ASTRO PAK®

WHITE PAPER

ULTRAPASS® PASSIVATION EFFICACY ON SANITARY TUBE WELDS

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BACKGROUND

Sanitary tubing is typically made of high quality austenitic stainless steel such as 316L. The interior surfaces are usually electropolished when used in high-purity systems such as those found in the pharmaceutical production and biopharma industries. The systems assembled from the electropolished stainless steel are often made of tubing runs comprised of sections of tubing joined by orbital welds.

Welds are problematic in a high-purity system due to their tendency to corrode faster than the undisturbed electropolished surfaces of the tubing. When the welds corrode, an iron oxide-rich rouge forms on the surface. This iron oxide can become a contaminant in the product carried in the line by dissolution of metals into solution and/or rouge particles detaching from the surface and becoming particulate contamination.

The welds corrode more easily than the undisturbed metal due to heat-induced damage. The heating is necessary to create the weld. The weld itself and the surrounding heat-affected zone (HAZ) have areas of chromium depletion, which is one of the more important changes seen in the weld and HAZ. This chromium depletion is seen as a decrease in the chromium to iron ratio (Cr/Fe) as measured by XPS (ESCA). Chemical passivation attempts to correct the effects of depletion of chromium at the surface of the weld and HAZ. This correction of the chromium to iron ratio is accomplished by the selective removal of iron atoms from the crystalline metal alloy structure, not by the addition of more chromium. The iron is removed on an atomic basis in the upper molecular layers of the metal, with a typical enhancement of the chromium to iron ratio to a depth of 20 – 50 angstroms.

The Astro Pak UltraPass® process will be tested to demonstrate the efficacy of this proprietary chemistry with regard to correction of chromium depletion on welds in 316L sanitary tubing.

TESTING

A supply of electropolished (EP) sanitary tubing was procured. The tubing was sectioned and welded by an orbital welder using inert purge gas during the welding operation. Post welding, the welds were cut into sections and coupons made that were approximately 0.75 inch by 0.75 inch square. The coupons were numbered on the outside surface, and the inner surface used for XPS measurement of the Cr/Fe and the chromium oxide to iron oxide ratio (CrOX/FeOX).

The UltraPass® process is proprietary, and the chemistry and techniques involved will not be disclosed in this document. Forty coupons were passivated using the UltraPass® process, five coupons were passivated separately with nitric acid, with a control group of six coupons that were cleaned but not passivated to provide a baseline measurement for comparison.

After the passivation of the 45 coupons was complete, all 51 coupons were subjected to XPS/ESCA analysis to determine the chromium to iron ratio. The control group and the UltraPass® groups also had the chromium oxide to iron oxide ratios measured. The coupons were sent to Evans Analytical Group (EAG) for XPS/ESCA analysis on the weld areas to determine the Cr/Fe and CrOX/FeOX ratios as an indirect measurement of improvement of corrosion resistance. The data generated at EAG was then analyzed by the Astro Pak Research & Development team to determine if any differences existed in the three groups – one group of six non-passivated controls, one group of 40 passivated by the UltraPass® process, and one group of five passivated with nitric acid as a "gold standard" for comparison. The results of the analysis are presented below.

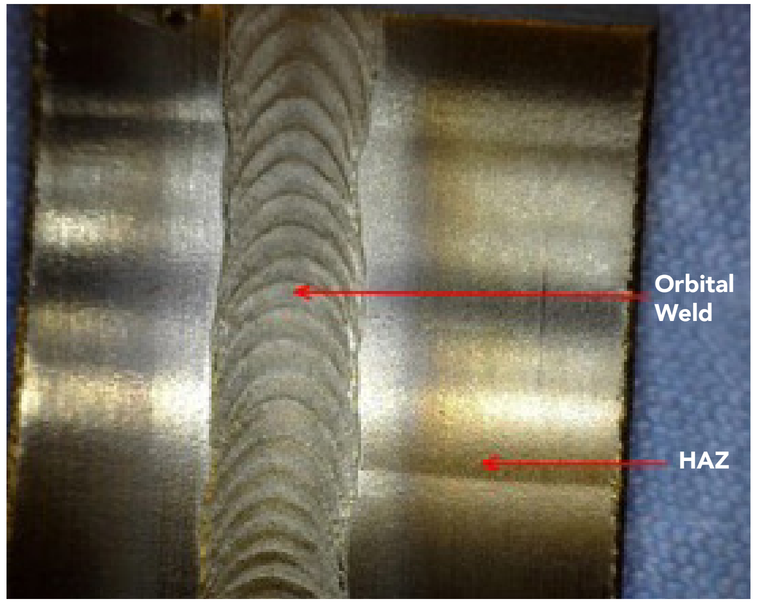


PHOTO 1:
UNTREATED ORBITAL WELD
(shown at 25 X magnification)

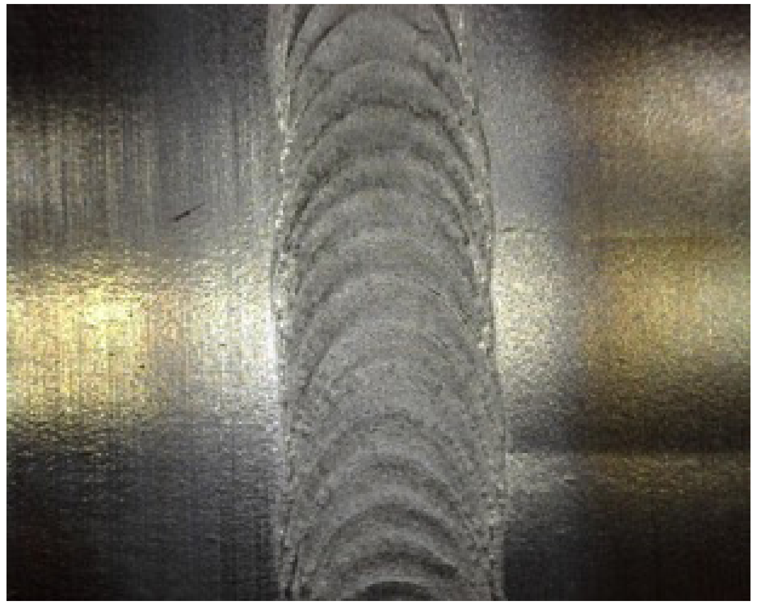


PHOTO 2:
UNTREATED ORBITAL WELD
(shown at 100 X magnification)

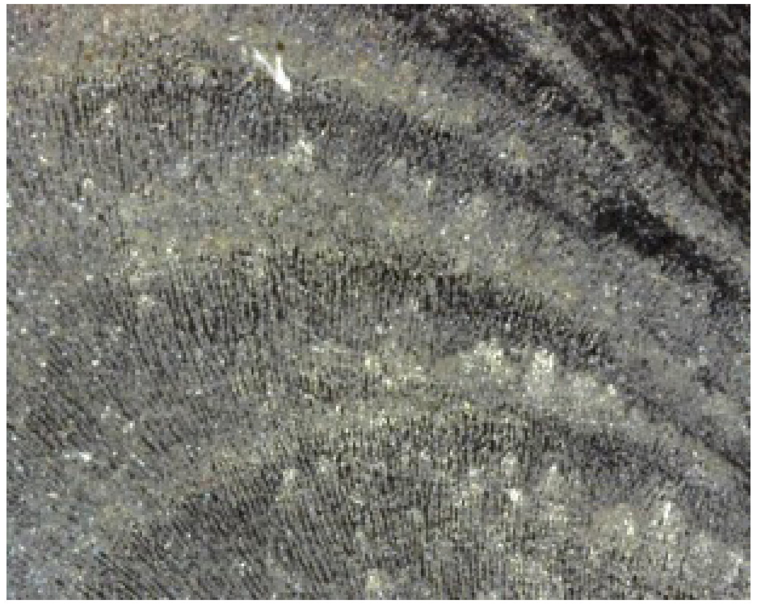


PHOTO 3:
UNTREATED ORBITAL WELD CLOSEUP
(shown at 215 X magnification)

EXPERIMENTAL RESULTS

TABLE 1A: XPS DATA		
CONTROL GROUP *(non passivated)*		
SAMPLE	Cr/Fe	CrOX / FeOX
C1	0.4	0.5
C2	0.4	0.4
C3	0.3	0.4
C4	0.8	1.1
C5	0.4	0.4
C6	0.2	0.2

TABLE 1B: DESCRIPTIVE STATISTICS		
CONTROL GROUP *(non passivated)*		
	Cr/Fe	CrOX / FeOX
Mean	0.417	0.500
Standard Error	0.08333	0.12649
Median	0.400	0.400
Mode	0.400	0.400
Standard Deviation	0.20412	0.30984
Range	0.600	0.900
Minimum	0.200	0.200
Maximum	0.800	1.100

TABLE 2A: XPS DATA	
NITRIC ACID GROUP *(passivated)*	
SAMPLE	Cr/Fe
#1	1.9
#2	2.5
#3	1.9
#4	1.3
#5	2.1

TABLE 2B: DESCRIPTIVE STATISTICS	
NITRIC ACID GROUP *(passivated)*	
SAMPLE	Cr/Fe
Mean	1.957
Standard Error	0.184005
Median	1.949
Mode	N/A
Standard Deviation	0.411447
Range	1.130
Minimum	1.319
Maximum	2.449

TABLE 3A: XPS DATA		
UltraPass® GROUP *(passivated)*		
SAMPLE	Cr/Fe	CrOX / FeOX
#1	2.4	3.3
#2	2.9	4.9
#3	3.3	5.3
#4	4.0	6.0
#5	3.0	4.8
#6	2.6	3.5
#7	2.6	3.6
#8	2.6	3.7
#9	3.5	5.3
#10	2.6	4.3
#11	1.9	3.1
#12	3.1	4.4
#13	2.6	4.2
#14	4.1	6.7
#15	3.5	5.1
#16	2.1	4.6
#17	2.2	4.4
#18	3.6	5.0
#19	4.6	6.5
#20	3.0	4.8

TABLE 3A (cont.): XPS DATA		
UltraPass® GROUP *(passivated)*		
SAMPLE	Cr/Fe	CrOX / FeOX
#21	3.0	5.5
#22	3.0	5.2
#23	3.2	5.5
#24	2.8	5.0
#25	2.8	4.7
#26	4.0	6.0
#27	3.2	5.0
#28	3.2	5.4
#29	3.0	3.8
#30	2.1	4.5
#31	2.1	4.7
#32	2.5	4.8
#33	3.2	5.6
#34	2.2	5.8
#35	2.2	4.6
#36	3.0	5.0
#37	2.4	5.5
#38	2.2	3.6
#39	2.4	4.2
#40	2.0	4.2

TABLE 3B: DESCRIPTIVE STATISTICS		
UltraPass® GROUP *(passivated)*		
	Cr/Fe	CrOX / FeOX
Mean	2.868	4.803
Standard Error	0.10002	0.13284
Median	2.850	4.800
Mode	3.000	5.000
Standard Deviation	0.63261	0.84017
Range	2.700	3.600
Minimum	1.900	3.100
Maximum	4.600	6.700

FIGURE 1: MEAN Cr/Fe & CrOX/FeOX for non passivated CONTROL and UltraPass® GROUPS

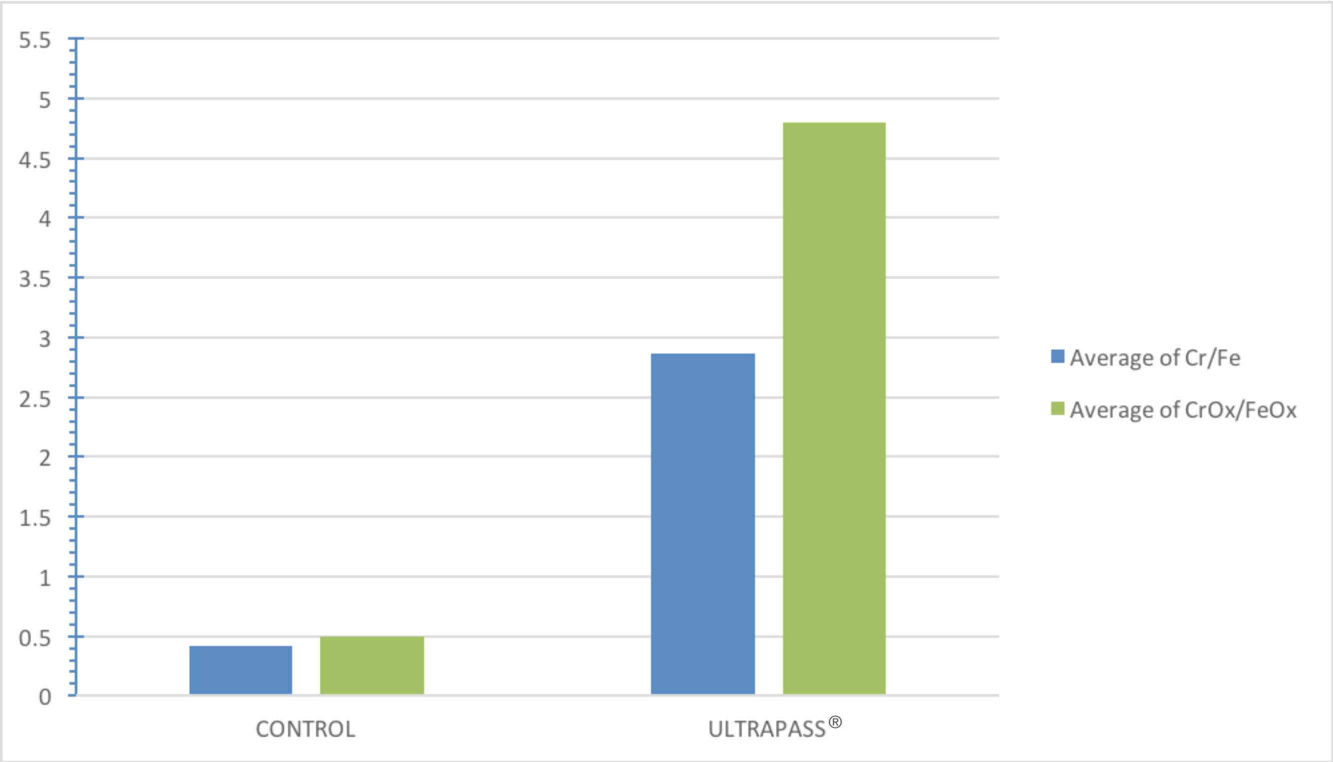
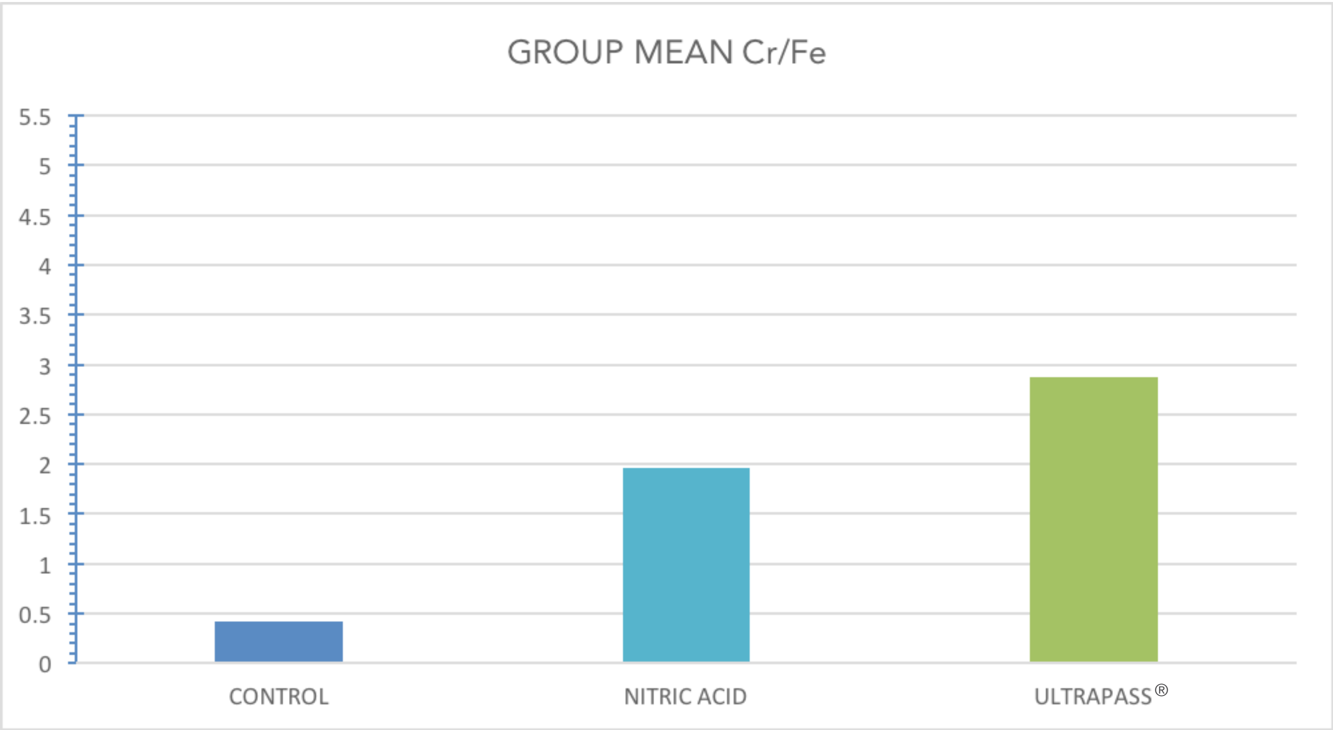


FIGURE 2: MEAN Cr/Fe for non passivated CONTROL, NITRIC ACID, and UltraPass® GROUPS



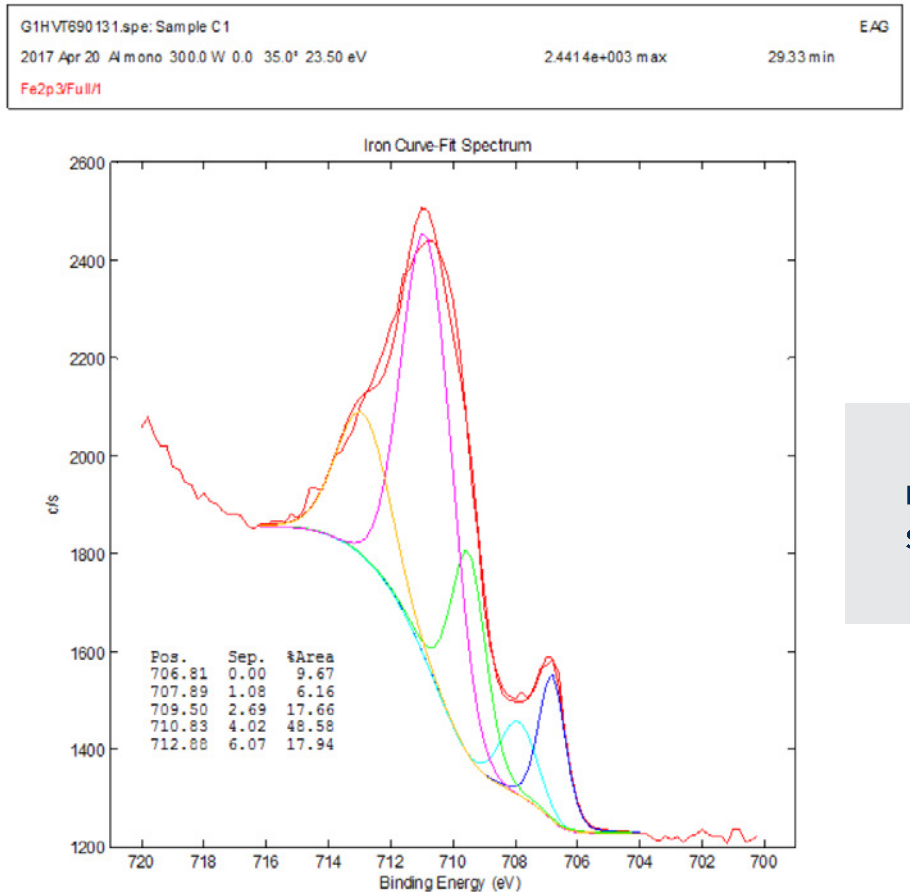


FIGURE 3:
Sample XPS Curve for Fe/FeOX

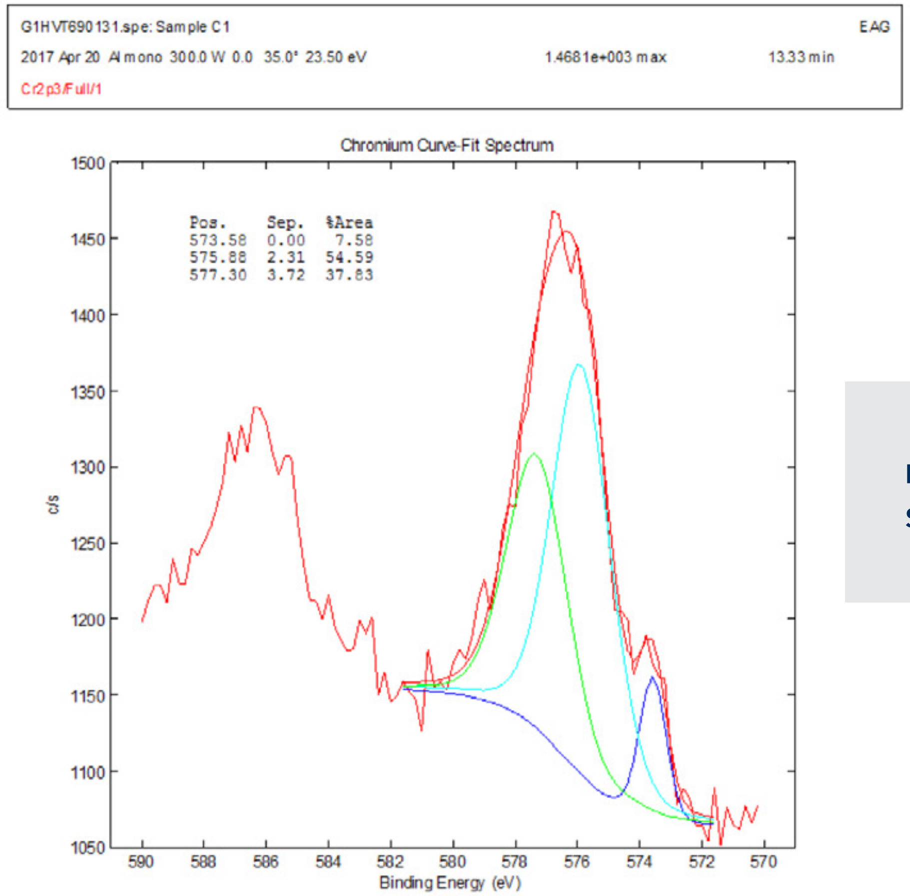


FIGURE 4:
Sample XPS Curve for Cr/CrOX

CONCLUSIONS

All weld samples from the control group (non passivated post welding) failed to meet the ASME BP recommended minimum Cr/Fe of 1.3, establishing the need for passivation.

All samples from the UltraPass® group exceeded the ASME minimum Cr/Fe of 1.3 when measured by XPS / ESCA (as stated in the ASME BPE NONMANDATORY APPENDIX E PASSIVATION PROCEDURE QUALIFICATION Table E-1 Minimum Surface Requirements for Process Qualification Samples). The mean or average Cr/Fe value for the UltraPass® group was 2.87.

The data was analyzed using the independent t-test to determine if the group means were significantly different. The independent t-test (also called the two sample t-test, independent-samples t-test, or Student's t-test) is an inferential statistical test that determines whether there is a statistically significant difference between the means in two unrelated groups. The differences in the group means for Cr/Fe and CrOX/FeOX for the two groups, control and UltraPass®, were highly significant, with values that were well below the generally accepted significance level (also called alpha) of 0.05. The calculated p value for the data which produced the Cr/Fe means was $5.30191E^{-12}$ and for the CrOX/FeOX means the p value was $7.41995E^{-16}$.

A comparison of the mean Cr/Fe produced by nitric acid per ASTM A-967 methodology and that produced by the UltraPass® formulation was also made. The mean value for the Cr/Fe for nitric acid passivated welds was 1.96 versus 2.87 for the UltraPass® passivated group. As the data from this experiment demonstrates, UltraPass® yielded considerably superior Cr/Fe results when compared to nitric acid passivation; however, to reach statistical significance at an alpha of 0.05, a larger sampling of nitric acid passivated coupons will be required.

The UltraPass® process resulted in effective passivation treatment that raised the Cr/Fe above the ASME BP recommended minimum, and raised the CrOX/FeOX as well. The data was statistically significant. The UltraPass® treatment resulted in surface chemistry of welds that was better than untreated samples in terms of the Cr/Fe & CrOX/FeOX as measured by XPS/ESCA.

The UltraPass® formulation also produced superior results when compared to the Cr/Fe produced by nitric acid. The passivated weld surfaces all exceeded the ASME BP recommended minimum Cr/Fe for stainless steel surfaces. As weld surfaces are typically more prone to corrosion when the depleted chromium condition induced by the heat of welding is in an uncorrected state, the UltraPass® chemical passivation process displays efficacy even in a worst-case scenario.

Dr. Brent Ekstrand

serves as Astro Pak Corporation's Vice President of Science & Technology. With over 20 years of experience in the industry, he is the company's primary subject matter expert for precision cleaning, cleanliness evaluation and measurement, cleanroom operations, corrosion remediation and prevention, and biological contamination / biofilm removal. Dr. Ekstrand writes many of Astro Pak's chemical processing procedures and has authored research papers that have been published in industry media such as the UltraPure Water Journal. His experience is extensive and varied. He has served as a member of an Industry Expert contributor panel at NASA Kennedy Space Center, Florida, and has worked with NASA at Jet Propulsion Laboratory in California. He acted as a consultant for the JPL Curiosity Mars rover program, and more recently, as an Independent Peer Review Board member for the upcoming JPL MARS 2020 mission. Dr. Ekstrand has given presentations to a wide variety of audiences, including speaking to the United States Environmental Protection Agency in Washington DC at a conference on halogenated solvent replacement with aqueous-based cleaning processes. Dr. Ekstrand received his doctorate degree from the University of the Pacific in Stockton, California in 1984.