

ADAPTED TUBE CLEANING PRACTICES TO REDUCE PARTICULATE CONTAMINATION AT HYDROGEN FUELING STATIONS

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Abstract

The higher rate of component failure and downtime during initial operation in hydrogen stations is not well understood. The National Renewable Energy Laboratory (NREL) has been collecting failed components from retail and research hydrogen fueling stations in California and Colorado and analyzing them using an optical zoom and scanning electron microscope. The results show stainless steel metal particulate contamination. While it is difficult to definitively know the origin of the contaminants, a possible source of the metal particulates is improper tube cleaning practices. To understand the impact of different cleaning procedures, NREL performed an experiment to quantify the particulates introduced from newly cut tubes. The process of tube cutting, threading and bevelling, which is performed most often during station fabrication, is shown to introduce metal contaminants and thus is an area that could benefit from improved cleaning practices. This paper shows how these particulates can be reduced, which could prevent station downtime and costly repair. These results are from the initial phase of a project in which NREL intends to further investigate the sources of particulate contamination in hydrogen stations.

1.0 Introduction

There are more than 30 hydrogen stations installed in California and more will be installed in the coming year [1]. Fuel cell electric vehicle (FCEV) customers depend on hydrogen stations to fuel their vehicles and station availability is critical to customer acceptance and operation success. New stations often experience more problems and have lower reliability [2], [3]. This paper analyzes metal particulate contamination found in field samples from failed parts and identifies tube cutting and conditioning, a process that occurs the most during the station build out, as a possible cause of this contamination.

FCEVs and hydrogen stations require high quality hydrogen fuel to perform efficiently and reliably. The State of California has adopted a fuel quality standard published by SAE International – SAE J2719: Hydrogen Fuel Quality for Fuel Cell Vehicles [4]. Contaminants may be gaseous, solid or liquid and can come from many different sources. Process conditions at a station are challenging. In order to meet customer demands, hydrogen gas flowing through a station must move at high velocity and experience temperatures ranging from -60°C to 200°C and above. The components in the hydrogen station are designed for high quality hydrogen fuel under these conditions. If particulates are introduced to the process stream, they travel with the gas at high velocities and can irreparably damage station components, which leads to station downtime, increased maintenance costs, lost profits and upset customers.

Gas purity is not a new concept and it is certainly not limited to only hydrogen stations. Gas systems that handle oxygen have a high degree of purity mandated by ASTM International in standard ASTM G93. Components, including tubing, are cleaned to the highest level and particulate contamination is not common. Hydrogen fueling stations, however, are governed by SAE J2719, which defines a bulk particulate limit of 1 mg of foreign particulate matter to 1 kg of hydrogen [4] but does not specify a maximum individual particle size. ASTM D7650-13 references a particulate size smaller than 0.2 μm for successful operation [5].

Researchers have performed a collection study in order to better understand the prevalence and composition of particulate matter encountered at forecourt hydrogen stations. In a U.S. Department of Energy fuel quality report [6], the authors summarize efforts and results by Quong and Associates, Smart Chemistry, California Fuel Cell Partnership, and NREL to capture and analyze contaminants collected at the fueling nozzle. These studies found particulate sizes ranging from 10 μm to larger than 1 cm with chemical compositions resembling dirt and metal dross. The report stops short of identifying the source of these particulates. Stations do include filters in the process stream to capture those expected particulates, but NREL has observed the catastrophic filter failure (i.e. shattered filters) that resulted in more particulate contamination. Identification of the particulate source is likely a more effective particulate risk mitigation strategy than filtration systems, because of filter failures and size limitations.

There are numerous pathways for contaminants to enter the hydrogen fuel so station operator awareness is crucial to preventing contamination. Ambient environment, component failure or improper cleaning techniques are three common pathways. Ambient environment particulate contamination such as dust, water or soot can enter the system when building, commissioning or performing maintenance on a station. Component failure may introduce material fragments into the process stream. Improper tube cleaning techniques, which are the focus of this paper, can result in metal shards or lubricant entering the process stream. Contaminants from many of these sources are preventable through consistent implementation of best-practice cleaning techniques for building and maintaining a hydrogen station. This paper will focus ways to reduce metal shards, which have been observed to be very harmful to station components.

Metal-to-metal sealing surfaces are very common at hydrogen stations. 304 and 316 stainless steel tubing are most commonly used for their strength and resistance to hydrogen embrittlement. Tubing in hydrogen stations can be connected using a variety of methods. This paper focuses on a method common to the most prevalent type of hydrogen stations, 70 MPa, where tubes are cut, beveled and threaded using hand tools or machines to form these metal-to-metal seals. The process results in metal shavings and cutting oil debris that can remain in the tubing after installation if not cleaned properly. The metal shavings will damage station components such as filters and elastomers. Additionally, cutting oil generally has high sulfur content, which is known to severely damage polymer electrolyte membrane fuel cells in vehicles [6]. Equipment suppliers provide guidance on cutting, beveling and threading of metal pipes, though they emphasize the importance of clean sealing surfaces and threads but not the importance of removing debris and cutting oil from the inside of the tube [7], [8], [9]. The Compressed Gas Association has published G-5.4-2012 Standard for Hydrogen Piping Systems at User Locations [10], wherein general mechanical and chemical cleaning procedures are given. This study will examine the effectiveness of specific cleaning methods to be employed after cutting, threading and beveling metal tubing to reduce the amount of particulate contaminant introduced when fabricating or repairing stations.

2.0 Approach

Data collected by NREL show that retail hydrogen stations experience significant downtime due to unplanned maintenance events. In order to better understand the causes of these events, NREL breaks out events by major station components. The results show that compressors and dispensers are leading categories for maintenance events, a large portion of which result from debris [11]. The types of

failures occurring in these components led NREL to believe that particulate contamination was the culprit, but the source of the particulates was unknown.

2.1 Contaminant Collection Program

NREL began distributing contaminant collection packets to station operators as part of the DOE's component technology validation project. The packets consist of swabs, vials, baggies and a form on which station operators can document the details of the sample collection. When a system failure occurs, or particulates are noticed during maintenance, the station operator collects a sample and mails it to NREL for the contamination to be analyzed.

When a sample is received, NREL first contacts the station operator that submitted the sample to confirm the location and conditions under which the sample was collected. NREL then performs a visual analysis using a microscope. The samples are often small and require magnification up to 1000x. NREL captured digital images from the microscope and used them in the analysis. NREL also performed scanning electron microscopy (SEM) to determine the specific composition of samples.

Samples were compared to show commonality. Samples from four separate stations exhibited a prevalence of 300 series stainless steel particulate matter. There are many 300 series stainless steel components in a hydrogen station, but few are likely to generate fragments of this size. Through experience gained at NREL's Hydrogen Infrastructure Testing and Research Facility, researchers suspected the particles came from tube cutting, threading and beveling.

2.2 Tube Cutting, Threading and Beveling Experiment

To better understand the contribution of tube cutting and conditioning to particulate contamination in hydrogen stations, NREL designed and performed a series of tests in which tubing was cut, conditioned, cleaned and then subject to 2 kg of hydrogen flow filtered at 20 μm . A Teflon filter was placed downstream of the tubing under test to catch any particulates that may come loose. The filters were weighed before and after testing to determine the total mass of particulate deposited. Additionally, Smart Chemistry performed microscopic analysis to determine the number and size of the collected particulates.

NREL staff cut, threaded and beveled a total of 18, 316 stainless steel tubes—nine 10-inch segments of 3/8" (0.086" wall thickness) and nine 10-inch segments of 9/16" (0.101" wall thickness) outer diameter (OD) tubing. Tubes were cleaned using three different methods: air and rag, tube brush (a.k.a. pigging) and sonication. The air and rag method is the most common and requires the least effort. After cutting and conditioning a piece of tubing, technicians blow 100 psi of compressed air through the tube and may wipe the outside of the tube using a shop rag. NREL replicated this procedure with a third of the tubes. A more advanced method for cleaning the tubing is to use a tube brush. This method involves more effort and can be difficult with long tube runs. It is not common for technicians to use a tube brush when cleaning tubing. NREL confirmed this through conversations with station builders and visits to station sites. On the next third of the tubes, NREL passed the tube brush through and back one time, then applied 100 psi of compressed air to the tube. NREL used a new 1/4" diameter nylon brush (Schaefer Brush 43702) for the 3/8" OD tubing and a new 3/8" diameter nylon brush (Schaefer Brush 93704) for the 9/16" OD tubing. To obtain a very clean tube to measure against, for the last third of the tubes NREL used sonication at 52°C for 60 minutes, after which the tubes were rinsed in DI water and blown out using dry nitrogen. NREL acknowledges that sonication is unrealistic for commercial construction of hydrogen stations. All samples were sealed in plastic bags to protect from debris until installation.

NREL weighed Pall Life Sciences TF-200 47mm 0.2 μm PTFE membrane filters (P/N 66143) prior to installation in a Millipore filter holder using a calibrated scale with ten microgram resolution in a laboratory environment. Each tube sample was connected between the Millipore filter holder and a WEH TN1 receptacle on NREL's Hydrogen Vehicle Simulator (HyVS). All fittings used were

sonicated prior to installation to ensure any contamination collected would not be from the test set up. NREL's 700 bar hydrogen dispenser was used to dispense the gas at a variable flow rate up to 0.5 kg/min. The mass of hydrogen passed through the test rig was measured with a Coriolis flow meter and using the PVT method on data from the HyVS tanks. The team targeted 2 kg of hydrogen per test, as advised by ASTM D7650. After testing, NREL removed and capped the filter holder apparatus. Disassembly took place in the same laboratory and filters were weighed again using the same scale.

Table 1. Cleaning technique and mass of hydrogen used for each test sample

Test Sample	Tube Size	Cleaning Technique	Mass of H ₂ Flow (kg)
1	3/8"	Air and rag	2.43
2	3/8"	Tube brush	2.36
3	3/8"	Sonication	1.78
4	3/8"	Air and rag	2.34
5	3/8"	Tube brush	2.44
6	3/8"	Sonication	2.44
7	3/8"	Air and rag	2.31
8	3/8"	Tube brush	2.38
9	3/8"	Sonication	2.36
10	9/16"	Air and rag	2.39
11	9/16"	Tube brush	2.34
12	9/16"	Sonication	2.37
13	9/16"	Air and rag	2.38
14	9/16"	Tube brush	2.44
15	9/16"	Sonication	2.60
16	9/16"	Air and rag	2.41
17	9/16"	Tube brush	2.35
18	9/16"	Sonication	2.27

Samples were transported to the Smart Chemistry analytical laboratory where microscopic analysis was used to determine the number and size of particulate matter deposited on the filters.

3.0 Results

3.1 Particulate Collection

This section provides examples of metal particulate contamination from the contaminant collection program at NREL. Samples presented are from retail hydrogen stations and the Hydrogen Infrastructure Testing and Research Facility at NREL. All samples were collected after a component failure occurred.

Magnified images of particulates collected after a compressor failure are shown in Figure 1.

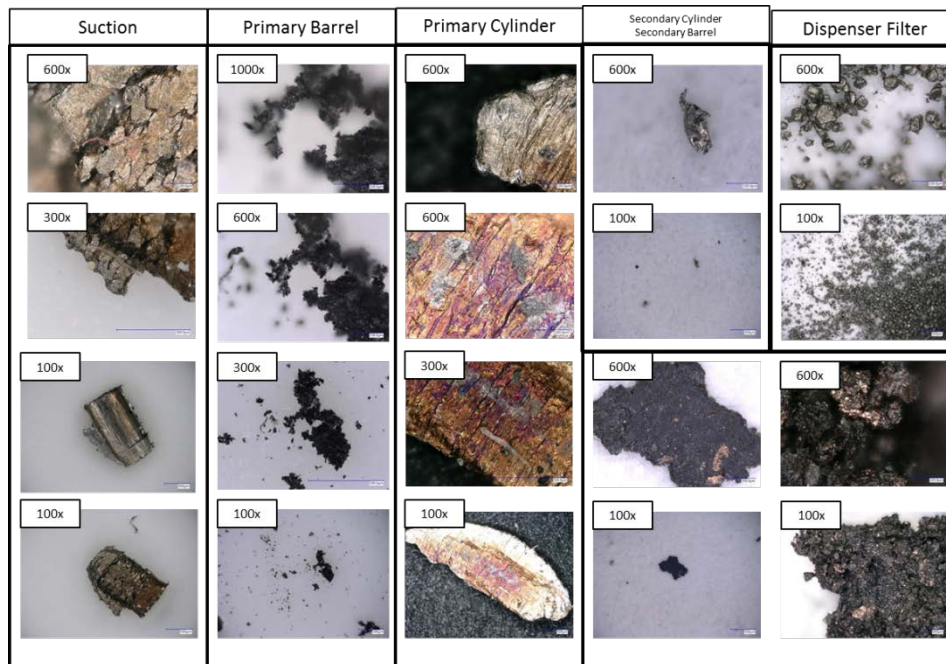


Figure 1. Images of particulates collected from a compressor and dispenser after a compressor failure magnified 100x to 1000x

Metal particulates were found throughout the system along with destroyed elastomers and a failed sintered filter. The metal particulate found in the inlet, or suction, side of the compressor, shown in the first column is about 1 mm by 1.5 mm and resembles half a cylinder. The metal particulate found in the primary cylinder, shown in the third column measures 3.6 mm by 1.3 mm and has discoloration consistent with high heat. Multiple particles were found in the secondary barrel. The particle shown in the fourth column and first row measures 0.25 mm by 0.1 mm and has no discoloration.

NREL analyzed the metallic debris collected from the suction, primary cylinder of the compressor and dispenser filter for chemical composition using SEM. The results showed compositions high in iron, nickel, chromium and molybdenum in the same ratio as 316 stainless steel [12]. The origin of these particles is not known.

In other samples, more metallic particulate was found in a failed check valve (Figure 2), compressor rider band (Figure 3) and valve seat material (Figure 4). The metal debris in Figure 2 appears to be magnetized, yet austenitic stainless steels are typically nonmagnetic. Heat treating and physical deformation, as may take place in a compressor environment, have been shown to magnetize austenitic steels and may be responsible for magnetizing the metal particulates here. Unfortunately, the amount of other material on the sample did not allow for SEM analysis.



Figure 2. Failed check valve from a leaking compressor. Metallic debris is shown in the top left.



Figure 3. Microscopic image of metal impregnated rider band collected from a compressor after a failure.



Figure 4. Microscopic image of a failed valve seat showing metal debris

3.2 Results of Tube Cleaning Testing

NREL compared the mass change of filters, the number of particles and the size of particles across cleaning methods and tubing size. The filters from tubing cleaned with the air and rag method had the highest mass change and highest number of particles, indicating the most contamination. Filters from tubing cleaned with the sonication method had the lowest mass change, indicating the least amount of particles by mass. Filters from the samples cleaned by tube brush had the lowest number of particles. The largest particles were found in the filters from tubing cleaned by the air and rag method. Filters from the 3/8" OD tubing had a higher mass change than filters from the 9/16" OD tubing did. The results were inconclusive for the number of particles collected on filters between 3/8" OD tubing and 9/16" OD tubing. Results for two samples (6 and 8) were thrown out due to an operator error in the testing procedure.

Figure 5 shows the mass difference results for each filter used in the tube tests. The first filters for the 3/8" and 9/16" tubing are outliers. Microscopic analysis showed that the outliers are a result of cutting oil deposition. The standard error in average mass difference across tube cleaning methods was 0.13 mg. Therefore, the air and rag (average = 0.53 mg, median = 0.24 mg) method is definitely worse than the sonication (average = 0.30 mg, median = 0.13 mg) method for mass difference, but within the standard error of the tube brush method (average = 0.11 mg, median = 0.08 mg). The tube brush method is within the standard error of the sonication method for mass difference and therefore not definitively better or worse.

On average the filters from 3/8" OD tubing showed a mass change of 0.56 mg (median = 0.20 mg) and filters from the 9/16" OD tubing showed a mass change of 0.15 mg (median = 0.13 mg), and thus on average the 3/8" OD tubing resulted in more particles than the 9/16" tubing. One explanation for this result could be that because the gas travels at higher velocity through smaller OD tubing for the same flow rate, it picks up larger particles. This effect was discussed in [6].

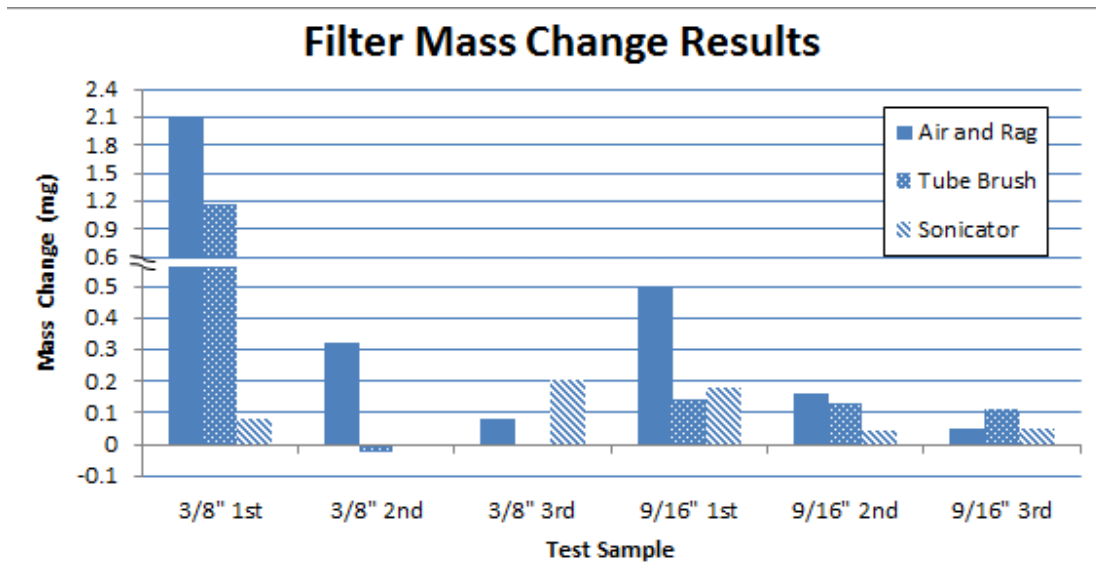


Figure 5. Results of laboratory tube cleaning tests, separated by cleaning procedure. The 2nd Sonicator sample for 3/8" OD and the 3rd Tube Brush for 3/8" OD samples were thrown out due to an operator error during collection.

Microscopic analysis gave the number and size of particles on each filter (Figure 6). With a standard error for the number of particles per filter of 11, the air and rag method (average = 54, median = 31) yielded definitively more particles than either the tube brush (average = 10, median = 8) or sonication methods (average = 22, median = 19) did. The results for the average number of particles between the tube brush and sonication methods were inconclusive. The number of particles collected on filters for the 3/8" OD (average = 19, median = 15) and the 9/16" OD (average = 39, median = 19) show more particles on the 9/16" tubing, but not outside of the standard error.

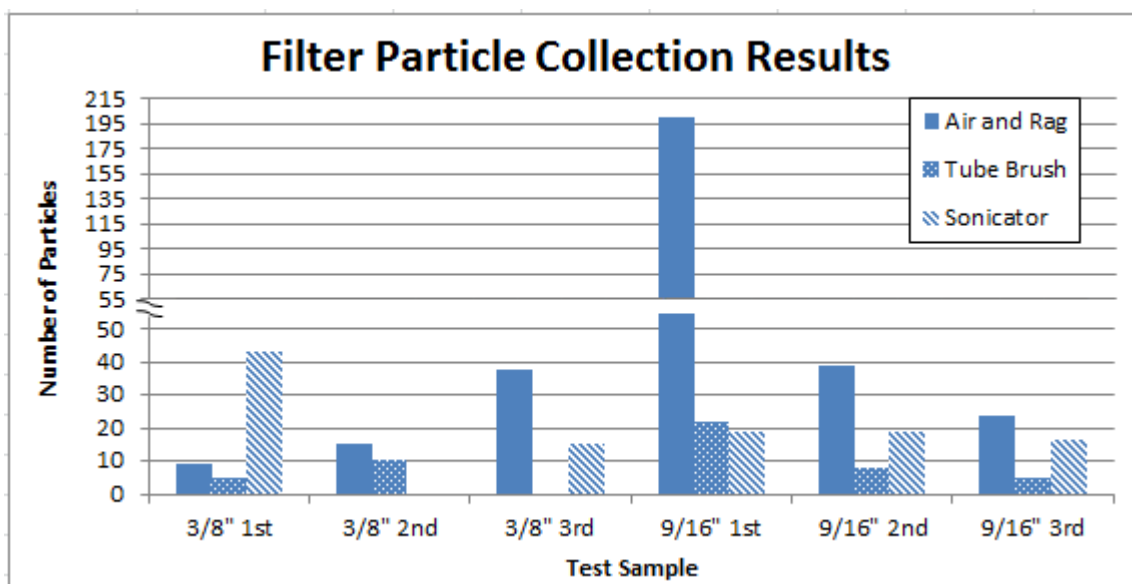


Figure 6. The number of particles collected on each filter, sorted by cleaning method. The 2nd Sonicator sample for 3/8" OD and the 3rd Tube Brush for 3/8" OD samples were thrown out due to an operator error during collection.

The average particle size was 72 μm . The largest three particles found during the study were 1,030 μm , 630 μm and 407 μm , and all three were found in tubing cleaned by the air and rag method. Over

200 particles were found in sample 10, which had the highest filter mass difference of all samples without visible oil deposits.

4.0 Conclusions

This study demonstrated the prevalence of metal particulate contamination in failed components collected from operating hydrogen stations. While the source of these metal particulates is unknown, this paper showed that metal particulate resulting from the tube cutting and condition process is a possible source.

NREL performed an experiment to quantify the amount of particulate contamination that resulted from tube cutting and conditioning after three separate cleaning techniques were employed. The cleaning techniques ranged from the most basic (compressed air and rag), to a simple improvement (tube brush), to an advanced method (sonication). The results showed that

- filters from sonicated tubing had less mass difference than filters from tubing cleaned with the air and rag method,
- using a tube brush instead of the common air and rag method when cleaning a tube can reduce the number and size of particulates,
- the tube brush and the sonication cleaning methods are statistically indistinguishable in reducing the number of particles introduced from tube cutting and conditioning,
- filters from 3/8" OD tubing had a higher mass difference than filters from 9/16" OD tubing and
- the number of particles on the filters were not statistically different for the two tubing sizes.

Regardless of the tubing size or cleaning method, any metal particulate can cause a problem in hydrogen stations or FCEVs, where they may be accelerated to high velocity and destroy filters or prevent a valve from operating properly. The specification for cleanliness of hydrogen dispensed to FCEVs (SAE J2719) specifies a maximum of 1 mg of particulate matter per 1 kg of hydrogen. Hydrogen stations contain tens of these tubes with cuts and conditioning on both sides. Thus it can be seen that particulate contamination from tube cutting and conditioning can result not only in station problems but also in a station dispensing hydrogen that is outside of specification.

This paper is an initial step in a study of identifying the source of particulate contamination and improving station cleanliness. Many more samples are necessary to accurately quantify the impacts of tube cutting and conditioning. A better understanding of metal particulate movement in a hydrogen station could also be gained by introducing bends, valves and filters into the test rig. NREL also acknowledges the aggregation of particulates caused by excess vacuum grease applies to elastomers in hydrogen service [13]. Pending more results, improved tube cleaning procedures could have significant impacts on the reliability of hydrogen stations.

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