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Evaluation of Alternate Stainless Steel Surface Passivation Methods (U)

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The WSRC Team: Westinghouse Savannah River Company LLC • Bechtel Savannah River, Inc • BNFL Savannah River Corporation
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STRATEGIC MATERIALS TECHNOLOGY DEPARTMENT

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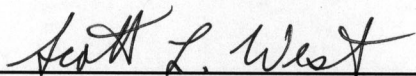
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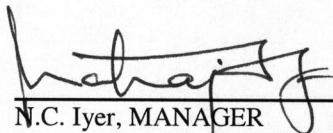
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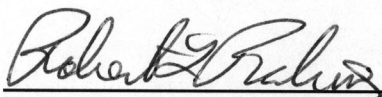
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31 May 2005

SUMMARY

Stainless steel containers were assembled from parts passivated by four commercial vendors using three passivation methods. The performance of these containers in storing hydrogen isotope mixtures was evaluated by monitoring the composition of initially 50% H₂ 50% D₂ gas with time using mass spectroscopy. Commercial passivation by electropolishing appears to result in surfaces that do not catalyze hydrogen isotope exchange. This method of surface passivation shows promise for tritium service, and should be studied further and considered for use. On the other hand, nitric acid passivation and citric acid passivation may not result in surfaces that do not catalyze the isotope exchange reaction $H_2 + D_2 \rightarrow 2HD$. These methods should not be considered to replace the proprietary passivation processes of the two current vendors used at the Savannah River Site Tritium Facility.

INTRODUCTION

The materials of choice for tritium gas processing systems are one of several austenitic stainless steel alloys, such as Types 304L, 316L, and 347. These alloys provide a combination of desirable properties for tritium systems: resistance to hydrogen embrittlement, general corrosion resistance, good toughness, fairly low hydrogen isotope diffusion rates, good strength and ductility, and a wide range of service temperature (cryogenic to 700 degrees F. and higher). These alloys are readily available, and the “wetted” parts (those contacting the process gas) of many common commercially available gas processing components such as pressure and temperature sensors, valves, fittings, and pumps are fabricated from them. Also, these materials have an excellent record of acceptance by industry: they are specified in many codes and standards, quality assurance processes are established for their manufacture, and they are used widely in the chemical processing and nuclear industries because of their desirable properties.

Because of the strict purity requirements of the product gas, it is vital to keep the tritium process at the Savannah River Site clean. Normally, when pipe, tubing, and all other processing system components are fabricated for or at the Savannah River Site Tritium Facilities, the surfaces of these components are cleaned (by various methods) and inspected for cleanliness [1]. Components procured for installation are similarly cleaned and inspected. Typical agents that are removed by cleaning include oil and grease common to stainless steel fabrication and dust and dirt from many sources. The purpose of cleaning is to remove foreign matter, and not specifically to alter the surface of the stainless steel component that is exposed to the tritium process gas (the “wetted” surface).

There are specific stainless steel components and tubing in the tritium process that when procured undergo a “passivation” surface treatment, to alter the properties of the surface. The purpose of the surface treatment is either to prevent hydrogen isotope exchange catalyzed by the stainless steel surface, or to block chemical impurities from the stainless steel itself from contaminating the process gas. An example of isotope exchange catalyzed by the surface is



An example of chemical contamination is the formation of methane from carbon dissolved in the stainless steel reacting with hydrogen isotopes in the gas stream. Components treated by surface passivation include i) tubing leading from sample points in the process to mass spectroscopy systems (to monitor gas composition), ii) the inlet manifolds and systems for these mass spectrometers, and iii) hydrogen isotope calibration standard containers. Historically and currently, this so-called “passivation” process is performed by one of two specific vendors. Both vendors’ processing is proprietary, although there is the general understanding that both treatments involve electropolishing the surface and a high temperature thermal treatment to remove hydrogen (protium) from the steel. An unpublished study performed by D. Blankenship of SRNL using Auger Electron Spectroscopy verified the information on one vendor’s web site that the chromium concentration within about 5-8 nm of the surface of passivated coupons was significantly higher than the bulk concentration.

The terminology related to passivation of stainless steel surfaces is confusing [2, 3, 4]. The definition of a stainless steel is an iron-base alloy having a minimum chromium content of 11% (by weight). This amount of chromium causes a so-called passive chromium-rich oxide surface film to form on the surface when exposed to oxidizing environments, such as air or water. It is this chromium-rich oxide passive film that protects stainless steels from aqueous corrosion. The family of austenitic stainless steels that is used in tritium systems is termed “18-8” stainless steel (including Types 304L, 316L, and 347 above), meaning that the chromium content is about 18% and the nickel content is about 8%. The additional chromium over the minimum 11% for these alloys has evolved over time to ensure that a sufficient chromium-rich passive film exists over the entire surface, including microstructural inhomogeneities such as grain and twin boundaries and slip bands that intersect the surface. So, any stainless steel exposed to air has a “passive” surface layer because of its chemical composition.

When 18-8 stainless steels are formed by cold working, impurities from rolling mills are impregnated into the surface. These impurities compromise the corrosion resistance of the surface, by forming local galvanic cells with the passive film. A common impurity is called “Free iron”, which results from previous rolling of carbon steel on the same mill (and other sources). Over the years, so-called chemical passivation treatments [4, 5] have been developed to treat the surface of stainless steels to remove these impurities and so to maximize corrosion resistance. There are a number of specific recipes based on nitric acid and a number based on citric acid [5]. Typical recipes are 20% to 40% HNO₃ at 50° to 60° C. for 20- 30 minutes, and 4% to 10% citric acid at 50° to 60° C. for 10 minutes. For both nitric acid and citric acid passivation, degreasing before the acid treatment, and neutralizing and rinsing after the acid treatment is very important. Citric acid passivation is relatively new, and is used increasingly for the food processing industry. Stainless steels can also be passivated by electropolishing [6]. In addition to removing any free iron, this method polishes the surface, which passivation by nitric acid or citric acid does not do.

Defense Programs considers both vendors of surface passivation to be at risk with respect to long term supply. Both are small companies, and one is almost a one man operation, with that man clearly at retirement age. From the expansion of semiconductor fabrication systems made of stainless steel in recent years, standard stainless steel surface treatment vendors have become much more numerous. The approach for this study, that was proposed and accepted as a Plant Manager Directed Research and Development funded task, was to find several commercial vendors who could passivate stainless steel parts by the standard nitric acid, citric acid, and electropolishing methods. The parts were chosen to form gas sample containers, and the surface treatments were evaluated by monitoring the H₂, D₂, and especially the HD content, using mass spectroscopy, of the containers after filling with a nominal 50% H₂ 50% D₂ mixture. The efficacy of different surface passivation methods was monitored by the effect on isotope exchange (Eq. 1 above).

EXPERIMENTAL PROGRAM

The literature indicated that passivating stainless steel by three general methods, nitric acid, citric acid, and electropolishing, is widely available and standard in industry. Based on this literature review, these three methods were chosen for study. Four vendors that could passivate parts by all three methods were chosen to surface treat parts for this study.

Sample Gas Container Passivation Treatment and Assembly

Stainless steel gas containers were designed to be assembled from stock Swagelok® company parts (Table I). The valves were disassembled, and the valve body, 25 cc gas cylinder, and reducer body were numbered such that each vendor could process each set of parts the same way, and the parts could be assembled into a gas sample container having the same type of surface treatment on all stainless steel surfaces. (The Swagelok® ferrules used to seal the parts together were not passivated, and the valve stem tip was also not passivated. The valve stem tips appeared to have the shiny appearance typical of electropolishing.) Three sets of parts were sent to each of four vendors. Each vendor passivated each set by one method (nitric acid, citric acid, and electropolish). No other instructions were given other than to passivate the parts per ASTM A-380, ASTM A-967, or ASTM B-912 as applicable. Thus, other than the generic terms “nitric acid”, “citric acid”, and “electropolish”, no other details about the treatments are known. The electropolished parts obviously had an altered, shiny surface finish (Fig. 1).

Part	Swagelok® Number
Miniature Sample Cylinder, 25 cc	SS-4CS-TW-25
Valve	SS-4BG-SC11
Plated Gaskets for Valve (to reassemble after passivating body)	SS-4BGO-K5-SV
Reducer	SS-600-R-4

Table I. Parts used for each sample gas container

When returned, the valves were reassembled, and the valves, reducers, and containers were in turn assembled into gas sample containers (Fig. 2). The Instrumentation and Examination Section leak tested each assembled container, and verified that the leak rate of helium out of the containers was less than 1×10^{-8} std cc He/s, which is the standard leak rate required for components in tritium service. Most measured leak rates were about 10^{-9} cc/s, for those containers that could be sufficiently tightened. One container could not be made leak tight. After vendor errors and rework, four electropolished, five nitric acid, four citric acid, and two untreated gas sample containers were evaluated.

Loading Containers with Hydrogen Isotopes

The containers were loaded with nominally 50% H₂ and 50% D₂ on the Hydride Test Manifold maintained by the Hydrogen Technology Section of SRNL. The sample gas containers were attached to the manifold in groups of three and evacuated. Three copper heater blocks were machined from round bar, each having a hole just large enough to accommodate the 25 cc cylinders. Two thermocouple wells were machined along the length of each copper heater block. Resistance heaters were clamped to the outside of the copper heater blocks, and the cylinder part of each sample gas container was heated to 125° C. while being evacuated for about 24 hours. This vacuum bakeout is used to initially clean isotope standard containers in the Tritium Facility, and was performed in this study to mimic Tritium Facility procedures as closely as possible.

After cooling to room temperature, each group of three cylinders was loaded with nominally 50% H₂ and 50% D₂ to a total pressure of nominally 1 atm (Table II). A 1 liter calibrated volume on the manifold was filled first with protium and then with deuterium to sufficient pressure (about 1200 torr) so that the nominally 50%-50% mixture was first used to flush each group of three sample containers twice (fill to the pressure in the calibrated volume and then evacuate) and then finally the group of three sample containers was filled with the gas mixture for evaluation. A separate sample container was also filled with the same gas; this container was brought to the Hydrogen Technology Section gas mass spectrometer for analysis of the initial fill for each loading group.

Gas from each sample container was sampled periodically and analyzed using the Hydrogen Technology Section mass spectrometer (Balzers Model GAM-400). Besides reporting quantitative results for % H₂, % D₂, and % HD, a general scan was made to detect other species if present through mass 60.

<u>Vessel No.</u>	<u>Surface Treatment</u>	<u>Loading Group</u>	<u>Load Pressure (Torr)</u>
1	Citric	E	713
3	Electropolish	E	713
4	Electropolish	A	714
6	Electropolish	B	719
6a	Electropolish	Refill of 6	822
7	Nitric	C	1121
8	As received	A	714
10	Electropolish	C	1121
11	Nitric	B	719
12	Citric	C	1121
13	As received	A	714
18	Citric	B	719
21	Nitric	D	865
22	Citric	D	865
23	Nitric	D	865
24	Nitric	E	713

Table II. Vessel Number, Surface Treatment, Loading Group and Pressure for Sample Containers. Containers in the same Loading Group were initially loaded at the same time.

RESULTS

The HD concentration in two of five nitric-acid-passivated containers and one of four citric-acid-passivated containers significantly increased with time (Figs. 3, 4). None of the four electropolished containers and none of the two as-received (untreated) containers significantly changed HD concentration. The original HD concentration in all the containers was about 0.4 % (Fig. 3), reflecting the HD concentration of the deuterium gas used. Container 6 had to be refilled- the first analysis after about 2 months revealed significantly lower pressure and significant nitrogen and oxygen, indicating air ingress. No evidence of methane formation, or any other hydrocarbon, was observed in any gas analysis.

DISCUSSION

The main result of this study is that commercial nitric acid and citric acid passivation treatments should not be considered for replacing the proprietary vendor passivation treatments for stainless steel at the Savannah River Site Tritium Facilities. The limited number of untreated containers tested does not allow a conclusion to be drawn about whether untreated Swagelok® parts are sufficient to eliminate isotope exchange. Swagelok® parts are cleaned according to a general specification. No special instructions were specified when the parts were procured for this study.

The inertness (absence of HD increase) of all the electropolished containers compared to the nitric acid and citric acid treated containers indicates the possibility that commercial electropolishing treatments may be sufficient to replace the proprietary processes. A study similar to this one using mixtures of deuterium and tritium on commercially electropolished test containers is needed to establish the feasibility of electropolishing.

The influence of the vacuum bakeout (125° C., 24 hours, above) on the results is unknown. The containers were baked out to mimic Tritium Facility practice as much as possible. Vacuum bakeouts are standard practice for high purity vacuum components. Future evaluations of electropolishing should explicitly study this variable as well.

Many materials properties such as grains size, degree of cold work at the surface, residual stress, and the intersection of twin boundaries and slip bands with the surface may contribute to the structure and properties of the passive film. For this reason, future studies of surface passivation by electropolishing should include samples fabricated by several vendors, and perhaps include “home-made” containers. It may be possible to achieve an inert surface by alternate methods other than the traditional electropolishing, for example by a short anneal in air.

CONCLUSIONS

Stainless steel containers assembled from parts passivated by four commercial vendors using three passivation methods were evaluated by monitoring the composition of initially 50% H₂ 50% D₂ gas. The conclusions drawn from this study are:

- 1) Nitric acid passivation and citric acid passivation likely will not result in surfaces that do not catalyze the isotope exchange reaction $H_2 + D_2 \rightarrow 2HD$. These methods should not be considered to replace the proprietary processes of the two current vendors used at the Savannah River Site Tritium Facility.
- 2) Commercial passivation by electropolishing appears to result in surfaces that do not catalyze hydrogen isotope exchange. This method of surface passivation shows promise for tritium service, and should be studied further and considered for use.

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- 5) ASTM Standard A-967 “Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts”, ASTM International, West Conshohocken, Pennsylvania (2001).
- 6) ASTM Standard B-912 “Standard Specification for Passivation of Stainless Steels Using Electropolishing”, ASTM International, West Conshohocken, Pennsylvania (2002).

ACKNOWLEDGEMENTS

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C. Johnson (Analytical Development), N. Wallace (Hydrogen Technology): Mass Spectroscopy

C. Mauldin (Tritium Facilities Laboratory), D. Speed (DP Engineering): Technical Advice



Figure 1. Photograph of untreated container (left) and electropolished container (right). Note lack of writing and shiny surface of electropolish container

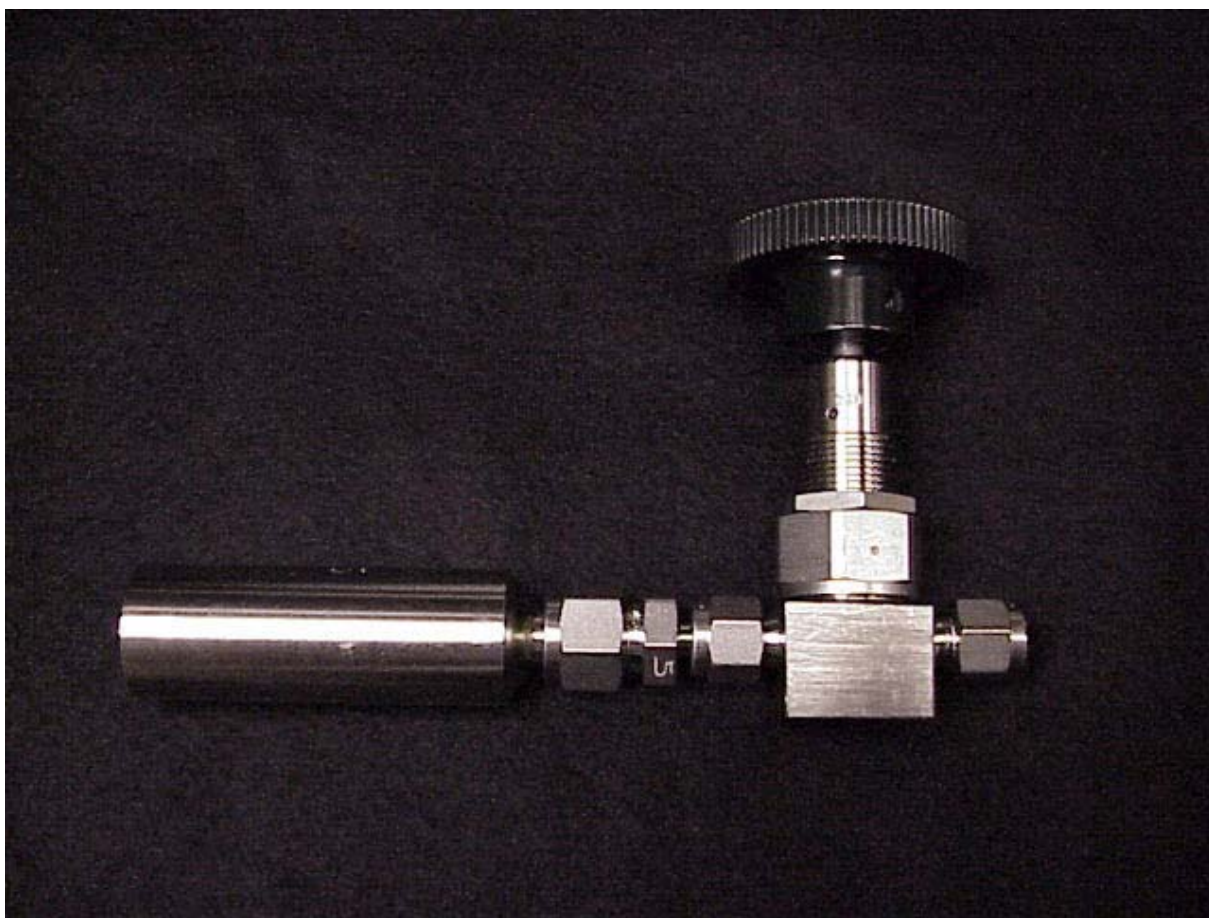


Figure 2. Photograph of Assembled Gas Sample Container. Left to Right: 25 cc Cylinder, reducer, 4 BG type valve.

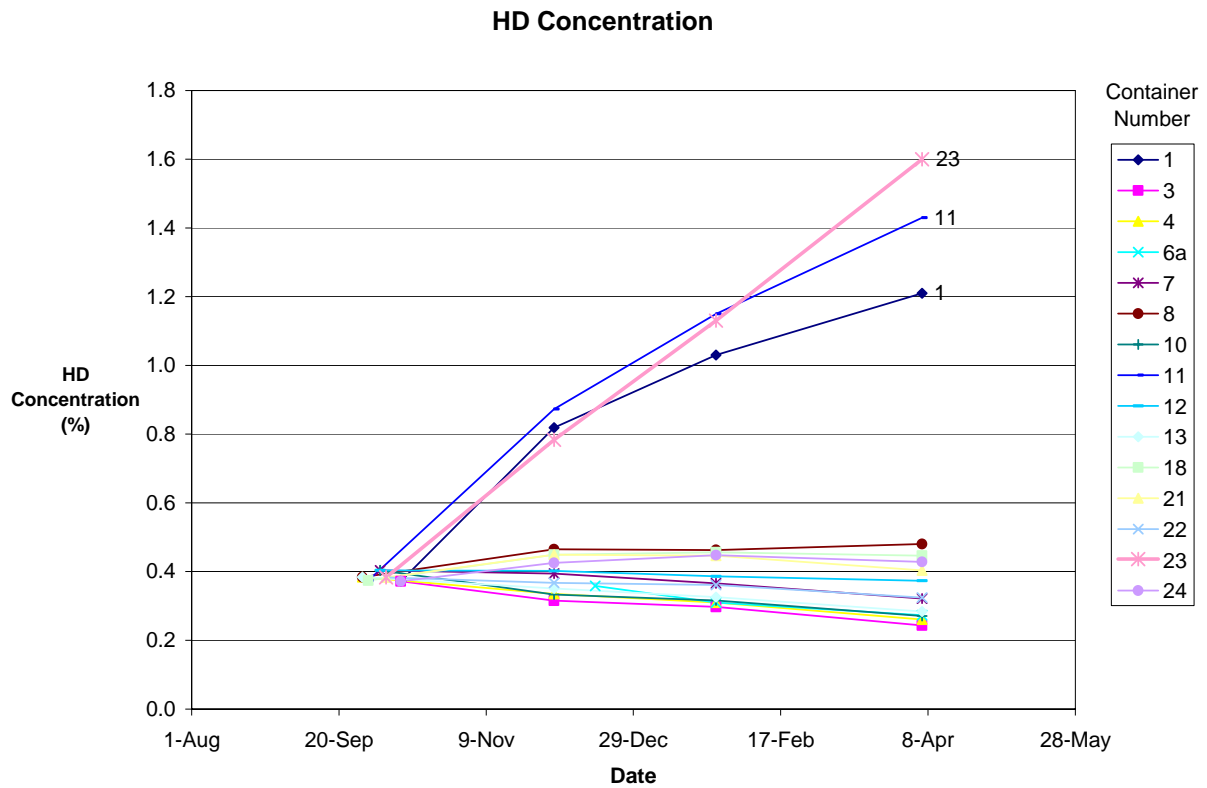


Figure 3. HD Concentration as a function of time for each container. Three containers, #23, #11, and #1, exhibited significant increase of HD with time. See Figure 4 for the same information graphed in a different way.

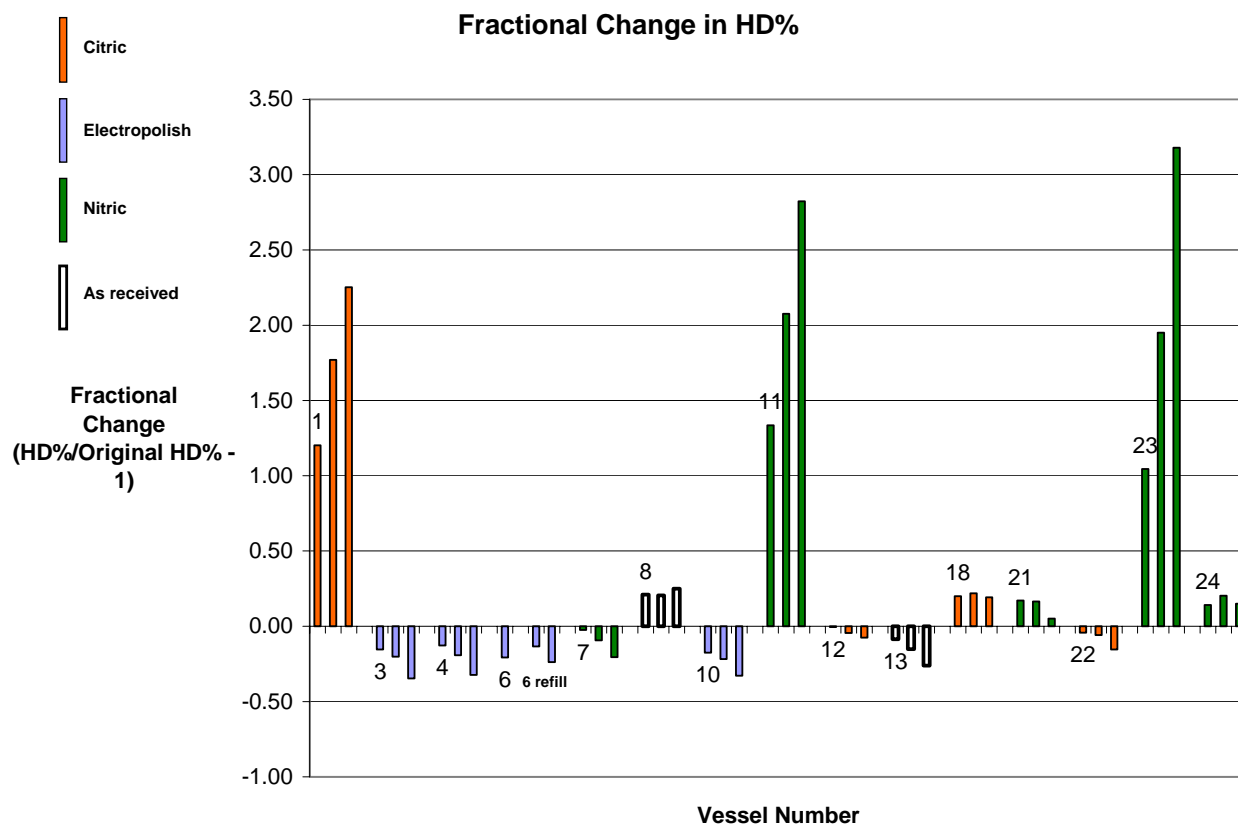


Figure 4. Fractional Change in HD Concentration for each container. Container number for each data set as marked. Note the steady increase in HD concentration for containers #1, #11, and #23. Note a Fractional Change of 1 means twice the original concentration, and a fractional change of 2 means three times the original concentration.