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**A Research Report
for Rockwell Hanford Operations**

**Evaluation of Silver Mordenite
for Radioiodine Retention at
the Purex Process Facility
Modification**

**R. D. Scheele
L. L. Burger**

July 1987

**Prepared for the U.S. Department of Energy
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SUMMARY

In 1985 and 1986 the Pacific Northwest Laboratory (PNL) evaluated the efficiency of silver zeolite, in particular silver mordenite (AgZ), as a trapping agent for radioiodine from the PUREX^(a) Process Facility Modification's (PFM) nuclear fuel dissolver off gas. The PFM is a new head-end treatment plant being designed by Rockwell Hanford Operations for the PUREX Plant at the Hanford Site. The tests were performed to determine AgZ performance at normal, off-normal, and standby conditions. Normal conditions were defined as 1 vol% nitric oxide (NO), 1 vol% nitrogen dioxide (NO₂), and an AgZ temperature of 150°C. Off-normal conditions, which could occur if the NO_x removal system failed or was placed downstream of the iodine removal system, would cause increases in the NO and NO₂ concentrations to 9 vol% each, and in the bed temperature to 230°C. Standby conditions would occur when the fuel dissolver was not operating; the off-gas system would continue to operate with air flow even though there would be no iodine or NO_x in the inlet air.

To determine the efficiency of AgZ under these various conditions, a series of experiments was designed to investigate the effect of NO concentration in the range 1 to 9 vol%, of NO₂ concentration in the range 1 to 9 vol%, and of bed temperature in the range 150 to 230°C, and to allow statistical analysis of the results. In addition, several special tests were performed to examine the effects of input iodine concentration, AgZ bed length, operation at standby conditions for extended periods, and the efficiency of reduced silver mordenite, Ag⁰Z.

With some qualifications, this experimental study showed that AgZ is an effective method for removing iodine from the PFM dissolver off gas at both normal and off-normal conditions. Bed loading and exit concentrations were independent of input concentration in the range 0.35 to 10.5 $\mu\text{mol CH}_3\text{I/L}$; however, bed loading was somewhat dependent on temperature. A 12-cm bed was routinely capable of reducing the effluent iodine concentration from

(a) Plutonium and Uranium Recovery by EXtraction. The facility is located at the Hanford Site in southeastern Washington state, and is operated for the U.S. Department of Energy by Rockwell Hanford Operations.

10 $\mu\text{mol I/L}$ to a nominal 10^{-4} $\mu\text{mol I/L}$. However, this low value is greater than the target 10^{-5} $\mu\text{mol I/L}$ set for the PFM. Some tests indicated that longer beds (16-cm) may be capable of reducing the effluent concentration to the target level. A disturbing aspect of these results, however, is that not all of the trapped iodine is firmly fixed on the AgZ. Some iodine will migrate when exposed to iodine-free air at standby conditions and could result in premature breakthrough.

The statistical analysis of the results of the parametric study to determine the effect of normal and off-normal operating conditions on the iodine loading of the AgZ at breakthrough showed that a higher loading of iodine on AgZ can be achieved at 150°C than at 230°C . Increasing the temperature from 150 to 230°C caused an average 10% decrease in the loading at breakthrough from 0.43 to 0.39 mmol I/g AgZ for a 12-cm bed. The NO and NO_2 concentration levels in the range of 1 to 9 vol% had no detectable effects. The results of this set of experiments indicate that operation of the iodine control system at normal or off-normal conditions will not greatly impact the final loading at breakthrough.

The special test to determine the effect of the input iodine concentration showed that the influent CH_3I concentration in the range of 0.35 to 10.5 $\mu\text{mol I/L}$ did not affect the effluent concentration during normal loading and standby operations before breakthrough. The results from this special test were compared with those of the run from the parametric study performed at normal conditions, and the results indicated also that the loading was unaffected by the change in input concentration.

The tests to determine the impact of increasing bed length produced several interesting results. The first is that a longer bed will improve the loading capacity of the AgZ at breakthrough. Secondly, a longer bed may reduce the effluent concentration to less than 10^{-4} $\mu\text{mol I/L}$, possibly to the target level, during loading and standby conditions. The effluent concentrations for these tests during loading trended downward with increasing bed length. Thirdly another test suggests that over an extended period of time with an iodine input of $\geq 10^{-4}$ $\mu\text{mol I/L}$, the effluent concentration will be 10^{-4} $\mu\text{mol I/L}$. In that test, the standby effluent from a 16-cm bed loaded to

0.4 mmol I/g AgZ was fed into a second 16-cm bed. After 20 days with the effluent concentration from the first bed at 10^{-4} $\mu\text{mol I/L}$, the effluent from the second AgZ bed was also 10^{-4} $\mu\text{mol I/L}$.

In all of the extended tests at standby conditions, the effluent concentration from a loaded bed increased to well above the target level. This increase indicates that a portion of the iodine is not initially bound firmly to the AgZ. In one of the extended standby tests, the chronic release decreased, after peaking, to 10^{-5} $\mu\text{mol I/L}$. In another test, the release decreased to 10^{-4} $\mu\text{mol I/L}$, suggesting that extended treatment at standby conditions or just at temperature would result in a stable iodine loading with an effluent concentration at the target level. If a stable loading does exist, achieving it may be a function of time and temperature.

The special test using Ag^0Z indicated that the achievable loading at breakthrough is about 30% less for Ag^0Z than AgZ. This finding was unexpected, based on past work which showed that a higher loading was obtained with Ag^0Z . This test suggested that the trapped iodine loaded onto an Ag^0Z bed at normal conditions is more tightly bound than iodine trapped on an AgZ bed. Before application of Ag^0Z to the PFM, further studies would be required.

This experimental program showed that even though AgZ was effective as an iodine trap at all potential conditions in the PFM, its performance did not meet all of the target criteria.

In addition to the iodine trapping studies, we measured several physical properties of the AgZ. Air-equilibrated -10+16 mesh AgZ had a density of 0.993 g/mL (10 wt% water) and a free volume of 40%. The pressure drop increased rapidly with a decrease in mesh size. The pressure drop for a 1.25-cm-diameter bed at 22°C ranged from 90 to 2210 mm $\text{H}_2\text{O/m}$ of bed length at a face velocity of 4.9 m/min for mesh sizes ranging from -10+16 to -40+70 mesh AgZ. Temperature also affected the pressure drop across the bed. Increasing the temperature from 22 to 100°C increased the pressure drop by 40 to 50%, and a change from 100 to 200°C caused an increase of 30%.

Additional studies of alternative materials and/or studies to understand and improve the chemistry and reactions rates of the trapping process may be required to meet the target control levels established by Rockwell for the PFM.

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INTRODUCTION

The Process Facility Modification (PFM) is being designed for head-end treatment of irradiated fuels, including N-Reactor and Fast Flux Test Facility (FFTF) fuels, for processing by the PUREX^(a) plant at the Hanford Site. Included in the design is a gas treatment system to remove radioiodine from the dissolver off gas. The currently proposed process uses heated beds of the silver-exchanged zeolite, silver mordenite (AgZ).

Rockwell Hanford Operations (Rockwell), operators of the PFM and PUREX Plant, requested that the Pacific Northwest Laboratory (PNL) determine the effectiveness of the proposed iodine removal system at normal, off-normal, and standby conditions. Off-normal conditions would occur if the removal system for nitrogen oxides (NO_x) were to fail or if the NO_x removal system were to be placed downstream instead of upstream of the iodine removal system. Standby conditions would occur when the dissolver was not operating, but normal flow of iodine-free air would still pass through the off-gas system. The iodine release from the AgZ beds at standby conditions is called chronic release. The target release level for the iodine control system is $<10^{-5} \mu\text{mol I/L}$. A previous PFM study^(b) demonstrated that AgZ would remove iodine from the gas stream, reducing the level to below $10^{-3} \mu\text{mol I/L}$.

To determine the bed-loading capacities and the effluent iodine concentrations at normal, off-normal, and standby conditions, PNL performed a series of statistically designed parametric tests using a bed of AgZ 12 cm long x 1 cm diameter. In addition, tests were performed to determine the effect of bed length, the effect of a second bed, the effect of extended standby conditions, and the efficiency of hydrogen-reduced AgZ (Ag^0Z). The results of these experiments are presented in this report.

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- (a) Plutonium and Uranium Recovery by EXtraction. The facility is located at the Hanford Site in southeastern Washington State.
 - (b) Letter report to Rockwell Hanford Operations by L.L. Burger, R.D. Scheele, and C.L. Matsuzaki. 1983. PFM Iodine Removal Studies, Pacific Northwest Laboratory, Richland, Washington.

EXPERIMENTAL DESIGN, APPARATUS, ANALYTICAL METHODS, AND PROCEDURE

The objective of the experimental program was to determine the efficacy of AgZ as an iodine-trapping agent at normal, off-normal, and standby operating conditions in the PFM. Table 1 presents these three operating conditions. In this section we describe the experimental design, the apparatus, and how a typical experiment or run was performed. In the appendices we present a brief description of a similar experiment performed several years ago to determine iodine loading. The appendices also contain measurements of several properties for the AgZ used, such as the density, water content, and the pressure drop at various conditions.

EXPERIMENTAL DESIGN

To measure the utility of AgZ under these possible conditions, D. J. Bates, a statistician, developed an experimental plan using a two-factorial statistical design to aid us in determining the effects of nitric oxide (NO), nitrogen dioxide (NO₂), and temperature. In this two-factorial design we used two levels of each independent variable with no replication and two runs at the mid-point levels of each variable. These latter two experiments at the center point of the experimental space are used to test for "lack-of-fit" of the resulting linear model for the experimental region of interest. The experimental design for the parametric study after randomization of the run order is shown in Table 2.

After the parametric study was complete, several special studies were performed to investigate other factors. These tests studied the effect of very low influent iodine concentration, bed length, extended standby operation, and the comparative efficiency of Ag⁰Z.

APPARATUS

The laboratory apparatus was designed to allow simulation of the expected or potential conditions in the PFM in terms of superficial face velocity, AgZ particle size, water content in the gas stream, NO and NO₂

TABLE 1. Normal, Off-Normal, and Standby Operating Conditions for PFM Iodine Control System

Operating Parameters	Level		
	Normal	Off-Normal	Standby
Gas Composition (Dry Basis)			
NO _x , vol%	2	18	0
NO, vol%	~1	9	0
NO ₂ , vol%	~1	9	0
O ₂ , vol%	12	14	21
N ₂ , vol%	86	68	78
CH ₃ I, μ mol/L	0.1	0.1	0
H ₂ O, vol%	3	3	3
mmol/L	1.3	1.3	1.3
Face Velocity, m/min	5	5	5
Bed Temperature, °C	150	230	50-150
Packing Size, Mesh	-10+16	-10+16	-10+16

TABLE 2. Experimental Design for Parametric Study

Experiment No.	NO, Vol%	NO ₂ , Vol%	Temperature, °C
1	9	9	230
2	9	1	150
3	5	5	190
4	1	9	150
5	9	9	150
6	1	9	230
7	5	5	190
8	9	1	230
9	1	1	150
10	1	1	230

concentrations, and temperature. The AgZ bed design was based on previous PFM studies (Letter report, Burger, Scheele, and Matsuzaki 1983) using AgZ and earlier work using Ag⁰Z for CH₃I trapping (Scheele, Burger, and Matsuzaki

1983; Burger and Scheele 1982a). A schematic of the laboratory apparatus is presented in Figure 1, and the standard experimental operating parameters are presented in Table 3.

In designing the system and selecting the operating conditions, it was necessary to select a bed size and iodine input concentration such that the time required to load a bed to 0.4 to 0.8 mmol I/g AgZ (50 to 100 mg I/g AgZ) was an acceptably small value. To reduce the loading time, we used a smaller bed than was used in previous PNL studies (Scheele, Burger, and Matsuzaki 1983; letter report, Burger, Scheele, and Matsuzaki 1983) and a higher input iodine concentration than will be found in plant.

Even though a smaller bed and a higher iodine concentration were used, the critical PFM operating conditions were preserved. The bed had a small diameter; yet it maintained normal face velocity, and it was long enough to

FIGURE 1. PFM Iodine Control Experimental Apparatus

TABLE 3. Standard Experimental Operating Parameters^(a)

<u>Bed Parameters</u>	<u>Level</u>
Diameter	1 cm
Length	12 cm
Material	AgZ, -10+16 mesh
Silver Content	19 wt%
Weight	9.3 g
Free Volume	40%
Water Absorption (ambient)	26 wt%
<u>Input Gas Parameters</u>	
Iodine Concentration	10.5, 21.0 μmol CH ₃ I/L
Carrier Gas	Air
Flow Rate	0.44 L/min
Face Velocity	5.6 m/min
H ₂ O Concentration	2.5 mmol/L

(a) One or two parameters vary for certain special tests.

accommodate the expected mass transfer zone of <10 cm (Scheele, Burger, and Matsuzaki 1983). The input iodine concentration was also preserved, existing in the tailing edge (downstream edge) of the iodine feed band.

The typical AgZ bed was prepared by adding 9.3 g of AgZ (purchased presized from Ionex Corporation) to the glass column and vibrating the material to pack the AgZ particles and reduce channeling. A constant temperature oven controlled the bed temperature to about $\pm 2^{\circ}\text{C}$, except for momentary excursions when an iodine influent or effluent sampler was introduced or removed from the oven.

The gaseous iodine sampler traps were 1-cm diameter by 5-cm long columns of 1.6-mm diameter silver faujasite (AgX) also purchased from Ionex. We selected AgX as a trap for the low concentrations of iodine in the effluent on the basis of past experience (Burger and Scheele 1982a). Samples of the influent iodine were obtained at the beginning and end of each working day.

The AgZ bed effluent was sampled at intervals of usually 1 to 2 hours during loading, and overnight or at selected intervals depending on the release pattern during standby.

Even though AgX is an excellent trap for iodine passing through or released from an AgZ bed, we recommended to Rockwell that AgZ be used for iodine control in the PFM because of its greater thermal stability and acid resistance compared with AgX. This greater stability is believed to be largely due to the higher Si/Al ratio (Venuto and Landis 1968) and the fact that AgX contains a clay binder.

The input gas stream was made up of air, O_2 , NO, CH_3I-N_2 , and H_2O . The gases were all supplied from commercial gas cylinders. Electronic mass flow meters controlled the gas flows; calibrated rotameters were also used to monitor the flow rates. Before the air was mixed with the NO_x gases, it was passed through a $40^\circ C$ water bubbler to obtain the desired water content; tests confirmed that water saturation of the gas was obtained. The NO was passed through the mixing bulb before being mixed with the air carrier gas. A stoichiometric amount of O_2 was added to the mixing bulb to react with the NO and produce the desired level of NO_2 .

Even though the reaction between pure O_2 and NO to produce NO_2 is very fast, further conversion of the remaining NO when mixed with air and at the higher temperature should be minimal because the rate drops rapidly with dilution. Kinetic calculations based on the data of Yost and Russell (1944) indicate that at the highest NO concentration and the lowest operating temperature, the NO concentration entering the bed might have been reduced by as much as 10%. The amount converted will be less at the highest temperature because the reaction rate slows as temperature increases. Thus the NO and NO_2 concentrations in the simulated off-gas stream were close to the desired experimental levels.

Methyl iodide was selected as the chemical form for iodine in these tests because it is the most difficult to trap of the major iodine species present in the dissolver off-gas stream, thus representing a worst case. If methyl iodide can be successfully controlled; so, then, can I_2 . The sources for the CH_3I were two gas tanks of a mixture of N_2 and ^{125}I -traced CH_3I obtained from New England Nuclear Corporation. The first contained

300 $\mu\text{mol CH}_3\text{I/L}$ and the second contained 154 $\mu\text{mol CH}_3\text{I/L}$. PNL measured the concentrations by means of gas chromatography using a 2-m Pora-Pak QS^(a) 80-100 mesh column at 200°C with a He flow of 100 mL/min. A photoionization detector (PID) with a 10.5 eV lamp was used. A concentration standard, prepared from reagent-grade CH_3I and air, was used to calibrate the output of the PID.

The experimental apparatus (Figure 1) was originally designed for a face velocity through the AgZ bed of 5 m/min. When the experiments were to begin, Rockwell requested that we consider increasing the face velocity through the bed. Without further reduction of the bed diameter, our installed instrumentation allowed a maximum face velocity of 5.6 m/min.

The apparatus was constructed of stainless steel, glass, and plastic. The gas transfer lines were stainless or plastic outside the oven; within the oven, glass was used for the transfer lines and the bed and sampler containers. Teflon^(b) tubing and screw clamps were used to seal butted glass joints. At first, polyethylene tubing was used for a portion of the transfer line for the CH_3I . After the first five runs were completed, however, we discovered that the CH_3I was diffusing through the tubing and was therefore not reaching the AgZ bed at the target nor at a predictable concentration. The problem was corrected by using all stainless steel tubing.

Because of the plastic tubing problem, the calculated loadings for these five runs were in error. The time-based loadings are calculated using the CH_3I concentration in the tank, the flow rate, and the time to reach breakthrough. Due to the loss of CH_3I through the plastic tubing, the input concentration was low, which caused the time-based loading to be high. The loadings at breakthrough based on gamma count are likely incorrect since they are calculated by correcting the measured final loading (by gamma count) using the ratio of the time to breakthrough and the total loading time as a

(a) Pora-Pak QS is a registered trademark of Waters Associates, Inc.
(b) Teflon is a registered trademark of E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

correction factor. Since the input concentrations for these five runs were erratic and unknown, the correction factor will not be accurate, nor will the calculated loading at breakthrough based on gamma count.

ANALYTICAL METHODS

To provide the necessary sensitivity to measure $<10^{-5}$ $\mu\text{mol I/L}$ in the effluent concentration from the AgZ, we used the radioactive iodine isotope ^{125}I to trace CH_3I at a specific activity of 1 mCi/mmol. Because of the low detection limit required, no analytical method was available to provide both quantitative measurement and identification of the effluent iodine chemical species.

To determine the iodine concentrations in the influent, in the effluent and on the beds, the gamma emission from the ^{125}I collected on the trap material and beds was counted with a NaI(Tl) crystal well counter. The gamma counting was calibrated using standards prepared by two methods: 1) adding a measured volume of traced CH_3I gas to a zeolite bed and 2) adding an aliquot of an aqueous Na^{125}I standard to a zeolite bed. Because the gamma activity on the iodine-loaded AgZ beds from the experiments was too great to count without attenuation, we used a copper cup shield to attenuate the activity for these high-activity samples.

EXPERIMENTAL PROCEDURE

The following procedure was used for a typical experiment or run. To initiate a run, the oven was turned on, the air flow started, and the water bubbler heated to temperature. Water-saturated air was passed through the heated AgZ bed for 1 to 2 hours, allowing the zeolite to become saturated at its equilibrium water content. After the NO and CH_3I lines were purged with N_2 , the gas flows of NO , O_2 , and CH_3I were started. The purge lines are omitted from Figure 1.

After about 1 hour with effluent trap E (see Figure 1) in place at the exit of the AgZ bed, the influent trap I was installed, the valve to the trap opened, and the flow through the AgZ bed stopped by closing the flow at point (a). Influent sample times were typically 2 minutes and were taken at the beginning and end of each working day. Because of the short collection

times, the influent concentrations measured were inaccurate and were only used to confirm that the input levels were approximately correct. They were not used to calculate bed loading. Instead, time-based loadings were calculated using known cylinder concentration, flow rate, and time. After the influent sampling was completed, an effluent trap was installed, and the valve to the influent sampler was closed and flow restarted through the AgZ bed. The effluent sampler traps were typically replaced every 1 to 2 hours throughout the working day.

At the end of the day, the CH_3I , O_2 , and NO flows were stopped, the NO and CH_3I gas lines purged with N_2 , and the airflow adjusted to 5.6 m/min. An effluent trap for iodine released during standby was installed and left in place until the CH_3I was restarted, or as needed to monitor the standby effluent concentration.

The progress of the iodine down the AgZ bed was tracked by monitoring the color of the iodine-loaded AgZ, which was used qualitatively to determine whether breakthrough had occurred. Another test for whether iodine had broken through was the color of the AgX effluent trap. If the trap was yellow, the color of AgI, breakthrough had occurred. At that point, the loading portion of the experiment terminated.

RESULTS

The results of the parametric study and the tests performed to determine the effect of specific factors are presented in this section. We first discuss some general observations, then the parametric study, and finally the tests of specific factors.

The results of the 21 experiments are presented in Table 4. Table 4 presents bed loadings and the average effluent concentrations during loading and standby conditions before breakthrough. We had originally planned to define breakthrough as the point when the effluent concentration exceeded 10^{-5} $\mu\text{mol I/L}$. However, in many experiments the effluent concentration was never lower than 10^{-5} $\mu\text{mole I/L}$, so breakthrough was redefined to be the point when the effluent concentration exceeded 10^{-3} $\mu\text{mol I/L}$ after a sharp, consistent increase in the effluent iodine concentration was observed. Occasionally breakthrough occurred during nightly standby operation; in those cases, the loading at breakthrough was taken to be the loading prior to standby operation.

The bed loadings at breakthrough reported in Table 4 were determined by two methods. In one method, an integrated value was based on the time to breakthrough, the concentration in the CH_3I feed tank, and the feed rate. The second method involved direct gamma counting of the loaded bed after termination of the experiment, corrected for the iodine lost during standby, and then adjusted using the ratio of the time to breakthrough to the total loading time as a correction factor.

GENERAL OBSERVATIONS

Table 4 illustrates our first general observation, that the loadings at breakthrough for a 12-cm bed ranged from 0.4 to 0.5 mmol I/g AgZ, and the effluent iodine concentrations during loading and standby before breakthrough were routinely 10^{-4} $\mu\text{mol I/L}$ and 10^{-5} $\mu\text{mol I/L}$, respectively. The effluent concentration during iodine loading before breakthrough was greater than the target 10^{-5} $\mu\text{mol I/L}$, and the standby concentration before breakthrough (average 2×10^{-5}) was near this desired level. These loading results are consistent with the 0.5 mmol I/g AgZ loading before breakthrough measured for

TABLE 4. Summary of PFM Iodine-Trapping Study Results

Run No.	Input CH ₃ I, μmol/L	NO ₂ , Vol%	Temperature °C	Loading at Breakthrough			Average Effluent Concentration Before Breakthrough, μmole I/L	Standby Concentration Before Breakthrough, μmole I/L
				By Time, mmol I/g AgZ	By Time, mg I/g AgZ	By Count, mmol I/g AgZ		
1	(a)	9	230	(a)	(a)	(a)	6.92E-06	2.3E-07
2	(a)	9	150	(a)	(a)	(a)	1.35E-04	2.6E-05
3	(a)	5	190	(a)	(a)	(a)	1.12E-04	1.1E-05
4	(a)	1	150	(a)	(a)	(a)	1.32E-04	2.9E-05
5	(a)	9	150	(a)	(a)	(a)	3.52E-04	4.3E-05
6	10.5	1	230	0.386	49.1	0.468	7.85E-04	1.5E-05
7	10.5	5	190	0.484	61.5	0.487	1.23E-04	1.9E-05
8	10.5	9	230	0.370	47.0	0.397	1.91E-04	1.0E-05
9	10.5	1	150	0.386	49.0	0.423	6.40E-04	6.0E-06
10	21.0	1	230	0.378	48.0	0.376	2.75E-04	NS
11	21.0	5	190	0.440	55.9	0.413	8.53E-05	NS
12	21.0	9	150	0.505	64.1	0.472	1.36E-04	NS
13	21.0	9	230	0.411	52.2	0.447	6.75E-04	NS
14	21.0	9	150	0.415	52.7	0.454	2.61E-04	NS
15	10.5	1	150	0.461	58.5	0.434	6.90E-05	2.2E-05
16(b)	0.35, 10.5	1	150	0.411	52.2	0.425	3.31E-05	9.2E-07
17(c)	10.5	1	150	0.620	78.7	(d)	8.59E-06	8.6E-07
18	10.5	9	230	0.373	47.4	0.384	1.85E-04	8.0E-06
19(e)	10.5	1	150	0.491	62.3	NM	8.46E-05	4.9E-05
20(f)	10.5	1	150	0.399	50.7	(d)	1.46E-05(g)	2.3E-06
22(h)	10.5	1	150	0.289	36.7	0.303	1.06E-05	<1E-05

NM = Not Measured.

NS = No Sample taken before breakthrough.

(a) CH₃I lost by diffusion through plastic transfer lines before delivery to AgZ bed, therefore unable to determine loading.

(b) Special test to determine effect of input iodine concentration level.

(c) Special test to determine effect of bed length. Bed length 16 cm.

(d) Treatment after loading precluded quantitative analysis of bed loading.

(e) 14-cm-long bed instead of 12-cm-long bed.

(f) Special test to determine effect of bed length and effect of standby on partially loaded bed. Bed length 16 cm.

(g) Does not include one non-consistent data point.

(h) Special test of Ag²Z.

a 13-cm bed (same breakthrough criteria) in our earlier studies (letter report, Burger, Scheele, and Matsuzaki 1983). See the Appendix A for a more detailed discussion of the results of this experiment.

Our second observation was that during standby operation iodine can migrate down the bed and breakthrough can occur. As iodine is trapped by AgZ, the loaded material turns yellow and then purple. This sharply colored iodine loading band was used to monitor the progress of the iodine down the bed. During standby with iodine-free air passing through the heated bed at 5.6 m/min, the purple loading band lightened in color and moved down the bed. Occasionally this migration caused breakthrough during the nightly standby operation, and the concentration would rise to a range of 10^{-1} to 10^{-2} $\mu\text{mol I/L}$. This migration indicates that some of the iodine is labile, as previously reported by Burger and Scheele (1982b). Analytical techniques used in these earlier release experiments were not sufficiently sensitive to detect such a slow iodine bleed.

Third, by using the color of the iodine-loaded bed as a guide, we found the mass transfer zone for these experiments to be 5 cm or less. This figure corresponds to the mass transfer zone of <10 cm measured for Ag⁰Z (Scheele, Burger, and Matsuzaki 1983) and 10 cm reported for AgZ by Thomas et al. (1977). These earlier experiments used different face velocities up to 15 m/min. Higher face velocities should cause the mass transfer zone to increase.

A fourth trend, which was observed occasionally, was that the effluent concentration decreased over the first few samples. This pattern suggests that the bed becomes more effective as it is conditioned.

PARAMETRIC STUDY

To determine the effects of NO concentration, NO₂ concentration, and temperature on the trapping of iodine by AgZ, B. A. Pulsipher of PNL used analysis of variance methodology (ANOVA) on a selected portion of the bed-loading results presented in Table 4.

The ANOVA was performed on both the integrated loading based on time and the loading based on the gamma count of the ¹²⁵I on the AgZ bed for runs 6 to

16 and 18. After runs 6 to 15 had been completed, Pulsipher performed an ANOVA using the loading results for those experiments and suggested that run 18 be performed to provide additional information about the system. Experiment 16 was performed specifically to determine the effect of input iodine concentration; however, after considering the lack of impact of input concentration, we decided to include the loading results in the statistical analysis.

The ANOVAs were performed iteratively. If a factor was determined to be statistically nonsignificant, that factor was dropped from consideration and the ANOVA repeated. For a simplified description of ANOVA, we refer the reader to Scheele, Burger and Matsuzaki (1983).

The loading curves for the first five runs and for each experiment used in the statistical analysis are presented in Figures 2 to 19. For the first five experiments and experiment 16, effluent concentration versus time is presented in Figures 2 to 6 and 18. For the remaining experiments and experiment 16, effluent concentration versus time-based loading is presented in Figures 7 to 17 and 19. In the first five experiments, a portion of the input CH_3I diffused through the plastic delivery line, which made the input concentrations extremely variable and the loadings indeterminate.

The results of the ANOVA analysis with the time-based loadings indicate that temperature has a statistically significant effect on the bed loading, while NO and NO_2 concentration do not. As shown in Figure 20, increasing temperature from 150 to 230°C caused an 11% reduction in the average loading for a 12-cm bed from 0.44 to 0.39 mmol I/g AgZ. The lack-of-fit test using the replicated center points (runs 7 and 11) indicated that the effects of temperature, NO , and NO_2 may not be strictly linear. As Figure 20 shows, the average loading at 190°C, 0.46 mmol I/g AgZ, is higher by 5% than the average loading at 150°C.

The statistical analysis of the data based on loading by count indicated that none of the tested factors had a significant effect. The inherent variation in the count data was of such magnitude that the small effects due

FIGURE 2. Effluent Concentration Versus Time for Run 1

FIGURE 3. Effluent Concentration Versus Time for Run 2

FIGURE 4. Effluent Concentration Versus Time for Run 3

FIGURE 5. Effluent Concentration Versus Time for Run 4

FIGURE 6. Effluent Concentration Versus Time for Run 5

to the three independent factors were not detectable. Figure 20 shows that both sets of loading data show the same trend, although the trend based on counting is less pronounced.

An attempt was made to examine statistically the effect of total NO_x on the loading. For the count-based loadings, total NO_x had no significant effect. For the time-based loadings there was a suggestion of some interaction between total NO_x and temperature at the 85% confidence level. It should be noted only a trend was suggested; additional studies would be required to clarify whether there was a significant effect.

In our earlier report on Ag⁰Z (Scheele, Burger, and Matsuzaki 1983) we discussed several chemical and physical factors that could affect the sorption of iodine by silver sorbents. One factor was NO₂ absorption by the zeolite with subsequent blockage of the iodine's access to the active silver sites. Another factor could involve the potential reaction between NO₂ and the CH₃I; in our earlier studies with Ag⁰Z, we observed that when NO_x was present in the gas stream the CH₃I was converted to I₂. It is possible that temperature and NO₂ concentration have different degrees of effectiveness, each depending on the level of the other. Because of the complexity of this

FIGURE 7. Effluent Concentration Versus Iodine Loading on AgZ for Run 6 (Parametric Study)

FIGURE 8. Effluent Concentration Versus Iodine Loading on AgZ for Run 7 (Parametric Study)

FIGURE 11. Effluent Concentration Versus Iodine Loading on AgZ for Run 10 (Parametric Study)

FIGURE 12. Effluent Concentration Versus Iodine Loading on AgZ for Run 11 (Parametric Study)

FIGURE 13. Effluent Concentration Versus Iodine Loading for Run 12 (Parametric Study)

FIGURE 14. Effluent Concentration Versus Iodine Loading on AgZ for Run 13 (Parametric Study)

FIGURE 15. Effluent Concentration Versus Iodine Loading on AgZ for Run 14 (Parametric Study)

FIGURE 16. Effluent Concentration Versus Iodine Loading on AgZ for Run 15 (Parametric Study)

FIGURE 17. Effluent Concentration Versus Iodine Loading on AgZ for Run 16 (Test of Input Iodine Concentration).

FIGURE 18. Effluent Concentration Versus Time for Run 16 (Test of Input Iodine Concentration)

FIGURE 19. Effluent Concentration Versus Iodine Loading on AgZ for Run 18 (Parametric Study)

FIGURE 20. Average Effect of Temperature on AgZ Bed Loading (Parametric Study)

system, consult our earlier detailed discussion of factors affecting the trapping of iodine by silver sorbents (Scheele, Burger, and Matsuzaki 1983).

The parametric study showed that of the factors tested, temperature was the only one to have a statistically significant effect. The reduction in time-based loading amounted to only 11% for an increase from 150 to 230°C. Because of the lack of effect of NO_x concentration, it appears that if the iodine removal system were to be placed in front of the NO_x recovery unit or if this unit were to fail, the loading would not be severely affected.

TEST OF INPUT IODINE CONCENTRATION

The purpose of experiment 16 was to determine whether input CH₃I concentration, in the range 0.3 to 10 μmol/L, affected the loading or the effluent concentration. Figures 17 and 18 present the effluent concentration as a function of the time-based loading and time, respectively. Figure 18 is presented to allow easier comparison between the loading periods for the two concentrations.

In experiment 16, the influent concentration of CH₃I was varied between 0.35 and 10.5 μmol/L on alternating days for the first three days. On day 4 the starting concentration was 10.5 μmol/L for the first 3 effluent samples; the input concentration was changed to 0.35 μmol/L for the next two samples, and finally back to 10.5 μmol/L for the remaining samples. As can be seen from Figures 17 and 18, the experiment was terminated before breakthrough was reached, although it appears to have been imminent. The final loading of 0.41 mmol I/g AgZ is reported in Table 4 as the loading at breakthrough.

As Figures 17 and 18 illustrate, the effluent concentrations during loading were near the target 10⁻⁵ μmol I/L independent of the input concentration. The standby concentrations were nominally 10⁻⁶ μmol I/L, which is below the target effluent concentration.

Experiment 9 was performed at the same conditions as experiment 16, differing only in input iodine concentrations. For these two experiments the loadings at breakthrough are comparable, 0.39 and 0.41 mmol I/g AgZ, respectively. However, the average effluent concentration before

breakthrough for run 16, 3×10^{-5} $\mu\text{mol I/L}$ is 5% of the average effluent concentration before breakthrough for experiment 9. We have no explanation for the difference in the two effluent concentrations.

Because the loading for experiment 16 was nearly the same as that for experiment 9, we included experiment 16 in the statistical analysis. The similarity in loadings is somewhat surprising considering that there were three standby operations in experiment 16 and one in experiment 9. One would predict, from the observed mobility of sorbed iodine during standby operation, observed in other runs, that increasing the amount of standby time would lessen the final loading at breakthrough. The length of the mass transfer zone may be the controlling factor. Additional testing is required to understand this phenomenon.

In summary, this experiment shows that at a bed temperature of 150°C , 1 vol% NO and 1 vol% NO_2 in the input gas, the bed loading and effluent concentration are independent of the input CH_3I concentration in the range 0.35 to $10.5 \mu\text{mol/L}$.

TESTS OF BED LENGTH AND EXTENDED STANDBY

After the initial phase of the parametric study was completed, we performed experiments 17 and 20 using a 16-cm bed at normal conditions to determine the effect of a longer bed and the stability during extended standby operations of the iodine trapped on the AgZ. These tests also simulated the scenario in which the PFM dissolver is not operated and a fully or nearly fully loaded AgZ bed is maintained at standby for an extended period of time before being removed. In addition to the two planned longer-bed tests, in run 19 we accidentally used a 14-cm bed instead of a 12-cm bed. Because this experiment provides additional information on the effect of a longer bed, it is discussed along with experiments 17 and 20 in this section.

Experiment 17 was performed in two parts. In the first part of experiment 17, as can be seen in Figure 21, a 16-cm bed was loaded to $0.62 \text{ mmol I/g AgZ}$ with a nominal effluent concentration of $10^{-5} \mu\text{mol I/L}$ before breakthrough. These loading and effluent concentration results were encouraging. When the bed length was increased from 12 to 16 cm, the loading at breakthrough increased 50% compared to the average loading of

FIGURE 21. Effluent Concentration Versus Iodine Loading on AgZ for Run 17 Loading and Standby Operations (Test of Bed Length and Extended Standby)

0.4 mmol I/g AgZ for experiments 9 and 16. In addition, the effluent concentration for the 16-cm bed met the target effluent concentration established for the PFM.

In the second part of experiment 17, the standby release was monitored for an extended period in two stages. In the first stage the chronic release was monitored for 20 days and the bed temperature was maintained at 150°C; then the temperature was increased to 200°C. With time, the effluent concentration at 150°C began to decrease with respect to the loading level. Extrapolating these standby data suggests that the bed might have stabilized at a loading of 0.5 mmol I/g AgZ, with a chronic release at $<10^{-5}$ μmol I/L. Increasing the temperature to 200°C increased the chronic release level to 0.1 μmol I/L suggesting an increase in the iodine vapor pressure.

In the second stage of the extended standby test, the bed was removed and divided into three parts of 4.93 g (inlet), 4.38 g (middle), and 3.81 g (outlet). The iodine loadings based on gamma count were 0.57, 0.44, and 0.35 mmol I/g AgZ, respectively, for the three bed portions. About 20% of the

original trapped iodine had been removed from the bed by standby operation. After the inlet third was treated for 11 days with an airflow of 200 mL/min at 180 to 200°C, the effluent dropped to the target release level of 10^{-5} $\mu\text{mol I/L}$. The inlet bed loading was now 0.43 mmol I/g AgZ. This test suggested that if a 16-cm bed is loaded to a maximum of 0.43 mmol I/g AgZ, the iodine loaded onto the bed might be fixed on the AgZ and might only allow an effluent concentration of $<10^{-5}$ $\mu\text{mol I/L}$. Experiment 20 was performed to test this hypothesis.

In experiment 20, a 16-cm bed was loaded to 0.40 mmol I/g AgZ and exposed to standby conditions for an extended period. After 7 days we inserted a second 16-cm bed in the effluent of the first bed to determine whether increasing the bed length further reduced the effluent concentration. The effluent concentration during loading as a function of bed loading is presented in Figure 22. The chronic release levels as functions of bed loading and time are presented in Figures 23 and 24, respectively.

During the loading cycle of experiment 20, the standby and loading effluent concentrations were similar to those for experiment 17. The loading

FIGURE 22. Effluent Concentration Versus Iodine Loading on AgZ for Run 20 (Test of Bed Length and Extended Standby)

FIGURE 23. Effluent Concentration During Standby Operations for Run 20 (Test of Bed Length and Extended Standby)

FIGURE 24. Effluent Concentration Versus Time for Run 20 Standby Operations (Test of Bed Length and Extended Standby)

effluent was typically 10^{-5} μmol I/L, and the standby averaged 2×10^{-6} μmol I/L. One loading effluent concentration was quite high and inconsistent with the other effluent concentrations. It was not used to calculate the average effluent concentration before breakthrough reported in Table 4.

After iodine loading was stopped in run 20, the standby concentration rose rapidly to 10^{-2} μmol I/L and remained in the 10^{-3} to 10^{-2} μmol I/L range, as can be seen in Figures 23 and 24. Thus our hypothesis that iodine loaded onto AgZ to 0.4 mmol I/g would be stable was not verified. It may be that a longer loading time or a higher bed temperature is required to stabilize the iodine on the bed.

The second 16-cm bed, downstream of the loaded first bed, initially reduced the effluent concentration to 10^{-4} μmol I/L. For the next 8 to 10 days, the effluent concentration from the second bed was typically lower than 10^{-5} μmol I/L with the exception of one sample. When measured, the effluent from the first bed was 10^{-4} μmol I/L. After another week, the effluent concentration from both beds appeared to level out at about 10^{-4} μmol I/L. This latter result suggests that the lowest achievable effluent concentration during long-term loading will be 10^{-4} μmol I/L independent of bed length up to 32 cm. It should be noted that the chemical species of the iodine released from the first bed during standby is unknown; however, we believe that it is probably I_2 .

Experiment 19, though accidentally run using a 14-cm bed instead of a 12-cm bed, provides supplementary information on the effect of increasing bed length. In this run the 14-cm bed was loaded to 0.5 mmol I/g AgZ before breakthrough, which occurred during standby operation. The effluent concentrations during loading and during standby before breakthrough were 10^{-4} and 5×10^{-5} μmol I/L, respectively. The effluent concentrations as a function of the bed loading are presented in Figure 25. Table 5 compares the results of this experiment with those of experiments 9, 16, 17, and 20.

Table 5 shows that increasing the bed length increases the iodine loading by a nominal 0.1 mmol I/g AgZ per 2 cm over 12 cm. The effluent concentration during short-term loading before breakthrough seems to decrease with increasing bed length, although the trend is not consistent. Additional

FIGURE 25. Effluent Concentration Versus Iodine Loading on AgZ for Run 19 (Test of Bed Length)

TABLE 5. Summary of Bed Length Test Results

Run	Bed Length, cm	Time-Based Loading at Breakthrough, mmol I/g AgZ	Average Effluent Before Breakthrough, μmol I/L	Average Standby Effluent Before Breakthrough, μmol I/L
9	12	0.39	6.4E-04	6.0E-06
16	12	0.41	3.3E-05	9.2E-07
19	14	0.49	8.5E-05	4.9E-05
17	16	0.62	8.6E-06	8.6E-07
20	16	ND	1.4E-05(a)	2.3E-06

ND = Not determined.

(a) Does not include second sample of first day; inconsistent with other samples.

studies would be required to determine the effect of bed length on the effluent concentration during loading at the iodine concentrations expected in the PFM. Standby concentrations do not appear to be affected by bed length.

In summary, these tests show that increasing the bed length will improve the achievable iodine loading on AgZ and may reduce the effluent concentration during loading. The extended standby tests indicate that a portion of the iodine loaded onto AgZ is not firmly fixed and will be removed during standby operations. The rate at which the iodine leaves the bed decreases with time, suggesting that with time the stability of the iodine increases and the iodine becomes less mobile. There is also some indication that the loading level before standby will affect the final stable loading.

TEST OF REDUCED SILVER MORDENITE

One alternative material which has received some attention as a trapping agent for gaseous radioiodine is hydrogen-reduced silver mordenite (Ag^0Z), AgZ that has been treated with hydrogen at an elevated temperature to convert most if not all of the ionic silver in the AgZ to metallic silver. Ag^0Z retains many of the attractive characteristics of its parent, such as its chemical stability in acidic systems, and offers potential improvements in loading capacity and stability of the trapped iodine. We chose to test Ag^0Z (-10+16 mesh) at normal conditions because a 12-cm bed of AgZ did not routinely reduce the iodine concentration in the gas to $<10^{-5} \mu\text{mol I/L}$.

Trapping of gaseous iodine by Ag^0Z was first studied by Thomas and coworkers (1977) at the Idaho National Engineering Laboratory (INEL). In succeeding studies at PNL, we showed that Ag^0Z was somewhat more effective in trapping elemental iodine and methyl iodide than AgZ (Scheele, Burger and Matsuzaki 1983). In PNL's studies the Ag^0Z was superior to AgZ in terms of iodine loading level at a breakthrough defined as reduction of the gaseous iodine concentration from 13 to $0.13 \mu\text{mol I/L}$.

It was our original belief that because of the relatively small quantities of iodine in the fuel to be processed at the PFM, the increased loading level that could be achieved using Ag^0Z was not worth the additional effort and hazard involved with hydrogen reduction. At that time, no studies had been performed to determine whether any iodine trapping material could achieve the PFM target release level for iodine, $<10^{-5} \mu\text{mol I/L}$.

As Figure 26 and Table 6 show, breakthrough occurred at a loading of 0.29 mmol I/g Ag^0Z . Loading was continued to a time-based loading of 0.38 mmol I/g Ag^0Z . The effluent concentration during loading after breakthrough slowly rose to $5 \times 10^{-3} \mu\text{mol I/L}$ at the end of the second day. Sample S-2, the standby sample immediately following this rise, and Sample S-3, which followed the short feed period on the third day, showed high concentrations. The remaining standby samples, including S-1, showed concentrations of $\leq 10^{-5} \mu\text{mol I/L}$. Several of the effluent samples were < 0 , as shown in Table 6. These samples were arbitrarily assigned effluent concentrations of $10^{-5} \mu\text{mol I/L}$ for plotting purposes in Figure 26. Unfortunately this experiment was performed when the ^{125}I had aged several half-lives, causing an increase in the detection limit. Because of this problem, the apparent results need to be confirmed.

FIGURE 26. Effluent Concentration Versus Iodine Loading on Ag^0Z for Run 22 (Test of Ag^0Z)

TABLE 6. Iodine Trapping by Ag⁰Z in Run 22

Day No.	Elapsed Time hrs	Sample No.	Effluent Concentration, $\mu\text{mol I/L}$	
			Loading	Standby
1	3	E-1	3.4-05	-
	6	E-2	1.3-05	-
	22	S-1	-	<0
2	23	E-3	1.0-05	-
		E-4	4.4-05	-
		E-5	3.1-04	-
		E-6	1.3-03	-
		E-7	1.9-03	-
	29	E-8	4.7-03	-
	46	S-2	-	2.4-04
3	47	E-9	3.0-05	
	50	S-3	-	1.1-04
	53	S-4	-	<0
4	70	S-5	-	3.1-05
	77	S-6	-	<0
5	119	S-7	-	1.4-05
	125	S-8	-	<0
8	190	S-9	-	2.0-06
9	216	S-10	-	<0

The loading at breakthrough for Ag⁰Z was 30% less than that achieved for run 9, which tested AgZ at comparable conditions. This result was surprising because of our past work (Scheele, Burger, and Matsuzaki 1983), which showed that higher loadings could be obtained using Ag⁰Z. It is unknown whether application of the same criteria for breakthrough used in the current study would affect the previously obtained results.

From this experiment, it also appears that the iodine trapped on Ag⁰Z at 0.4 mmol I/g Ag⁰Z is less mobile than iodine trapped on AgZ at a comparable

loading. After a few days of standby operation, the chronic release from this 12-cm bed of Ag^0Z was near the target concentration. In contrast, the chronic release from the 16-cm bed of AgZ loaded to 0.4 mmol I/g AgZ (experiment 20, Figures 23 and 24) decreased to and stabilized at 10^{-4} μmol I/L after 20 days. The results of this single test suggest with Ag^0Z that it may be possible to achieve a higher loading and still have a stable trapped iodine. Further experimentation is required before the utility of Ag^0Z can be fully assessed for application at the PFM.

CONCLUSIONS

With some qualifications, silver mordenite (AgZ) is an effective trap for iodine, capable of reducing the effluent iodine concentration in the PFM dissolver off gas to a nominal 10^{-4} $\mu\text{mol I/L}$. Although this concentration is about a factor of 10 greater than the target level for the PFM, there are reasons to believe that the larger zeolite bed to be used in the PFM and the longer time for reaction may improve the efficiency even more.

If a nearly loaded AgZ bed is exposed to a gas stream without iodine present, a breakthrough can occur during these standby conditions. Indications are that the bed will stabilize after an extended period at a loading of 0.4 $\mu\text{mol/g AgZ}$. At PFM a backup adsorber bed will be provided to prevent unacceptable releases after breakthrough of the first bed. The data indicate that the backup bed will be effective for this purpose.

The statistical analysis of the parametric study to determine the effect of normal and off-normal operating conditions showed that there is no NO or NO_2 effect and only a small negative, though statistically significant, temperature effect when temperature is increased from 150 to 230°C. These experiments showed that on a practical basis the loading is not significantly (>10%) affected by changes in operating conditions.

The special tests produced several significant findings. The first is that a longer bed will improve the short-term load capacity of the AgZ and, before breakthrough, will reduce the effluent concentration to the target level during loading at normal and standby conditions. Secondly, the iodine input level in the range 0.35 to 10.5 $\mu\text{mol CH}_3\text{I/L}$ will not affect the effluent concentration or the bed loading at normal conditions. Thirdly, a second bed in series will initially reduce the effluent concentration from an off-gas system to the desired level (i.e., equivalent to a longer bed); however, over time the effluent will increase to the nominal 10^{-4} $\mu\text{mol I/L}$. Finally, on the basis of the breakthrough criteria of this study, the achievable iodine loading on $\text{Ag}^{\text{O}}\text{Z}$ is 0.3 mmol I/g $\text{Ag}^{\text{O}}\text{Z}$, which is 30% less than the loading for AgZ loaded at comparable conditions. The iodine loaded on $\text{Ag}^{\text{O}}\text{Z}$, however, appears to be less mobile than that loaded onto AgZ.

This experimental program showed that even though AgZ was effective as an iodine trap at all potential conditions in the PFM, the performance of a 12-cm bed did not meet all of the target criteria. Before it is possible to ensure that the target control levels of the PFM will be met, additional studies may be required. These studies might include a long-term test using the expected PFM iodine concentration and PFM bed length, comparison of alternative materials and studies to understand and control the chemistry and reaction rates of the trapping process.

RECOMMENDED FUTURE WORK

In light of the results showing higher-than-targeted iodine effluent concentrations and poor retention of iodine at standby conditions, we recommend an experimental program to include a screening study of other state-of-the-art silver sorbents and a fundamental study to determine the mechanism of iodine trapping and a method to reduce the mobility of trapped iodine during standby operations. Further special tests, such as an extended loading experiment using the process iodine concentration and a long bed (>12 cm) to confirm the results of the long-bed tests, are also suggested.

A fundamental study could use thermoanalytical techniques such as differential scanning calorimetry (DSC) and thermogravimetry (TG) to measure enthalpy and rate of the sorption reaction. The DSC and TG techniques could also be used to determine the stability of sorbed iodine on silver sorbents. Other studies could use surface analysis or spectroscopic techniques to analyze iodine-loaded materials.

The screening study to determine which of the current state-of-the-art silver-containing sorbents would be most effective under the conditions of PFM operation could be approached in many different ways. Experiments such as those already completed could be performed to allow comparison with AgZ. If one of the materials offers promise, a more extensive set of experiments could be performed similar to the parametric study described in this report. Alternatively, or in addition, shallow beds of silver sorbent could be used to determine the kinetics of the sorption reaction. No kinetic data are currently available; the shallow-bed tests could also be considered the fundamental studies. These kinetic studies should all be done using all of the individually suspected iodine forms in a dissolver off gas.

As can be seen from the above list of suggested studies (this list is by no means comprehensive), there is much to be learned about the trapping of iodine from a dissolver off-gas stream. Previous studies have concentrated on the empirical demonstration of the process and have not looked at the basic mechanism of trapping. Nor have earlier studies attempted to determine the limits of use for each state-of-the-art silver sorbent.

REFERENCES

- Burger, L. L., and R. D. Scheele. 1982a. Recycle of Iodine-Loaded Silver Mordenite by Hydrogen Reduction. PNL-4490, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., and R. D. Scheele. 1982b. "Iodine Fixation Studies at the Pacific Northwest Laboratory," in Management Modes for Iodine 129, W. Hebel and G. Cottone, eds. Harwood Academic Publishers, New York.
- Scheele, R. D., L. L. Burger, and C. L. Matsuzaki. 1983. Methyl Iodide Sorption by Reduced Silver Mordenite. PNL-4489, Pacific Northwest Laboratory, Richland, Washington.
- Thomas, T. R., L. P. Murphy, B. A. Staples, and J. T. Nichols. 1977. Airborne Elemental Iodine Loading Capacities of Metal Zeolites and A Method for Recycling Silver Zeolite. ICP-1119, Idaho National Engineering Laboratory, Idaho Falls, Idaho.
- Venuto, P. B., and P. S. Landis. 1968. "Organic Catalysis Over Crystalline Aluminosilicates." In Advances in Catalysis and Related Subjects Vol. 18. Ed. D. D. Eley, H. Pines, and P. B. Weisz. Academic Press, New York.
- Yost, D. M., and H. R. Russell, Jr. 1944. Systematic Inorganic Chemistry of the 5th and 6th Group Non-Metallic Element. Prentice-Hall Inc., New York.

APPENDIX A

PREVIOUS AgZ - METHYL IODIDE TESTS

APPENDIX A

PREVIOUS AgZ - METHYL IODIDE TESTS

In the preliminary iodine-trapping experiments carried out for the PFM Project^(a), several tests were performed to demonstrate the effectiveness of AgZ as a trap for CH₃I. At the time, the PFM plan was to use a caustic scrub to remove the bulk of the I₂, which was estimated to be more than 90% of the total iodine, and to use AgZ to capture the remaining I₂ and the organic iodides.

The first tests performed in conjunction with the caustic scrubbing experiments showed that a 5-cm-diameter by 15-cm-long bed at 150°C could reduce the gas phase concentration of CH₃I from 2.5, 14, and 25 μmol I/L by a retention factor (RF) of >10³. The last test was to demonstrate that an AgZ bed could reduce the effluent concentration to <10⁻³ μmol I/L.

The objective of this single experiment was to determine the efficiency for CH₃I capture and the loading capacity at the target effluent concentration of 10⁻³ μmol I/L. The experimental parameters are shown in Table A.1. The bed had sampling ports at 3, 8, 13, and 18 cm from the top (inlet) of the AgZ bed. The CH₃I was traced with ¹²⁵I. We measured the iodine concentration in the effluent by passing a 100 mL/min sample stream through a 1.3-cm-diameter by 11-cm-long bed of 20 to 40 mesh AgZ held at 200°C to collect the radioiodine. The radioiodine was then measured with a NaI(Tl) scintillation gamma detector.

At the end of each day of loading, the side ports were sealed, the temperature was lowered to ambient, ~23°C, and the air flow adjusted to 0.5 L/min (0.25 m/min face velocity). Charcoal traps were placed at the bed exit during this standby operation to detect possible leakage of the iodine. A small amount, ~10⁻⁶ fraction, was found. The bed temperature was raised to 150°C 1.5 hours before the next loading began.

(a) Letter report to Rockwell by L. L. Burger, R. D. Scheele, and C. L. Matsuzaki. 1983. PFM Iodine Removal Studies, Pacific Northwest Laboratory, Richland, Washington.

TABLE A.1. Operational Parameters for CH₃I-AgZ Experiment

Parameters	Level
I ₂ concentration, $\mu\text{mol I/L}$	0
CH ₃ I concentration, $\mu\text{mol I/L}$	10
NO _x concentration, vol %	0.5
NO concentration, vol%	0.38
NO ₂ concentration, vol%	0.12
Carrier gas	Laboratory air ^(a)
Gas Flow, L/min	10
Gas Face velocity, m/min	5
AgZ column diameter, cm	5.0
AgZ column height, cm	18.0
Packing	14-20 mesh AgZ, 18 wt% Ag
AgZ bed temperature, °C	150
Bed Mass	~300 g

(a) Water concentration about 5×10^{-4} mol/L.

The results of the test are shown in Figure A.1 which shows the effluent concentration as a function of bed loading. If the momentary spikes evident from the 8-, 13- and 18-cm sample ports are ignored, the loading at a breakthrough concentration of 1×10^{-3} $\mu\text{mol I/L}$ can be compared. These are shown in Table A.2.

TABLE A.2. Bed Loading at Breakthrough

Bed Depth, cm	Bed Loading at 1.0×10^{-3} $\mu\text{mol I/L}$ Breakthrough (mmol I/g AgZ)
3	0.06
8	0.31
13	0.61
18	0.97

Recognizing that the higher concentration spikes seen in Figure A.1 may be significant, a more conservative loading may be identified. For the 13- and 18-cm beds this would be about 0.5 and 0.75 mmol I/g AgZ respectively.

FIGURE A.1. Effluent Concentration Versus Iodine Loading for 18-cm Bed of AgZ (Previous Work)

APPENDIX B

AgZ DENSITY AND PRESSURE DROP MEASUREMENTS

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AgZ DENSITY AND PRESSURE DROP MEASUREMENTS

ZEOLITE DENSITY

Three batches of AgZ ranging in silver content from 18.76 to 19.08 wt% were combined. The -10+16 mesh material showed density variation from 0.985 to 1.02 g/mL. The variation was probably due to slight differences in size distribution and hence packing. The free volume was about 40%. The composite density after air equilibration was 0.993. The water content, as indicated by drying at 450°C, was about 10%.

PRESSURE DROP STUDIES

The pressure drop through AgZ beds of different mesh sizes was measured with nitrogen gas at flow rates from 1.7 to 17 m/min face velocity, and at 22, 100, and 200°C. The data are given in Tables B.1 and B.2. The pressure drop will depend on the particle size distribution within a mesh range and upon the degree of settling reached in preparing the bed samples. The measured densities of the samples represented in Table B.1, for example, varied by $\pm 5\%$. It would not be surprising to have pressure drops vary from 10% to 20% for different batches of as-received zeolite of a given mesh range.

The pressure drop increases rapidly as the mesh decreases. For a flow of 600 mL/min (4.9 m/min face velocity), the pressure drop for the 1.25-cm-diameter bed at 22°C is about 90, 165, 470, 790, and 2210 mm H₂O per meter of bed length for -10+16, -14+20, -20+30, -30+40, and -40+70 mesh, respectively. The pressure drop increase from room temperature to 100°C is 40 to 50% and from 100 to 200°C is 30%. For the experimental arrangement used in the iodine sorption tests, the observed pressure drop in the bed and connecting tubing was about 16 to 20 mm H₂O.

TABLE B.1. Pressure Drop in AgZ Beds^(a)

Flow, mL/min	Pressure Drop (ΔP), mm H ₂ O			
	14-20 Mesh	20-30 Mesh	30-40 Mesh	40-70 Mesh
200	52	141	237	756
400	89	274	474	1410
500	126	--	--	--
600	163	467	785	2210
700	--	--	--	2610
800	237	637	1030	--
1000	333	844	1330	--
1200	444	1090	1710	--
1400	533	1330	2020	--
1600	600	1470	2230	--
1800	652	1560	2380	--
2000	770	1900	2760	--

Coefficients for
Equation $\Delta P = A (\text{Flow})^B$

A	0.0597	0.304	0.770	3.95
B	1.245	1.148	1.080	0.988
R ²	0.991	0.997	0.999	0.997

(a) Dia. 1.25 cm, temp. 23°C.

TABLE B.2. Temperature Dependence of Pressure Drop^(a)

Flow, (b) mL/min	Face Velocity, m/min	Pressure Drop (ΔP), mm H ₂ O/m		
		at 22°C	at 100°C	at 200°C
300	2.44	--	58	95
325	2.64	44	--	--
600	4.88	90	--	--
800	6.50	128	191	251
1000	8.15	169	245	345
1500	12.2	--	410	567
2000	16.3	442	617	803

(a) Dia. 1.25 cm, mesh -10+16, length 12.7 cm, gas N₂.

(b) Measured at 23°C.

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