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Capture of elemental and organic iodine from dilute gas streams by silver-exchanged mordenite

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Abstract

The treatment of off-gas streams arising from reprocessing of used nuclear fuel (UNF) is an area of active study by the U.S. Department of Energy. Such off-gas streams contain volatile fission products, including long-lived ^{129}I. Although ^{129}I is released into the off-gas at multiple points within the chemical reprocessing flowsheet, previous research has focused on removal from the dissolver off-gas stream (DOG). The DOG is expected to contain up to 98% of iodine in UNF at ppm levels within the stream. Other off-gas streams will also contain iodine but at substantially lower concentrations. Recent work has shown that compliance with U.S. regulations will likely require capture of iodine from these dilute streams in addition to capture from DOG.

In particular, the vessel off-gas (VOG) stream is expected to contain 1-3% of the total iodine inventory at ppb concentrations. A review of literature also indicates that the speciation of iodine in the VOG stream will differ from that of the DOG, with the DOG containing primarily I_2 and the VOG containing a mixture of I_2 and organic iodine species.

Silver-exchanged mordenite (AgZ) has been identified for use in the removal of iodine from off-gas streams. It is an effective capture material for I_2 at the concentrations expected in the DOG, but little is known about its performance in gas streams that may contain both I_2 and organic iodides at very dilute concentrations.

The experiments to be described were designed to separately characterize the adsorption of I_2 and methyl iodide on AgZ through extended duration testing. Simulated vessel off-gases containing low levels of either I_2 or methyl iodide were contacted with AgZ sorbent beds for up to four months. Through the use of sorbent beds in series and varied sampling times, key parameters such as adsorption rate, decontamination factor, and performance over time could be determined for the capture of each species by AgZ.

This paper will discuss the literature relating to the speciation of iodine in the VOG and will discuss the results of adsorption experiments. An examination of the difference between capture of I_2 and organic iodides will be conducted, and the impacts of those results on future iodine removal work will be considered.

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1. Background

The release of volatile radionuclides from a used nuclear fuel (UNF) reprocessing plant is governed by three regulations in the United States: these are 40 CFR 61, 40 CFR 190, and 10 CFR 20. These regulations limit emissions of ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I based on the potential combined total dose received by the public from the four radionuclide emissions to the environment. They also establish total release limits for ^{85}Kr and ^{129}I. Analysis of the impact of these regulatory requirements on a potential reprocessing plant shows that compliance will require iodine removal from the combined plant off-gas prior to its discharge to the environment. It is expected that the necessary plant decontamination factor (DF) for iodine is likely to be > 1,000.[1]

To provide a high overall plant DF, the treatment of multiple off-gas streams within the plant is required. The dissolver off-gas (DOG) stream contains approximately 95 to 98% of the iodine found within the UNF.[2] Complete removal of iodine from this stream, without treatment of other streams such as the cell off-gas (COG), vessel off-gas (VOG), or waste off-gas (WOG), would thus result in a plant DF of < 100. As interest in iodine capture has expanded to consider these additional streams, several key factors and their effects on the iodine capture process and iodine capture media must be considered.

First, the chemical characteristics of the gas streams will vary. The DOG will contain a significant amount of reactive NO and NO_2 species, with other streams containing much lower NO_x concentrations. VOG streams may contain volatile organics from the solvent extraction processes. Second, the total quantity of iodine present in the stream will vary: It is expected that the DOG will contain iodine at ppm levels, with the VOG closer to ppb levels. Third, total gas flow rates will differ. The DOG flow rate will be the lowest, with the VOG up to 100x higher, and the COG 1000x the flow rate of the DOG.

One of the most important factors requiring investigation is the presence of *penetrating species* of iodine in the off-gas streams. Penetrating species are those species other than elemental iodine (I_2) that are expected to be captured poorly by many traditional iodine sorbents. These are likely to include organic iodine species such as methyl iodide (CH_3I), or other alkyl iodides, as well as some inorganic forms such as hypoiodous acid (HOI). A full treatment of the potential species found in each off-gas stream can be found in Bruffey et al., 2015.[3]

One iodine sorbent under consideration for use in a reprocessing plant is reduced silver-exchanged mordenite (Ag^0Z). It has been demonstrated that Ag^0Z is more easily penetrated by CH_3I under prototypic DOG conditions, but there is no information available regarding the adsorption of organic iodine species onto Ag^0Z under prototypic VOG conditions.[4] As it is thought that the VOG will contain the highest percentage of organic iodine species, the characterization of organic iodine adsorption onto Ag^0Z under VOG conditions merits further study.

CH_3I adsorption onto zeolite minerals such as Ag^0Z has been investigated to determine important factors such as the mechanism of adsorption[5,6], CH_3I capacity of the sorbent, and the effect of other gas species on the adsorption process.[4,7] This is not a comprehensive list, but reviews of the literature do indicate that there are no documented studies of the adsorption of CH_3I onto zeolites at concentrations that might be expected in a VOG stream.

The experiment and findings of the authors regarding the adsorption of I_2 onto Ag^0Z under VOG conditions are summarized here and will be used for comparison to the results described within this paper.[8] The test exposed three beds of Ag^0Z to a prototypical VOG stream composed of 7 ppb I_2 within a moist feed stream of 0°C dew point. An unexpected spike in iodine feed concentration (to approximately 1 ppm I_2) within the first days of the experiment was observed and must be considered when interpreting the results. First, there was no breakthrough above the experimental detection limit of 0.1 mg I/g Ag^0Z. Second, iodine was observed to penetrate approximately 10 cm into the bed. Finally, it was observed that the sorbent performance degraded as a function of time online. This aging effect has been demonstrated previously by Jubin, 2011.[9]

The experiment described in this paper builds on the work of Jubin et al.[8] by testing in which Ag^0Z is exposed to a simulated VOG stream containing very low levels of CH_3I for four months. The experiment was designed to maximize the amount of information that could be obtained from these experiments and provides information on mass transfer zone, DF across the sorbent bed, rate of iodine uptake, and the degradation of Ag^0Z upon extended exposure to a VOG stream.