Evaluation of Getters for Methane and Ammonia Decomposition

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Getters are used in many tritium purification systems for impurity removal. One getter material, SAES® ST909, can be used to decompose various impurities (methane, carbon oxides, ammonia and others), and release the hydrogen bound in these compounds for further processing. Because, ST909 absorbs eight to nine percent of its initial weight in nitrogen, alternate materials may provide greater operational flexibility to accommodate variable operating carrier gases. The gettering capability of ST909 is related to the tri-metallic alloy (zirconium, manganese, and iron) composition. However, simply using a material with the same composition may not provide similar methane and ammonia decomposition conversion efficiency. For this testing, alternative materials to ST909 are compared to track methane and ammonia decomposition performance. Bench scale tests were performed at elevated temperature using various gas mixtures. Changes in methane and ammonia decomposition performance were tracked using RGA analysis during bench scale testing. Analytical comparisons of chemically equivalent materials to ST909 were also performed and correlated to bench scale test results. Characterization testing performed to evaluate chemically equivalent materials included: X-ray fluorescence, X-ray diffraction, and inductively coupled plasma-mass spectrometry (ICP-MS). Results are expounded upon and differences in gettering capability of alternate materials are highlighted.

Keywords: Getters; Tritium Purification; Methane Decomposition, Ammonia Decomposition

1.0 Introduction

The purpose of impurity removal is to generate high purity product streams and waste streams with minimal product loss. Impurity removal techniques that are used must account for the conditions of the gas streams. In a tritium process, the gases involved are varied and in one location a gas which is desirable can be considered an impurity in another. Getter materials are a technology that can be used to remove select impurities from a process stream; however, their effectiveness is dependent on gas composition and operational conditions. This means that looking for interactions of the gases as well as interactions with related equipment, also needs to occur.

SAES ST909 is the trade name for a zirconium-manganese-iron alloy getter produced by SAES Getters. The getter, ST909, is useful for the removal of carbon oxides and oxygen. This getter material can also decompose compounds of tritiated water, methane, and ammonia that are contained in process gas streams. ST909 getters a number of gas species at elevated temperatures by the formation of Zr-based compounds [1, 2]. One drawback to the usage of ST909 is that it can absorb up to eight to nine percent of its initial weight in nitrogen as determined in this testing and expressed in literature [3]. However, while gas processing streams are likely to be tritium rich, tritium-related gloveboxes could have 'inert' atmospheres - such as argon, nitrogen, or helium - which may also need to be treated.

Impurity/product removal of the glovebox gases requires a material that can handle the varied nature of process streams in which they are subjected. For ST909, zirconium reacts preferentially first with oxygen, next with nitrogen found in nitrogen containing compounds (e.g. ammonia, nitrogen gas), then carbon from carbon based impurities, such as methane, and finally hydrogen. However, ST909 is relatively expensive (up to $5300/kg depending on the quantity ordered) and alternate materials may provide greater operational flexibility to accommodate variable operating carrier gases.

Testing was performed to identify a more effective and hopefully less expensive combination of materials (or a material) that can perform same overall functions of gettering oxygen from water, and carboxides, then nitrogen from ammonia, and carbon from methane gas; with comparable performance capabilities to ST909 for use with nitrogen and argon carrier gases. This test series focused on methane and ammonia removal. A similar study was previously reported on in the literature [2]. This paper presents additional materials that were evaluated and specifically compares how the preparation methods of similarly composed materials will change conversion efficiencies.

2.0 Experimental Methods

2.1 Materials

The original patent relating to ST909 covered compounds with the formula ZrM_1M_2, where M is any transition metal selected from the group consisting of Cr, Mn, Fe, Co, Ni and mixtures thereof [4]. Group IV metals of the periodic table seem to do well for gettering while transition metals, in general, show good potential for decomposing NH_3 and CH_4.

The following materials were selected for study based on their potential as an alternate to ST909 for CH_4 and NH_3 decomposition: ST909 (to establish baseline), nickel on kieselguhr (Ni/k), SAES ST707 which is a ZrVFe getter, American Elements (AME) TiMoZr, AME AlNiFe, AME ZrMnFeAl and AME ZrNi.

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2.2 Experimental Set-up

Testing was performed using a flow through test manifold and test cells described previously in literature [5]. The manifold is equipped with vacuum pumps, pressure transducers, flow controllers, various gas supplies, thermocouples, and residual gas analyzers (RGAs). The test cell is constructed of 9.525 mm (3/8 inch O.D.) 0.889 mm (0.035 in wall) 316L stainless steel tubing.[2] The total test cell length is just over 22.86 cm (9 inch) long and has two VCR fittings welded to the ends with a fritted disk welded in place approximately 1/3 the way up the test cell. The test cell is placed in a vertical configuration during operation. Both ends of the test cell have 0.5 micron stainless steel fritted gaskets to protect the system from the potential migration of particulates. Test cells were loaded with approximately 6 grams of material per test. ST909 pellets are right cylinder pellets approximately 6 mm in diameter by 4 mm tall. Similar particle/pellet sizes were used for the other materials.

Tests were performed to look for comparisons based on mass. However, this method in itself is only relevant for scoping studies. A more in depth look would use a method such as mercury intrusion to determine the surface area of the materials and comparisons could be made with that basis. Within the test cells, materials were loaded in a stacked configuration for regular shaped pieces and a packed configuration for irregular shaped particles.

The test cells were heated using clam shell heaters. Temperature was measured with thermocouples placed on the surface of the test cell. Unless otherwise noted, the gas flow rate was maintained at ~30 sccm and the system had a nominal pressure of ~2.8*10^5 Pa (~2100 Torr). Test cell temperature was maintained at 670°C.

2.3 Gas Compositions

Gas mixtures used during tests are indicated in Table 1. Gases include high nitrogen mixtures as well as elevated argon mixtures with nitrogen. Impurities in the gas mixtures included: NH_3, CH_4 or a combination of both. The decomposition conversion efficiency of NH_3 and/or CH_4 was determined for each of the materials using residual gas analysis of a test system slip stream.

Table 1 : Gas Compositions Selected for Study

Composition (vol %)
99.5% N_2, 0.5% CH_4
99.5% N_2, 0.5% NH_3
93% N_2, 1.5% Ar, 0.5% He, 5% CH_4
32% N_2, 67% Ar, 0.5% He, 0.5% CH_4
32% N_2, 66% Ar, 1% He, 0.5% NH_3, 0.5% CH_4
99% N_2, 0.5% He, 0.5% NH_3

3.0 Material Comparisons

Although SAES ST909 and AME ZrMnFeAl have similar compositions, the preparation method of the materials differs greatly. ST909 is prepared from powdered metallurgy, whereas the AME ZrMnFeAl is prepared from melted ingots. However, the cost of the ZrMnFeAl alloy pellet produced by American Elements is roughly 60% less than the cost of ST909 from SAES for the same quantity ordered.

Testing was performed to determine the chemically comparability of the two materials. Characterization testing performed included: X-ray fluorescence, X-ray diffraction, and inductively coupled plasma-mass spectrometry (ICP-MS). XRD and EDXRF results are discussed in general due to space consideration.

3.1 XRD / EDXRF

XRD results indicated similar overall composition based on peak presence and intensity. However, a slight broadening of a peak from the AME equivalent material compared to the ST909 was seen at the two theta value near 40 to 45. Peak broadening in this case is likely due to crystal lattice distortion due to concentration gradients. This is inferred from the formation of small magnetic particles decrepitated AME sample materials found post testing analysis. Visual observations of the ST909 and AME equivalent are shown in Fig 1. AME sample are prone to have golden discoloration from use.

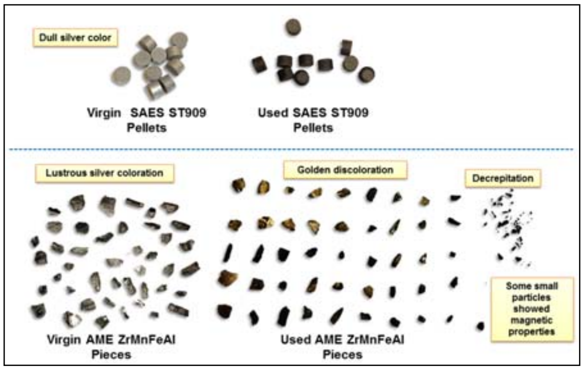

Fig 1: Visual Comparison of ST909 with AMEZrMnFeAl

EDXRF K ratios (Ka, Kb, La) from the two samples were similar for zirconium, iron, and manganese. Differences were observed in minor elements. The ST909 sample showed indications of V, Cr, Ni, Cu, and Sn (all at < 0.5%) which were missing from AME. Whereas, the AME equivalent sample contained trace Hf at <0.5% which was not observed in ST909.

3.2 ICP-MS

Results of the Perkin Elmer ICP-MS comparative tests are presented in Table 2. The residual standard deviations (RSD) of the results are not provided in the table. The RSD accounts for the sum of the columns not adding to 100%. It is observed that trace elements are more prevalent in the ST909 material in comparison to the AME equivalent sample. Trace elements are likely artifacts of sample preparation. The inclusion of tin is thought to be related to the binder used in sintering the ST909 pellets.

Table 2: Compositional Comparison of ST909 to AME ZrMnFeAl

	ST909 (wt%)		AME (wt%)	
Element	Expected	Measured	Reported	Measured
Al	**10**	10.5	**10**	10.5
Ba		0.006		< 0.008
Co		0.0499		< 0.065
Cr		0.0424	0.0026	< 0.038
Cu		0.0549	0.0045	< 0.122
Fe	**25**	24.1	**25**	23.2
Mn	**24.5**	25.4	**24.5**	19.8
Ni		<0.024	0.0032	<0.072
O			0.068	
other				10.35
Si		0.915	0.0028	1.55
Sn		0.634		< 0.32
Ti		< 0.014	0.0008	< 0.042
V		0.0596		< 0.085
Zr	**40.5**	39.5	**40.5**	34.6

Results from AME equivalent sample indicate that specifications with new vendors may require greater levels of scrutiny. Significant differences were observed in the weight percentages of AME ZrMnAl for zirconium at 34.6 wt% as compared to the reported 40.5 wt% as well as that indicated for manganese wherein the reported value was 24.5 wt% as opposed to the measured 19.8 wt%.

Analytical results show that the materials are similar in chemical composition overall. However, similar composition does not necessarily relate to similar CH_4 and NH_3 decomposition efficiencies. Factors such as surface area and packing efficiencies likely play a role but were not studied in these experiments.

4.0 Methane and Ammonia Conversion Results

For this paper, the CH_4 and NH_3 conversion efficiency is determined from the RGA signal of the mass spectrometer. Because RGA signals can vary based on fluctuations in pressure, an inert gas constituent was used during test to normalize the signal strength. Conversion efficiencies were determined using the following relationship:

$$\boldsymbol{Conversion\ Efficiency} = \left[\mathbf{1} - \frac{\left(\frac{\boldsymbol{Signal}_{\ \boldsymbol{test}}}{\boldsymbol{Signal}_{\boldsymbol{inert,test}}}\right)}{\left(\frac{\boldsymbol{Signal}_{\ \boldsymbol{feed}}}{\boldsymbol{Signal}_{\boldsymbol{inert,feed}}}\right)}\right]\%$$

where the subscripts ‘test’ and ‘feed’ indicate the feed gas ratio and the reactor effluent during testing ratios respectively.[2]. The subscript ‘inert’ refers to the comparative mass signal of an inert gas (argon or helium). Tests looked at the conversion efficiency after ~24 hours for comparison purposes.

4.1 Methane Decomposition

Methane conversion efficiencies observed during testing suggests that the different sample preparation method will affect conversion efficiency performance. As shown in Fig 2, a methane decomposition conversion efficiency of ~10% was observed for AME ZrMnFeAl when exposed to an argon rich gas stream. ST909 had a conversion efficiency of ~20% when exposed to a gas of similar composition. The AME TiMoZr conversion efficiency was also fairly consistent but only reached a decomposition efficiency of ~15%. It is unclear if packing efficiency also played a role in the decomposition. The ST909 pellets were in a cylindrical stacked configuration; however, the AME ZrMnFeAl pieces were of verious sizes and shaped that had less void space per given length of tubing. The statistical impact of this phenomena was not isolated.

Materials such as AME TiMoZr and AME ZrMnFeAl had fairly stable methane decomposition capabilities over the course of the test. The steep incline in ST909’s conversion ability is likely an artifact of the sample loading time (approximately two hours) to establish equilibrium. Because the AME TiMoZr and AME ZrMnFeAl were prepared from melted ingots the surface area and thus active sites for methane conversion would be lower and time to establish equilibrium would be less influenced by pore diffusion.

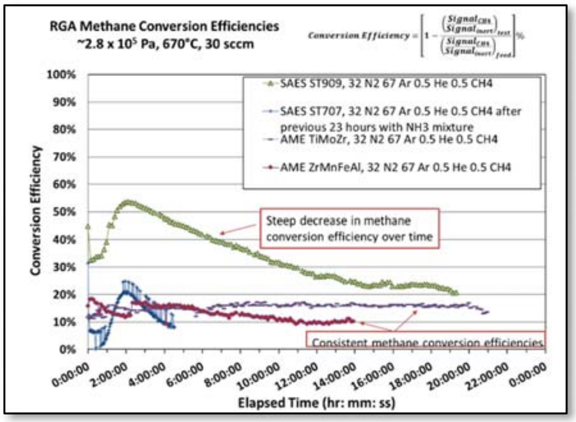

Fig 2: Methane Decomposition Efficiencies of ST909, ST707, AME TiMoZr, and AME ZrMnFeAl exposed to a 32% N_2, 67% Ar, 0.5% He, and 0.5% CH_4 gas mixture

In Fig 2, it is shown that both the AME ZrMnFeAl and ST909 H_2 signals decreased over time. However, though the signal is much lower than either the ST909 or the AME ZrMnFeAl, the AME TiMoZr shows a slight increase over time. This increase could be related to the hydriding nature of Ti and Zr materials of the alloy. It may take longer for the partial pressure of H_2 over AME TiMoZr to be reached and thus the curve may represent changes that occur to the sample while the H_2 is loading. The decrease in the H_2 signals for the ST909 and AME ZrMnFeAl is likely related to the active sites being blocked for more CH_4 decomposition by the nitrogen reactions and the CH_4 on the surface.

Lower N_2 gas concentration does improve initial conversion efficiency. The N_2-rich gas causes reduced conversion efficiency for many of the materials selected for study. It is likely that the gettering efficiency is lowered for many of the zirconium based materials due to the more favorable bond dissociation energies of the nitriding reactions in comparison to CH_4 based reactions.

Fig 3 shows that many of the materials nearly equally became blanketed by the presence of excess impurities (such as CH_4). A gas stream of 93% N_2, 1.5 % Ar, 0.5% He and 5% CH_4 was unable to be effectively treated for all but the Ni/k material. The Ni/k has excellent conversion efficiency in a N_2 rich gas mixture.

The decomposition conversion efficiencies for all materials were below 8%, other than the Ni/k, for the 5% CH_4 gas concentration. Coking on the surface of particles implies that sufficient time is needed for most of the materials to allow gettered elements to move inward within the material so that a clean surface for reaction is available. Coking also indicates that given the right conditions the CH_4 reformation is possible. It is recommended that the CH_4 concentration be maintained at a minimum. If excessive coking has occurred it may be necessary to replace a getter bed to remove the gettered atoms from a process.

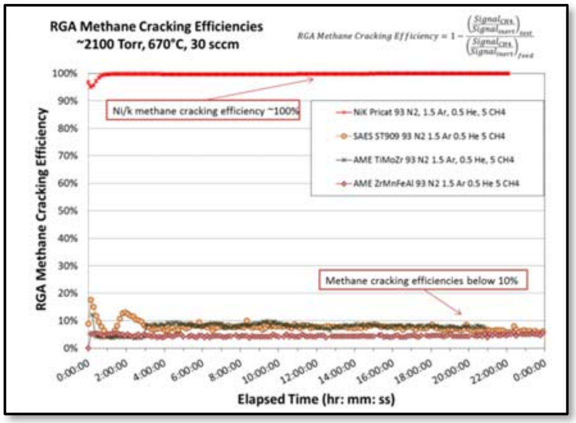

Fig 3: Methane Decomposition Efficiencies of Ni/k Pricat, ST909, AME TiMoZr, and AME ZrMnFeAl exposed to a 93% N_2, 1.5% Ar, 0.5% He, and 5% CH_4 gas mixture

4.2 Ammonia Decomposition

Equilibrium between NH_3, H_2 and N_2 was the driving factor for most of the material's decomposition efficiency. The NH_3 decomposition efficiency of the sample AME material was only slightly higher (1 to 2%) than ST909 (results not shown). Both materials performed similar to one another for a 99.5% N_2 with 0.5% NH_3 gas mixture. Other materials also had similarly high NH_3 decomposition efficiency. A 99% N_2, 0.5% He, and 0.5% NH_3 gas mixture was used to determine NH_3 decomposition efficiency of the materials shown in Fig 4.

The efficiency of NH_3 decomposition was reduced to roughly 60% and stayed relatively constant for Ni/k over the course of testing. The stable decomposition efficiency of the Ni/k is related to the catalytic activity of the material which could indicate that a greater mass would have better conversion efficiency. Ni/k has a lower density than any of the other materials tested. Each pellet had roughly 1/3 the mass of the ST909 material.

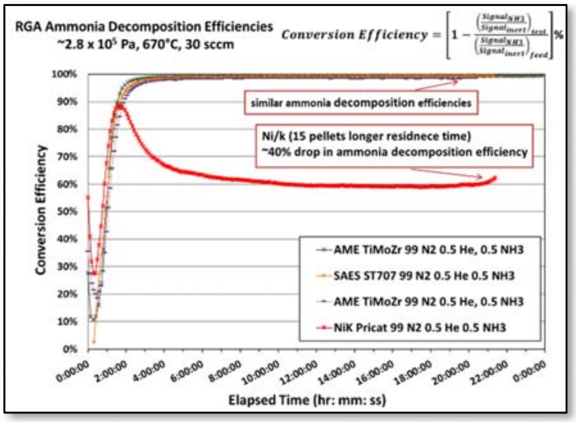

Fig 4: Ammonia Decomposition Efficiencies of AME TiMoZr, ST707, and Ni/k Pricat exposed to a 99% N_2, 0.5% He, and 0.5% NH_3 gas mixture

4.3 Combination Testing

Combination tests were performed which varied the mass of the sample material within the test cell. The two materials were loaded into two test cells that were then placed in series. In one test, the first test cell contained AME ZrMnFeAl and the second test cell contained AME NiFe. The gas mixture was 32% N_2, 66% Ar, 1% He, 0.5% NH_3 and 0.5% CH_4. Single material tests were also performed with the same gas mixture for AME NiFe and AME ZrNi for comparative analysis of different Ni containing materials. ZrNi is a hydride material and was therefore not chosen for initial combination testing.

One difficulty in RGA signal analysis of the downstream gases is that the molecular weight related to mass 16 can represent both CH_4 and NH_3 gas species. However, this is overcome by using mass 15 for CH_4 conversion instead of only mass 16. Graphs in which the lines are relatively parallel indicate similar parent gases. Mass 15 better represents the potential for less hydrogen fragmentation from the RGA for the CH_4 than would be required by the NH_3 to get the same mass. A reduction of mass 15 signal with low efficiency does not imply that the conversion efficiencies of any of the materials tested will be that low. The mass 15 signal is based on radicals formed from the test by the RGA. Mass 17, 16, and 15 RGA signals are shown in Fig 5 to Fig 7.

The more favorable bond dissociation energies of the nitriding reactions in comparison to carbon reactions cause decomposition efficiencies for NH_3 to be greater than for CH_4 gas mixtures in combination testing. For an Ar-rich gas with NH_3 and CH_4 impurities present, combination testing of AME ZrMnFeAl with AME AlNiFe showed CH_4 decomposition efficiencies greater than 35%. AME ZrNi had a better CH_4 conversion efficiency at ~48%. AME AlNiFe had 80% NH_3 decomposition efficiency and AME ZrNi had a

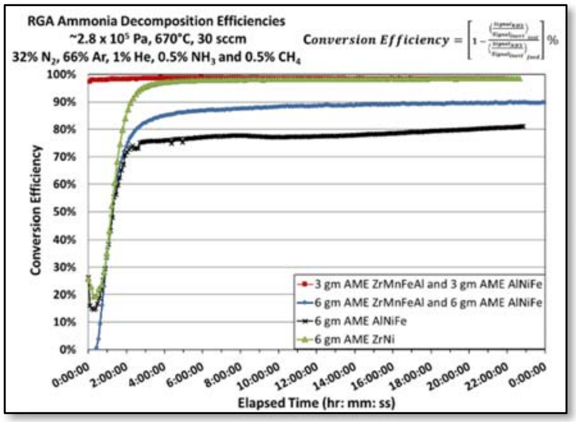

Fig 5: Combination testing for materials exposed to a 32% N_2, 66% Ar, 1% He, 0.5% NH_3 and 0.5% CH_4 gas mixture, RGA Mass 17

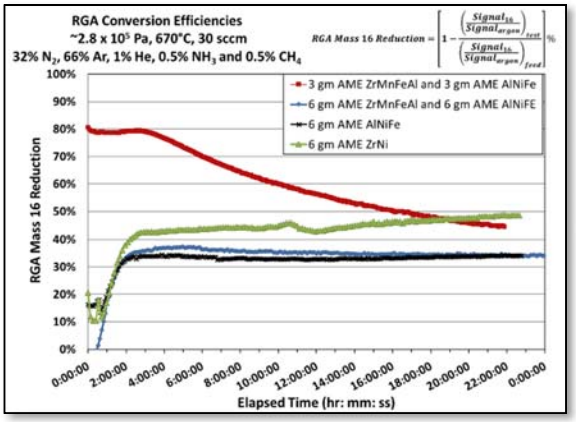

Fig 6: Combination testing for materials exposed to a 32% N_2, 66% Ar, 1% He, 0.5% NH_3 and 0.5% CH_4 gas mixture, RGA Mass 16

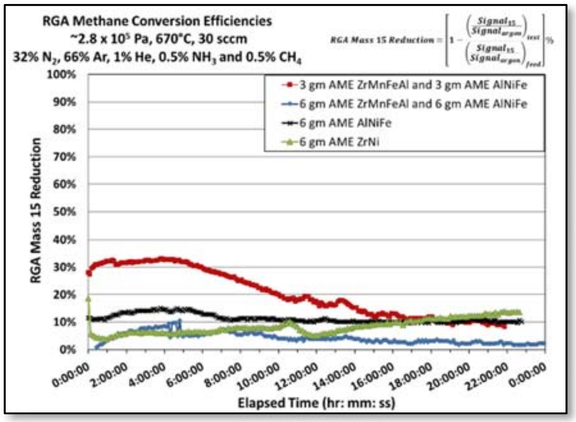

Fig 7: Combination testing for materials exposed to a 32% N_2, 66% Ar, 1% He, 0.5% NH_3 and 0.5% CH_4 gas mixture, RGA Mass 15

decomposition efficiency of ~97% when exposed to the same gas. Combination test of the AME ZrMnFeAl with AME AlNiFe made little difference compared to tests with just the AME AlNiFe. Increasing masses of ZrMnFeAl and AME AlNiFe also did not appear to increase conversion efficiency. It is unclear why this is the case; but, it may be an artifact of the space velocity of the test cell. Combination testing shows that the AME alumina nickel iron alloy has an improved CH_4 conversion efficiency even though NH_3 was initially present. An improvement of 8% at the end of the test is noted compared to other materials such as ST909 subjected to gas mixture without NH_3. Combination testing showed increased CH_4 conversion capability.

5.0 Conclusions

Several materials were tested as alternative to SAES ST909. Based on the results presented in this report other materials perform better than ST909 under the conditions tested. The sample preparation method of ST909 has an impact on CH_4 decomposition performance. American Elements produced a material of similar composition that had a CH_4 conversion efficiency of ~10% when exposed to an argon rich gas stream. ST909 had an ~20% CH_4 conversion efficiency.

For an argon rich gas with both NH_3 and CH_4 impurities present, combination testing of AME ZrMnFeAl with AME AlNiFe showed CH_4 conversion efficiencies greater than 35%. AME ZrNi had a better CH_4 conversion efficiency at ~48%. AME AlNiFe had 80% an NH_3 conversion efficiency and AME ZrNi had a decomposition efficiency of ~97% when exposed to the same gas. Combination test of the AME ZrMnFeAl with AME AlNiFe made little difference compared to tests with just the AME AlNiFe.

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