver zeolite, prepare and investigate the properties of other metal zeolites for airborne iodine species, to more fully evaluate the most promising materials, and finally to provide support for full scale testing. Current laboratory studies include various methods for the preparation of silver zeolite; methyl iodide adsorption as a function of humidity, temperature, face velocity, and bed depth; desorption of iodine; loading capacity as a function of airborne iodine species concentration and flow rate; and product solubility. Similar studies have also been conducted for other selected metal zeolites. A limited number of charcoal adsorption tests have been conducted to provide comparison data.

Introduction

Since the proposed use of silver zeolite as an airborne iodine species adsorbent was presented at the Tenth AEC Air Cleaning Conference, a program has been established in our laboratory to systematically evaluate the possible use of metal zeolites in reactor cleanup systems and nuclear fuel processing plant off-gas streams. The objectives of this program are to: (1) thoroughly investigate the iodine species adsorption properties of silver zeolite, (2) prepare and investigate the adsorption properties of other metal zeolites, (3) more fully investigate the materials showing the greatest promise for the adsorption of the various airborne iodine species, and (4) provide support for full scale testing of the selected materials.

The conditions under which these materials are being tested include variations in face velocities or residence times, relative humidity, temperature, and pressure. Other factors being considered which may affect the iodine species adsorption are poisoning effects due to various contaminants, shelf and service life, and radiation damage. Results of methyl iodide and elemental iodine adsorption tests conducted on various metal zeolites are presented. Impregnated charcoal adsorption data are also presented for comparison purposes.

Test Apparatus

Two test systems are being used in these investigations. The system for the high temperature and pressure experiments is shown schematically in Figure 1. The basic design of the system is similar to one reported by Wilhelm(1) except the system is constructed of metal, primarily stainless steel, to withstand high pressures. It was designed to operate over a range of flow rates, relative humidities, temperatures, pressures, and iodine concentrations. The details of the apparatus are contained in another report(2). Also, an all-glass system, Figure 2, has been constructed for ambient temperature and pressure studies. Most of the studies of elemental iodine adsorption and poisoning effects from contaminants are being done with this system. In both systems, 1-inch diameter by 2-inch long test bed holders were used.

The major problems encountered in the operation of the test systems have been temperature control and relative humidity measurement. Because of the physical size of the system, it is impractical to place the entire system in a thermostated oven. Therefore, various portions of the metal system external to the oven have been heat-traced with heating tapes to maintain the desired temperature limits of ±0.25°C. Calibrated I-C thermocouples and platinum resistance thermometers with the appropriate bridges are used for temperature measurement.

The relative humidity is determined using two techniques depending on the conditions. For the lower temperature studies, 25 to 90°C, the relative humidity is measured at a point in the gas stream just prior to the test bed holders with a thermistor psychrometer. For tests conducted at temperatures of greater than 90°C, the relative humidity is determined by a calculation method similar to that reported by Ackley and Adams(3).

Metal-Ion Exchange

Sodium ions in pure Linde Molecular Sieve powder are readily replaced by silver ions. However, the zeolite used in these tests is in the extrudate form which contains 20 percent inert binder. This material exchanges more slowly than the powder. Batch exchange and ion-exchange column techniques have been studied. The batch exchange technique when used alone was inefficient and time consuming. With the ion-exchange column technique, a 95-percent silver-sodium exchange was relatively easy to attain. However, for more complete exchange, the addition of heat was required. The following procedure has been used to obtain 99+-percent silver-exchanged material: After the 1/8-inch diameter Linde Molecular Sieve 13X extrudate was ground, sieved, and blended to the proper mesh size distribution, 100-gram quantities of the material were water-washed by decantation to remove the fines,

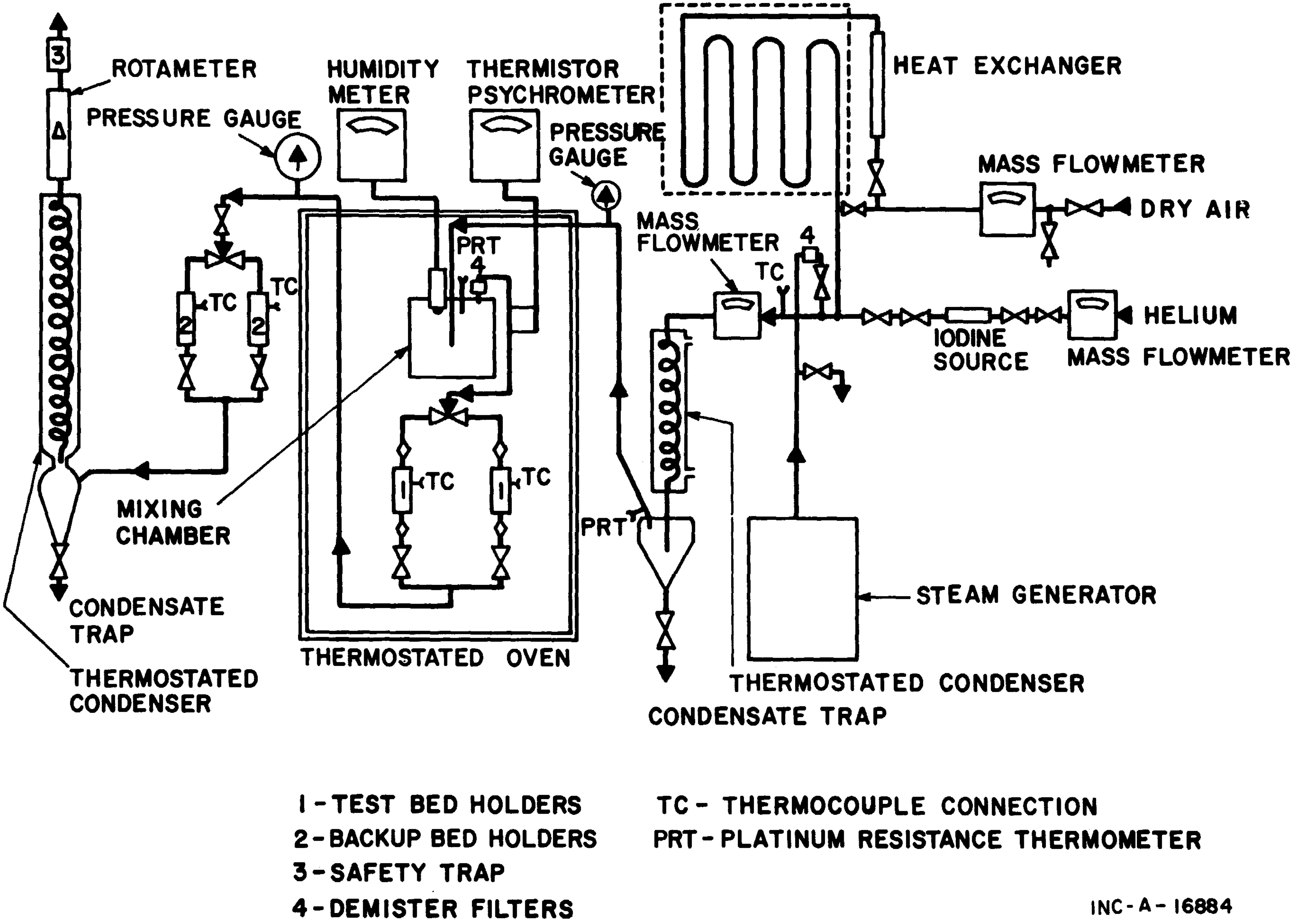

Fig. 1 Schematic Diagram of High Temperature, High Pressure Test Apparatus

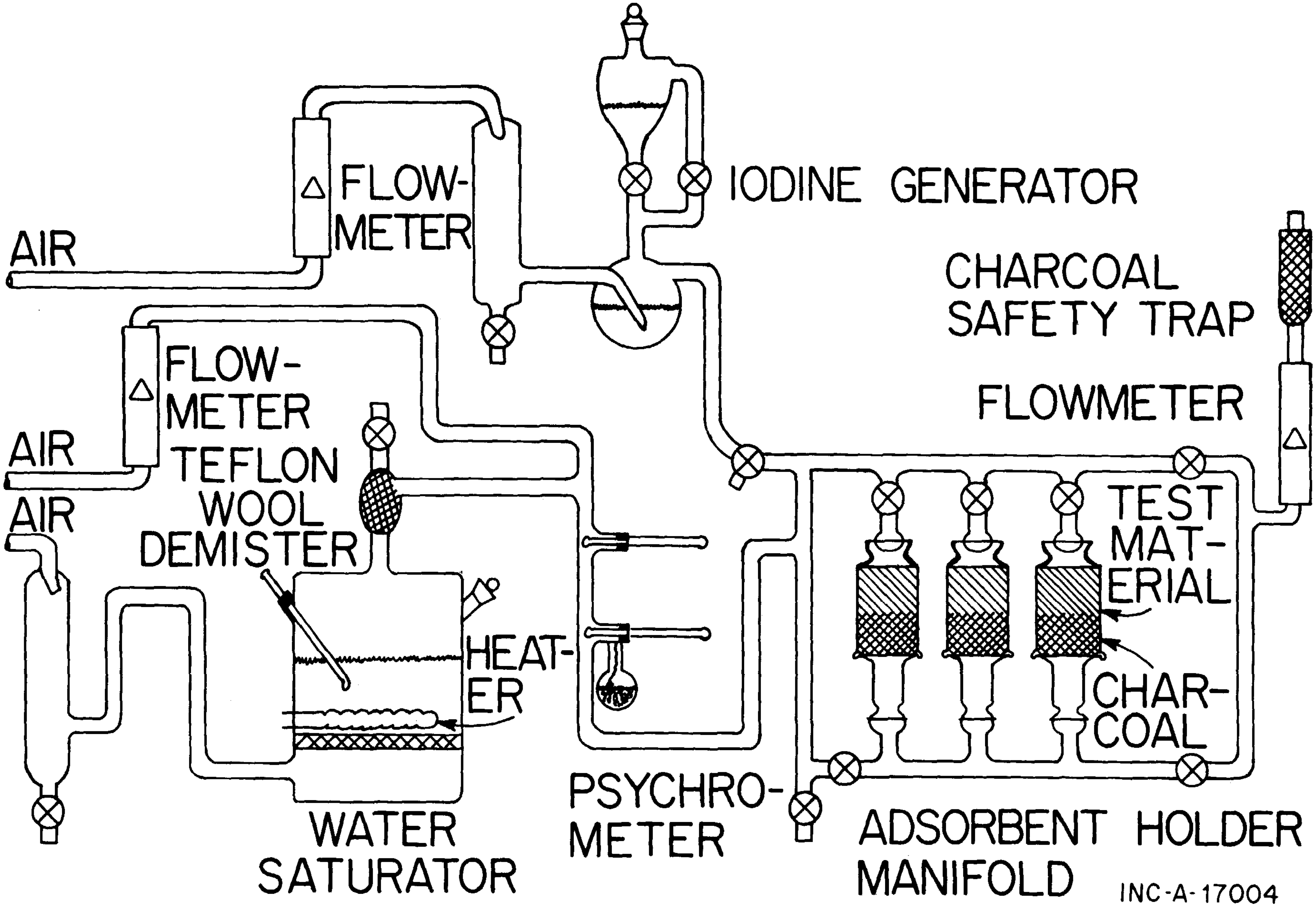

Fig. 2 Schematic Diagram of All-Glass Iodine Adsorption Test Apparatus

loaded into a glass ion-exchange column, 1-inch in diameter by 16-inches long, with water, and 700 ml of a 200 g/l silver nitrate solution was passed through the column at a rate of 2 to 3 ml/min. The partially-exchange material was transferred to a 1-liter round bottom flask with 250 ml of 200 g/l silver nitrate solution, the flask was heated to about 80°C, and the mixture was refluxed for 4 to 6 hours. The mixture was transferred to a Buchner funnel, washed with water until a negative silver test was obtained, air dried in the funnel for about one hour, and transferred to a vacuum over for final drying at a temperature of 100°C under vacuum.

Specific ion-exchange procedures to attain the most efficient exchange have not been developed for the other metal zeolites. The most successful exchange of metal ions with sodium have been done in a water-jacketed, ion-exchange column with the water-jacket temperature maintained at 75 to 80°C. An exchange of 97 percent has been attained for thallium and 98 percent for lead. The extent of exchange for cadmium and copper were not determined.

Test Procedures

The test procedures used in both systems are essentially the same. The test material is preequilibrated at the test conditions in the test apparatus for a period of one hour before the iodine species is introduced into the system. The results of water adsorption studies have shown that equilibration of the metal zeolite test material at test conditions is essentially complete within 45 minutes. For charcoal, a preequilibration time of 1½ to 2 hours has been found sufficient for the size of the test beds used in these tests. Several methyl iodide adsorption tests were made on both silver zeolite and impregnated charcoal beds which had been preequilibrated for up to 18 hours; but, no significant differences were observed in the adsorption properties compared with the shorter preequilibration times. The mesh size distribution of the metal zeolites was chosen so that the pressure drop across the bed of metal zeolite would be approximately the same as that of the charcoal. This distribution is 10 weight percent -10 +12 mesh and 90 weight percent -12 +14 mesh, U.S. Standard Series.

A loading period of one hour was used in the methyl iodide adsorption tests. Carrier-free I-131 was used to prepare the methyl iodide which was adsorbed on a bed of Porapak Q. The methyl iodide was then purged from the Porapak bed with helium. The methyl iodide concentration levels were varied from 0.1 to 10 $\mu g/M^3$ by regulating the helium flow rate through the Porapak Q bed. In initial studies, the adsorption beds were purged for one hour following the adsorption tests; however, the results of a number of subsequent tests showed that once the methyl iodide was adsorbed on the silver zeolite it remained in place. Therefore, the purge time was reduced to 15 minutes.

The preequilibration, loading, and purging times in the elemental iodine adsorption tests were similar to those used in the methyl iodide tests. In the elemental iodine adsorption tests, the iodine was generated by the reaction of iodate and iodide-131 in acid and was purged into the system with air.

In both the elemental iodine and methyl iodide adsorption tests, the test beds were radiometrically scanned to determine the longitudinal activity distribution on the test bed before it is disassembled and gross counted for quantitative distribution data.

Adsorption Test Results

The results of the methyl iodide adsorption tests with metal zeolites and some with impregnated charcoal are presented in Tables I, II, and III. The data in Table I were collected while a method for fully exchanging the sodium ions in Linde Molecular Sieve 13X was still in the developmental stage. Consequently, considerable scatter in the adsorption efficiencies was observed. Therefore, the data reported in this table represents an average of several tests conducted at the specified conditions. This is also the case, to a limited extent, for the methyl iodide adsorption efficiencies for silver zeolite at 60°C reported in Table II.

Studies were conducted to determine the effect of bed temperature on the adsorption efficiency of methyl iodide by silver zeolite. In these tests, heating tapes were wrapped around the stainless steel test bed holders, and the temperature was increased until the centerline temperature of the test bed was 10°C above the test atmosphere temperature. The results of these tests are given in Table IV. Because the metal zeolites are good heat conductors, the temperature gradient across the metal zeolite adsorption beds would not be expected to be large and the measured temperature gradient across a bed of silver zeolite was 1 to 2°C in a dry-air atmosphere and a face velocity of 92 ft/min.

A systematic study of the adsorption properties of metal zeolites for airborne elemental iodine has recently been started. The data collected to date are reported in Table V.

Effect of Contaminants on Adsorption

Tests in which the effect of various gaseous contaminants on the iodine adsorption of silver zeolite were studied are summarized in Table VI. Several procedures were used in conducting these tests. In some of the tests, samples of aluminum metal were dissolved in nitric acid with a mercuric nitrate catalyst, and the dissolution gases passed through the silver zeolite adsorption beds with the contaminant gas. When the dissolution was nearly complete, I-131 in the iodide form was introduced into the dissolution flask, and the generated iodine purged through the adsorption bed with the contaminant gas. In other tests, the contaminated gas was passed through the adsorbent bed, after being water saturated, and the iodine was generated by adding I-131 to a

TABLE I

METHYL IODIDE ADSORPTION EFFICIENCIES OF VARIOUS METAL ZEOLITES AND IMPREGNATED CHARCOALS AT 25°C FOR VARIOUS FACE VELOCITIES AND RELATIVE HUMIDITIES

Material	Actual Face Velocity (ft/min)	Relative Humidity (Percent)	Adsorption Efficiency (Percent)
AgX	46	90	99+(a)
AgX	46	95	99+(a)
AgX	46	100	99+(a)
BC 727(b)	46	90	76
BC 727	46	100	70
AgX	92	90	94(a)
AgX	92	95	92(a)
AgX	92	100	90(a)
BC 727	92	90	67.0
Whitco #42(c)	92	90	92.4
MSA 85851(d)	92	90	89.1
NACAR G 615(e)	92	90	94.3
CdX	92	90	1.4
PuX	92	90	1.5
PbX	92	90	0.8

(a) Incompletely exchanged material

(b) Barnebey-Cheney Co.

(c) Whitco Chemical Co.

(d) Mine Safety Appliance Co.

(e) North American Carbon Co.

TABLE II

METHYL IODIDE ADSORPTION EFFICIENCIES FOR SILVER ZEOLITE AND IMPREGNATED CHARCOALS AT 60 AND 90°C FOR VARIOUS FACE VELOCITIES AND RELATIVE HUMIDITIES

Material	Actual Face Velocity (ft/min)	Relative Humidity (Percent)	Adsorption Efficiency (Percent)
At 60°C			
AgX	58	90	99.3
NACAR G 615	58	90	96.9
MSA 85851	58	90	90.8
AgX	114	80	99.8
AgX	116	90	96.2
AgX	118	95	95.7
AgX	119	100	92.5
MSA 85851	116	90	76.6
MSA 85851	119	100	44.8
At 90°C			
AgX	63	89	99.7
AgX	65	88	99.7
AgX	81	83	99.7
AgX	87	90	99.3
AgX	89	84	99.5
AgX	150	96	94.9
AgX	151	96	92.0
MSA 85851	59	94	98.1
MSA 85851	85	83	97.7
MSA 85851	89	84	93.6
MSA 85851	88	91	89.5

TABLE III

METHYL IODIDE ADSORPTION EFFICIENCIES OF METAL ZEOLITES AND IMPREGNATED CHARCOALS AT 125°C FOR VARIOUS FACE VELOCITIES AND RELATIVE HUMIDITIES

Material	Actual Face Velocity (ft/min)	Relative Humidity (Percent)	Adsorption Efficiency (Percent)
AgX	48	85	99.94
AgX	47	89	99.91
AgX	48	90	99.62
CdX	49	85	1.77
CuX	51	86	0.82
PbX	48	85	7.47
TlX	50	86	1.02
MSA 85851	47	84	99.35
MSA 85851	48	89	98.23
MSA 85851	50	98	90.70
AgX	100	84	99.72
AgX	99	91	99.37
AgX	99	96	98.94
MSA 85851	102	83	96.73
MSA 85851	97	90	93.18
MSA 85851	93	97	89.29
NACAR G 615	99	85	99.43
Witco #42	99	85	98.70
BC 727	97	83	98.39

TABLE IV

METHYL IODIDE ADSORPTION EFFICIENCIES OF HEATED ADSORPTION BEDS OF METAL ZEOLITES

Material	Actual Face Velocity (ft/min)	Relative Humidity (Percent)	Test Atm. Temp. (°C)	Test Bed Center-line Temp. (°C)	Adsorption Eff. (Percent)
AgX	92	90	25	35	99.9+
AgX	92	95	25	35	99.9+
AgX	92	100	25	35	99.9+
CuX	92	70	25	30	20.8
PbX	92	70	25	30	82.6
CdX	48	85	125	135	1.20
CuX	48	85	125	135	0.03
PbX	44	82	125	135	1.70

TABLE V

ELEMENTAL IODINE ADSORPTION EFFICIENCIES OF VARIOUS METAL ZEOLITES AT AMBIENT TEMPERATURE (22°C) FOR VARIOUS FACE VELOCITIES AND RELATIVE HUMIDITIES

Material	Actual Face Velocity (ft/min)	Relative Humidity (Percent)	Adsorption Efficiency (Percent)
NaX (13X)	46	90	4.24
PbX	46	90	7.21
TlX	46	90	27.37
AgX	92	100	99.99+
CdX	92	100	0.82
PbX	92	100	5.16

sulfuric acid solution. As before, the generated I-131 was passed through the adsorbent bed with the contaminant gas.

In all of these tests, the adsorption beds were at ambient temperature, about 25°C, and the face velocity across the 1-inch diameter by 2-inch long glass test bed averaged about 92 ft/min. The humidity was maintained close to saturation, and in some cases, considerable condensation occurred in the beds. The iodine injection period was usually relatively short--15 to 30 minutes. Several impregnated charcoal adsorption beds followed the silver zeolite beds; and after the tests were completed, each adsorption bed was counted and the I-131 distribution calculated.

Adsorption Capacity Studies

Adsorption capacity tests for methyl iodide on silver zeolite have been conducted and are reported in Table VII. Similar data for Barnebey-Cheney 727 impregnated charcoal are also included. The experiments were done with a dry-air atmosphere and 46 ft/min face velocity in the stainless steel test apparatus using the same adsorbent bed holders previously described. In this experiment, the backup adsorption bed material was silver zeolite. It was placed in a lead cave over a sodium iodide detector which was connected to a count rate meter with a recorder output. The tests were conducted using a variety of methyl iodide concentration levels and loading times. For the silver zeolite tests, the methyl iodide flow was stopped when the activity level reached 10 times background. The test bed was then purged with air. A similar procedure was used for charcoal; but, because methyl iodide is easily purged from the charcoal, the methyl iodide flow was stopped at lower activity levels in an attempt to obtain comparable data. Typical methyl iodide adsorption and desorption curves observed for silver zeolite and Barnebey-Cheney 727 charcoal are shown in Figures 3 and 4, respectively. The maximum methyl iodide adsorption obtained on silver zeolite at the given test conditions

TABLE VI

EFFECT OF VARIOUS GASES ON IODINE ADSORPTION CHARACTERISTICS OF SILVER ZEOLITE

Gas	Amount of Gas (Total Flow Time)	Dissolver Contents	Percent I_2 Adsorption
NO_2	55 liters (4 hr)	Al-HNO_3	99.7
CO_2	50 liters (7 hr)	Al-HNO_3	94.2
	600 liters (1.3 hr)	Al-HNO_3	99.2
	430 liters (1.5 hr)	H_2SO_4-$NaNO_2$	99.9+
O_2	630 liters (1.2 hr)	Al-HNO_3	98.4
	1200 liters (2 hr)	H_2SO_4-$NaNO_2$	99.9+
SO_2	500 liters (10% SO_2) (1.5 hr)	H_2SO_4-$NaNO_2$	99.9+
H_2S	70 liters (8% H_2S) (2 hr)	H_2SO_4-$NaNO_2$	99.9+
Propane	560 liters (1.2 hr)	H_2SO_4-$NaNO_2$	99.9+
Hexone	200 ml distilled through bed	H_2SO_4-$NaNO_2$	99.9+

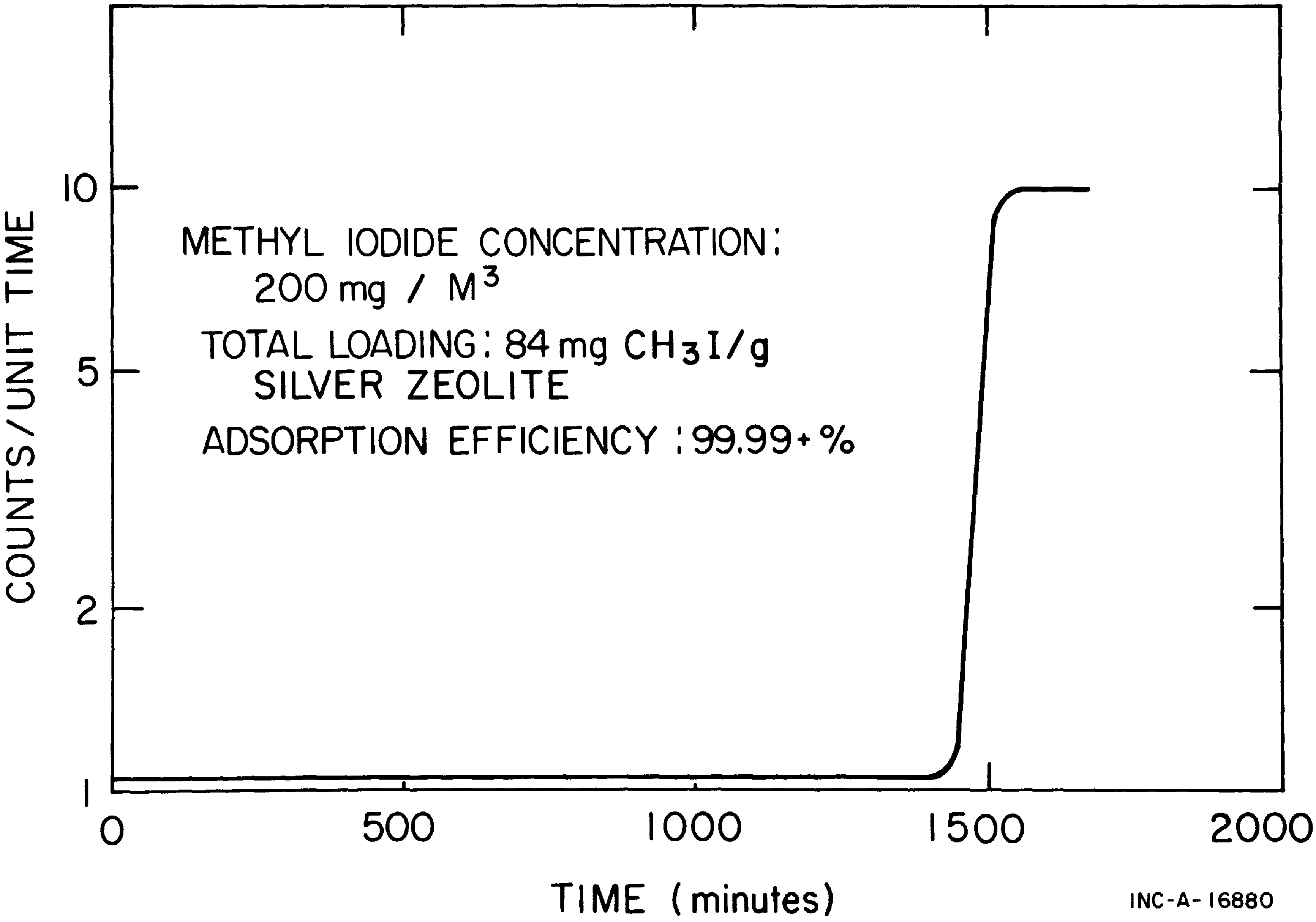

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Fig. 3 Adsorption Curve for Silver Zeolite in Dry Air at 25°C

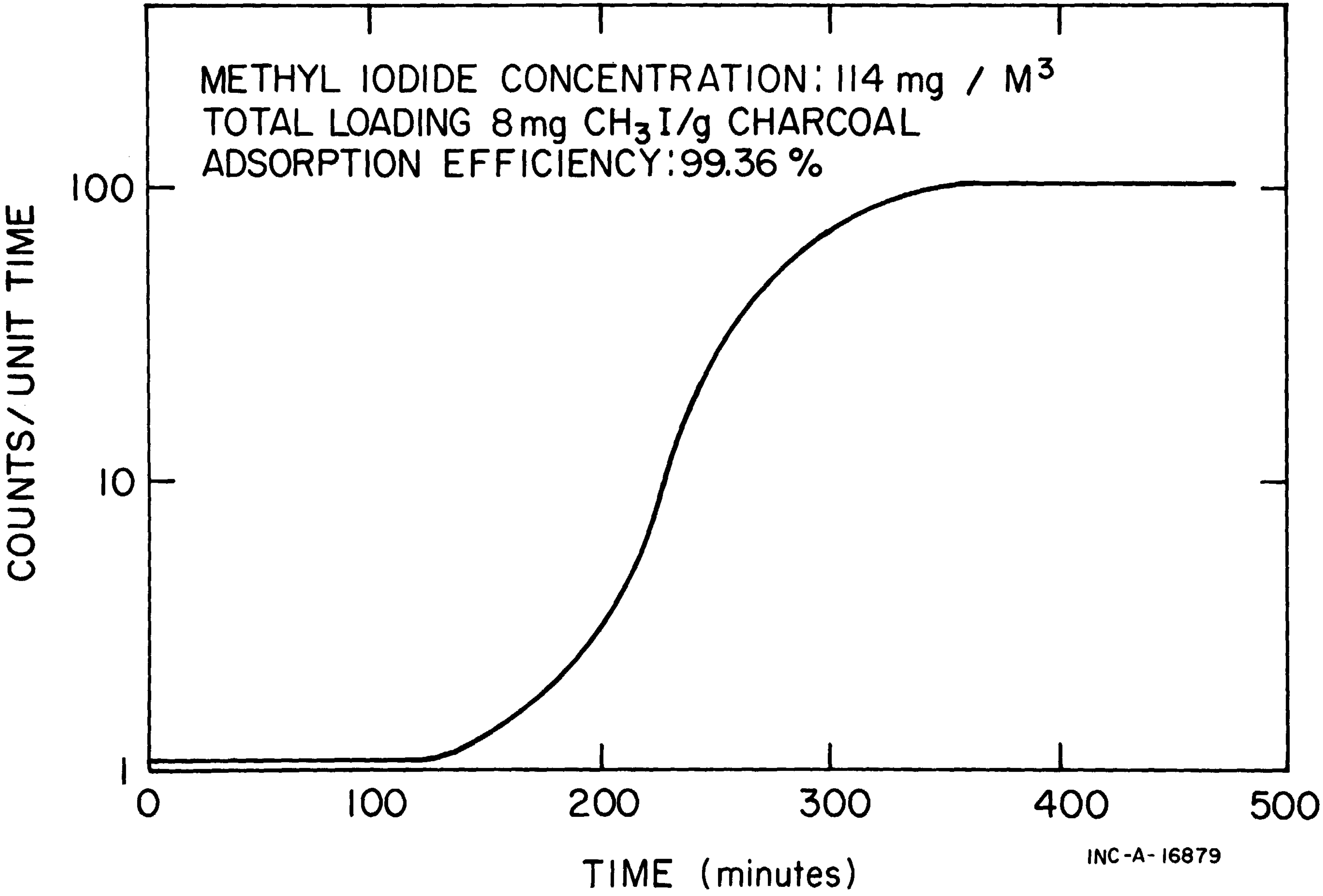

Fig. 4 Adsorption Curve for Charcoal (BC-727) in Dry Air at 25°C

TABLE VII

METHYL IODIDE LOADING CAPACITY OF SILVER ZEOLITE AND BC 727 CHARCOAL IN DRY AIR AT 25°C

Material	Actual Face Velocity (ft/min)	Loading Time (min)	Purge Time (min)	Airborne CH_3I Conc, (g/M^3)	Load. Capacity (mg CH_3I/g bed)	Ads. Eff. (Percent)
AgX	46	30	90	5.1	37	99.99+
BC 727	46	21	90	4.5	51	91.68
AgX	46	177	30	1.5	63	99.97
BC 727	46	56	120	1.4	44	93.09
AgX	46	1560	20	0.23	84	99.99+
BC 727	46	180	210	0.20	20	97.33
BC 727	46	137	263	0.15	11	99.10
BC 727	46	128	525	0.11	8	99.36
AgX(a)	46	240	30	1.20	68	99.99+

(a) Test bed material heated to 100°C.

was 84 mg CH_3I/g AgX, which is about 14 percent of the theoretical test bed capacity. Less than 8 mg CH_3I/g charcoal were adsorbed by Barnebey-Cheney 727 charcoal at about half the airborne methyl iodide concentration and with a lower adsorption efficiency.

Aqueous Leaching of Methyl Iodide from Silver Zeolite

The leachability of methyl iodide adsorbed on both silver zeolite and Barnebey-Cheney 727 charcoal was determined. In this study, 30 g of silver zeolite and 13 g of charcoal, each loaded with I-131 tagged methyl iodide, were placed in separate beakers containing 5 ml of water per gram of adsorbent material. The mixture was swirled several times, transferred to glass columns containing glass wool filters, and the liquid phase was drained from the columns at a rate of 2 ml/min. Each column was then leached three more times with like quantities of water. The solutions were counted and passed, successively, through 3-micron and 0.22-micron Millipore filters. After each filtration, the liquid phases and the filters were counted for I-131 activity.

Results from these tests show that: (1) fines are associated with each material and collect on the 3-micron filter but represent less than one percent of the total activity, (2) little or no activity was deposited on the 0.22-micron filter, (3) methyl iodide adsorbed on the charcoal is easily removed with water, and (4) methyl iodide adsorbed on silver zeolite is not removed with water. Approximately 65 percent of the activity was leached from the charcoal by the rinsings while less than 0.01 percent of the activity was removed from the silver zeolite.

Mechanism Studies

To study the mechanism for the adsorption of methyl iodide by silver zeolite, a water-saturated stream of nonradioactive methyl iodide and helium purge gas was passed through a bed of silver zeolite until it became saturated with methyl iodide. The collected effluent was analyzed by gas chromatography, and methyl alcohol was identified as the primary reaction product. If it were assumed that for every mole of methyl iodide adsorbed, a mole of methyl alcohol was liberated,about 70 percent of the adsorbed methyl iodide could be accounted for.

Discussion and Conclusions

The results of the methyl iodide adsorption studies on silver zeolite show that, like impregnated charcoal, its adsorption characteristics are adversely affected by high humidity atmospheres, but to a lesser degreee. Although a thorough study has not been completed, results to date indicate that the methyl iodide adsorption properties of silver zeolite at high relative humidities are very sensitive to the extent of silver-sodium exchange.

The precision of the methyl iodide adsorption data on silver zeolite shows that the test apparatus is sufficiently controlled and the measuring devices sufficiently accurate to yield reproducible data.

The contaminant gas studies show silver zeolite to be reasonably resistant to poisoning by a number of contaminant gases. Silver zeolite exhibits a high loading capacity per gram of adsorbent material. The fact that it forms an insoluble product is of particular importance.

The mechanism by which the iodine species is adsorbed and retained by the silver zeolite is not completely understood. Based on the evidence obtained on its thermal stability(4), insolubility, and the analysis of the reaction products, it seems likely that silver iodide is being formed in the zeolite structure. In the case of methyl iodide adsorption, the methyl radical probably combines with a hydroxyl group, presumably from water, and is liberated as methyl alcohol. Because hydrogen replacement of the silver ion in type X zeolite is extremely difficult, it is doubtful that the proposed mechanism would occur without some crystalline degradation of the zeolite structure.

Fully-exchanged silver zeolite is the most efficient material examined to date for the adsorption of airborne iodine species under the adverse conditions expected in the event of a loss-of-coolant accident in a PWR. Other metal zeolites, though less efficient, may also be useful for this purpose. Silver zeolite appears to be ideally suited for use as an airborne iodine species adsorbent in other phases of the nuclear industry, such as , nuclear fuel processing plant off-gas streams.

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DISCUSSION

KOVACH: You might have mentioned it, but it probably escaped me. What was the particle size of your zeolite?

PENCE: You are right; I neglected to mention that. The standard mesh size distribution we used in our tests was 10 wt. percent 12 mesh and 90 wt. percent 14 mesh, U. S. Standard series. As you have indicated in your reports and as does Dr. Wilhelm, the adsorption efficiency is highly dependent upon the particle size. And we found this to be particularly true when we compared the results of the adsorption tests of silver zeolite with those of the chemically impregnated charcoal.

DOMNING: Have you considered the possibility that the production of your methyl alcohol is from a perhydroxol ion rather than from a hydroxol ion in the surface of the filter?

PENCE: This could very well be. We don't claim to really know what's going on in the zeolite structure.

WILHELM: In your zeolite studies, I think the preconditioning time for humid air was 45 minutes? Is that correct?

PENCE: Forty-five minutes to an hour, yes.

WILHELM: Did you run some experiments on 100% relative humidity with much longer preconditioning times too?

PENCE: Yes, we conducted tests in which we used preconditioning times up to 24 hours, and we did not tetect any appreciable differences in the adsorption efficiencies between the tests in which we used one hour preconditioning and those in which we used 24 hour preconditioning times.

One thing I might comment on, in regards to some of your earlier statements concerning the acid stability of the zeolites is that the Y-type zeolite is supposedly more acid resistant than the X-type zeolite. We found the Y-type zeolite we tested had a poor binder for our purposes. When we attempted to exchange it, the particles collapsed. And this we concluded to be associated with the binder. The type of binder has tremendous influence on the usefulness of the materials for this purpose. I don't know of any self bonded X- or Y-type zeolites that are commercially available, but I think this would make the zeolite more desirable for our use.

WILHELM: Well, concerning the stability of the binder I think that we both agree.

PENCE: I think you had better success than we did with the Y-type zeolite.

WILHELM: I believe the lattice of the zeolite itself gets hurt by the acid. You see what happened to us was that the whole material broke down in wet gas containing NO_2. This happened also in pure steam of high temperature and pressure.

PENCE: We certainly agree that there is some degradation occurs during the exchange with silver nitrate. How much this effects the properties we have not really determined. So far it has been no problem for us.

ANALYSIS OF CONCURRENT ADSORPTION AND CHEMICAL REACTION IN PACKED BEDS*

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ABSTRACT

A series of equations were developed to describe accurately concurrent adsorption and chemical reaction of gases in packed granular beds. These equations use analysis by statistical moments to develop a straightforward, rapid method for calculating breakthrough curves. A useful feature of these equations is that they provide a method for calculating the fraction of adsorbate which will pass through the bed unreacted.

Introduction

Presented in this paper is a set of equations which were derived to facilitate the study of concurrent adsorption and chemical reaction of air pollutants at low concentrations in a packed granular bed (such as a bed of chemically treated charcoal or reactive molecular sieves). These equations differ significantly from those usually used in chemical engineering practice for the analysis of this particular problem. These differences are:

A. Inclusion of certain factors which are often omitted in chemical engineering practice, but which may be important here. These factors are: 1) interparticle diffusion; 2) hold-up in the interparticle void volume; and 3) an exact equation for intraparticle mass transfer.

B. Exclusion of effects expected only at high concentrations of adsorbate. These effects are: 1) a nonlinear isotherm; 2) changes in the carrier gas velocity as a result of adsorption and chemical reaction of the adsorbate; and 3) secondary effects resulting from the heat of adsorption and chemical reaction.

C. Analysis of the breakthrough curve by the method of statistical moments.

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1. The Basic Differential Equation

The differential equation for mass transfer within the bed is:

$$D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - \frac{\partial C}{\partial t} - k\frac{\partial}{\partial t}\int_0^t C(t-\tau)g(\tau)e^{-\alpha\tau}d\tau$$
$$-\alpha k\int_0^t C(t-\tau)g(\tau)e^{-\alpha\tau}d\tau = 0. \qquad (1)$$

where

D = effective interparticle diffusion coefficient, cm^2/sec
C = concentration of adsorbate in the mobile phase
x = distance from inlet, cm
V = interparticle mobile phase velocity, cm/sec
t = time following introduction of pulse of adsorbate, sec
k = partition coefficient for adsorbate between mobile and stationary phase, measured statically, assuming $\alpha = 0$.
$g(\tau)$= mass transfer function for equilibrium between stationary and mobile phases, sec^{-1}.
α = first order reaction constant, sec^{-1}.

The first two terms in Equation 1 represent, in order, the amount of adsorbate added to a differential strip by 1) diffusion and 2) convection. The last three terms give in order 3) the increase of adsorbate in the mobile phase, 4) the increase of adsorbate in the stationary phase, and 5) the amount of adsorbate lost by chemical reaction.

The function $g(\tau)$ describes the rate of mass transfer between the stationary and mobile phases. If the adsorbent particles consist of homogeneous spheres there is no simple equation for $g(\tau)$, but the Laplace transform of $g(\tau)$, $\bar{g}(s)$ can be shown to be:(1)

$$\bar{g}(s) = \frac{12\beta}{s}\left\{\sqrt{\frac{s}{4\beta}}\coth\left[\sqrt{\frac{s}{4\beta}}\right] -1\right\} \qquad (2)$$

$$\beta = D_p/d_p^2 \tag{3}$$

where

β = time constant for intraparticle diffusion, sec^{-1}
D_p = coefficient for intraparticle diffusion, $\mathrm{cm}^2/\mathrm{sec}$
d_p = diameter of the adsorbent particles, cm.

The Laplace transform of Equation 1 with respect to time yields the following differential equation,

$$D\frac{d^2\bar{C}(s)}{dx} - V\frac{d\bar{C}(s)}{dx} - s\bar{C}(s) - k(s+\alpha)\bar{C}(s)\bar{g}(s+\alpha) = 0. \tag{4}$$

which, with the boundary condition that a unit pulse of adsorbate was injected into the bed at time, t = 0, integrates to give the following equation for the Laplace transform of the breakthrough curve:

$$\bar{C}(s) = \exp\left\{-\left[\sqrt{V^2 + 4D(s+\alpha)k\bar{g}(s+\alpha) + 4Ds} - V\right]\frac{x}{2D}\right\}. \tag{5}$$

2. Analysis by Statistical Moments

The method of analysis proposed here, following a similar procedure in gas chromatography,(2,3) is to determine the statistical moments of the breakthrough curve from the equation for its Laplace transform, and then use these moments in a Gramm-Charlier series to calculate the observed breakthrough curve.

The nth ordinary moment of the breakthrough curve

$$M_n' = \int_0^\infty t^n C(t)dt \tag{6}$$

is calculated from the Laplace transform of the breakthrough curve as follows:

$$M_n' = \lim_{s\to 0}(-1)^n \frac{d^n}{ds^n}\bar{C}(s). \tag{7}$$

In the equations which follow, we will use the zeroth ordinary moment, the normalized first ordinary moment, which is defined as

$$M_1 = \int_0^\infty tC(t)dt \Big/ \int_0^\infty C(t)dt, \tag{8}$$

i.e.,

$$M_1 = M_1'/M_o', \tag{9}$$

and for all the higher moments we will use the normalized central moment, defined as

$$\underset{n>1}{M_n} = \int_0^\infty (t - M_1)^n C(t)dt \Big/ \int_0^\infty C(t)dt. \tag{10}$$

These moments are readily calculated from the ordinary moments.

Even without further formal mathematical analysis, these moments supply useful information about the adsorbate breakthrough curve. The zeroth, first, second and third moments supply, in order, information about the fraction of adsorbate which reacted, the mean holdup time for unreached adsorbate, the variance in the holdup time of the unreacted adsorbate, and the skewness in the breakthrough curve of the unreacted adsorbate.

The formal analysis which we suggest for this analysis is a reconstruction of the breakthrough curve as a Gramm-Charlier series. The breakthrough curve as a function of the first three terms of this series is:

$$C(t) = \frac{M_o}{\sqrt{2\pi}} e^{-\xi^2} \left[1 + \frac{M_3}{6M_2^{3/2}} (\xi^3 - 3\xi) + \frac{1}{24} \left\{ \frac{M_4}{M_2^2} - 3 \right\} \left\{ \xi^4 - 6\xi^2 + 3 \right\} \right]. \tag{11}$$

where

$$\xi = \frac{t-M_1}{M_2^{1/2}} \tag{12}$$

4. Significance of this Analysis

Quite often breakthrough curves appear to be, within the limits of experimental error, Gaussian curves. This is because the many random movements of the molecules passing through the bed result in a distribution that, from the central limit theorem of statistics, ultimately assumes a Gaussian form. The Gramm-Charlier series is particularly suited for the analysis of breakthrough curves of this nature. Indeed, the first term of the Gramm-Charlier series gives the breakthrough curve in the form of the nearest Gaussian approximation and the remaining terms can be considered to be corrections to the Gaussian approximation.

In this analysis it is necessary to have only the zeroth, first and second moments to calculate the breakthrough curve as a Gaussian approximation. These moments are, in order:

$$M_o = e^{-\left(\sqrt{V^2 + 48D\beta(\phi\coth\phi-1)} - V\right)\frac{x}{2D}}, \tag{13}$$

$$M_1 = \frac{x\left\{3k\left(\sqrt{\frac{\beta}{\alpha}}\coth\phi - \frac{1}{2}\mathrm{csch}^2\phi\right) + 1\right\}}{\sqrt{V^2 + 48D\beta(\phi\coth\phi - 1)}}, \tag{14}$$

$$M_2 = \frac{\frac{3xk}{4}\left\{2\sqrt{\frac{\beta}{\alpha^3}}\coth\phi + \frac{1}{\alpha}\operatorname{csch}^2\phi - \frac{1}{\sqrt{\alpha\beta}}\operatorname{csch}^2\phi\operatorname{ctnh}\phi\right\}}{\sqrt{V^2 + 48D\beta\,(\phi\coth\phi - 1)}} ,$$

$$+ \frac{2Dx\left\{3k\left(\sqrt{\frac{\beta}{\alpha}}\coth\phi - \frac{1}{2}\operatorname{csch}^2\phi\right) + 1\right\}^2}{\left[V^2 + 48D\beta(\phi\coth\phi - 1)\right]^{3/2}} \qquad (15)$$

where

$$\phi \equiv \sqrt{\frac{\alpha}{4\beta}} . \qquad (16)$$

We have also derived the third, fourth and fifth moments, and these moments, when needed, should permit breakthrough curves which deviate from a simple Gaussian curve to be calculated with increased accuracy.

There are modifications of this type of analysis leading to even simpler results. One needs to know the range of convergence of such procedures before advocating their application to engineering. The main point to be made in this paper is to show that analysis by statistical moments can lead to a straightforward, rapid calculation of the performance of packed beds in which both adsorption and chemical reaction is taking place. In fact one result already obtained, the zeroth moment, gives the fraction of adsorbate which will pass through the bed unreacted, and this was one of the main goals of the analysis.

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APPLICATION OF METAL ZEOLITES TO RADIOIODINE AIR CLEANING PROBLEMS

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ABSTRACT

The use of fully loaded zeolite as an adsorbent for airborne iodine in reactor containment filter systems was first proposed by Idaho Nuclear Corporation at the Tenth Air Cleaning Conference. Since that time, detailed investigations of the iodine adsorption properties of silver and other metal-loaded zeolites have suggested several other potential applications for these materials. One important application is the removal of iodine from the off-gas of nuclear fuel processing plants. The high temperature operability of metal zeolites make them attractive for this application. The use of tandem beds containing different metal-loaded zeolites and the advantages of using heated beds are discussed. An examination of the economics of metal zeolites shows the use of these materials to be practical for many iodine air cleaning applications.

Introduction

Since the use of silver zeolite as an adsorbent for airborne iodine species was first proposed(1) at the Tenth USAEC Air Cleaning Conference in 1968, a considerable number of R & D programs, both here(2,3,4) and abroad(5,6) have been initiated to more fully evaluate the iodine species adsorption properties of silver and other metal loaded zeolites. To date, the results of these investigations are most promising. It is encouraging that not only are different materials being investigated, but also that different air filtration hardware concepts are being studied.

Because of the wide operational flexibility of inorganic adsorbents, especially that of silver zeolite, the potential usefullness of these materials extends to many areas. Among these are: (1) on-line or emergency air cleaning filtration units for nuclear power reactors, (2) iodine removal from off-gas streams in nuclear fuel processing plants, (3) iodine scrubbing from natural gas released by Plowshare experiments, (4) face masks and air filtration units for military use, (5) air filtration systems for civil defense fallout shelters, and (6) use in monitoring and sampling devices for Health Physics surveillance. A more novel use of silver zeolite is as a molecular hydrogen getter.

This paper briefly reviews existing iodine species adsorption data for metal zeolites, discusses the operational flexibility of metal zeolites as applied to various air cleaning problems with emphasis on reactor and nuclear fuel processing plant applications, and presents a preliminary examination of the economics of metal zeolites compared with existing systems.

Iodine Species Adsorption on Silver Zeolites

The adsorption of methyl iodide by silver zeolite as a function of relative humidity and temperature at 100 afpm face velocity is shown in Figure 1. Also shown are the 90, 95, and 99 percent adsorption isotherms for methyl iodide. The determined percent methyl iodide adsorption for each test condition is also given. The purpose of this plot is to show the operational limitations of silver zeolite as a function of atmospheric conditions and to show the methyl iodide adsorption systematics of silver zeolite.

For a given temperature, the adsorption of methyl iodide decreases with increasing relative humidity; however, this effect is temperature dependent, being less at higher temperatures. For a given relative humidity, the methyl iodide adsorption increases with increasing temperature. We believe the increased adsorption efficiency is related to an increase in reaction rate at the higher temperatures. It is evident that high temperature and low humidity promote increased adsorption efficiency. Similar tests were conducted at about 50 afpm face velocity, with greater than 99 percent methyl iodide adsorption being obtained for all test conditions.

Based on the adsorption data obtained at 50 afpm face velocity and at 100 afpm face velocity, the methyl iodide adsorption efficiency (A) should be calculable as a function of relative humidity (RH), temperature (T), and face velocity (FV) for any given set of conditions. Rigorous treatment of the relationship:

$$A \sim (f)\mathrm{RH,T,FV}$$

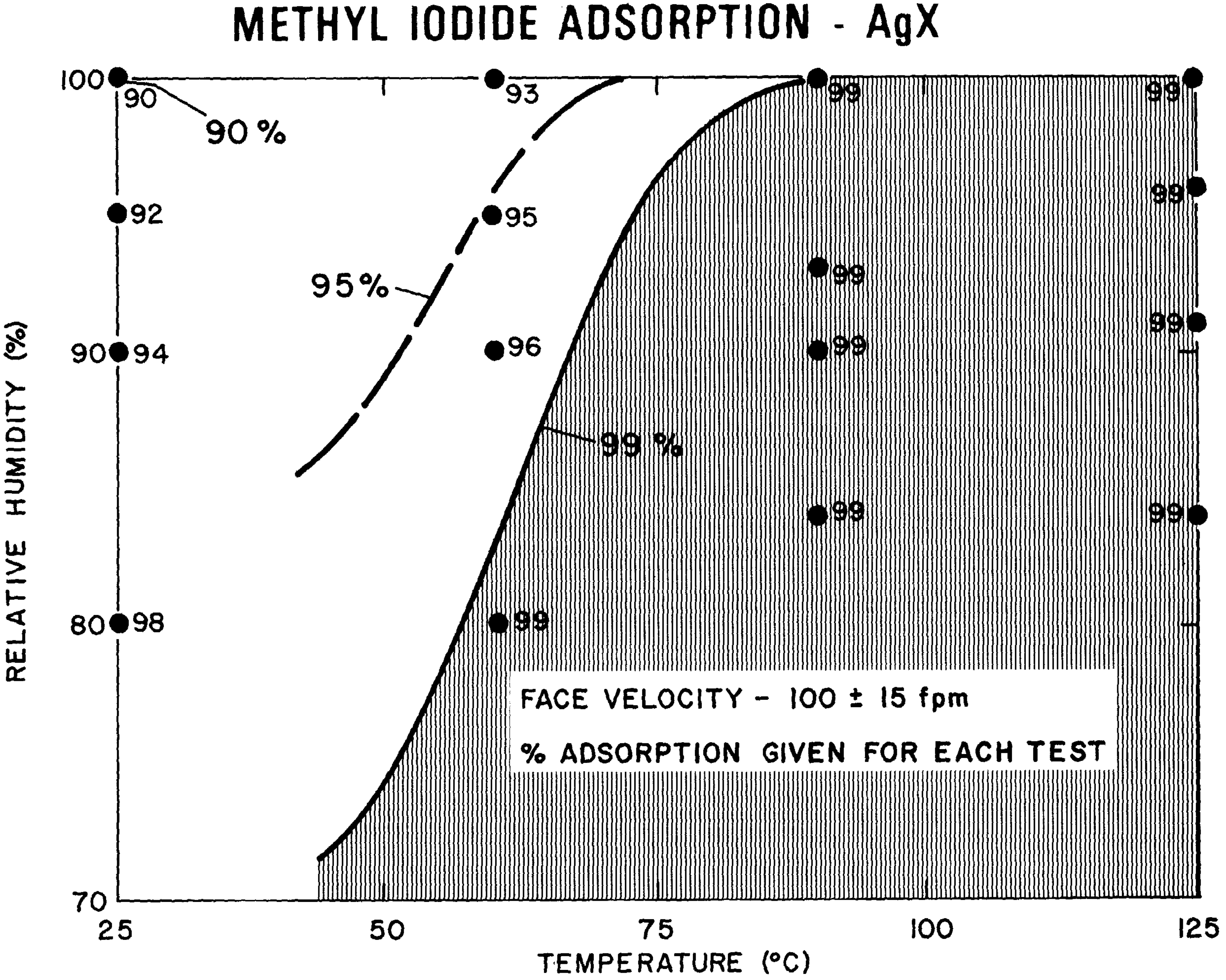
requires more experimental data. Such data is being collected.

Considering the systematics and reproducibility of the data obtained to date, we believe a working relationship can be established for a wide range of conditions. This information is important for the design and establishment of the optimum operating characteristics of silver zeolite filter systems.

Operational Flexibility of Metal Zeolites

One of the important properties of metal zeolites is nonflammability. This property allows for the design of air filtration systems incorporating heated beds. Studies in our laboratory and others(7) have shown that heat significantly increases the methyl iodide adsorption

Figure 1



METHYL IODIDE ADSORPTION - AgX
RELATIVE HUMIDITY (%)
TEMPERATURE (°C)
100
90
80
70
25
50
75
100
125
90
92
94
98
93
95
96
99
90 %
95 %
99 %
FACE VELOCITY - 100 ± 15 fpm
% ADSORPTION GIVEN FOR EACH TEST

efficiency of silver zeolite. This increase is related to two factors: lowering of the effective relative humidity of the incoming air stream, and an increase in reaction rate. The relative significance of each has yet to be determined. Other advantages associated with the use of heated beds are increased bed capacity, the use of higher flow rates, and the use of other metal-loaded zeolites.

Based on the preliminary data shown in Figure 2, the methyl iodide adsorption efficiency of silver zeolite is much less flow rate dependent than for charcoal. With silver zeolite, flow rates up to four times that for charcoal can be used with comparable efficiency. Even higher flow rates can probably be tolerated with heated beds.

Although lead zeolite shows little adsorption efficiency for methyl iodide, greater than 97 percent elemental iodine adsorption can be obtained with lead zeolite for 90 percent relative humidity air streams when the bed is operated at elevated temperatures. The adsorption efficiency of lead zeolite for elemental iodine as a function of bed temperature is shown in Figure 3. In these studies, the incoming air stream was maintained at 21°C and 90 percent relative humidity. The adsorption beds were heated externally to give a centerline temperature of approximately 20°C and 40°C above the incoming air stream. Significant increases in elemental iodine adsorption efficiency were obtained.

To determine the significance of heating the beds, two additional tests at lower relative humidity were conducted. In the first, the bed temperature was 21°C and the relative humidity of the incoming air stream at 21°C was less than 5 percent. For this case the elemental iodine adsorption was greater than 99.9 percent. In the second test, the bed temperature was 21°C and the relative humidity of the incoming air stream was 40 percent, which approximates the moisture content of a 90 percent relative humidity air stream at 21°C when the temperature is rasied to 40°C. For this case, the elemental iodine adsorption was 5 percent. These data indicate the following: (1) a high relative humidity dependence on the adsorption of elemental iodine by lead zeolite, (2) at very dry conditions the reaction is rapid and no additional heat is required, and (3) small amounts of water vapor (40%RH) seriously affect the adsorption properties of lead zeolite and that energy (heat) must be added to the system to increase the reaction rate. Based on these observations, it appears that for normal conditions the controlling factor in increasing the elemental iodine adsorption efficiency of lead zeolite through the application of heat is an increase in reaction rates rather than a reduction in relative humidity. More extensive studies are planned for lead and other metal-loaded zeolites.

The potential use of metal zeolites, other than silver, for the adsorption of elemental iodine is most encouraging and suggests the use of mixed beds for maximum material utilization. With this system, the use of two or more beds in tandem is proposed. The first beds conceivably

ADSORPTION EFFICIENCY vs FACE VELOCITY

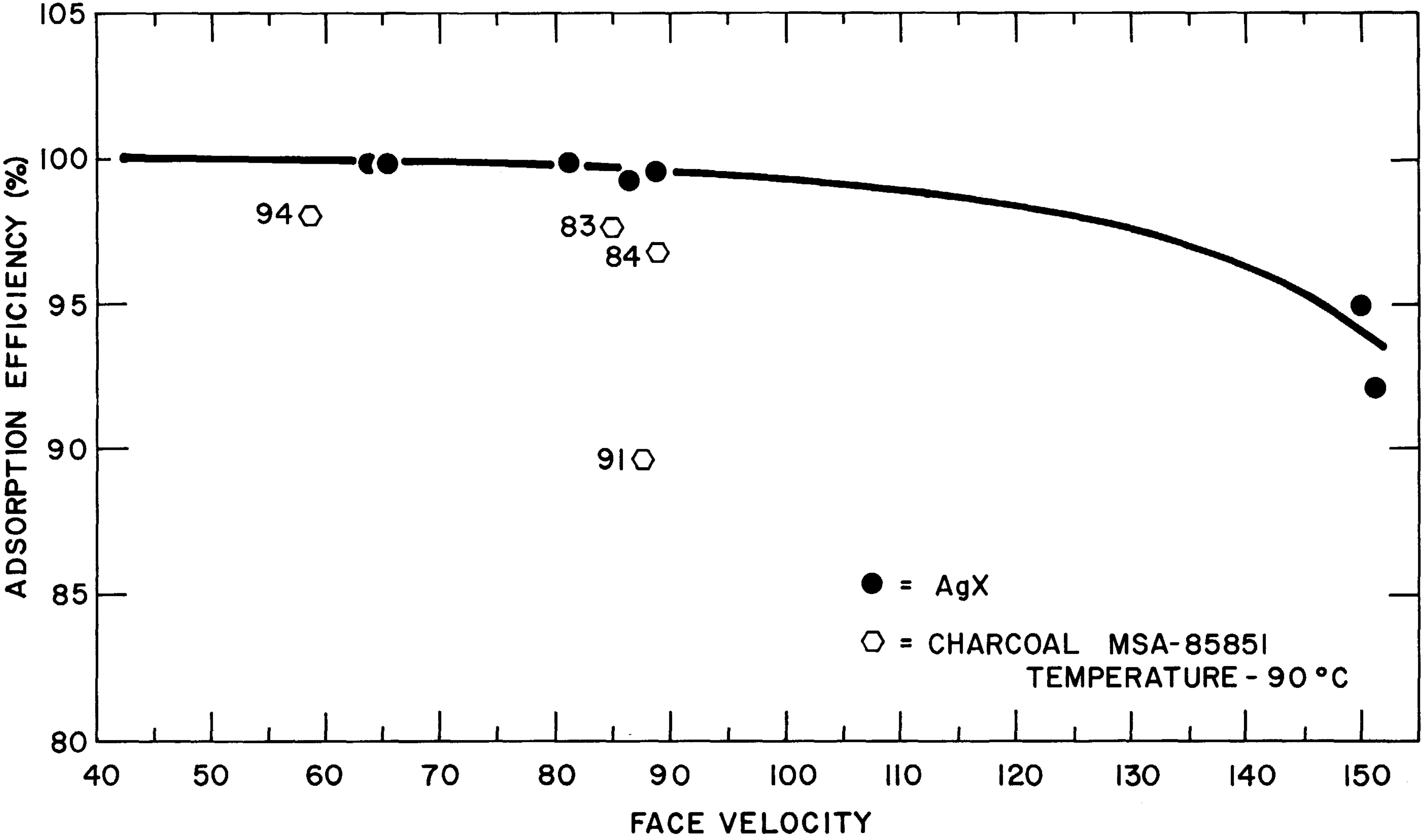
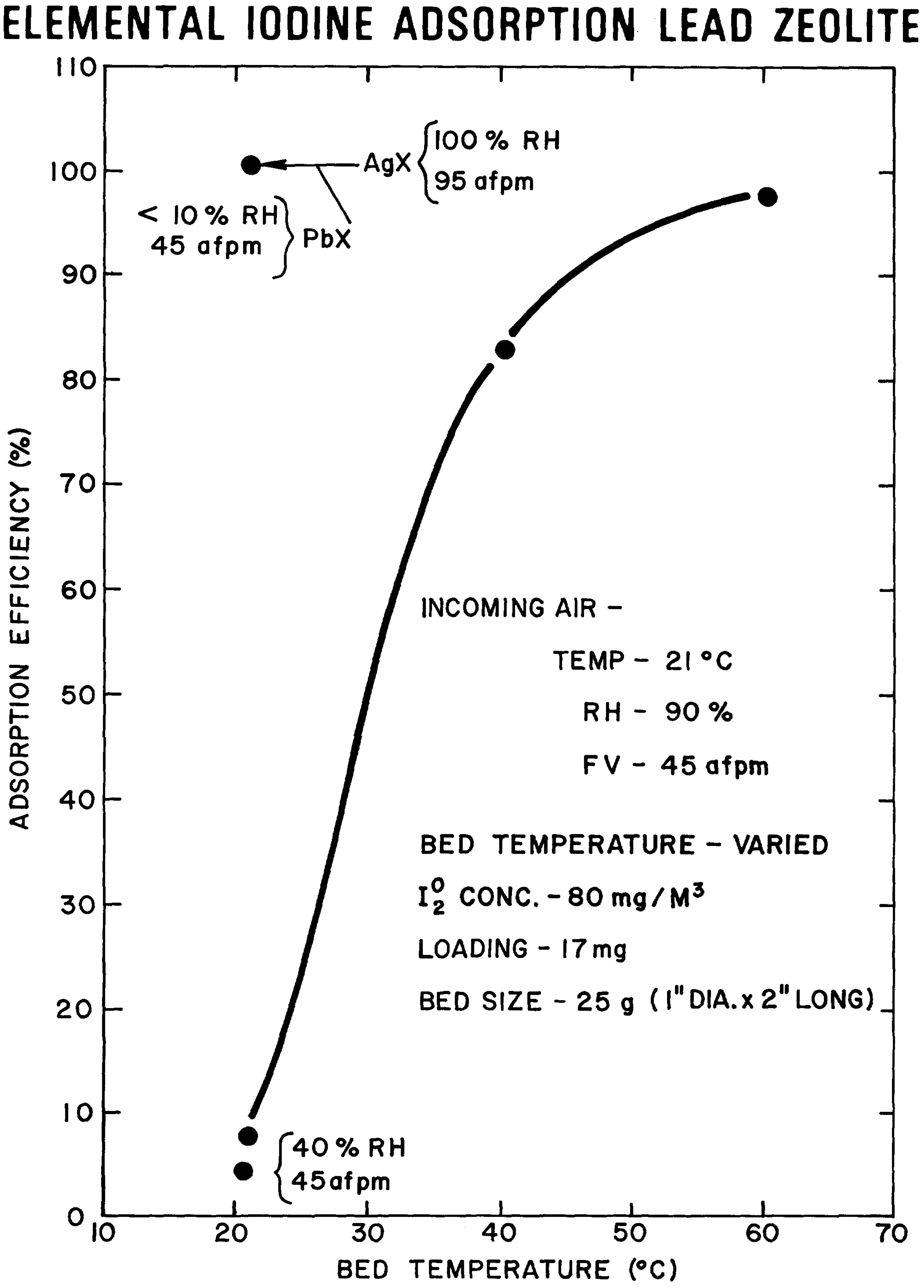


Figure -2-

Figure 3


ELEMENTAL IODINE ADSORPTION LEAD ZEOLITE
ADSORPTION EFFICIENCY (%)
0
10
20
30
40
50
60
70
80
90
100
110
BED TEMPERATURE (°C)
10
20
30
40
50
60
70
AgX
100 % RH
95 afpm
< 10 % RH
45 afpm
PbX
40 % RH
45 afpm
INCOMING AIR -
TEMP - 21 °C
RH - 90 %
FV - 45 afpm
BED TEMPERATURE - VARIED
I_2^0 CONC. - 80 mg / M^3
LOADING - 17 mg
BED SIZE - 25 g (1" DIA. x 2" LONG)

composed of lead zeolite would function primarily as elemental iodine adsorbents and the final bed composed of silver zeolite would serve as an adsorbent for organic iodides and for traces of elemental iodine passing the first bed, thus maximizing the use of the more expensive material. We strongly urge that this concept be more fully explored and be considered for those applications where feasible.

Another method of increasing the usable capacity of an adsorbent bed is the use of stacked removable beds. In this system, a series of beds are stacked in tandem in lieu of one large bed. When breakthrough occurs, the first bed is discharged from the assembly. The remaining beds are then advanced, with the second partially used bed now in the first position. A new bed is then inserted at the end of the train. Thus, increased utilization of the bed material can be attained. This concept should be especially attractive for use in nuclear fuel reprocessing plants off-gas streams.

A seldom discussed property of silver zeolite is its capability to function as a hydrogen getter. In this mode of operation, hydrogen reduces the silver ions in the zeolite structure to the metal and the hydrogen enters the zeolite structure where it associates with hydroxyl ions. A limited number of experiments conducted in our laboratories have shown that hydrogen can be adsorbed from a water saturated-air stream if the silver zeolite bed is operated at 100°C. The operational limitations of silver zeolite for use as a hydrogen getter have not been fully established. Based on these limited data for hydrogen adsorption and the advantages of using heated beds for methyl iodide adsorption, it is conceivable that a heated silver zeiolite bed could serve both as a hydrogen getter and as an airborne iodine species adsorbent. Of importance in such a consideration is the effect of the hydrogen reduction of the silver ions upon the methyl iodide adsorption properties of silver zeolite. Studies to evaluate this dual role of silver zeolite are in progress.

Because of the operational flexibility of metal zeolites, we believe they offer more potential for use in a wider variety of airborne iodine air cleaning problems than other materials currently in use.

Application of Metal Zeolites to Airborne Iodine Air Cleaning Problems

A major potential use of metal loaded zeolites is in air filtration units for gaseous reactor effluents. Currently two types of systems are in use. One is a recirculating system and the other is a "single-pass" system, which discharges to the surrounding environs. The iodine species adsorbent material now in use in these systems is chemically impregnated charcoal.

For this application metal-loaded zeolites offer many advantages compared to charcoal. For the recirculating systems, which are relatively small, the use of heated beds could result in improved adsorption efficiency, the use of smaller bed sizes, or higher flow rates.

In the case of an accident, a system operating at high efficiency and high flow rates would more quickly remove the airborne iodine species from the atmosphere. This could result in more of the iodine being fixed on a solid adsorbent and less deposited on the walls of the containment building or available for leakage to the environs.

Especially attractive is the use of mixed beds in which the bulk of the elemental iodine would be removed by an inexpensive lead zeolite bed and the organic iodides would be removed by a silver zeolite bed.

The large "once-through" filter systems currently in use require many tons of charcoal for efficient operation. Because of the flow rate limitations (50 fpm) imposed by charcoal for efficient methyl iodide adsorption and the large volume (2-3 x 10^6 ft) of containment vessel air which must be filtered, these systems are by necessity designed with large surface areas. In addition, large ventilating systems are required to move the air, and demisters and cooling devices are required to condition the atmosphere for efficient bed operation.

Because of the superior methyl iodide adsorption properties of silver zeolite we believe these systems can be reduced in size and the need for auxiliary conditioning equipment reduced. The data in Figure 1 shows that silver zeolite functions well as a methyl iodide adsorbent at high temperatures and high relative humidity. These conditions exist early in the reactor accident sequence and at a time when the airborne iodine species concentration is at a maximum. Considering these factors, a high airborne iodine removal could be obtained at the most preferred time--early in the accident sequence. As the temperature of the containment atmosphere decreases the flow rate through the beds could be reduced to retain maximum adsorption efficiency. By employing heated beds, even higher adsorbent bed capacity and efficiency could be obtained. Likewise, higher flow rates could be used.

We believe the existing filter systems can be modified to use the more efficient silver zeolite adsorbent. However, based on the operational flexibility of this and other new materials, we suggest that the presently used air cleaning techniques be thoroughly reviewed to determine if they represent the most efficient and economical design.

A second important source of airborne iodine contamination is the nuclear fuel processing plant. This situation is different from the accident release conditions of the reactor in that constant iodine removal from the off-gas is required. The magnitude of this source of iodine release is a function of the plant capacity and the age of fuel.

With the advent of more processing plants and the apparent desire to process shorter cooled fuels to minimize the fuel cycle cost, the iodine release from this source must be closely controlled.

To date, iodine removal systems for processing dissolver off-gas have employed liquid scrubbers or silver nitrate coated on an inert support. Both of these systems have operational drawbacks. The liquid scrubbers are not highly efficient and the silver nitrate system must be closely controlled to prevent dissolution or destruction of the silver nitrate. Because charcoal presents a potential explosion hazard in the presence of nitric acid vapors, its use is limited. Metal zeolites appear most suited for this problem.

In most cases, the principal iodine species present in an aqueous fuel processing plant off-gas stream is elemental iodine. Generally, the composition of this stream is well characterized and constant. These conditions are most favorable for efficient iodine removal with metal zeolite. For this application, we are investigating the concept of mixed removable beds consisting of series of lead zeolite beds operated at elevated temperatures to provide efficient elemental iodine removal followed by a bed of silver zeolite to adsorb the organic iodides and any elemental iodine passing the first beds.

Because acidic vapors can be present in a processing plant off-gas stream, serious consideration must be given to the type of zeolite used in the system. The X-type zeolite is a slightly basic material which is easily decomposed in acid; thus, if this material is used in either the lead or silver form, the incoming air stream must be free of acidic vapors. To circumvent this problem, other more acidic type zeolites are being investigated to determine their ion-exchange properties and to determine the iodine adsorption efficiency of their various metal exchanged forms.

Laboratory tests(2) pertaining to the poisoning of silver zeolite by a variety of atmospheric pollutant have shown little or no effect upon the elemental iodine adsorption efficiency of silver zeolite. Similar studies with other potentially useful metal zeolites are planned.

Considering the data available to date, we believe metal zeolites are ideally suited to the removal of various airborne iodine species from nuclear fuel processing plant off-gas streams.

Economics of Silver Zeolite

Of primary concern to any potential user of silver zeolite for the adsorption of airborne iodine species is the cost factor. To date, we have not conducted a detailed cost analysis regarding either the substitution of silver zeolite for charcoal in existing installations or placement in new installations. Currently, insufficient laboratory data exist to conduct a reliable cost evaluation; however, such an evaluation is planned.

Based on available information, a preliminary examination of the cost factor can be made. The estimated cost of fully-loaded silver zeolite is approximately ten times the cost of chemically impregnated charcoal. Of prime importance in making a cost comparison is the loading capacity factor for silver zeolite. Based on a loading of 5 mg of methyl iodide per gram of charcoal and about 100 mg of methyl iodide per gram of silver zeolite, the capacity factor in terms of mg of methyl iodide per gram of adsorbent is 20 in favor of silver zeolite.

For use in reactor filter systems, this high capacity factor for silver zeolite immediately suggests the possibility of smaller filter beds, operation at higher flow rates, or a combination of these. Based on the capacity factor alone, the material cost for adsorbing a unit of methyl iodide is less for silver zeolite than charcoal.

A second consideration is the use of heated beds to attain higher adsorption efficiencies; thus, reducing the amount of bed material compared to operating the bed at ambient temperatures. The economics of heating versus reduced bed sizes must be evaluated. Another factor to consider with heated beds is elimination of demisters and/or cooling coils which are currently employed to condition the atmosphere such that the charcoal beds will function as desired.

A third consideration is the use of mixed metal zeolite beds. Because elemental iodine is more easily adsorbed than methyl iodide, it is conceivable that a bed of another metal zeolite, whose metal ion reacts with iodine (i.e., lead), could precede the silver zeolite bed. Thus, a less expensive material could be used to adsorb the bulk of the iodine activity, which is elemental iodine, and hence require a smaller bed of silver zeolite to remove the more persistent species.

For application in the removal of iodine from aqueous type nuclear fuel processing plant off-gas streams, a mixed metal inorganic adsorbent system seems feasible. Here, the question of the base material is not well defined.

With regard to regeneration, silver zeolite which has been used to adsorb airborne iodine species cannot be regenerated in the normal sense; however, the silver can be reclaimed by destroying the zeolite. The reclaiming cost is estimated to be approximately $0.80/pound of zeolite disregarding the radioactive handling problem.

Other important factors in the economics of silver zeolite are effective service life and the poisoning effect of various atmospheric pollutants. To date, no extended service life experiments have been conducted because of continuing product development. When a suitable product has been developed, extended service life tests are planned. If silver zeolite is not adversely affected by weathering as is charcoal, then periodic replacement of the bed material is not a factor; and additional cost savings could be attained.

Based on this review of the economics of silver zeolite, it appears that the use of this material in air cleaning systems is practical. One intangible item of comparison not considered is safety. Included are such properties as product stability and flammability. If, for a given operation, the material cost of silver zeolite and charcoal are equal, the additional safety features of silver zeolite are obtained without cost.

Conclusions

Laboratory studies have shown that silver zeolite is a highly efficient adsorbent for airborne methyl iodide and elemental iodine. The operating characteristics of silver zeolite have been more fully defined and the usefullness of other metal zeolites is being established. The use of heated beds increases the operational flexibility of metal loaded zeolites, and the use of mixed beds shows promise for better utilization of the bed material. The use of metal loaded zeolites in both reactor and nuclear fuel processing plants air cleaning systems is feasible from both an operational and economic viewpoint. Because of the promising data obtained to date, detailed engineering studies should be conducted. Included should be the testing in large scale systems.

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DISCUSSION

KOVACH: Well, I think I like this last table you showed, but I would like to point out that you are using both the carbon and the zeolite by volume. So from an equal volume basis, the density ratio changes your cost ratio, to about doubling your zeolite costs from the volume ratio, which I think will be more realistic. Density being about a little over twice what the carbon is, and I think all other efficiencies were equal. The other question I had is do you feel that evaluating these materials solely on efficiencies and relationship to methyl iodide or even if you want to go to any of the other strange species which might, probably, could, would occur, is realistic, when it is still fairly well agreed that something like, I'll even lower my number, 75 percent is a elemental iodine.

MAECK: The predominant species is elemental iodine, possibly 99 percent.

KOVACH: Well, I'm saying that I see more and more of these evaluations based on the small rather strange species. I'm afraid that we start forgetting about the bulk of the material. I'm talking about reactor applications and not necessarily reprocessing or others where you run into the more exotic species. I think that you have to remember the efficiencies and evaluations, particularly when you compare economic data, based on the elemental iodine.

MAECK: I fully agree with that. And this is why we are trying to look at some of the other materials. If we can use a cheaper material to get the bulk of the activity why not do it? Why go to a more expensive situation. But, for the added safety, I think that it is required to get that last little bit. If we want to go along with your filtration ideas we've not to take that philosophy.

KOVACH: Every absorber will have a silver zeolite lining.

WILHELM: I would like to comment on this. We made calculations for the temperature in the adsorber material and started with a temperature of 140°C for the atmosphere in the containment shell under MCA conditions. This is really an average number considering the heat transfer from the core into the steam and the containment. On top of this, additional decay heat will be generated in the filter beds. We calculated that for the LOCA of a PWR and medium flow rates and found that we could have an increase in temperature in the adsorber material of more than 100°C just by decay heat. In a LOCA you may get up to 10^7 curies on the filter bed.

PARKER: Pardon me, may I break in, for the people who are leaving the afternoon session will be held at 1:15 in order to accommodate the lateness of the hour.

WILHELM: Now you are in the range of 200°C or more. This will be what can be expected for a filter system of the recirculating type or for a once-through system. The only system where you must not expect that high temperatures is the filter for the annulus between the shells of a double containment. There you will be inside the region where you can work with charcoal. So we thought materials like zeolite would be of extremely high value and the only thing which bothered us was the extremely high price.

MAECK: I think that with the higher temperature you can use other metal-exchanged zeolites very effectively.

KOVACH: I think even if you compare your silver zeolite costs, it's a lot cheaper to put in a condenser. Which you have to have anyway, because you want to cool your recirculating system. I don't agree with you that you can't have carbon in the containment. As a matter of fact I think even a silver heat exchanger would be slightly less expensive than exchanging the same volume rates of carbon with the highly loaded silver zeolite. I am not talking here about some of the newer materials, but the carbon systems can be designed which do not exceed 150°C.

WILHELM: If you have already your activity trapped in that volume of adsorber material you can't take it away. It will just heat up your adsorber material. By cooling of the air upstream you may lower the temperature to a value let's say 50°C lower than I mentioned, but you still run into trouble with larger power plants. I think carbon can be of use up to 150°C. From experiments at higher temperatures we learned that desorption gets serious. Considering the limit in temperature and the amount of decay heat that may be generated in the adsorber bed you just can't use impregnated activated carbon for such filter devices.

KOVACH: The decay heat caused temperature rise is still a function of iodine loading, if you have sufficient carbon you will not reach desorption temperatures. Of course there are systems where combination of materials could be more advantageous.

WILHELM: Right, and if you calculate temperatures in recirculating type filter systems for big power reactors, 1000 MW_e or more you are also in trouble. We don't like the large amount of money we have to invest in new adsorber materials. But at least we have problems. We have densely populated areas. So, we must look for a safety system that will work safely under those conditions. That's just our problem.