



Evaluation of getters for methane and ammonia decomposition

David W. James*, Gregg A. Morgan

Savannah River National Laboratory, Aiken, SC, United States



ARTICLE INFO

Keywords:

Getters
Tritium purification
Methane decomposition
Ammonia decomposition

ABSTRACT

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.

1. 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.

* Corresponding author.

E-mail address: david.james@srnl.doe.gov (D.W. James).

2. 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.

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 μ m stainless steel fritted gaskets to protect the system from the potential migration of particulates. Test cells were loaded with approximately 6 g 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 $\sim 2.8 \times 10^{-5}$ 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. 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 chemical 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 40–45. 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.

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.

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%.



Fig. 1. Visual Comparison of ST909 with AMEZrMnFeAl.

Download English Version:

<https://daneshyari.com/en/article/6742897>

Download Persian Version:

<https://daneshyari.com/article/6742897>

[Daneshyari.com](https://daneshyari.com)