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The poisoning of silver zeolite by organics

J. G. JOLLEY, H. G. TOMPKINS
EG & G Idaho, Inc., PO Box 1625, Idaho Falls, Idaho 83415, USA

Silver zeolite was exposed to various organics to measure their effect on the silver zeolite's ability to subsequently adsorb iodine. The organics examined were alkanes, alkynes, aromatics, ketones, alcohols, and halocarbons (methyl and ethyl based). The reduction in iodine removal efficiency ranged from zero to 96%. Adding additional radicals to the base organic generally had the effect of decreasing the silver zeolite's iodine removal efficiency.

1. Introduction

One of the fission products in nuclear reactors is radioactive iodine. This species normally remains trapped in the fuel element. In the event of a meltdown accident or during the reprocessing of spent fuel, the radioiodine may be released to the atmosphere and present serious biohazards. Air filtration systems using silver-exchanged zeolite (AgX) to remove gaseous iodine species were developed to replace older systems which used activated charcoal. (Silver zeolite is made by replacing the normal cation in the zeolite with silver.) The advantages silver zeolite has with respect to activated charcoal are non-flammability, high removal efficiency per unit volume, long service life, and permanence for disposal [1, 2]. Its negative attributes are silver cost and "poisoning" by some organics. Poisoning, in this context, is the adsorption of extraneous matter which impedes the adsorption of iodine species.

Some nuclear facilities have experienced premature decrease in iodine removal efficiency. Cursory examination of silver zeolite in those cases revealed the presence of organics, such as aromatics [3].

In this study, silver zeolite was exposed to various organics (alkanes, alkynes, aromatics, ketones, alcohols, and halocarbons) to measure their effect on the silver zeolite's ability to subsequently adsorb iodine.

2. Experimental details

2.1. Materials

The materials used, with supplier and purity, are listed in Table I. The organics were various alkanes, alkynes, aromatics, ketones, alcohols, and methane- and ethane-based halocarbons. The carrier gases were nitrogen and air, and the purge gas was helium.

2.2. Techniques

The apparatus used to load the AgX test column is shown schematically in Fig. 1. Pyrex glass test columns, 12 cm long by 0.4 cm inside diameter, were filled and packed with one gram of AgX and plugged at both ends with Pyrex glass wool. Each test column was preconditioned with a helium purge at 200° C for 24 h to remove any impurities in the AgX. Fifteen millilitres of the organic were pipetted into the evaporation flask. An activated carbon filter was attached to the gas inlet of the evaporation flask to filter the purge gas.

The carrier gases, nitrogen and ambient air (air from the laboratory at ~ 40% humidity), had a flow rate of ~ 400 $\mathrm{cm}^3\,\mathrm{sec}^{-1}$ (face velocity of 50 $\mathrm{cm\,sec}^{-1}$). A water aspirator was used to provide vacuum assistance on the exit end of the AgX column. Carrier gas was bubbled into the organic liquid in the evaporator flask to carry the resulting vapour into the AgX test column. The gas flow was continued for 30 min after all of the liquid had vaporized (as observed visually). Loading was done at ambient temperature.

The amount of organic adsorbed by the AgX was determined by weighing the column before and after the loading process.

The iodine removal efficiency of the AgX was measured using the apparatus shown in Figs. 2

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TABLE I Candidate poisons and materials

Reagent	Supplier	Quality
Candidate poisons		
benzene	J. T. Baker Co.	99.8%
bromomethane	Linde	99.5%
bromotrichloromethane	Pfaltz & Bauer, Inc.	Research
bromotrifluoromethane (Halon 1301$^{\text{TM}}$)	Linde	99.0%
2-butanone (methyl ethyl ketone)	J. T. Baker Co.	Photrex reagent
chloromethane	Linde	99.5%
cyclohexane	Fisher Scientific Co.	Spectranalysed
dibromomethane	Pfaltz & Bauer, Inc.	Research
1,3-dichloroethane	J. T. Baker Co.	Photrex
dichloromethane	J. T. Baker Co.	Reagent
1,3-dimethylbenzene (*m*-xylene)	Eastman Kodak Co.	95.0%
ethanol	U.S. Industrial Chemicals Co.	Reagent
ethyne (acetylene)	Liquid Air, Inc.	Industrial Grade
n-hexane	J. T. Baker Co.	Spectrophotometric
methanol	Fisher Scientific Co.	Certified ACS
methylbenzene (toluene)	J. T. Baker Co.	99.8%
4-methyl-2-pentanone (methyl isobutyl ketone)	J. T. Baker Co.	Photrex reagent
2-propanol	American Drug and Chemical Co.	Reagent
2-propanone (acetone)	American Drug and Chemical Co.	99.5%
tetrachloromethane (carbon tetrachloride)	J. T. Baker Co.	Instra-analysed
1,1,2,2-tetrachlorethane	J. T. Baker Co.	Reagent
trichloromethane (chloroform)	J. T. Baker Co.	Instra-analysed
1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113$^{\text{TM}}$)	J. T. Baker Co.	100.0%
Carrier and purge gases		
helium	Liquid Air, Inc.	High Purity
nitrogen	Liquid Air, Inc.	High Purity
Zeolite and iodine		
iodomethane	Pfaltz & Bauer, Inc.	Research
iodomethane [^{131}I]	New England Nuclear	Reagent
Silver Zeolite Ionex Ag-400, 10 × 6 (US) mesh granules	Ionex Research Corp.	98% Ag Exchange
Miscellaneous materials		
activated carbon	Linde	Industrial Grade
potassium bromide	BDH Chemicals, Ltd.	IR Grade

and 3. The first two columns of AgX were used for the efficiency test, and the third one was for normal radiation safety. A rough vacuum pump was attached to the exit to assist in the flow. One mCi of CH$_3^{131}$I was diluted with non-radioactive iodomethane to produce a 1 ml solution of ~ 10 mrem of activity on contact. 10 μl of the CH$_3^{131}$I dilution were injected into the septum with a Hamilton 104N syringe. The CH$_3^{131}$I vapour was carried through the test apparatus for 1.5 h by either nitrogen or air.

The amount of iodomethane which was removed from the gas stream by the loaded AgX was measured using radioactivity measuring techniques. Contents of the loaded AgX test column and back-up AgX test column were transferred to

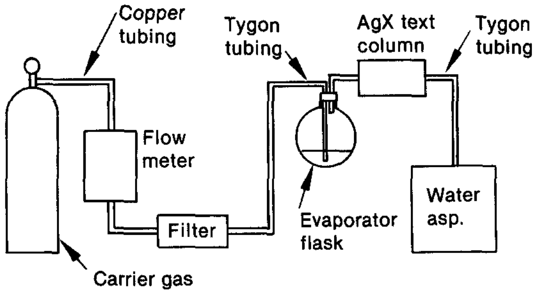

Figure 1 Loading apparatus.

7 ml scintillation vials. Due to the radioactivity, double containment was required to ensure safe handling (see Fig. 3). Each 7 ml scintillation vial was then inserted into the holder in the 100 ml scintillation vial and placed in the well of a NaI(TI) detector for counting. (Each sample vial assembly had been counted for background.)

The amount of ^{131}I in each of the sample vial assemblies was monitored by counting the 0.364 MeV gamma being emitted. The equipment used is listed in Table II. To provide adequate counting statistics, number of counts ranged from 1 to 3 x 10^6 counts per 5 min.

The efficiency of each AgX sample was determined using the following expression:

$$\frac{A}{A+B} \times 100\% = \%\ \text{Efficiency}$$

where A is the number of counts per 5 min for the poisoned AgX test column and B is the number of counts per 5 min for the back-up AgX test column.

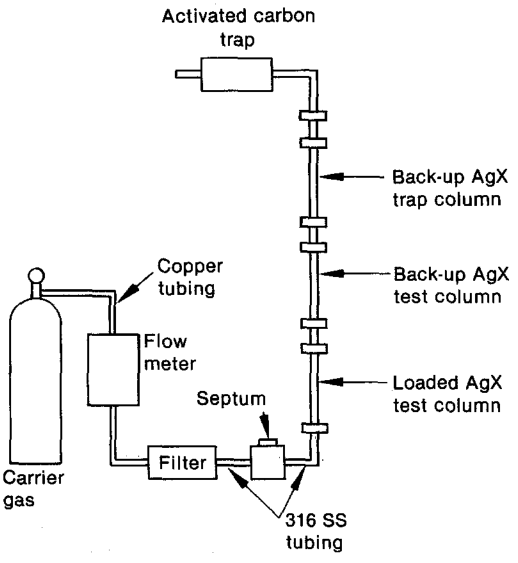

Figure 2 Efficiency apparatus.

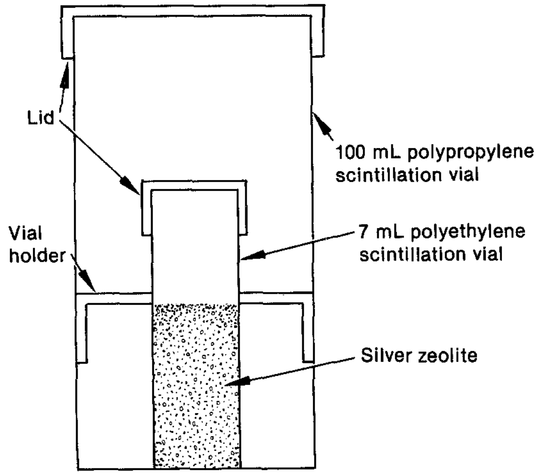

Figure 3 Double containment sample holder.

Efficiency thus reflects the amount of iodine trapped in the poisoned AgX compared to the total amount of iodine injected into the system. The radioactivity of the third column was measured to verify that all of the radioiodine was collected by the first two columns. This was the case, since no radioactivity was detected in the third column for any of the efficiency experiments.

Ancillary measurements were made using Fourier transform infra-red spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and energy dispersive X-ray spectroscopy on a scanning electron microscope. Infra-red (IR) spectra were taken by a Digilab FTS-15C Fourier transform infra-red spectrometer (FT-IR). The sample of loaded AgX was finely ground in a mortar and pestle and diluted to 0.1 g/1 g with IR grade KBr. A sample of diluted AgX (loaded) was placed in a DRA-3CD diffuse reflectance cell manufactured by Harrick Scientific Corp.

Halogen content was monitored with energy dispersive spectroscopy (EDS) with a Unispec System 7000, manufactured by Kevex International Corp.; X-ray photoelectron spectroscopy (XPS or ESCA), manufactured by Physical Electronics Industries;

TABLE II Gamma counting equipment

Equipment	Manufacturer and model
Well-type [NaI(TI)] detector	Ortec
Timer and counter	Ortec 871
Amplifier and single-channel analyser	Ortec 490B
Minibin and power supply	Ortec 401M/402M
PMT base with preamplifier	Ortec 276
HV power supply	Ortec 456

and X-ray diffraction (XRD), manufactured by Philips Electronic Instruments, Inc.

3. Results and conclusions

The glass tube packed with AgX weighed approximately 12 g and the weight gain measurements after loading showed that the AgX adsorbed roughly 0.10 to 0.13 g of organic per gram of AgX for all of the candidate poisons. It should be noted that enough vapour passed over the AgX to completely saturate the AgX so that the uptake was not governed by adsorption kinetics or amount of organic vapour. Infra-red spectra confirmed the adsorption of organics on the AgX for the non-halogenated hydrocarbons. Spectra with the non-halogenated organics were essentially the same as for the bulk organics [4, 5]. The spectra for the AgX loaded with the halocarbons, however, did not show the presence of the organic species.

EDS and XPS analyses indicated that the AgX adsorbed chlorine from tetrachloromethane, chlorine from trichloromethane, bromine and chlorine from bromotrichloromethane, bromine from dibromomethane, and iodine from iodomethane. Negligible adsorption by the AgX was indicated from dichloromethane and bromotrifluoromethane. Formation of silver halides (AgI, AgCl, and AgBr) by AgX poisoning (CH_3I, CCl_4, and CH_2Br_2) was confirmed by XRD [6].

These results indicate that, for non-halogenated species, AgX simply adsorbed the molecule as is, with the exception of the alcohols (OH stretch band of 3200 to 2330 cm^{-1} is eliminated), and for halogenated species a chemical reaction occurs in which halogens are removed from the organic molecule by chemical bonding to the silver.

TABLE III AgX efficiency

	N_2 (%)	Air (%)
Unpoisoned AgX	> 99	> 99
AgX "poisoned" with:		
Aromatics		
benzene	93	99
1,3-dimethylbenzene	38	99
methylbenzene	56	> 99
Alcohols		
ethanol	99	> 99
methanol	> 99	> 99
2-propanol	69	> 99
Ketones		
2-butanone	96	97
4-methyl-2-pentanone	46	96
2-propanone	> 99	> 99
Chlorocarbons		
chloromethane	86	93
1,2-dichloroethane	93	93
dichloromethane	> 99	> 99
1,1,2,2-tetrachloroethane	21	78
tetrachloromethane	26	28
trichloromethane	60	62
Bromomethanes		
bromomethane	35	34
dibromomethane	64	64
Miscellaneous		
bromotrichloromethane	41	4
bromotrifluoromethane	> 99	> 99
cyclohexane	> 99	> 99
ethyne	51	39
n-hexane	99	> 99
1,1,2-trichloro-1,2,2-trifluroethane	48	> 99

The results of the iodine adsorption efficiency tests are shown in Table III and Figs. 4 and 5. As the table indicates, there is some dependence on the carrier gas, but the trends are similar. For the

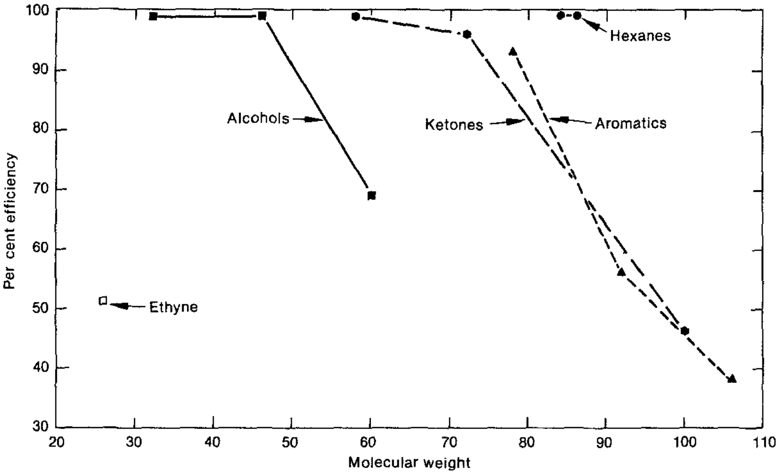

Figure 4 Iodine adsorption efficiency against molecular weight for non-halogenated organics. The efficiency is the fraction of the total amount of radioiodine which was removed by the first column.

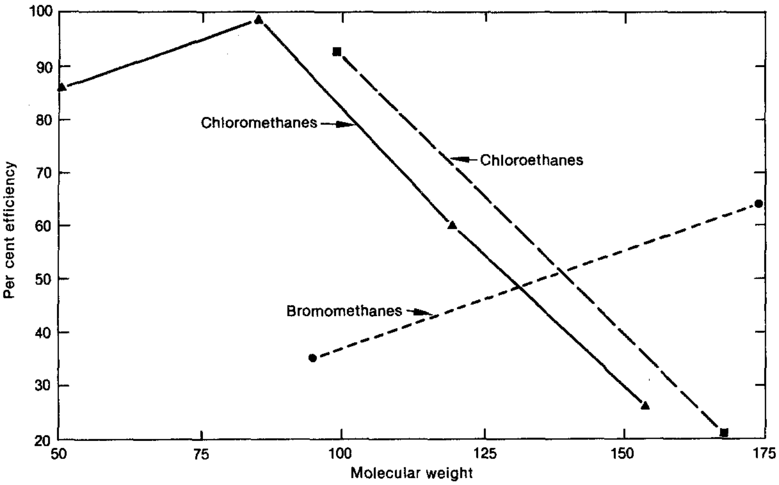

Figure 5 Iodine adsorption efficiency against molecular weight for halocarbons. The efficiency is the fraction of the total amount of radioiodine which was removed by the first column.

non-halogenated species, the simpler organic molecules of each type did not reduce the efficiency significantly. The addition of CH_3 groups to the basic molecule had the effect of reducing the efficiency. This is shown particularly well in Fig. 4, a plot of the molecular weight against the efficiency for the alcohols, ketones, aromatics, alkanes, and alkynes. The general trend appears to be that the efficiency is degraded by moving from the alkanes to the ketones and aromatics to the alcohols to the alkynes. With the exception of the bromomethanes, for a given type of halogen the efficiency of the AgX is reduced more by molecules containing larger numbers of the halogen atoms.

5. Discussion

It is clear that although size plays a significant part in the effectiveness of the organic in reducing the efficiency, size is not the primary factor. Fig. 4 shows that the variation in the effectiveness due to the primary functional group, e.g., ketone as opposed to alcohol, overrides size. The key point here is that the organic molecules are not just blocking the pores in the zeolite, keeping the methyl iodide from interacting with the silver. In the case of the halogens, this is particularly true: the organic is fragmented and the organic fragments appear to desorb, leaving only the silver halide. Infra-red spectra indicate that the organic part of the halocarbon is not retained by the AgX whereas X-ray diffraction, X-ray photoelectron spectroscopy, and weight gain measurements indicate that the halogen part of the halocarbon reacted chemically with the AgX and is retained. It appears that the bonding of the organic to the silver plays a significant part in whether the organic acts as a poison or not. Future work should address this phenomenon. Work is in progress to obtain desorption kinetic data as a function of temperature.

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