Evaluation of a cleaning method for the tritium environment

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Solvents can be used to clean process equipment and piping that will come in contact with tritium containing gas streams; but, the ways in which solvents interact with catalysts is also of interest. This method of cleaning does not account for impurities within the bulk of a material that could be released from catalyst or containment barriers during high temperature operation. One solvent of interest which can be used because of its ability to both degrease and be analyzed for carbon content is Vertrel^{TM} MCA. Tests were performed to determine carbon, sulfur, and chlorine concentrations for two candidate materials which were subjected to Vertrel MCA cleaning. Comparisons with high temperature hydrogen reduction are provided. Solvent analysis, LECO carbon/low sulfur determination testing, and neutron activation testing were performed to provide comparisons. Results show potential risks of using solvent cleaning and analysis as the only method of determining impurity concentration of materials which will be exposed to high temperature testing.

Keywords: Tritium purification, Ammonia decomposition, Solvent cleaning

1.0 Introduction

Several methods of preventing and removing impurities from the tritium environment exist. These methods include, among others, getters and catalysts which are effective at capturing and breaking bonds of tritiated compounds which represent tritium-holdup. Carbon contaminants can form into methane and halogens can be the source of acid gases which can lower the purity of the tritium product if not removed. Although, getters and catalysts can be used to remove impurities the desire is to prevent impurity introduction by removing impurities before they can be introduced. Procurement of materials with low impurity content is an effective method of minimizing impurities; however; this is not always possible. Cleaning of materials may also be needed. Both options can result in significant cost avoidance related to equipment damage due to impurity processing; but, may not be completely practical when it comes to materials such as catalysts.

Although, piping and tubing can be cleaned using solvents, little attention has been given to cleaning methods of catalysts and getters which may be used in a tritium environment. It may be that catalyst and getters are assumed to be free of impurities. The presence of impurities causes catalysts and getters to lose effectiveness. In many cases that assumption would therefore be true.

The challenge of cleaning materials which can go into a tritium process is a matter of history. Ozone depleting solvents such as hydrofluorocarbons, which have historically proven effective as degreasers, are a greenhouse gas and are considered not environmentally friendly [1, 2]. However, other alternatives have been developed. One non-ozone depleting solvent of interest is Vertrel MCA. The benefit of this degreaser for a tritium environment is that it reportedly leaves minimal residue and the effluent generated from cleaning can be analyzed to determine surface carbon content [3]. This makes Vertrel MCA potentially useful for cleaning piping and tubing in industrial applications which require the minimization of carbon impurities. However, just like industrial applications, the typical cleaning methods used to prevent impurity introduction in a tritium environment must also account for end-use operating conditions.

During use, impurities found in the bulk of a material such as a getter or a catalyst as well as piping and tubing can migrate to the surface over time through diffusion. The hydrogen reducing environment inherent to a tritiated environment encourages the migration/leaching of impurities from the bulk to the surface where interaction can occur. Operating conditions such as elevated temperatures also play a role in the release of impurities over time. Once released, impurities can accumulate and cause corrosion to process piping and tubing. Impurities can also poison catalysts, getters, hydride materials; or can damage other general process equipment.

Catalysts come in many forms and are made from a variety of feed stocks. Some catalyst materials also have rough surfaces whereas others are smoother. These factors affect how they can be cleaned and whether they can be cleaned via solvent cleaning. For both the nickel coated ceramic and the sintered iron catalysts, the feedstock materials used in manufacturing have inherent impurities. The purity of iron is subject to the smelting process used to purify it. The surface area of nickel is enhanced by dispersing it on a support such as a ceramic material. The ceramic support may have its own impurities but the impurities of the nickel metal may also need treatment.

Two proprietary materials (shown in Fig 1,) a nickel coated ceramic as well as sintered iron pellets, were used to determine the carbon-and-sulfur-removal effectiveness of Vertrel MCA. These materials are representative of rough and smooth surfaced catalysts which could be used to crack tritiated impurities. They also have differing quantities of chlorine, carbon, and sulfur. These elemental

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impurities are of interest for their potential to form tritiated acid gases.

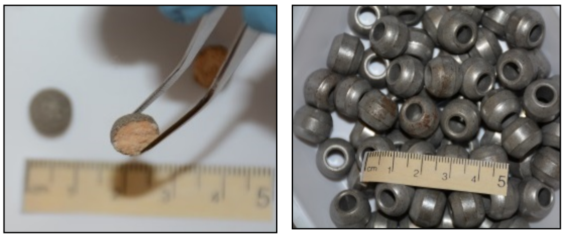

Fig 1: (left) Nickel on ceramic pieces showing an eggshell coating; (right) sintered iron pellets

2.0 Experimental methods

2.1 Analytical evaluation

Cleaning methods such as washing with solvents and or performing protium reduction prior to introducing a material to a tritium environment may be able to remove impurities. Analytical evaluation of materials is needed to determine if impurities have been removed prior to introducing them to a tritium environment.

Several instruments and related techniques were used to determine impurity concentrations of the samples. These instruments and their associated methods include: neutron activation, oil-in-solvent analysis, and carbon sulfur determination. Descriptions of each technique are summarized below.

Neutron activation analysis can be used to quantify the chlorine content of the sample materials. Neutron activation analysis uses a californium source contained in a water-filled pool to provide a flux of neutrons for activation analysis. The induced activity is measured and the components of interest are determined by ratio to a standard.

Oil-in-solvent analysis is reportedly useful for determining carbon concentration. This method assumes that the surface is representative of the bulk material. Oil-in-solvent analysis requires a known volume of clean solvent, (Vertrel MCA) to be flushed over the surfaces to be analyzed. The flushed wash mixture is then analyzed with a Horiba S-316: Wilks InfraCal total oil and grease (TOG) and total petroleum hydrocarbon (TPH) analyzer and compared to a standard 100 ppm carbon concentration solution.

Carbon and sulfur concentrations are also determined using a LECO carbon/sulfur determinator. The LECO CSLS600 determinator uses a tungsten accelerator to measure carbon and/or sulfur contents of materials with a melting point as high as 1500°C [4]. To determine carbon and sulfur contents, a weighed sample is combusted in an oxygen rich environment. If carbon and/or sulfur are present, then carbon dioxide and sulfur dioxide are byproducts of combustion. These byproducts are swept into an absorption cell and the gas is quantified by infrared (IR) spectroscopy. Calibration standards are run before and after use.

2.2 Hydrogen reduction test cell description

For hydrogen reduction, batch materials are loaded into a quartz cylinder fitted with a metal cap. An image of the test system is shown in Fig 2. Ports on the metal cap include those for thermocouples, the water cooling coil, and the gas lines for the inlet as well as the exhaust gas streams. Test cell interior dimensions are 15.875 cm (~6.25”) diameter and 91.44 cm (36”) height. Only a portion of the test cell is filled with material but it is kept within the heated zone of the furnace.

Quartz wool and a quartz plate were included to prevent damage to the test cell during loading. As expansion of metals occurs during heating, a sacrificial inner quartz tube of 10.795 cm (~4.25”) inner diameter is used to contain the sample within the larger tube. This diameter and length of the test cell were chosen to minimize channeling and axial conduction effects [5]. The test cell is placed in a furnace to ensure uniform heating of the materials. The bottom of the furnace is capped with insulation to prevent unwanted heat loss. At the top of the test cell, a metal baffle is used to ensure that the maximum operating temperature of the sealing O-ring is not exceeded. In addition to the baffle, a copper cooling coil is placed on the exterior and interior of the quartz tube for added protection of the O-ring gasket material. Tap water is flowed through the cooling coils to allow the rapid temperature change (from 775°C to 21°C) to occur within 38.1 cm (15”). The exhaust line is equipped with a water column to ensure that in the event of a loss of power or gas flow rate, oxygen ingress would be limited.

Fig 2: Apparatus used for hydrogen reduction testing

2.3 Hydrogen reduction operating conditions

Operating conditions play a role in the kinetics involved with hydrogen reduction. For the given materials, hydrogen reacts with iron at temperatures greater than 300°C and reaches equilibrium quickly at temperature greater than or equal to 500°C [6, 7]. It is also noted that the transitional change in the crystalline structure of nickel from α-nickel to β-nickel occurs at ~320°C within a hydrogen reducing environment [8]. Hydrogen reduction in terms of a tritium environment must account for the final use of the material. However, as the purpose of the related tests is a scoping evaluation to determine the potential for impurity release, temperatures related to material phase changes are of less significance. Operating temperature of the test cell was maintained at 775°C for the majority of the tests.

For all aspects of related tests, the gas flow rate is maintained at ~1416 sccm and the system has a nominal pressure of ~101325 – 106658Pa (~760 - 800 Torr). To reduce materials with hydrogen, argon is first used to displace residual air from the ambient temperature test cell. After several hours of argon purge, activation activities proceeded. Protium (Air Liquide, 99.9998% H_2) is used to activate the materials. To ensure that the material temperature limits are not exceeded, furnace temperature set points are increased in a stepwise manner (generally with 150 – 175 °C steps). Between steps, conditions are stabilized (by holding temperature constant for 30 min to 1 h) before continuing. In this manner, the temperature is ramped from ambient conditions to 775°C. Upon reaching the desired operating test conditions, the temperature is maintained at 775°C for at least 72 h. At the end of this time, the furnace temperature is increased to 800°C and held for 30 min. The test cell/material is then allowed to cool to room temperature. Once cooled, the hydrogen gas is turned off and argon is then used to displace hydrogen in the test cell.

3.0 Results

Various samples of the nickel-coated ceramic and the sintered iron were prepared for analytical analysis to determine impurity content of both the cleaned and the untreated materials. The samples included virgin materials (either sintered iron and nickel coated ceramic), virgin materials cleaned with Vertrel MCA, and samples which underwent hydrogen reduction while in a 50:50 mixture by volume wherein both the nickel coated ceramic and the iron pellets jointly underwent hydrogen reduction in the same test cell. Tested samples were also analyzed.

3.1 Neutron activation

Neutron activation was used to determine the chlorine content of the samples. Both materials had chlorine contents below 250 ppm before cleaning. The chlorine content of the sintered iron pellets was below the calibrated detection limits of the equipment used for neutron activation. Results are provided in Table 1.

Although cleaning caused the chlorine content of the nickel coated ceramic pellets to drop by 30 ppm the rough surface of this catalyst makes the application of Vertrel MCA less appropriate. Although no liquid was observed, the aroma of the solvent was still present. Neutron activation testing was only performed on the nickel coated ceramic and sintered iron materials which underwent hydrogen reduction in the 50:50 mixture hydrogen reduction test.

Table 1: Neutron Activation Results

Material	Chlorine μg/g
Nickel-Coated Ceramic	
Virgin	170
50:50 Mixture Post Testing	167
Solvent Cleaned	137
Sintered Iron	
Virgin	63.0
50:50 Mixture Post Testing	48.4
Solvent Cleaned	48.0

3.2 Oil-in-solvent analysis

The results for oil-in-solvent analyses show that the surface concentration of both virgin samples was below 100 ppm carbon based on the comparative standard. From one wash, the concentration of the surface carbon impurities was 19 ppm and 43 ppm for the nickel-coated ceramic pieces and sintered iron pellets, respectively. These values are given with a degree of uncertainty as standards were not tested for carbon content below 100 ppm.

It is unclear how effective the Vertrel cleaning method is at removing some hydrocarbons. Two stainless steel tubes, which were used as thermowells, were provided for surface cleaning of both the inner and outer surfaces of the tubing. Results indicate that the 3/8" stainless steel tubing had < 100 ppm carbon. However, as presented in Fig 3, visual inspection shows that the vendor stamp remained on the surface after cleaning. This stamp was easily removed with acetone and manual wiping.

Fig 3: Stainless steel tubing showing vendor stamp after Vertrel MCA cleaning

For the purposes of this test series, the stainless-steel tubing was also subjected to hydrogen reduction prior to contact with the sintered iron pellets to prevent cross-contamination of the sintered iron pellets. The complete test assembly was heated to 775°C in a H_2 reducing environment.

3.3 Carbon/sulfur determination

Sulfur/Carbon determination test results are included in Table 2. Results show the average impurity concentration determined with respective standard deviation using the Microsoft Excel spreadsheet program's built-in *Confidence* function. The 95% confidence intervals of the results from the average impurity concentrations are provided. Confidence intervals are based on the standard deviation of the respective sample populations.

Table 2: Sulfur /Carbon Determination Results

Material	Sulfur, ppm	Carbon, ppm	Sample Size
Nickel-Coated Ceramic			
Virgin Oil-in-Solvent Comparative Result		19	
Virgin	1 ± 2	19 ± 10	8
Solvent Cleaned	1 ± 1	15 ± 4	4
50:50 Mixture Post H_2 Reduction	10 ± 5	8 ± 6	5
Sintered Iron Group A, initial carbon content > 1000 ppm			
Virgin	29	1337	1
Solvent Cleaned	38 ± 13	1471 ± 214	5
Sintered Iron Group B, initial carbon content < 1000 ppm			
Virgin	62 ± 12	358 ± 22	6
Solvent Cleaned	52 ± 19	350 ± 36	6
Sintered Iron Total Population Tested (A & B)			
Virgin Oil-in-Solvent Comparative Result		43	
Virgin	57 ± 17	498 ± 370	7
Solvent Cleaned	45 ± 18	860 ± 602	11
Single Material Solvent Cleaned prior to H_2 Reduction	29 ± 10	7 ± 6	13
50:50 Mixture Post H_2 Reduction	49 ± 13	14 ± 1	3

The sintered pellets did not have uniform carbon content. The carbon content of the sintered iron is an artifact of both the iron powder used to make the pellets as well as the lubricant used during sintering. Two distinct carbon concentration populations were observed which account for the large confidence interval of the post-tested materials. Testing of the carbon and sulfur content of the materials (virgin and Vertrel MCA surface cleaned) indicated that the sintered iron pellets have a small population with carbon content greater than 1000 ppm (Group A in Table 2), whereas the majority of the pellets have a virgin carbon content near 360 ppm (Group B shown in Table 2). Because sulfur concentrations between the two subsets have a comparable order of magnitude, the variable carbon content is likely an artifact of the lubricant used during sintering.

Minimal initial sulfur content was observed for the virgin nickel on ceramic material (1 ± 2 ppm). However, the sintered iron pellets' total population had a sulfur concentration of 57 ± 17 ppm sulfur. It is likely that the sulfur is inherent to the sintered iron because the sulfur concentrations of the virgin and solvent cleaned samples have overlapping confidence intervals.

Evaluation of results from post hydrogen reduction testing of the 50:50 mixture indicates that a portion of the sulfur content of the sintered iron was mobile and transferred to the nickel coated pieces. The sintered iron sulfur concentration dropped, whereas the sulfur concentration of the nickel-coated ceramic pieces increased by ~10 ± 5 ppm for 50:50 mixture test.

The quartz tube provided visual observation of the loss of sulfur and carbon wherein striated layers of yellow and gray-black residue formed on the wall of the test cell as is shown in Fig 4.

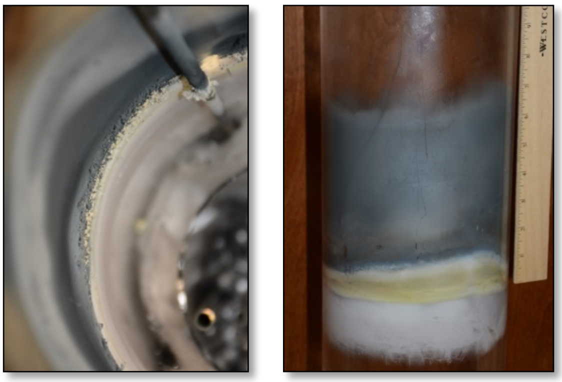

Fig 4: Residue deposited on test cell wall following hydrogen reduction testing; (left) interior and (right) exterior view

Low initial carbon and sulfur content on the virgin nickel on ceramic material (19 ± 10 ppm) was observed. However, the sintered iron pellets had much higher initial carbon content. The cleaned sintered iron material had overlapping confidence intervals with the virgin material indicating that the carbon is inherent. Post testing of the 50:50 mixture sample set indicates that the carbon content reduced for both the nickel on ceramic and sintered iron materials. The nickel on ceramic dropped by ~11 ppm to 8 ± 6 ppm and the sintered iron dropped to only 14 ± 1 ppm for the total population. Sintered iron hydrogen-reduction tests performed without Ni catalyst present showed slightly better final carbon concentration (7 ± 6 ppm) but with a larger confidence interval.

4.0 Conclusions

Since most of the related hydrocarbons of the sintered iron pellets are not surface contaminants, the effectiveness of removing hydrocarbons with Vertrel MCA was limited. Measurements of the effluent of Vertrel cleaning indicate that the carbon content of the catalyst was less than 100 ppm. However, the total carbon content of the sintered iron pellets measured by LECO carbon sulfur determination was far greater. The effectiveness of the initial cleaning by Vertrel MCA for the removal of hydrocarbons from piping and tubing is also a potential area of concern for tritiated processes wherein hydrogen leaching is a potential.

As verified via LECO carbon sulfur determination, hydrogen reduction provides a means to remove bulk impurities. Hydrogen reduction of sintered iron pellets demonstrated the potential to reduce average carbon content by two orders of magnitude (down to 7 ± 6 ppm) and sulfur content by nearly half (down to 29 ± 10 ppm). Visual observations of the quartz tubing used in tests also confirm the value that hydrogen reduction provides for removing impurities.

Because the impurities of the materials can transfer during activation, separately cleaning high impurity containing materials with hydrogen reduction prior to combining them could prove beneficial. The carbon concentration determined from analyzing the Vertrel MCA solution provides order of magnitude differences for the sintered iron pellets. This factor makes using the analysis potentially unsuitable for materials that do not have homogenous compositions or that will likely have impurity migration during operation due to such factors as temperature and hydrogen reduction.

By reducing a material with protium prior to introduction to a tritium gas stream, a carbon source could potentially be eliminated. Thus, tritiated methane production could be prevented. If more than one catalyst is to be used, it is recommended to perform hydrogen reduction of the catalyst independently if impurity migration is possible. This would prevent the transfer of impurities such as sulfur from one material to the other. Some materials may not require the same level of hydrogen reduction because the impurity levels are low and in some cases.

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