Preliminary Evaluation of Exchange of Hydrogen Isotopes in the Structure of a Mordenite-Based Sorbent

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SUMMARY

Silver-exchanged sodium mordenite (AgZ) is being evaluated as a sorbent to remove iodine from process effluent streams of used nuclear fuel (UNF) treatment plants. Previous studies have shown that AgZ adsorbs significant quantities of water, in addition to the iodine, from a humidified gas phase. The water within the plant is contaminated with tritiated water, particularly the water arising from the head-end treatment processes. Although methods to reduce or prevent the accumulation of water with the iodine have been devised and demonstrated, a concern arises that contact with tritiated water will permit an exchange of some of the stable hydrogen in the mordenite structure for tritium. The tritium thusly incorporated into the structure will likely remain in the mordenite even after thermal treatment to remove the physisorbed surface water. Subsequent processes that might destroy the structure (e.g., vitrification where the crystal may dissolve in molten glass) have the potential to release the tritium (or tritiated water), thereby representing another potential pathway for release of tritium to the environment. The purpose of the present study is to evaluate the exchange of hydrogen isotopes in the mordenite structure with hydrogen isotopes associated with fluids in contact with the mordenite.

Calculations were performed to estimate the effect of isotopic exchange on the overall plant decontamination factor (DF) for tritium, with the extent of isotopic exchange varying from 0 to 100% (the latter meaning that atomic fraction of tritium to all hydrogen would be the same in the structure as in the water in the off-gas stream). In the calculation it is assumed that all the tritium in the mordenite structure is released without controls from a waste form preparation process. The DF can be strongly affected by the extent of exchange; it can also be partially restored by adding natural water (e.g., steam) to the gas stream to dilute the tritiated water.

Samples of sodium mordenite (NaZ) and silver mordenite that had been reduced with hydrogen (Ag^0Z) were dried in ambient air at 270°C before contact with humid air. The sorbents were exposed to humid air bearing either natural water (i.e., water having a natural abundance of deuterium) or deuterium oxide (D_2O) at 100% relative humidity at room temperature (~22°C). Hydration under these conditions resulted in sample weight-gain ranging up to 18.9% for NaZ and 15.7% for Ag^0Z. Some samples remained at room temperature while others were placed in stainless steel capsules, which were then sealed and heated to an elevated temperature (150°C) for varying lengths of time. Under these conditions the concentration of deuterium would be over three orders of magnitude greater than the tritium found in off-gas streams. The large concentration gradient should permit exchange of the deuterium with the hydrogen integral to the structure of the mordenite, if it occurred, to a greater extent and more rapidly than exchange of tritium in the fuel recycle plant. (It should be noted that the studies reported here were performed without radiological materials and in a non-radiological environment. Consequently, no allowance is given for any enhancement of molecular transfer or exchange that might be caused by ionizing radiation normally encountered in a fuel recycle plant.) All samples were dried at 215°C before analysis because (1) drying of the silver loaded mordenite after iodine loading is the anticipated baseline in deployment of AgZ sorbent and (2) drying removes much of the surface water that might interfere with analysis of the structural water.

Thermogravimetric analyses indicated the removal of water from NaZ at temperatures below 500°C; the peaks usually centered around 260°C and indicated water and deuterated water loss from the surface. Spectra did not reveal water or deuterated water peaks at temperatures above 500°C for NaZ samples, although there was a loss of sample mass in some cases. Ag^0Z exhibited peaks at two separate temperatures indicating water removal; the first below 500°C, similar to the NaZ samples, and the second around 800°C. It is speculated that the presence of the silver enables a substantial structural change that is accompanied by the release of water at the higher temperature. In no case did the water released at the higher temperature include measureable amounts of deuterated water.

Nuclear magnetic resonance analyses were used to detect and measure deuterium in a solid sample at room temperature. It could not discern differences between surface or pore-adsorbed water and structural water. Deuterated water was measured in the Ag^0Z samples prepared as described above. In addition, premeasurement sample preparation showed about half the deuterium was removed under vacuum at room temperature within 2 h, and it was completely removed under vacuum at 100°C within 2 h. It was surmised that this easily removed water was sorbed on the surface or embedded in pores for those samples that had undergone thermal treatment (150°C) for durations of ~192 h. No detectable quantities of deuterium remained after the evacuation at 100°C. The detection limits were equivalent to an isotopic exchange of $\leq 0.091\%$. Calculations at this level of exchange indicate very little effect on the plant DF, should the structural water somehow be released.

Because the atom fractions of deuterium in the water in these tests were orders of magnitude greater than those of tritium found in humid fuel recycle plant off-gas streams, the extent of tritium exchange with the structural hydrogen of the mordenite is expected to be extremely low in actual practice.

It is recommended that additional tests of longer duration be performed. Duration should be comparable to the time between AgZ bed replacements anticipated for the plant. In addition, most (if not all) the structural water in the mordenite remains even at temperatures of 1200°C. Analysis methods that destroy the structure (possibly dissolution in glass) would have the best chance of releasing all the structural water for measurement with mass spectroscopy techniques.

CONTENTS

LIST OF FIGURES

Figure **Page**

LIST OF TABLES

ACRONYMS

AgZ	silver mordenite
Ag^0Z	Hydrogen-reduced silver mordenite
DF	decontamination factor
DTA	differential thermal analysis (analyzer)
MS	mass spectroscopy
MTIHM	metric tons initial heavy metal
$^m/_zN$	mass to charge ratio with N being a numerical value
NaZ	sodium mordenite
NMR	nuclear magnetic resonance
ORNL	Oak Ridge National Laboratory
PWR	pressurized water reactor
TGA	thermogravimetric analysis (analyzer)
UNF	used nuclear fuel
3AMS	type 3A molecular sieve

Preliminary Evaluation of Exchange of Hydrogen Isotopes in the Structure of a Mordenite-Based Sorbent

1. INTRODUCTION AND OBJECTIVES

Silver-exchanged sodium mordenite, or simply silver mordenite (AgZ), is being evaluated as a sorbent to remove iodine from process effluent streams of a used nuclear fuel (UNF) treatment plant.[1] Previous studies have shown that the AgZ adsorbs significant quantities of water, in addition to the iodine, from a humidified gas phase.[2] Methods to reduce or prevent the accumulation of water with the iodine have been devised and demonstrated. In essence, these methods accept that water will be co-adsorbed with iodine and that the water can be desorbed by heating the iodine laden mordenite—the major fraction of the iodine remaining on the thermally treated mordenite. By appropriate sequencing of the AgZ and molecular sieve sorbents, and thermal cycling, it has been shown that the water may be recovered separately from the iodine.[3]

However, in the previous evaluations of the mordenite sorbent, no structural component of the mordenite other than the silver is considered a participant in any chemical reactions or exchanges. The composition of sodium mordenite (NaZ) is represented by $(Na_2O)_4 \cdot (Al_2O_3)_4 \cdot (SiO_2)_{40} \cdot 24H_2O$, and the ion exchange process to incorporate silver replaces part, or all, of the sodium with silver. The water, or more specifically the hydrogen, in the mineral structure remains. In certain reprocessing plant off-gas streams, part of the water will contain tritium. A concern arises that the stable hydrogen in the mordenite structure will exchange with the tritium in the (temporarily) sorbed tritiated water, incorporating tritium into the structure of the mineral. Thermal treatment to remove the physisorbed surface water may not remove the tritiated water thusly incorporated into the mineral structure. Subsequent processes that might destroy the structure (e.g., vitrification where the crystal may dissolve in molten glass) have the potential to release the tritium (or tritiated water), thereby representing another potential pathway for release of tritium to the environment. A literature search (moderately thorough, certainly not exhaustive) found no data on the exchange of hydrogen isotopes between mordenite or zeolite structures and fluid phases in contact with the mineral.

The objective of the present study is to evaluate the extent of isotopic exchange of tritium in AgZ. To simplify handling and reduce costs associated with experiments using tritium, deuterium was used as a surrogate for tritium.

2. POTENTIAL EFFECT OF ISOTOPIC EXCHANGE ON OFF-GAS DECONTAMINATION

This section contains the results of *calculations* performed to evaluate the potential effect on the overall plant's tritium decontamination factor (DF) caused by isotopic exchange of tritium in the mordenite. A simplified off-gas processing arrangement shown in Fig. 1 was used as a basis for material balances. In this arrangement the DF is defined as the amount of tritium introduced to the system (in stream 2) divided by the amount of tritium escaping the plant (sum of that in stream 11 and that held on the AgZ). The basis included pressurized water reactor (PWR) fuel irradiated to 55 GWd/MTIHM and cooled for 5 years before processing. Off-gas was assumed to arise from voloxidation which was further assumed to release 100% of both tritium and halogens (e.g., iodine). This is a good assumption for tritium, but poor for release of iodine in voloxidation processes using oxygen as the reagent. For NOx-based voloxidation, both assumptions may be reasonable.

The amount of silver mordenite required per tonne of fuel was calculated on the basis of 100% retention of halogens, limited by an equivalent iodine capacity of 7 wt%. The water in the crystalline matrix was based on the composition of sodium mordenite, $(Na_2O)_4{\cdot}(Al_2O_3)_4{\cdot}(SiO_2)_{40}{\cdot}24H_2O$. Type 3A molecular sieve (3AMS) was selected as the baseline sorbent for removing water (and thus the tritiated water) from the off-gas stream. The total amount of water in the gas stream is the sum of the water arising from all isotopes of hydrogen in one tonne of fuel and any water added to the gas stream from other sources during processing of that quantity of fuel, and the concentration of tritium in the gas stream was calculated from these values. Overall tritium DFs may require the addition of water because 3AMS may reduce the dew point of the gas stream no lower than about −70°C. Thus trace quantities of water are lost to the stack, limiting the DF. Addition of water is upstream of the AgZ column (as shown) because isotopic exchange of tritium with the mordenite would be lessened when tritium is dilute. First order estimates of the amount of tritium exchanged into the mordenite were based on the concentration of tritium in the combined sources of water (gas stream and within mordenite structure) and the assumption that for 100% exchange the atomic ratio of tritium to all hydrogen approached the same value in all water-containing phases (i.e., mordenite structure, surface sorbed water, and off-gas). Lower percentages of exchange were calculated by reducing the fraction of tritium transferred to the mordenite phase. Fractional extents of exchange are expected if the rate of isotopic exchange is limited. In these calculations, exposure time of the AgZ bed to the off-gas stream is not a variable. Calculation of the overall tritium DF is based on the amount of water escaping the 3AMS sorption column (usually very small) and amount of tritium exchanged into the mordenite, which is also assumed to fully escape during subsequent processing of the mordenite into a waste form.

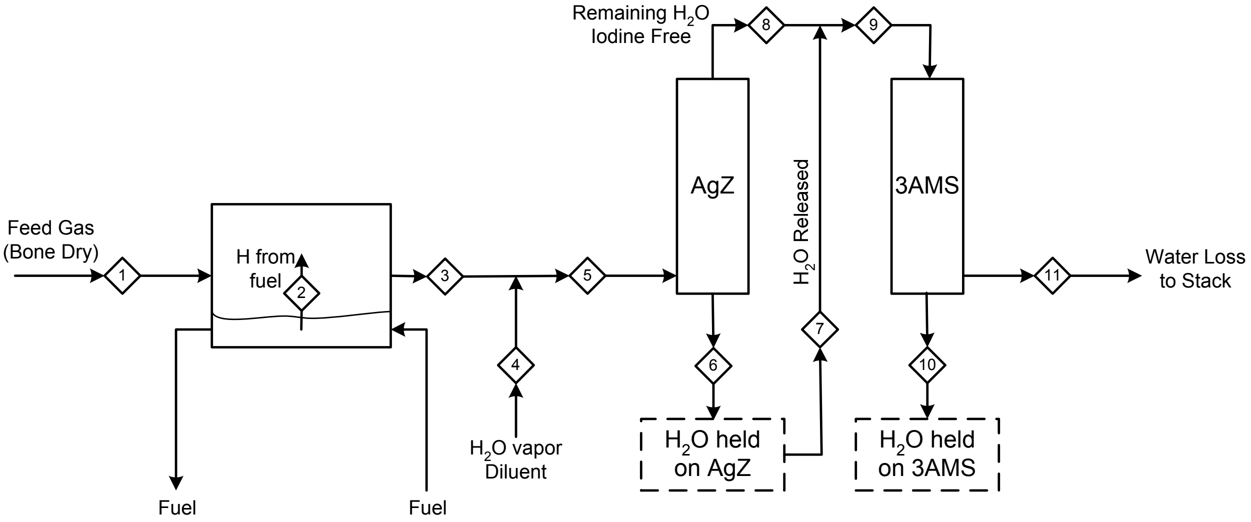


Fig. 1. Simplified material balance diagram for iodine and tritium capture from a fuel treatment process.

Results of the material balance calculations are shown in Figure 2. Tritium DFs decrease as the extent of isotopic exchange with AgZ increases. As shown, high DFs are sensitive to small extents of exchange. Dilution with (natural) water increases the DFs substantially. Required DFs for tritium retention are in the range of ca. 30 or less, depending on fuel burnup and time since the fuel was removed from the reactor.[4] Reductions in the DF, caused by isotopic exchange of up to about 5%, can be partially restored by the addition of modest amounts of natural water to the process (remembering it is necessary to achieve an overall DF of only ~30). Conversely, large extents of isotopic exchange require large amounts of water to restore acceptable DFs, which tends to result in large amounts waste requiring solidification (e.g., grout).

The need to reduce waste quantities might then encourage secondary systems to sequester tritium arising from AgZ waste production activities.

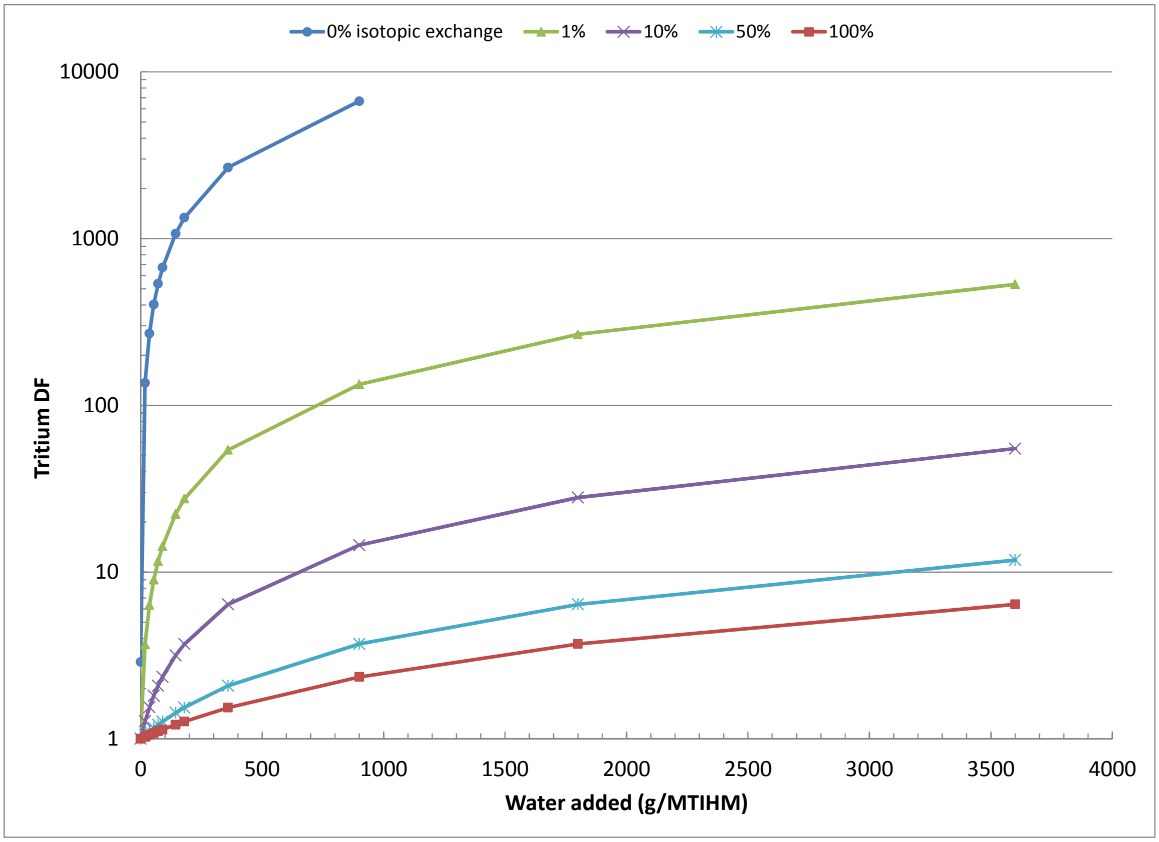


Fig. 2. Estimated plant tritium DF decreases with increased ^{3}H exchange to AgZ (representing ^{3}H loss) and increases with natural water addition to off-gas stream.

3. INITIAL EVALUATION OF PHASE CHANGES WITH DTA/TGA

Differential thermal analysis (DTA)/thermogravimetric analysis (TGA) was used in a set of initial evaluations to ascertain the temperatures at which phase changes in the AgZ occur and water is removed from the AgZ. Measurements were made on both an engineered AgZ product (previously described[2]) and on AgZ powder. A summary of the tests performed and the weight loss that occurred at a final temperature of ~700°C is given in Table 1.

The engineered form of the AgZ was in the shape of cylinders approximately 1/16 in. diam. and 1/16 in. long. This type material is manufactured by adding clay binder(s) to the powdered crystalline zeolite, followed by extrusion and baking. Ion exchange is used to replace a fraction of the sodium in the mordenite by silver, and this particular product contained 9.5 wt% silver (total mass basis which includes the binder). The sample had also been treated with hydrogen at 230°C to reduce the silver—the usual preparation step used just before introduction of the sorbent to an off-gas treatment system used to recover iodine. Two samples of the reduced AgZ (i.e., Ag^0Z) were tested—one sample which was stored under argon following reduction and one similarly stored but allowed to hydrate in air at 100% relative humidity and room temperature (~22°C). The hydrated sample lost considerably more weight (12.3% vs.

5.6%) in the TGA. Results are shown in Figs. 3 and 4, respectively. Data on the hydrated sample indicate a phase change under 150°C, presumed to be loss of surface sorbed water. Because the hydrogen reduction process had taken place at 230°C, little water remained on the unhydrated sample that could be desorbed at temperatures below 200°C. Above about 200°C there is a continuous loss of mass, presumed to be water, but no obvious phase changes were noted in either sample. Between about 450°C and 550°C the sample mass ceases to change, and up to about 700°C it remains essentially constant.

Table 1. Summary of samples for initial DTA/TGA measurements.

Sample #	Material	Reduction	Hydration Temp. (°C)	Air Dew Point For Hydration (°C)	Ultimate Wt Loss [b] (%)
ZN1	Engineered AgZ, with binder,[a] silver concn. 9.5 wt%	230°C w/H_2	N/A	N/A	5.6
ZN2	Engineered AgZ, with binder,[a] silver concn. 9.5 wt%	230°C w/H_2	22	22	12.3
ZN3	Powdered AgZ, no binder, silver concn. 20.0 wt%	N/A, as prep'd.	N/A	N/A	2.9
ZN4	Powdered AgZ, no binder, silver concn. 20.0 wt%	N/A, as prep'd.	22	22	15.2
EN1	Powdered AgZ, no binder, silver concn. 20.0 wt%	230°C w/H_2	N/A	N/A	2.8
HN1	Powdered AgZ, no binder, silver concn. 20.0 wt%	230°C w/H_2	22	22	19.3

[a] Engineered form is pelletized, and was crushed to a powder before analysis.

[b] At temperature >550°C.

Four tests were performed with the AgZ powder. It was prepared by contacting procured NaZ with silver nitrate solution, followed by washing and drying the powder. The prepared AgZ contained 20 wt% silver and no binders. Analysis was performed on the AgZ powder and on the AgZ that was hydrated in air at 100% relative humidity and room temperature (22°C). Aliquots of the AgZ powder were subjected to hydrogen reduction at 230°C and stored under argon (hereafter called Ag^0Z). One sample of the Ag^0Z was analyzed with no further treatments, and another was hydrated as before and then analyzed.

Analysis of the powdered AgZ sample (ZN3), exhibited little water loss below 200°C, and the sample mass was nearly constant above 200°C. No remarkable phase changes were evident above 200°C and up to 700°C. The powdered Ag^0Z sample (EN1) behaved similarly.

The hydrated silver mordenite samples, having greater water content, exhibited sharper phase changes at temperatures below 150°C, again thought to be desorption of surface sorbed water. Data are shown in Fig. 5 for the AgZ sample that had been hydrated in air at 100% relative humidity and room temperature (ZN4). Between 200°C and 700°C, continuous but small mass losses took place with no remarkable phase changes. Another AgZ sample that was reduced in hydrogen at 230°C and then hydrated under similar conditions (HN1) was analyzed, and the results are shown in Fig. 6. A strong phase change is noted at temperatures below 200°C with accompanying weight loss thought to be water. Between 200°C and

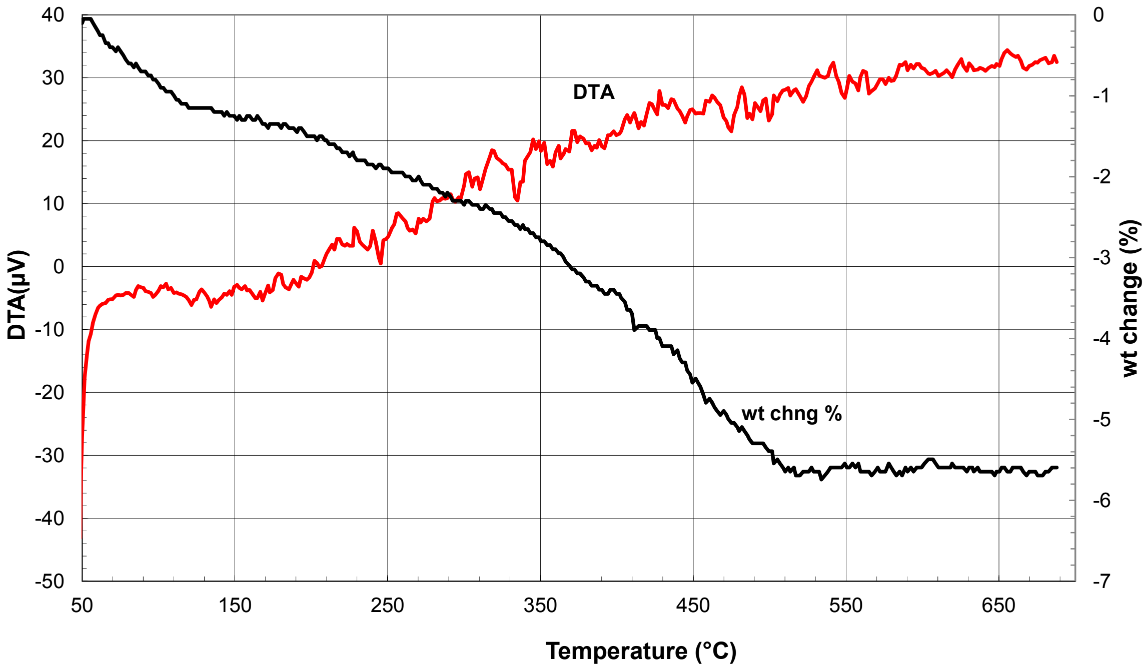


Fig. 3. DTA/TGA of engineered AgZ reduced with hydrogen and storage under argon (sample ZN1).

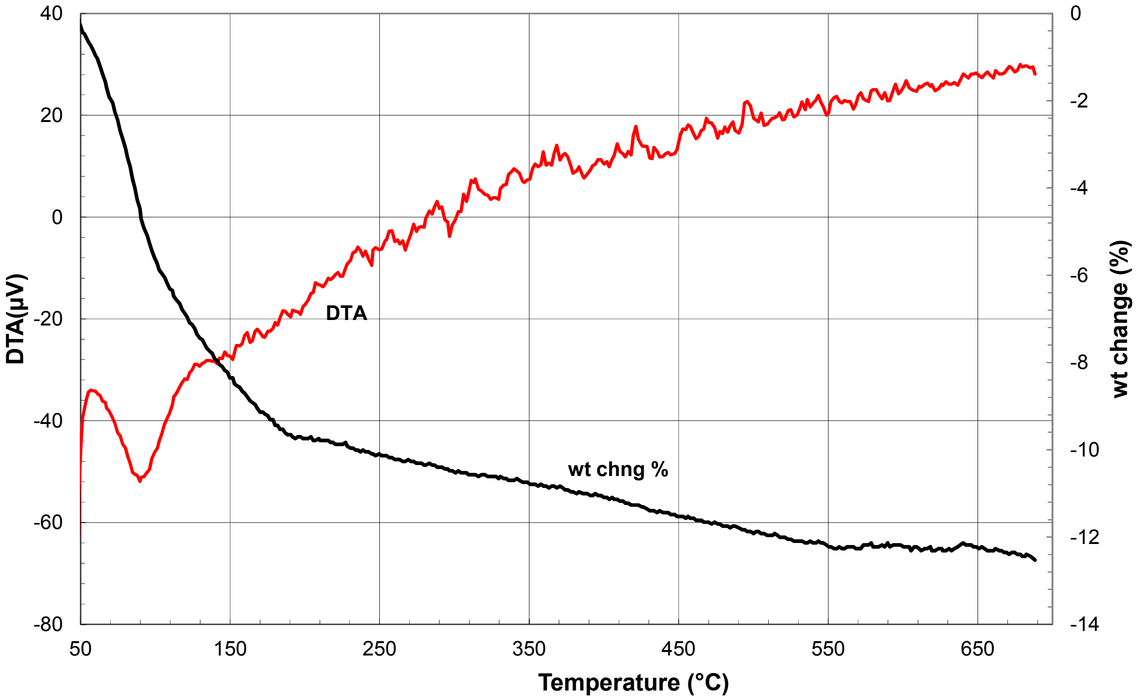


Fig. 4. DTA/TGA of engineered AgZ reduced with hydrogen, stored under argon, and hydrated (sample ZN2).

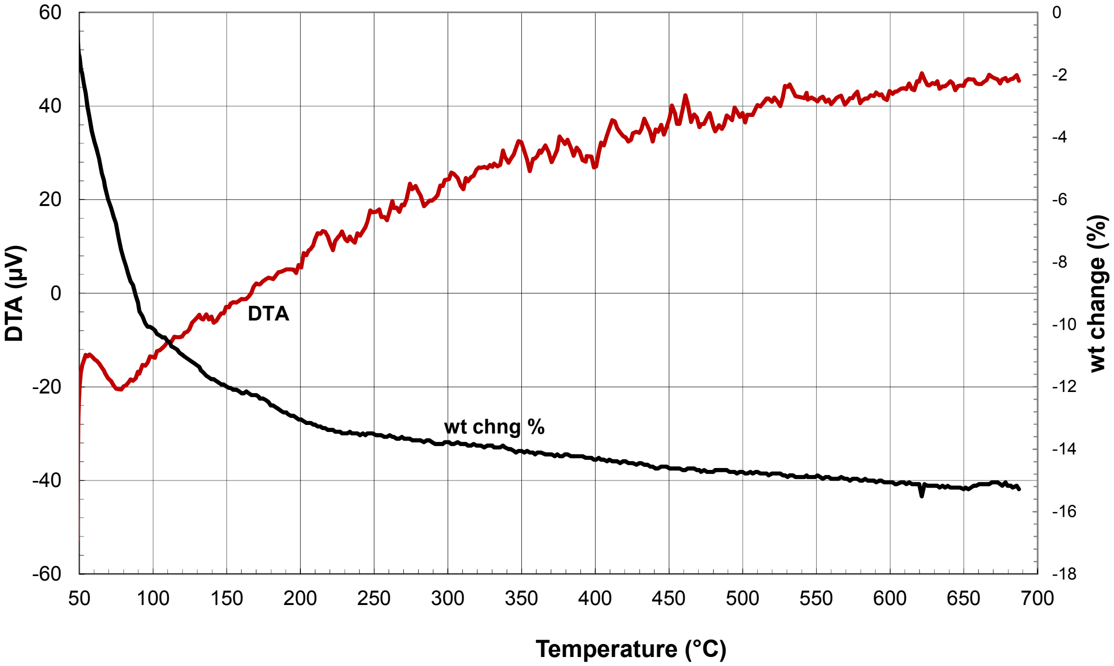


Fig. 5. DTA/TGA of as-prepared silver mordenite powder that had been hydrated (sample ZN4).

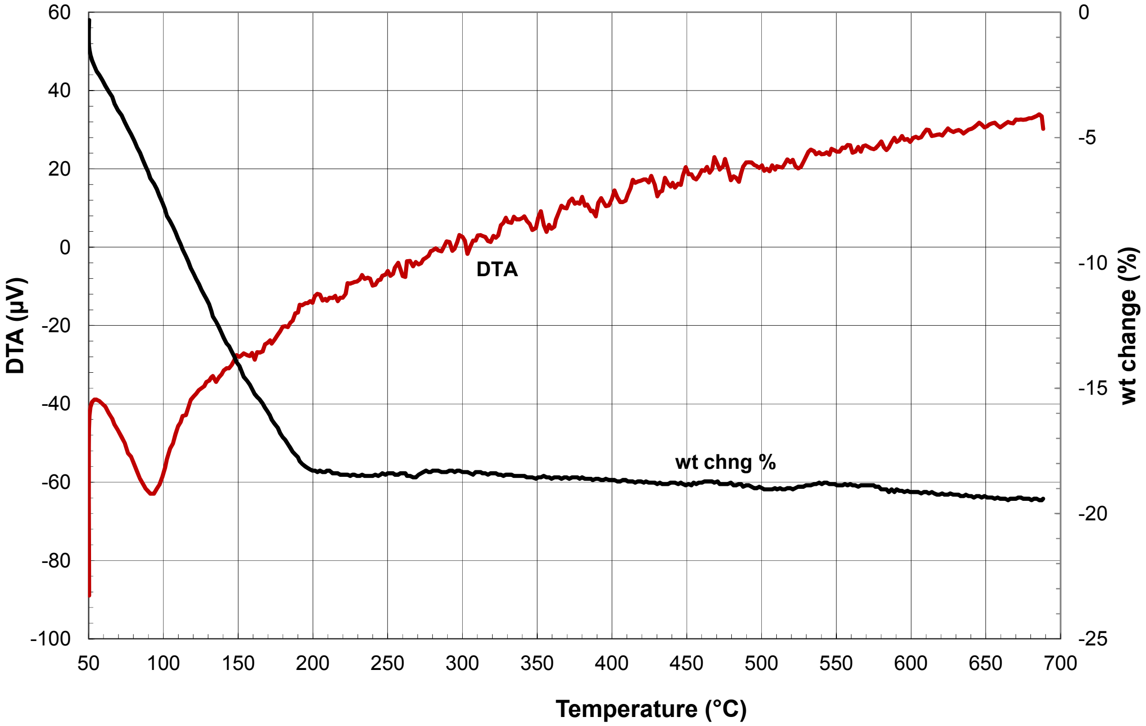
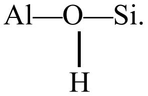


Fig. 6. DTA/TGA of as-prepared, then reduced and hydrated, silver mordenite powder (sample HN1).

700°C very little mass loss was observed. Comparison of Figs. 5 and 6 may be indicative of loss of mass due to thermal reduction of silver in the sample that did not undergo hydrogen reduction (i.e., sample ZN4).

Few phase changes were observed in these initial evaluation tests—the most notable change occurring at about 150°C. Literature data on the thermal decomposition of natural mordenite have been reported (Pechar and Rykl[5]), and the following phase changes as ascertained by DTA/TGA and x-ray spectroscopy were claimed:

$\xrightarrow{\text{start w/}}$ mordenite
$\xrightarrow{140^{\circ}\text{C}}$ metamordenite
$\xrightarrow{510^{\circ}\text{C}}$ mordenite + amorphous phase
$\xrightarrow{840^{\circ}\text{C}}$ mordenite + amorphous phase + anorthite + SiO_2
$\xrightarrow{1000^{\circ}\text{C}}$ anorthite + SiO_2 + amorphous phase.

The loss of "surface" water at ~150°C observed in the present tests seems to correspond to the transition from mordenite to "metamordenite" reported by Pechar and Rykl.[5] In addition, those authors also state that "over the temperature of 510°C, the remaining water forms structural hydroxyl groups which persist up to the highest temperatures", which was 1000°C. Such structural groups are of the form  $\mathrm{Al{-}\underset{\overset{|}{H}}{O}{-}Si}$.

4. TGA WITH MS ANALYSIS OF VOLATILIZED COMPONENTS

Samples of NaZ and Ag^0Z powders (no binder) were contacted with deuterium oxide (D_2O) at elevated temperature for varying lengths of time to permit exchange of the deuterium with the hydrogen integral to the structure of the mordenite. TGA analyses were performed at temperatures up to ~1200°C to remove all surface sorbed water and attempt to decompose the mordenite, thereby releasing the structural water. The off-gas from the TGA system was analyzed continuously by mass spectroscopy (MS) to determine whether deuterium is released when the mordenite decomposes to silicon dioxide and aluminum oxides, and how much is released.

4.1 Preparation of Samples

The two mordenite powders used in the experiments to ascertain the extent of isotopic exchange of hydrogen in the mordenite structure were prepared by drying and hydration operations. Both mordenite powders contained no binder—one type powder was as-received NaZ, and the other was as-prepared AgZ that was reduced in-house under hydrogen at 230°C (often referred to as Ag^0Z). Both were dried at 270°C for about 27 h to provide source material for further testing and provided the baseline samples.

Baseline samples of Ag^0Z and NaZ were hydrated with water having natural abundances of hydrogen isotopes. Hydration took place in air at room temperature (~22°C) and 100% humidity. The samples were in open-top containers and were placed in a small enclosure alongside an open-top container of water. The samples were exposed to the moist atmosphere for ~3 days. Measurement of sample mass before and after hydration indicated weight gains of 16.0% and 13.8% for for NaZ and Ag^0Z, respectively. The samples were then dried for 4 h at 215°C to reduce the amount of surface sorbed water. The drying results shown in Table 2 indicate that slightly more water was associated with the sample after drying than was in the pre-hydrated samples—a result consistent with reduction of AgZ having taken place at 230°C.

Table 2. Preparation of baseline samples with ordinary water

Sample		Humid Air	Drying		Dried Sample	
No.[a]	Mass (g)	Temp. (°C)	Temp. (°C)	Time (h)	Mass (g)	Loss (%)
NaZ-baseline	>10 [b]	—	—	—	—	—
NaZ-W1	0.711 [c]	22	215	4.1	0.625	12.1
Ag^0Z-baseline	>10 [b]	—	—	—	—	—
Ag^0Z-W1	0.618 [c]	22	215	4.1	0.551	10.8

[a] First part of sample number indicates form of mordenite; second part is a test identifier.
[b] Source materials that had contacted only natural water: NaZ as-received or Ag^0Z powder—no additional hydration or drying performed. Aliquots taken from these sources as required for further treatment.
[c] Measured sample mass following exposure to humid air (100% relative humidity, 22°C) for ~3 days.

Aliquots of both NaZ and Ag^0Z, dried as described earlier, were hydrated with deuterium oxide (100% deuterated water or D_2O). Again, open-top containers of the mordenite material were placed in a small enclosure alongside an open-top container of D_2O. The aliquots were weighed before hydration began, and they were removed and weighed periodically over a 12-day period. The mass increase of each aliquot is shown in Fig. 7 as a function of time. Uptake of heavy water is rapid at first, and then slows as

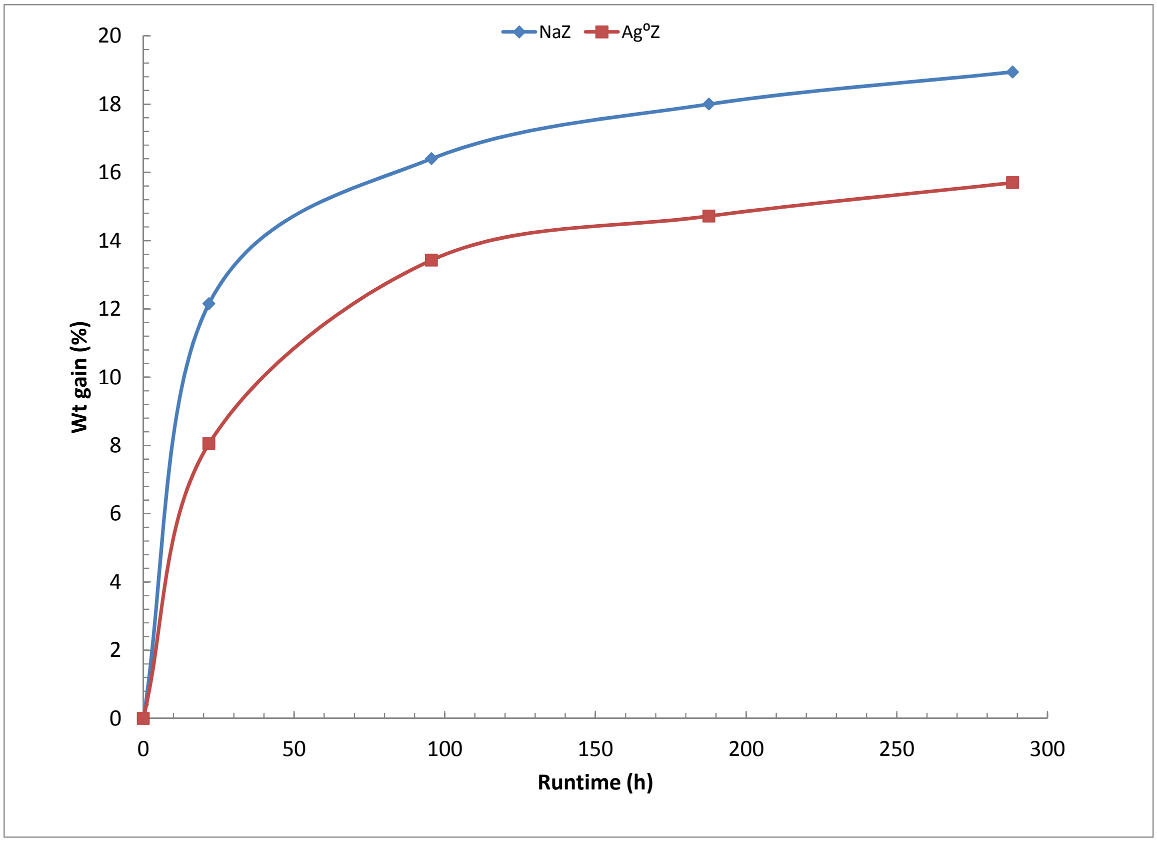


Fig. 7. Hydration of NaZ and Ag^0Z with D_2O.

expected. When the hydration was terminated, equilibrium had not been fully achieved, but the data indicate that Ag^0Z has less capacity for water than does NaZ. Measured mass increases of ~19% and ~16% for NaZ and Ag^0Z, respectively, are considerably higher than the 2%–4% water expected to be retained at a temperature of 150°C. This excess was exploited to provide the deuterium for isotopic exchange, if any, with the hydrogen in the structure of the mordenite.

Samples of approximately 1 g of hydrated mordenite were placed in each of several stainless steel capsules. These capsules were made of ¾-in. Swagelok® tubing couplings and plugs, as shown in Fig. 8. The internal volume of each capsule was calculated to be ~6.5 cm^3. Now consider the following: The vapor pressure of water at 150°C is ~4.76 atm. The amount of D_2O vapor that can be contained in the volume of a capsule, at this temperature and pressure, is 0.018 g. One gram of hydrated mordenite (either silver or sodium) can lose water amounting to at least 10% of the sample mass, or 0.10 g by weight, at 150°C to an unconfined gas phase. This represents a considerable excess of water compared to the amount that would transfer to the vapor phase within a sealed capsule heated from room temperature to 150°C. This implies that most of the D_2O remains on the surface of the mordenite and should enhance isotopic exchange with the structural hydrogen. In addition, a partial pressure of water around 4.76 atm is over two orders of magnitude greater than the partial pressure of water in the off-gas stream that would normally be treated with Ag^0Z (i.e., ~0.014 atm); the tritiated water is a small fraction of the water in this much leaner stream. This contacting method was selected because (1) it avoided the need to operate a bubbler and flow-through system that would consume large quantities of D_2O, (2) it achieves high D_2O concentrations in contact with the solid without introducing a separate liquid phase, and (3) the high concentrations of D_2O in contact with the mordenite would give the best chance of incorporating deuterium into the structural matrix of the solid.

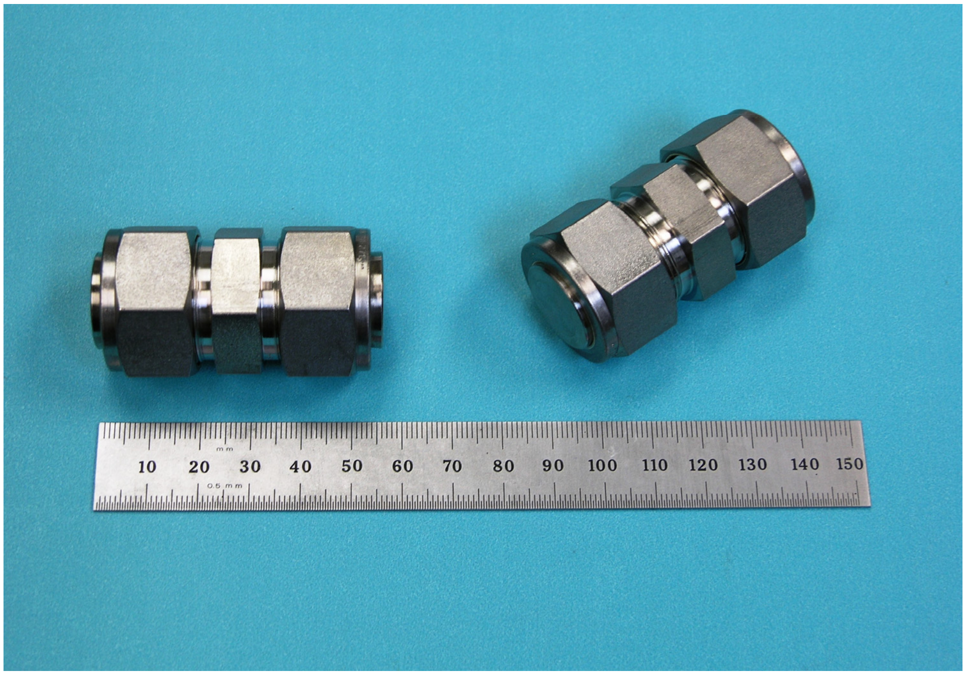


Fig. 8. Stainless steel capsules used to contain the heated mordenite samples and associated moisture.

A list of samples of NaZ and Ag^0Z treated with D_2O is given in Table 3. Samples NaZ-003 and Ag^0Z-003 were contacted with D_2O vapor at room temperature for 12 days and then dried at 270°C. Weight losses of up to 29% are indicative of the amount of deuterated water that was surface sorbed.

Table 3. Summary of D_2O treated samples

Sample		**Capsule Heating**		**Post Heating**		**Drying**		**Dried Sample**	
No.[a]	**Mass**[b] **(g)**	**Temp (°C)**	**Time (h)**	**Mass (g)**	**Loss (%)**[d]	**Temp (°C)**	**Time (h)**	**Mass (g)**	**Loss (%)**[d]
NaZ-003	1.003	23	*c*	*c*	*c*	270	24.0	0.711	29.1
NaZ-004	1.051	150	48.0	1.040	1.0	215	4.5	0.877	16.6
NaZ-005	1.033	150	192.1	1.022	1.1	215	4.5	0.866	16.2
Ag^0Z-003	1.077	23	*c*	*c*	*c*	270	24.0	0.836	22.4
Ag^0Z-004	1.010	150	48.0	0.929	8.0	215	4.5	0.866	14.3
Ag^0Z-005	1.006	150	95.3	0.997	0.9	215	4.5	0.860	14.5
Ag^0Z-006	1.017	150	192.1	0.935	8.1	215	4.5	0.872	14.3

[a] First part of sample number indicates form of mordenite; second part is a test identifier.

[b] Measured sample mass following exposure to D_2O humid air (100% relative humidity, 22°C) for ~12 days.

[c] These capsules were not heated and remained at room temperature until dried.

[d] Percentage loss is based on hydrated sample mass (2nd column).

The post heating percentage weight loss may be used as an indicator of capsule integrity. Most samples exhibit a mass loss of around 1%, which indicates the capsules were well sealed. Two samples (Ag^0Z-004 and Ag^0Z-006) exhibited a weight loss of ~8%, which might indicate that some of the surface sorbed water leaked from the capsule, and the D_2O partial pressure was closer to 1 atm than 4.7 atm. Nonetheless, sufficient deuterated water remained for isotopic exchange (i.e., 18 mg D_2O available compared to an estimated 105 mg of water in the sample structure).

4.2 Results of TGA-MS Analyses

The TGA-MS data included the total change in mass of the sample and the mass spectroscopy of volatile components emanating from the sample as a function of temperature. The MS data were in the form of ion current for several molecule fragments having mass to charge ratios, *m/z*, as shown in Table 4.

Table 4. Presumed molecular fragments found in mass spectra

m/z	**Potential fragments**
1	H
2	H_2, D
16	O
17	OH
18	H_2O, OD
19	HDO
20	D_2O, Ar^{+2}

The ratio $m/z = 20$ always showed a constant current indicating that doubly charged argon (argon was the carrier gas) was the primary observable species. The ratio $m/z = 19$ is the unique marker for deuterium-containing water (even though D_2O was used as the source of deuterium, the presence of natural water associated with the sample would have permitted free ionic exchange resulting in HDO).

The mass spectra for NaZ and Ag^0Z samples are presented and discussed in the next two subsections. (The NaZ sample dried at 270°C before TGA analysis was not considered further because the little remaining water did not result in substantial or interesting MS peaks for further analysis.)

4.2.1 Sodium Mordenite

Data for a sequence of tests with NaZ are shown in Figs. 9–11. The baseline sample (NaZ-baseline) was not contacted with D_2O and no peak for $m/z = 19$ (or $^m/_z19$, etc., for simplicity) is noted. Peaks for $^m/_z16$, $^m/_z17$, and $^m/_z18$ are evident and appeared centered at ~260°C where most of the mass loss occurred. This is consistent with the sample having been dried at 215°C in a standard laboratory oven before analysis with TGA-MS. There is a small but continuous loss of mass from ~400°C to ~1080°C, with no evidence of water loss cause by abrupt phase changes. Above ~1080°C the sample mass begins to decrease more rapidly, but no associated peaks in $^m/_z16$, $^m/_z17$ or $^m/_z18$ are evident. Analysis of sample NaZ-W1 showed similar trends.

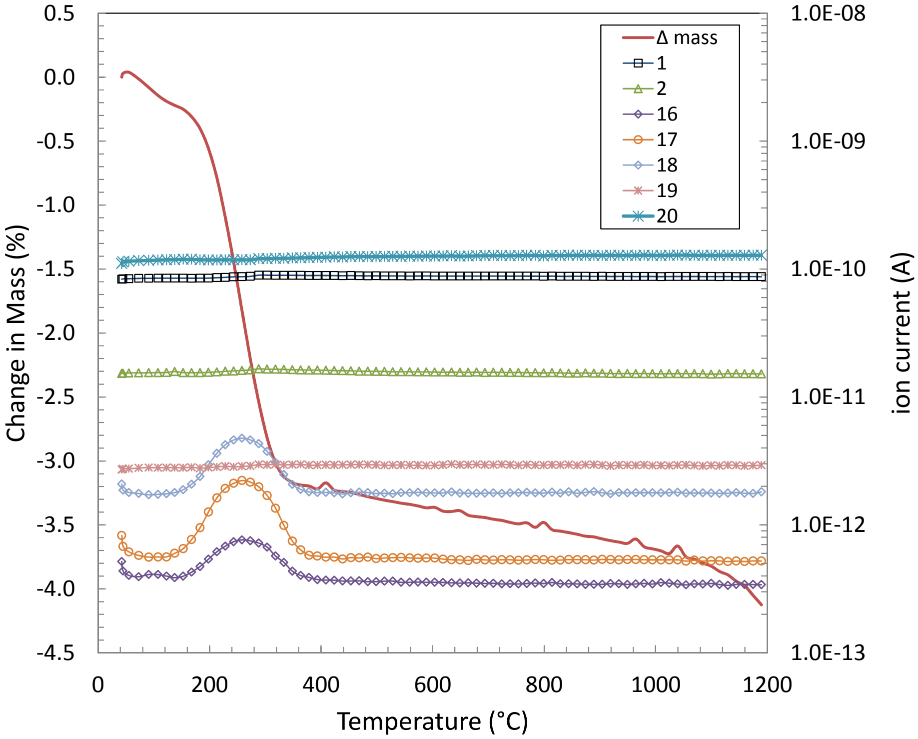


Fig. 9. TGA-MS data for NaZ-baseline; deuterated water in natural abundance.

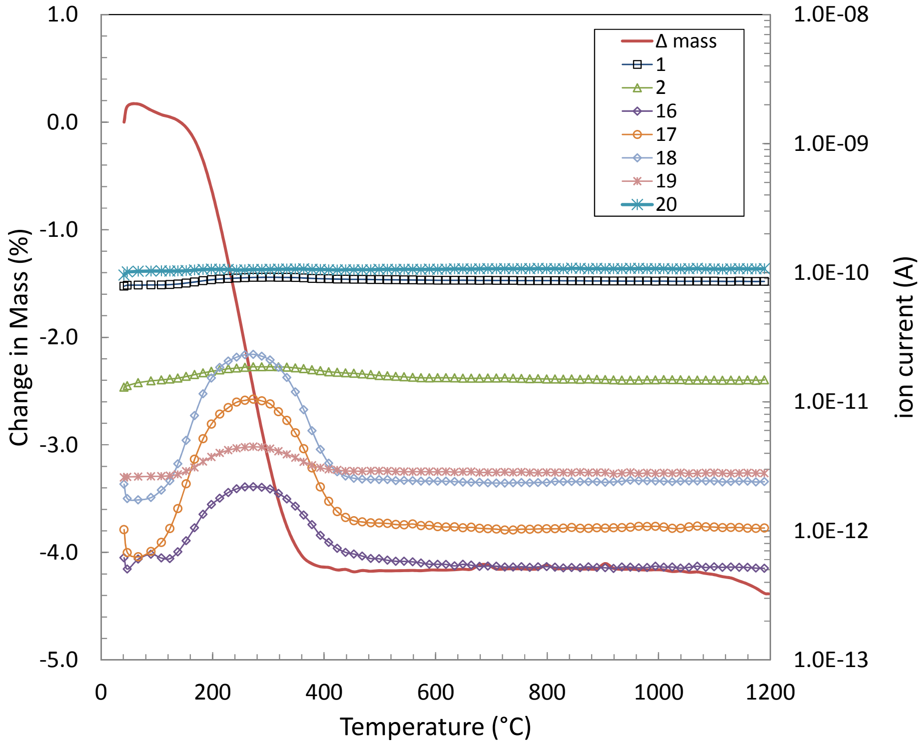


Fig. 10. TGA-MS for NaZ-004, contacted with deuterated water for 48 h at 150°C.

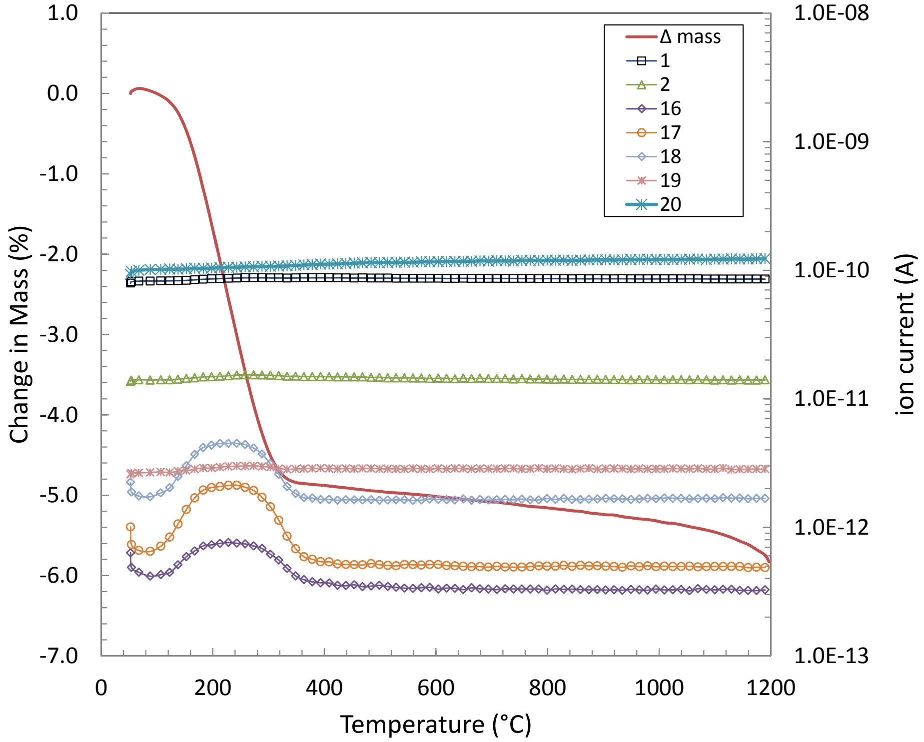


Fig. 11. TGA-MS for NaZ-005, contacted with deuterated water for 192 h at 150°C.

Samples NaZ-004 and NaZ-005 were contacted with D_2O and held at 150°C for ~48 h and ~192 h, respectively (see Figs. 10 and 11). As shown in Fig. 10, data on NaZ-004 show clear peaks at $^{m}/_{z}16$, $^{m}/_{z}17$, $^{m}/_{z}18$ and $^{m}/_{z}19$ centered at a temperature of ~260°C. A small increase in $^{m}/_{z}2$, and even smaller in $^{m}/_{z}1$, can also be seen. There appears to be no overall mass change between ~400°C to ~1080°C. Above ~1080°C the sample mass begins to decrease again, but no changes in water fragment ion currents are evident. Data on sample NaZ-005 (Fig. 11) exhibited similar peaks, although differences in peak heights could be caused by a change in the sensitivity setting on the instrument. In this case, however, there was a slight decrease in the overall sample mass between ~400°C to ~1080°C. In all cases, the decrease in total mass above ~1080°C without changes in the water fragment ion currents indicate volatility of an unidentified component of the NaZ.

Because of differences in background ion current, and potentially instrument gain, between tests, direct comparison is not revealing. For curves representing $^{m}/_{z}16$, $^{m}/_{z}17$, $^{m}/_{z}18$ and $^{m}/_{z}19$, the background signal was estimated from the constant portion of the curve. The background was subtracted from the curve to leave only the peaks, and the area under the peaks was calculated by numerical integration (designated A*m/z*, e.g., A18). The ratios of the calculated areas were computed and are listed in Table 5 for samples NaZ-004 and NaZ-005. These values indicate that less deuterated water is released at temperatures below 500°C for the sample maintained at the elevated temperature for the longer time interval. One possible explanation is that the natural structural water exchanged hydrogen isotopes with the surface sorbed deuterated water and that the water is not released from the structure albeit at the highest temperatures of the test. If the chemical formula for mordenite shown in Sect. 1 is used to calculate the structural water remaining in the samples after heating to 510°C and given the total amount of ‘surface’ water available after the room temperature hydration step, then the ratio of surface water to structural water was 2:1 for both NaZ-004 and NaZ-005. If isotopic blending were complete, there would be a reduction in the $^{m}/_{z}19$ found in the MS data, but not as large a reduction as indicated in Table 5.

Table 5. Ratios of areas under MS peaks for indicated ion pairs.

	Sample	
Ratio	**NaZ-004**	**NaZ-005**
A18/A16	10.2	4.88
A19/A16	0.814	0.182
A18/A19	12.5	26.9

4.2.2 Silver Substituted Mordenite

Results for a sequence of tests using Ag^0Z samples are shown in Figs. 12–15. The most obvious difference between the tests using Ag^0Z and the tests using NaZ is that there are double peaks in the MS data on the Ag^0Z. The first peak occurs at temperatures below ~500°C, and the second occurs at ~800°C. The second peaks in the data on Ag^0Z-baseline and Ag^0Z-006 samples are more pronounced than those in Ag^0Z-004 and Ag^0Z-005. (Analysis of sample Ag^0Z-W1 revealed similar trends as analysis of Ag^0Z-baseline.) The difference in the intensity of the second peak signal does not correlate to the inferred leak from a couple of the sample capsules in the Ag^0Z test series. The reason for the difference in peak intensities is unclear, but it is likely due to changes in instrument setup or calibration drift. The data lead to the conjecture that the presence of silver causes release of water from the mordenite structure at ~800°C with an accompanying phase change not seen with NaZ.

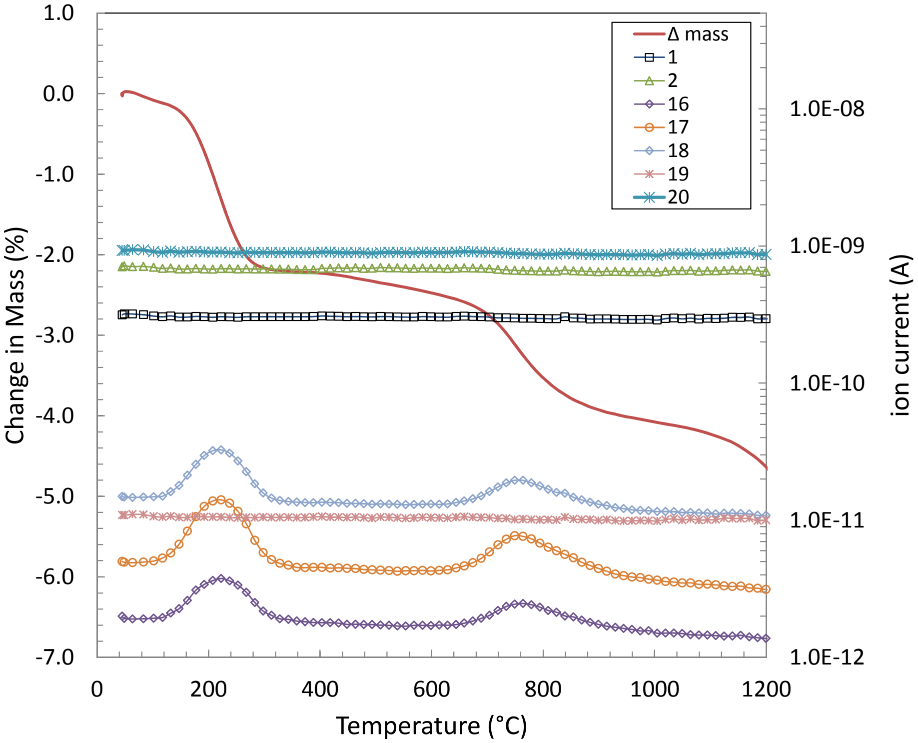


Fig. 12. TGA-MS data for Ag^0Z-baseline; deuterated water in natural abundance.

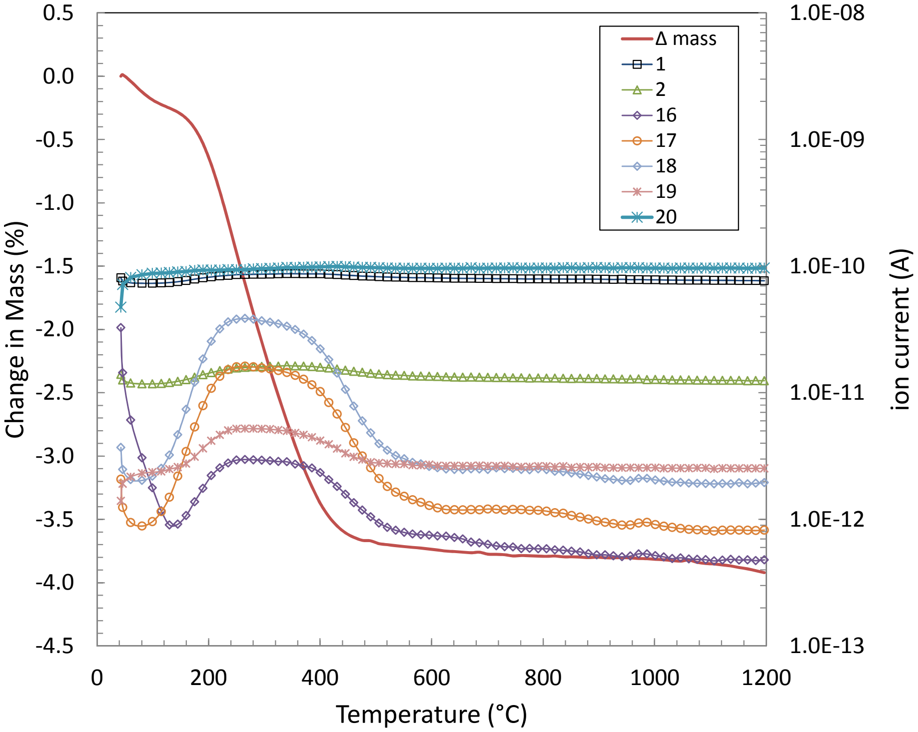


Fig. 13. TGA-MS for Ag^0Z-004, contacted with deuterated water for 48 h at 150°C.

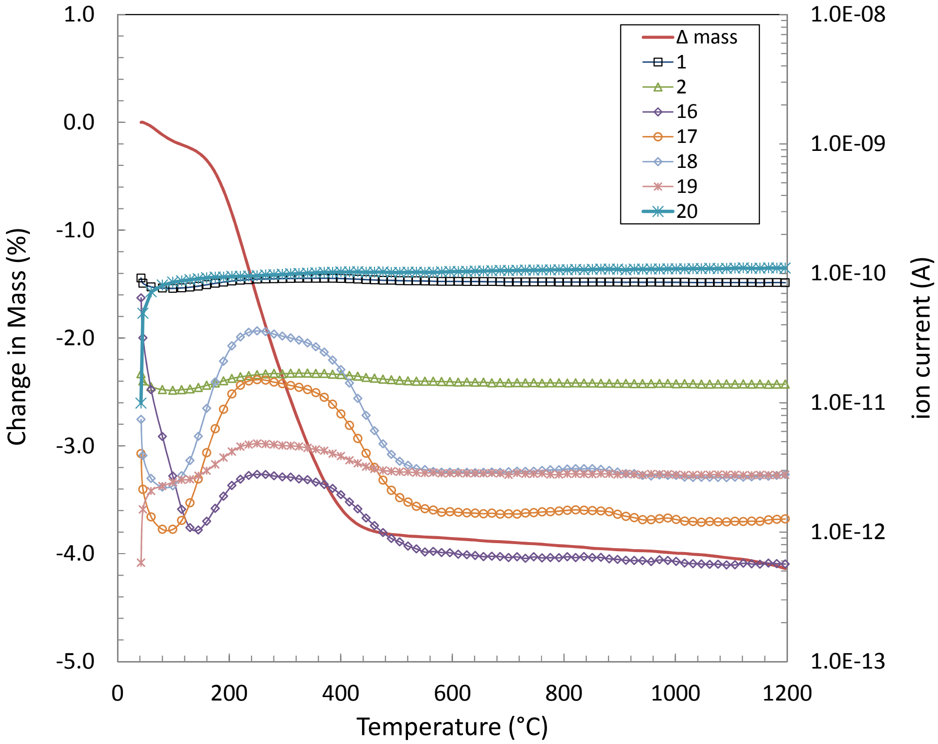


Fig. 14. TGA-MS for Ag^0Z-005, contacted with deuterated water for 95 h at 150°C.

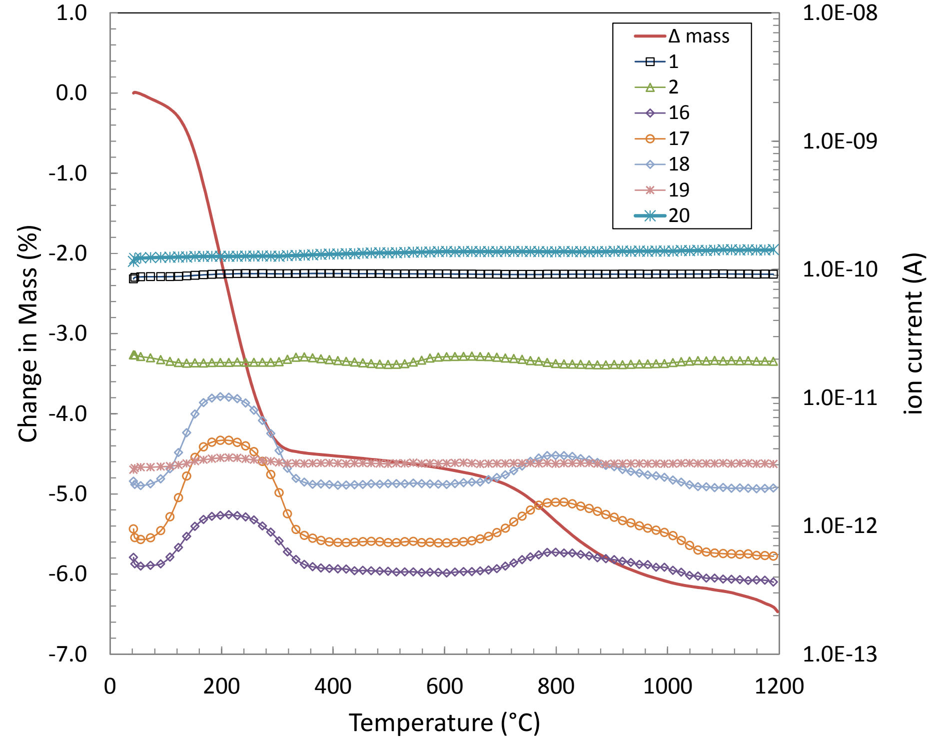


Fig. 15. TGA-MS for Ag^0Z-006, contacted with deuterated water for 192 h at 150°C.

At temperatures below 500°C, the MS data on Ag^0Z-004 and Ag^0Z-005 exhibit a strong peak for $^m/_z19$ and a weaker peak for $^m/_z2$. Both *m/z* ratios are indicative of deuterium bearing species in the vapors evolved from the samples. No peaks for these *m/z* ratios can be discerned at temperatures above ~500°C. This supports the proposition that isotopic exchange of hydrogen isotopes between surface sorbed (or gaseous) water and mordenite structural water does not take place or takes place to a very limited extent under the conditions tested. Similar tests at greater contact times and/or higher temperatures might cause a measureable exchange and should be investigated in the future.

As before, the areas under the MS peaks were calculated by numerical integration of the spectra, and ratios of the areas corresponding to specific *m/z* ratios were computed. The results are shown in Table 6. Where the second peak was large enough to obtain values larger than the noise in the signal, the ratio A18/A16 was slightly smaller than at the first peak. The trend would indicate that $^m/_z18$ may have been replaced with, for instance, $^m/_z19$, but the difference is not significant. In addition, no $^m/_z19$ is observed in the second peaks. The ratio A19/A16 from the first set of peaks indicates a decreasing concentration of deuterated water in the volatilized phase as the sample treatment time increased; treatment consisting of subjecting the encapsulated, hydrated sample to a temperature of 150°C. Considering that no second peaks in the $^m/_z19$ signal were observed (even when the graphing scale was greatly expanded), it is surmised that there is little, if any, isotopic exchange that places deuterium in the mordenite structure at the conditions of these tests.

Table 6. Ratios of areas under Ag^0Z MS peaks for indicated ion masses

	Sample			
Ratio	**Ag^0Z-baseline**	**Ag^0Z-004**	**Ag^0Z-005**	**Ag^0Z-006**
First peak				
A18/A16	8.14	12.9	13.3	9.16
A19/A16	0	0.951	0.813	0.302
A18/A19	n/a [a]	13.6	16.3	3.03
Second peak				
A18/A16	7.32	n/m [b]	n/m	8.07
A19/A16	0	n/m	n/m	0
A18/A19	n/a	n/m	n/m	n/a

[a] Not applicable because of zero value in indicated denominator.

[b] Not measured because observed peaks in associated mass spectra too small to obtain reliable results.

5. NUCLEAR MAGNETIC RESONANCE (NMR) ANALYSIS

Samples were prepared as described in Sect. 4.1, and aliquots of Ag^0Z-003 and Ag^0Z-006 were analyzed with NMR. The lower limit of detecting deuterium (in atomic form, ^2H) was estimated at 50 nmol, and the largest sample that could be placed in the rotor was 4 mg of mordenite sample. Based on the chemical formula of the mordenite (Sect. 1), about 55,000 nmol of hydrogen would be present in the mordenite structure. These values imply that deuterated water in concentration $\leq 0.091\%$ of the structural water would not be detected. The measured resonance lines in the experiments with the solid mordenite samples indicated that surface sorbed deuterium could not be distinguished from structural deuterium (e.g., SiOH, etc).

No deuterium was detected in the solid state analysis of sample Ag^0Z-003. This sample, as described in Sect. 4.1, was dried at 270°C followed by hydration with D_2O at room temperature and redrying at 215°C. Elevated temperature (150°C) treatment of this sample was not performed.

Recall that sample Ag^0Z-006 was hydrated at room temperature with D_2O, placed in a closed capsule and heated to 150°C for 192 h, and then dried at ambient pressure and 215°C. Portions of Ag^0Z-006 were prepared for analysis using three (3) different methods: (1) no further treatment, (2) placed in a vacuum of 7.5×10^{-5} Torr at room temperature for 2 h, and (3) placed in a vacuum of 7.5×10^{-5} Torr and heated to 100°C for 2 h. In sequence, the first sample portion exhibited a ^2H spectrum with a single line at 7.4 ppm after an overnight accumulation of resonance signals; analysis of the second sample portion produced a peak height of the ^2H resonance signals of about 50% of that of the first sample; and the third sample portion exhibited no ^2H resonances.

The conclusions drawn from these data are (1) elevated temperatures (e.g., 150°C) are required to drive deuterium species into pores or vacancies where drying at 215°C leaves deuterium in detectable concentrations, and (2) evacuation at room temperature and 100°C removes most to all of the detectable deuterium from heat treated samples. It may be inferred that deuterium exchanged into the structure of the mordenite is below detectable concentrations and that the deuterium is removable because it is sorbed in the surface or in pores.

6. CONCLUSIONS AND RECOMMENDATIONS

Samples of NaZ and Ag^0Z were hydrated at 100% relative humidity D_2O at room temperature, heated to 150°C in closed capsules for durations ranging from 0 to 192 h, and dried at ambient pressure (open capsules) at 215°C. The samples were then analyzed to ascertain if deuterium had exchanged with the hydrogen in the structure of the mordenite. Methods of analysis included DTA/TGA, TGA-MS, and NMR.

TGA-based analyses indicated the removal of water from NaZ at temperatures below 500°C; the peaks usually centered around 260°C indicating water and deuterated water loss from the surface. Spectra did not reveal water or deuterated water peaks at temperatures above 500°C for NaZ samples. Ag^0Z exhibited two peaks indicating water removal, the first below 500°C, similar to the NaZ samples but broadened in peak width, and the second around 800°C. It is speculated that the presence of the silver enables a substantial structural change that is accompanied by the release of water. In no case did the water released at the higher temperature include measureable amounts of deuterated water.

NMR analyses could not discern differences between surface or pore adsorbed water and structural water. Deuterated water was detected in the Ag^0Z samples, but about half was removed under vacuum at room temperature and it was completely removed under vacuum at 100°C. It was surmised that this easily removed water was sorbed on the surface or embedded in pores for those samples that had undergone thermal treatment (150°C) for a duration of 192 h. No detectable quantities of deuterium remained after the evacuation at 100°C, which was taken to mean that deuterium in the structure was below detectable limits. The detection limits were equivalent to an isotopic exchange of $\leq 0.091\%$. Calculations at this level of exchange indicate very little effect on the plant DF should the structural water somehow be released.

Because the atom fractions of deuterium in the water in these tests were orders of magnitude greater than those of tritium found in humid fuel recycle plant off-gas streams, the extent of tritium exchange with the structural hydrogen of the mordenite is expected to be extremely low.

It is recommended that additional tests of longer duration be performed. Duration should be comparable to the time between AgZ bed replacements anticipated for the plant. In addition, most (if not all) of the structural water in the mordenite remains even at temperatures of 1200°C. Analysis methods that destroy the structure (possibly dissolution in glass) would have the best chance of releasing all the structural water for measurement with MS techniques. Because radiation is known to enhance the diffusional transfer of molecules into a solid substance, its effect on the isotopic exchange of tritium with mordenite structural hydrogen could also be investigated by exposing heated samples to a high gamma-radiation source.

7. REFERENCES

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