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Consolidated Fuel Reprocessing Program

ORGANIC IODINE REMOVAL FROM SIMULATED DISSOLVER
OFF-GAS SYSTEMS UTILIZING SILVER-EXCHANGED MORDENITE

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ORGANIC IODINE REMOVAL FROM SIMULATED DISSOLVER OFF-GAS STREAMS UTILIZING SILVER-EXCHANGED MORDENITE*

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ABSTRACT

The removal of methyl iodide by adsorption onto silver mordenite was studied using a simulated off-gas from the fuel dissolution step of a nuclear fuel reprocessing plant. The adsorption of methyl iodide on silver mordenite was examined for the effect of NO_x , humidity, iodine concentration, filter temperature, silver loadings, and filter pretreatment. The highest iodine loading achieved in these tests was 142 mg CH_3I per g of substrate on fully exchanged zeolite. This is approximately the same as the elemental iodine loadings. The experimental results indicate that a filter using fully exchanged silver mordenite operating at 200°C obtained higher iodine loadings than a similar filter operating at 150°C. Pretreatment of the sorbent bed with hydrogen rather than dry air, at a temperature of 200°C, also improved the loading. Variations in the methyl iodide concentration had minimal effects on the overall loading. Filters exposed to moist air streams attained higher loadings than those in contact with dry air.

Partially exchanged silver mordenite achieved higher silver utilizations than the fully exchanged material. The partially exchanged mordenite also achieved higher loadings at 200°C than at 250°C. The iodine loaded onto these beds was not stripped at 500°C by either 4.5% hydrogen or 100% hydrogen; however, the iodine could be removed by air at 500°C, and the bed could be reloaded.

A study of the regeneration characteristics of fully exchanged silver mordenite indicates limited adsorbent capacity after complete removal of the iodine with 4.5% hydrogen in the regeneration gas stream at 500°C. The loss of adsorbent capacity is much higher for silver mordenite regenerated in a stainless steel filter housing than in a glass filter housing.

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1. INTRODUCTION

Iodine-129 is produced by both natural and man-made sources. The natural sources include the spontaneous fission of uranium and the interaction of cosmic rays with xenon in the atmosphere. The annual production through these natural paths is approximately 10 mg/year. With its long half-life (1.6×10^7 years), ^{129}I tends to accumulate worldwide. As of 1940, the estimated accumulation has been reported to be 2×10^5 g.¹ A single light-water reactor (LWR) will produce 234 g of ^{129}I based on a uranium burnup of 30,000 MWd/t.² In handling the spent fuel, a single 5-t/d nuclear fuel reprocessing plant would have to process 3.2×10^5 g of ^{129}I /year.

In addition to ^{129}I , various amounts of other short half-life iodine isotopes are also produced; however, none of these appear in significant amounts after long (>200-d) decay times. On the other hand, in the reprocessing of liquid-metal fast breeder reactor (LMFBR) fuels, reducing the decay times to as little as 90 d might have economic incentive. This shorter decay time would mean that larger amounts of the short half-life isotope ^{131}I ($t_{1/2} = 8.05$ d; specify activity, 1.24×10^5 Ci/g) would also become a significant factor.

During the past two decades, various systems have been studied to reduce the iodine released to the environment. Two liquid scrubber systems are currently available: the Iodox system and the mercuric nitrate-nitric acid (Mercurex) system. Solid sorbents have also been studied, either as secondary systems to provide final filtering following use of either the Iodox or Mercurex system or as primary systems to replace the liquid methods.

These solid sorbents include silver faujasite, silver mordenite, alumina silicates, and macroreticular resins. Activated carbon has also been examined as a reference material; however, this material cannot be considered as a primary sorbent for treating reprocessing plant off-gas because of its low ignition temperature and its adverse reactions with nitrogen oxide which could lead to the formation of explosive compounds and to poisoning by organic contaminants in the off-gas.

If high decontamination factors (DF's) are required, one of the more promising systems for primary iodine removal is the Iodox system; otherwise, solid sorbent-based processes tend to be favored. The Iodox system has already been tested on an engineering scale and has demonstrated good capabilities and operability. Decontamination factors in excess of 10^6 have been obtained. There are, however, concerns about the long-term integrity of the materials of construction that come in contact with the 20 to 23 M HNO_3 scrub solution.

Silver-impregnated solid sorbents offer a much simpler iodine removal scheme in comparison to liquid systems. In this case, however, iodine DF's are limited to about 10^3 , and high operating costs can be expected, particularly if the silver is not recovered. In the past few years, regenerable adsorbents have been receiving considerable attention.

At the 14th ERDA Air Cleaning Conference,³ it was reported that silver-exchanged faujasite (AgX) loaded with elemental iodine could be regenerated in situ with a pure hydrogen stream at 500°C; however, a 50% loss in loading capacity was observed after five loading cycles. Silver-exchanged faujasite is capable of adsorbing iodine at temperatures as high as 500°C; and like most other sorbents, it is adversely affected by water

vapor, especially when condensation occurs. Faujasite is also adversely affected by acid vapor which would be found in the dissolver off-gas system. Average I_2 loadings were 100 to 200 mg I_2 per g AgX or 23 to 47% utilization of the available silver.

A silver-containing alumina silicate, AC-6120, also showed potential on a once-through basis. Silver utilizations of ~59% have been reported with AC-6120.

Similar studies with silver mordenite (AgZ) showed only a negligible reduction in loading capacity after eight cycles.⁴ Average I_2 loadings were 100 to 130 mg I_2 per g AgZ or 42 to 55% utilization of the available silver. However, these tests were limited to elemental iodine loading.

The high cost of silver, the lack of an available AC-6120 regeneration scheme plus limited regeneration potential, and the lack of acid resistance of the AgX make these materials less attractive than AgZ for large-scale use.

Previous work at the Oak Ridge National Laboratory was reported at the 16th DOE Air Cleaning Conference.⁵ This work demonstrated the increased loading of CH_3I following hydrogen pretreatment of the AgZ. Hydrogen stripping of the iodine loaded bed was also demonstrated; however, the regeneration procedure caused a dramatic loss in the bed loading capacity.

The objectives of the solid sorbent studies reported here were to evaluate:

1. the suitability of silver-exchanged mordenite as a backup or secondary iodine removal system to the Iodox process in nuclear fuel reprocessing plants;
2. the removal capabilities of silver-exchanged mordenite for organic iodides;
3. the use of low silver content mordenite for iodine removal; and
4. the regeneration potential of both fully and partially exchanged silver mordenite.

2. EXPERIMENTAL PROCEDURE

Silver-exchanged mordenite (AgZ) was prepared by ion exchange with 0.16-cm-diam extrudates of the sodium form of Norton Zeolon 900; silver-exchanged faujasite (AgX) and lead-exchanged faujasite (PbX) were prepared from 0.16-cm-diam extrudates of Linde molecular sieve, type 13X. Fully exchanged AgZ or PbX was prepared by loading fifteen hundred grams of the unexchanged zeolite into an ion exchange column and batch contacting with 3 L of 1 M silver nitrate or lead nitrate solution at 40°C. At regular intervals the spent solution was replaced with fresh solution until no change in silver or lead concentration was detected. The solution was drained, and the exchanged zeolite was air dried at 60°C for 24 h. Fully exchanged silver mordenite was also purchased from Ionex Corporation under the trade name of Ionex Ag-900. Partially exchanged silver mordenite (LAGZ) was prepared by contacting unexchanged mordenite once with a limited amount of silver nitrate solution and air dried at 60°C in air. During this exchange, virtually all of the silver from the solution is substituted for sodium in the zeolite structure. Thus, the degree of exchange is easily controlled by limiting the silver nitrate concentration. The AgZ beds were pretreated *in situ* prior to sorbent tests by heating to 200°C and purging with 4.5 H₂-95.5% Ar at a flow rate of 5 L/min for 24 h. The bed was then isolated and brought to the operating temperature. The same procedure was used to pretreat the LAGZ beds. The hydrogen pretreated condition of AgZ and LAGZ is denoted by AgZ and LAGZ respectively.

Methyl iodide loading tests were conducted using an apparatus similar to that used by Staples et al.³ A schematic of the equipment is presented

in Fig. 1. Heated air streams containing the desired amount of NO, NO₂, CH₃¹²⁷I tagged with CH₃¹³¹I, and water vapor were passed through the segmented filter bed located in the heated main filter enclosure. Initial studies were conducted using a glass filter casing. A stainless steel filter divided into six segments (see Fig. 2) was used in later experiments. The breakthrough of the bed was monitored by collecting the CH₃I leaving the main filter of AgX. At regular intervals, this trap was removed and counted for ¹³¹I. When >0.1% of the iodine in the feed gas stream was found to be passing through the main filter, the run was stopped. The bed segments were counted for ¹³¹I using a sodium iodide crystal and a single channel analyzer set on the 364-KeV gamma-ray of 8-d half-life ¹³¹I. Using a 100-KeV window, the gross count over a 1-min period (corrected for background) was used as a measure of the iodine content of the bed. The total amount of CH₃I loaded on the test bed was then calculated from the known ratio of ¹²⁷I to ¹³¹I.

Fig. 1. Test apparatus for methyl iodide loading studies.

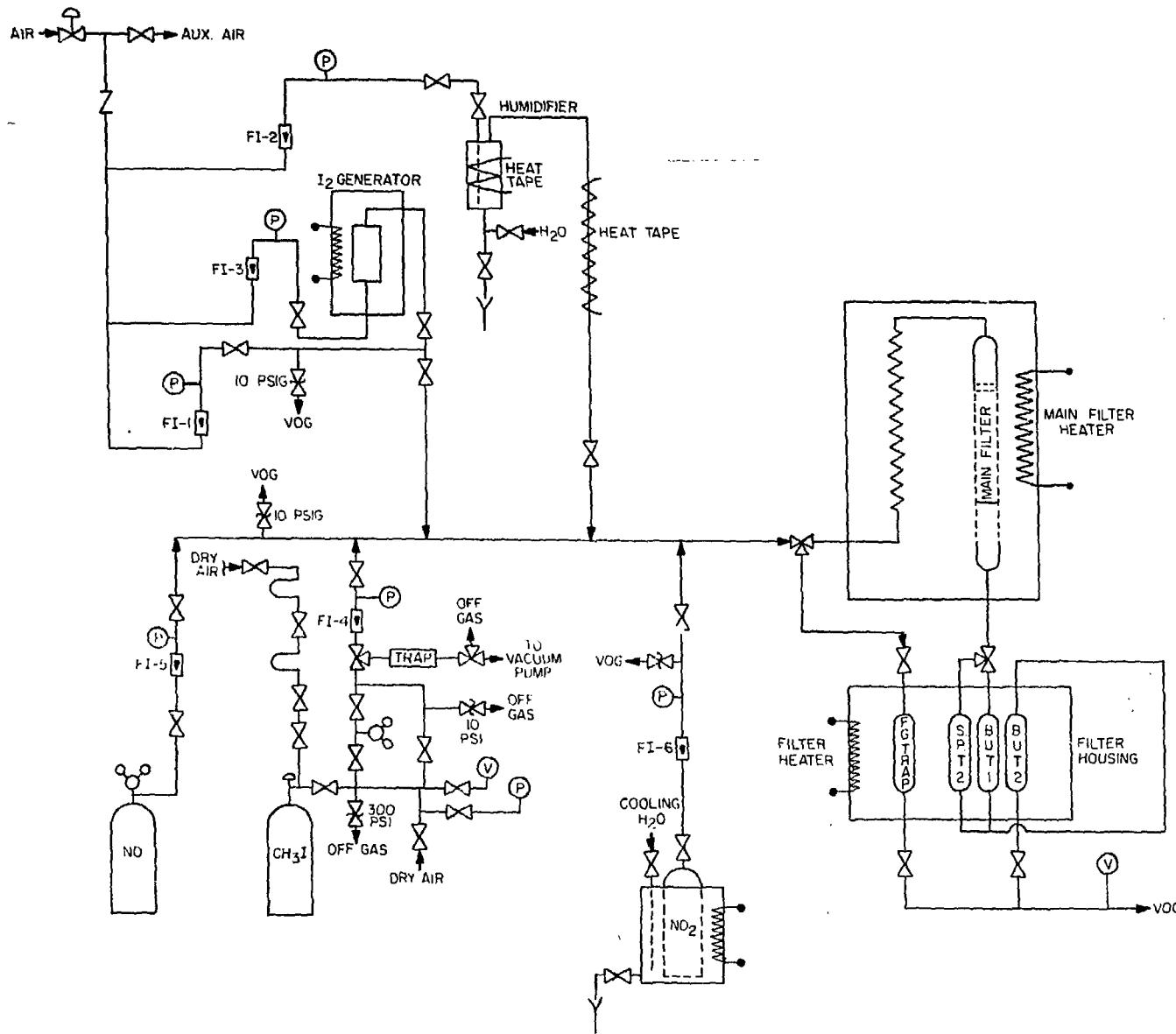
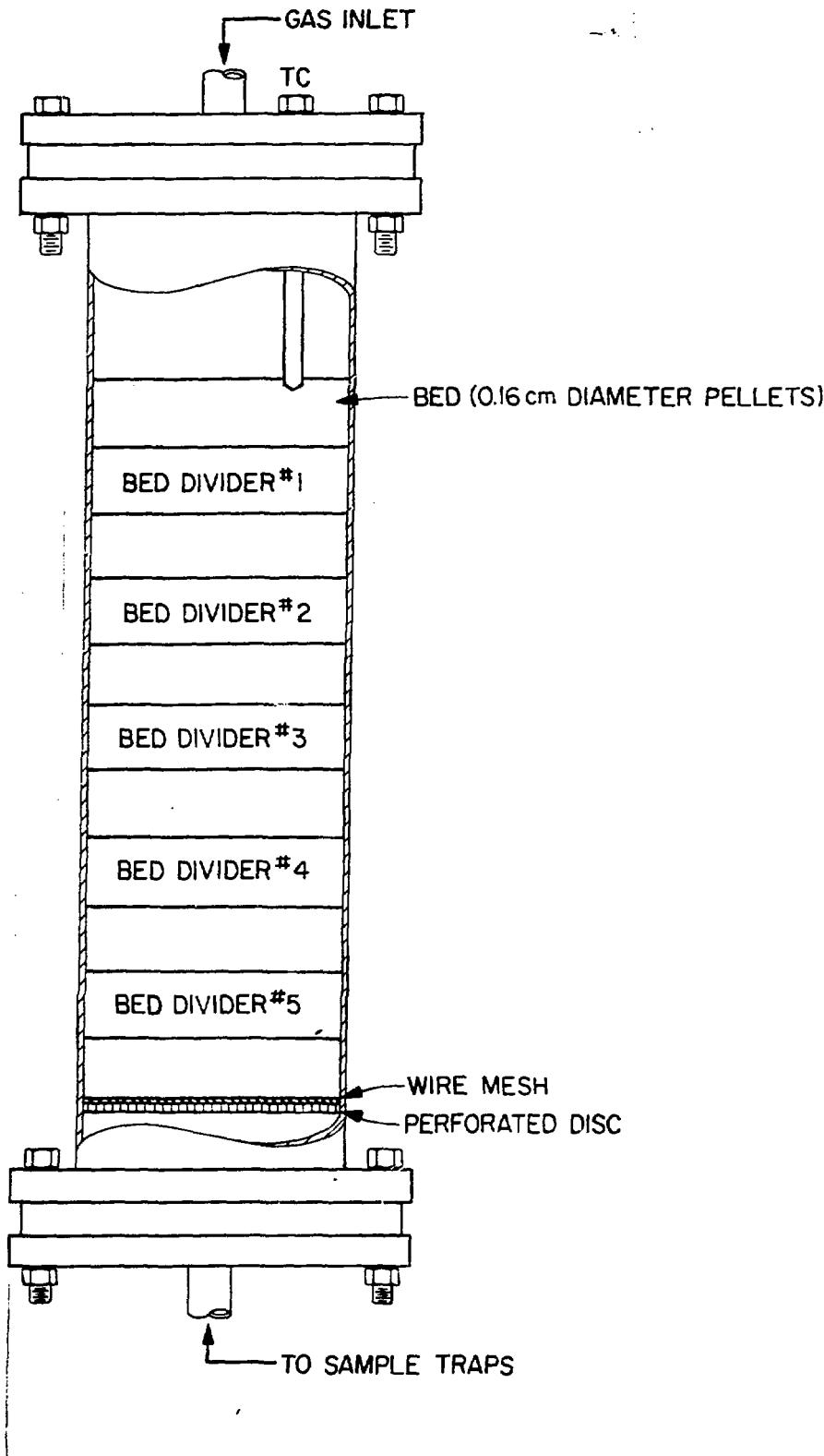


Fig. 2. Stainless steel main filter.



3. EXPERIMENTAL RESULTS

3.1 Temperature and Humidity Effects on AgZ

The effects of NO, NO₂, humidity, pretreatment conditions, operating temperature, and CH₃I concentration on the loading capacity of AgZ were evaluated using an eight-run fractional 2ⁿ factorial-designed experiment.

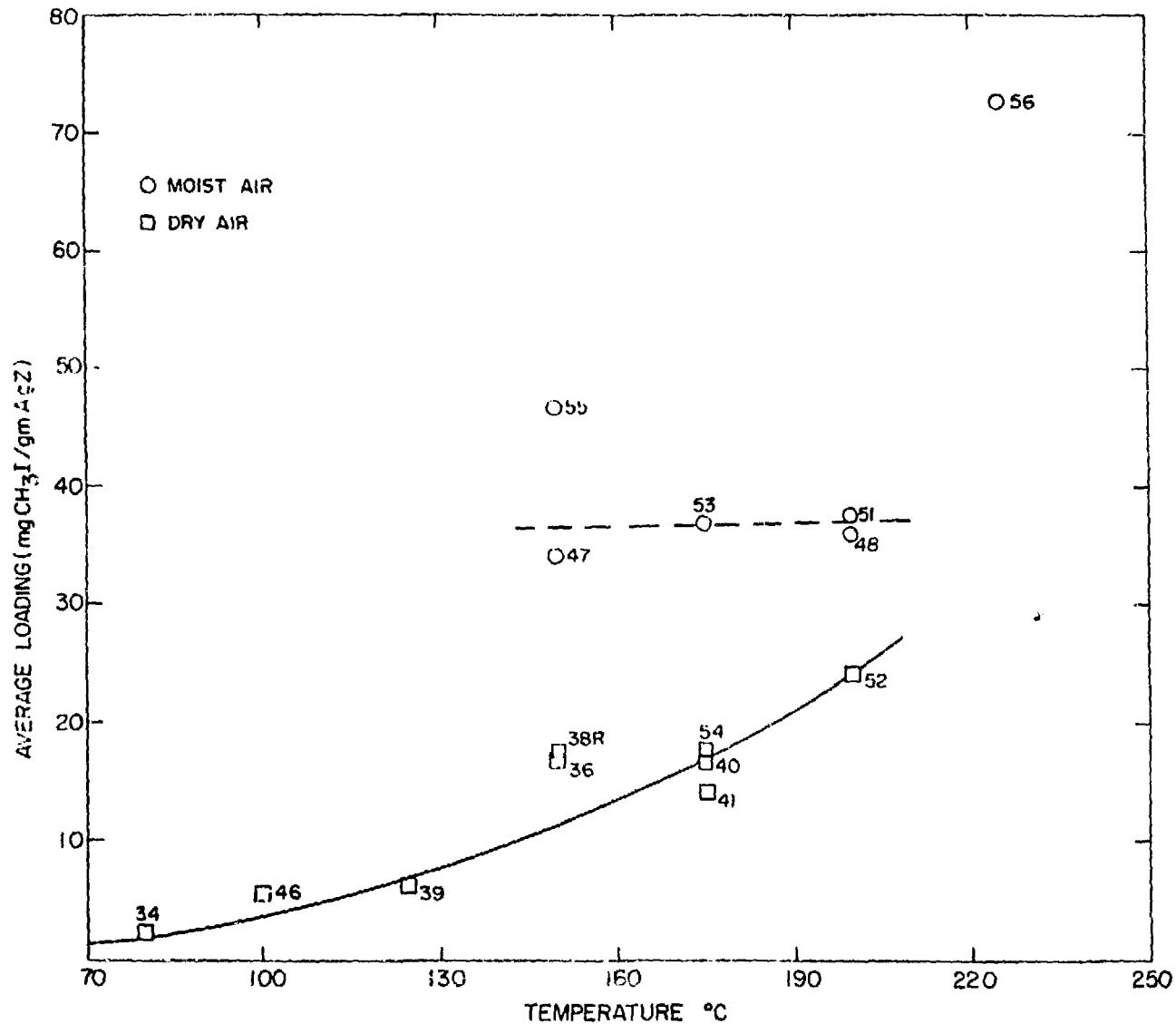
Analysis of those data indicated that (1) pretreatment with 4.5% H₂-95.5% Ar at 200°C for 24 h improved loadings; (2) loadings were improved at higher operating temperatures; (3) loadings were improved in moist air conditions; and (4) the other variables, NO, NO₂, and CH₃I concentration, produced variations in loadings that were less than the response error.

A follow-on study was conducted to examine the effects of temperature and humidity on AgZ. An air stream containing 1000 mg of CH₃I per m³ and a dewpoint of either ~-54°C or ~+35°C was passed across four hydrogen pretreated beds operated at 75, 100, 125, 150, 175, 200, or 225°C. The average amount of CH₃I loaded on the four 2.54-cm-thick beds is shown in Fig. 3 as a function of temperature.

As indicated by the original scoping study, the presence of water in the system resulted in higher CH₃I loadings. As the operating temperature is increased, loadings are also increased, but the mass transfer zones (MTZ) are also increased. At 150°C, the MTZ for both the humidified bed and the dry bed is 5 cm to 7.5 cm in length. At 200°C, the MTZ is over 10 cm.

The higher bed loadings are probably the result of improved mass transfer into the pores of the AgZ since the gas molecules increase in kinetic energy with temperature.

Fig. 3. Average CH_3I loading from feed gas stream (containing 1000 mg CH_3I per m^3) onto a 10.16-cm-deep bed of AgZ as a function of temperature.

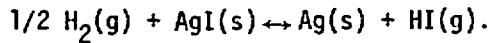


Improved loading was also observed in a run that was stopped at breakthrough; that is, a DF <1000, which was allowed to remain at its operating temperature (150°C) overnight. When loading was reinitiated 18 h later, the DF across the bed remained above 1000 for 2 h, allowing the additional loading of ~20 mg/g on the first bed before breakthrough occurred again. During the heat soaking period, the iodine apparently distributed into the AgZ pellet thus freeing some of the more accessible silver sites for the second loading period. The elevated temperatures probably facilitate similar movement of iodine into the more inaccessible silver sites, thus increasing the overall silver utilization.

Tests at 200 and 225°C in the presence of moist air have achieved loadings of 139.5 and 141.5 mg of iodine per gram of AgZ respectively. Possibly, higher loadings could be achieved on longer beds since the entire mass transfer zone was not observed on the four beds used in these experiments.

3.2 Regeneration Test of AgZ

Loaded AgZ beds were regenerated with the equipment, shown in Fig. 4, using both 4.5% H₂-95.5 Ar and pure H₂. Both satisfactorily remove the chemisorbed iodine. The assumed reaction is:

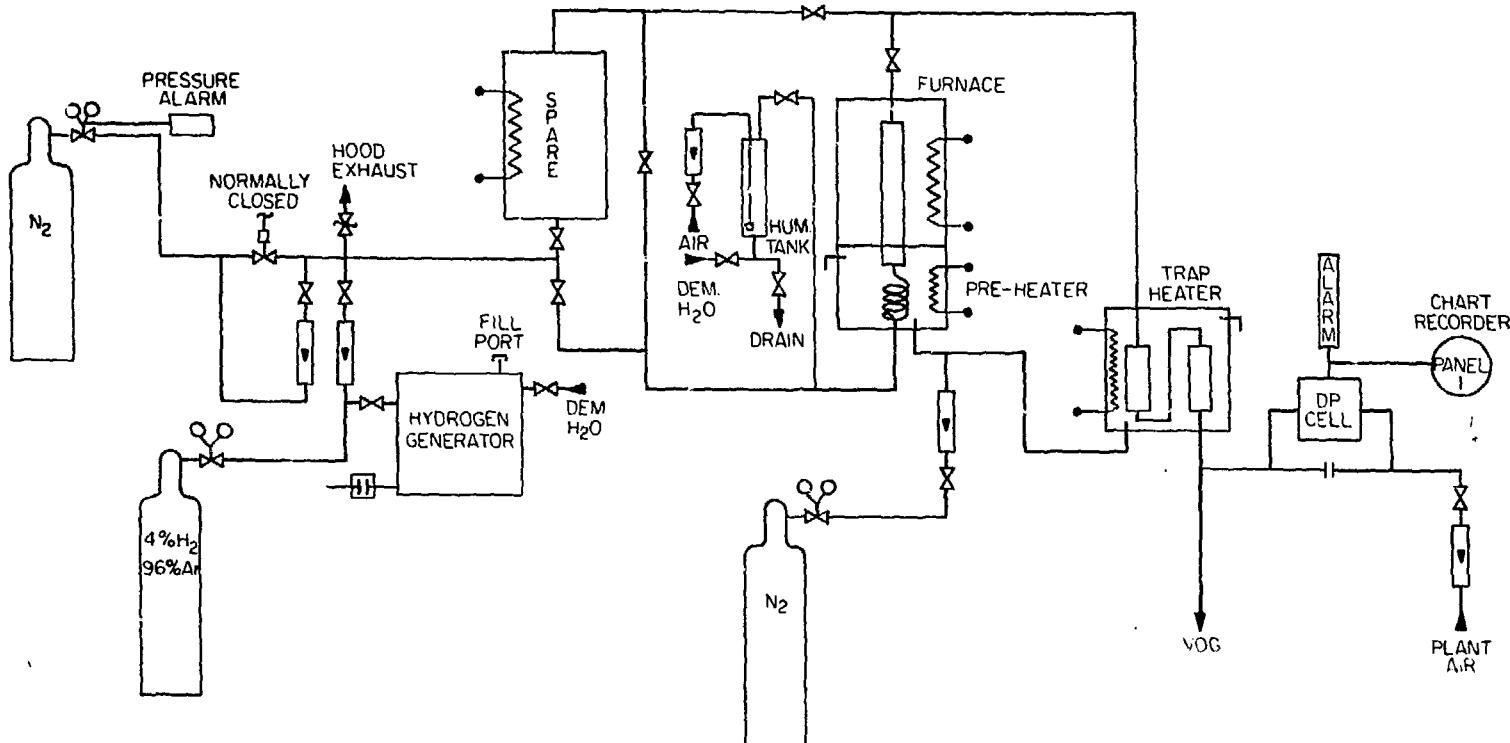


Equilibrium vapor pressures of HI at an operating temperature of 500°C are 26.5 and 119.1 Pa for 5% and 100% H₂ respectively.

The hydrogen flow was countercurrent to the original iodine flow. The iodine in the form of HI was then trapped on the PbX bed. During 24 h of regeneration with a H₂ flow of 0.5 SLPM, >50% of the I₂ is removed in 6 h and >98% in 24 h.

Fig. 4. Hydrogen regeneration flowsheet for silver mordenite.

ORNL DWG. 80-15053



The second loading of the regenerated bed using the same feed conditions as the initial loading resulted in significantly lower loadings than the original loading. The addition of water vapor to the feed gas improved loads to approximately one-third of the original loadings at 150°C.⁵ This loading is significantly lower than the post regeneration loadings reported by Thomas et al.⁴

An examination of the AgZ by x-ray diffraction and scanning electron microscopy showed:

1. the presence of free silver following 4.5% H₂ pretreatment,
2. the formation of small (<2000 Å) nodules of silver,
3. no free silver or silver nodules on air pretreated AgZ, and
4. large (<8000 Å) nodules of silver following regeneration at 500°C with 4.5% H₂.

To determine the effects of temperature and time on the formation of the silver nodules and subsequent CH₃I loading on the AgZ, a series of beds was treated with 100% H₂ for 24 or 48 h at temperatures of 200°, 400°, or 500°C. Following this treatment, the beds were loaded with CH₃I in dry air. The results of the bed loadings are shown in Table 1.

Loadings showed decreased retention capacity for CH₃I as exposure time to H₂ increased and as temperature of exposure increased. Photomicrographs showed small increases in the module size from 200 to 400°C and a significant increase in nodule size at 500°C. It is the migration of the silver to these nodules that we believe to (at least partially) account for the decrease in CH₃I loadings. The migration of silver in the presence of hydrogen was also noted by Yates in 1965.⁶ Yates reported silver crystallites of 170 Å formed in the presence of H₂ at 250°C. These temperatures of interest are

Table 1. CH_3I loadings of 100% hydrogen
treated AgZ in dry air

Run	Temperature (°C)	Time (h)	Loading (mg/g)
57	200	24	35.6
58	200	48	12.3
59	400	24	11.0
61	400	48	8.0
60	500	48	0.26

well below the melting point of silver (961°C). The vapor pressure is correspondingly low (10^{-5} nm Hg at 757°C).

Work by Scheele et al, reported by Burger,⁷ using glass housings for the AgZ did not show the same large nodules following a hydrogen pretreatment at 500°C nor was the loading as low. A series of tests was conducted using a 5.08-cm-diam glass column to explore the possible effects of filter housing material. This column was loaded with AgZ and treated with 100% H₂ at 500°C for 24 h. The bed was then loaded with CH₃I to 54 mg/g at 200°C in moist air. This is approximately half the loading observed for AgZ under the same loading conditions but treated with 4.5% H₂ at 200°C and 10 times higher than loadings following hydrogen treatment at 500°C in stainless steel. Additional work remains to be completed in this area to determine the role stainless steel plays in the apparent "deactivation" of the AgZ.

3.3 Scoping Tests on Partially Exchanged Silver Mordenite

Tests on fully exchanged AgZ indicate the iodine first chemisorbs at the easily accessible silver sites. Experience in exchanging the sodium for silver has also shown that the last 25% of the exchange is more difficult. With this in mind, the CH₃I loading characteristics of partially exchanged silver mordenite (LAgZ) were examined using a fractional factorial designed experiment. The experiment examined the effects of NO, NO₂, humidity, bed temperature, dilute hydrogen, and silver content on the loading capacity. Experimental conditions are presented in Table 2. The eight-run design, along with the loading on the first bed, and the effects of each variable are shown in Table 3.

Table 2. Experimental conditions for scoping studies

Variable	Value
Bed weight, g	~40
Bed diameter, cm	5.08
Bed thickness, cm	2.54
Number of beds	6
Carrier gas	Air
Superficial velocity, m/min at STP	10.0
CH ₃ I concentration, mg/m ³ at STP	1000
NO concentration, %	0 or 3.0
NO ₂ concentration, %	0 or 3.0
Relative humidity (dewpoint), °C	-54 or ~35
Pretreatment	4.5% H ₂ in Ar for 24 h
Bed temperature, °C	200 or 250
Hydrogen, %	0 or 1.0

Table 3. Summary of screening runs on LAgZ^a

Run	Bed loading ^b (mg CH ₃ I/g LAgZ)	NO (%)	NO ₂ (%)	Dewpoint (°C)	Temp. ^c (°C)	Ag (%)	H ₂ (%)	Dummy
1	17.74	0.0	0.0	-54	200	1.5	0.0	+
2	21.63	3.0	0.0	-54	250	3.0	0.0	-
3	11.13	0.0	3.0	-54	250	1.5	1.0	-
4	30.10	3.0	3.0	-54	200	3.0	1.0	+
5	37.44	0.0	0.0	35	200	3.0	1.0	-
6	7.48	3.0	0.0	35	250	1.5	1.0	+
7	12.95	0.0	3.0	35	250	3.0	0.0	+
8	14.18	3.0	3.0	35	200	1.5	0.0	-
Σ								
$\Delta\Sigma$								
Effect		-1.468	-3.983	-2.138	-11.567	12.898	4.913	-4.028

^aRun conditions: six beds each, 2.54-cm-thick, 5.08 cm in diameter, gas rate 20 SLPM; pretreated 24 h at 200°C with dry 4.5% H₂-95.5% Ar; average decontamination factor >10³.

^bLoadings are based on a dry density of 0.78 g/cm³.

^cBed temperature.

A response error for this experiment can be estimated using the dummy variable.⁸ Using this technique, a value of 2.83 mg/g was obtained. However, this method probably overestimates the response error because of potential interaction between the measured variables.

Analysis of the data has indicated that (1) increased loadings occur with increased silver content as would be expected, (2) higher loadings occur at 200°C rather than at 250°C, (3) the presence of 1% hydrogen in the gas stream improves loading, (4) moisture has a detrimental effect on the loading of CH_3I , (5) the presence of NO_2 also has a detrimental effect on the loading, (6) the effect of NO (although showing a negative effect on loading) is smaller than the response error and cannot be seriously considered.

The negative temperature effect may be the result of the limited silver sites in the interior of the LAgZ pellet that were present in the AgZ pellet and were reached by iodine atoms with higher energies.

Silver utilization averaged 72% for both the 1.5 and the 3% LAgZ , whereas silver utilizations of over 50% were rare with AgZ ; the highest silver utilization on AgZ seen to date is 64%. One hundred percent silver utilization on 3% LAgZ was seen in run 5 of the scoping study.

Regeneration studies of the LAgZ indicate that the use of 4.5% H_2 in Ar at 500°C does not perform in the same manner as it does with fully exchanged silver mordenite. Very little (<5% in 24 h) of the iodine loaded onto the LAgZ is removed by the 4.5% H_2 treatment at temperatures up to 500°C, and only limited iodine removal (~13%) was achieved using pure hydrogen at 500°C for 48 h. Air purges at temperatures up to 250°C are also inadequate for removal of the iodine; however, air at 500°C will remove >90% of the iodine in 24 h. The regenerated material has been reloaded

with CH_3I to ~90% of the original iodine loading and regenerated three times with similar results. During the air regenerations at 500°C, 30 to 40% of the iodine is removed in the first hour and an additional 30 to 35% is removed during the second hour of regeneration.

3.4 LAgZ Potential as Main Filter Material

The high degree of silver utilization achieved by LAgZ makes this material attractive for use in a main filter. Of concern during early studies was the high cost associated with the use of silver substituted zeolites; however, the cost associated with LAgZ is quite low. For example, assuming the following:

3% Ag loading by weight,

95% silver utilization,

\$16 per troy oz of silver, and

\$5 per pound for 1/16-in.-diam Norton Zeolon 900, |

a 0.5 t/d nuclear fuel reprocessing plant would require 7.5 kg/d of sorbent to remove the 0.25 kg/d of halogens present in the plant off-gas. The cost of the sorbent amounts to ~\$82 for the substrate and \$95 for silver per day or a total cost of \$7.40/h of operation. The total volume of waste generated would be approximately $2.5 \text{ m}^3/\text{year}$.

Future efforts to optimize the degree of silver loading should reduce the total cost and waste volume.

4. CONCLUSIONS

The following conclusions can be made from the experimental results and interpretation of the data:

1. Loadings of ~ 142 mg of CH_3I per g of AgZ can be obtained. This represents a silver utilization of $\sim 60\%$.
2. Bed temperature has a positive effect on the loading capacity of the AgZ and AgZ .
3. Water vapor with a dewpoint up to 35°C has a positive effect on the CH_3I loadings on AgZ .
4. Nodules of free silver are formed in AgZ during hydrogen pretreatment. The size of the nodule appears to be a function of the temperature more than the exposure time. Nodules approximately 2000 \AA in diameter are formed in beds up to 400°C . At 500°C , nodules are 10 to 20 times as large.
5. Loading decreases with increasing temperature hydrogen exposure.
6. Higher loadings are achieved using glass filter housings vs stainless steel when using high temperature hydrogen for regeneration.
7. High silver utilizations $> 95\%$ can be achieved for LAGZ .
8. A bed temperature of 200°C produces higher CH_3I loadings on LAGZ than 250°C .
9. The presence of H_2O has a slight negative effect on CH_3I loadings for LAGZ .
10. LAGZ cannot be regenerated using hydrogen at 500°C as can AgZ .

Future plans include:

1. Further examination of the effects of stainless steel on AgZ regeneration.
2. Examination of the effect of operating conditions on the length of the mass transfer zone.

3. Determine the optimum silver loading on $\overset{\circ}{\text{AgZ}}$ to minimize waste volume and maximize silver utilization.
4. Investigate the mechanisms involved in CH_3I loads on $\overset{\circ}{\text{AgZ}}$ and LAgZ .
5. Mixed I_2 and CH_3I loadings on LAgZ .

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