Protection Against Metal Ion Leaching due to Organic Solvent Exposure

Technical Insight

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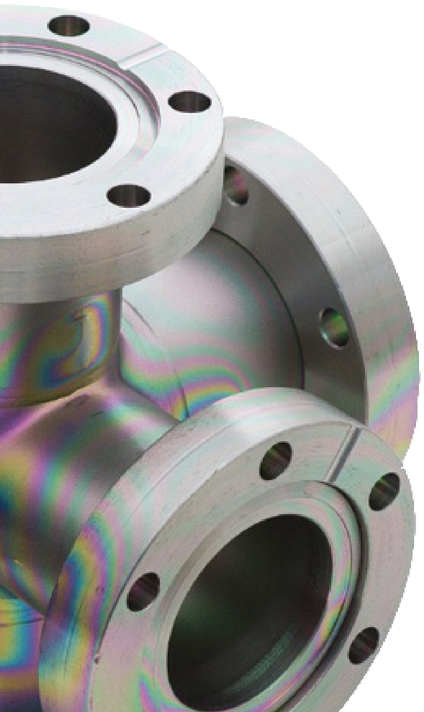

Background

Identifying corrosion of metal substrates is often done by visual inspection with the appearance of rust or monitored by mass changes showing that metal ions are being removed from the substrate. There are times that leaching of metal ions (aka corrosion), for example with neat organic solvents, are far less obvious, requiring a different approach to quantifying this corrosion. It would be valuable to evaluate and prevent this process, as it can have a significant impact on improving certain HPLC experiments.

The corrosion of titanium in the presence of neat methanol has been known since the 60's when NASA found that Ti-6Al-4V (a common titanium alloy) will experience stress-corrosion cracking when exposed to methanol. Since titanium is the metal of choice for many biocompatible HPLC systems, it is critical to eliminate the exposure of the metal components to pure organic solvents. Mauro De Pra of ThermoFisher Scientific presented a talk on this subject at HPLC 2019 in Milan. He showed that titanium ions will migrate from the solvent frits to the silica packing material in the HPLC column. Once there, the titanium ions will react and bind with silanols on the surface of the silica. These immobile ions can cause issues with certain compounds which chelate to them. One such compound is ciprofloxacin, a common antibiotic, which will show significant tailing and peak distortion if run through a titanium contaminated column.

This issue is not limited to titanium. Mel Euerby is currently a scientist with Shimadzu, and he wrote a paper in 1995 while he worked for Fisons Pharmaceuticals (now a part of AstraZeneca) that showed a similar issue can occur with stainless steel. He showed that both acetonitrile and methanol could cause iron ions to leach into the silica bed causing poor peak shapes when running a separation with a metal chelating compound, 2,3-dihydroxynapthalene. He also showed that soaking frits in methanol can extract up to 1µg of total iron, which is not measurable via visual changes nor via mass change with a standard lab balance.

SilcoTek has previously shown that the Dursan coating process can assist with any metal chelating compound separation by providing a barrier layer between the stainless steel substrate and the analytical flow path. This TI will investigate whether Dursan and other SilcoTek coatings can prevent metal ions from leaching into pure organic solvents.

Data and Discussion

Porous metal discs with 10 µm nominal pore sizes were purchased from McMaster Carr. Coatings to be tested were Dursan, Silcolloy, and RD5-SiN. Once the coatings were complete, the coated frits and an uncoated frit were placed individually in polypropylene plastic containers which were filled with 100 mL of HPLC grade methanol and closed. One plastic container was filled with 100 mL of HPLC grade methanol and closed without a sintered disc present to act as a baseline for the experiment. After an exposure time of one month, the sintered discs were removed from the methanol and the samples were delivered to the Energy and Environmental Sustainability Laboratories at Penn State University. Samples were then prepared by evaporating 10 mL of the methanol in a PTFA vial. The remains were dissolved in approximately 5 mL of dilute nitric acid which was then analyzed using a Thermo Fisher iCap RQ ICP-MS. Iron, nickel, and chromium were measured and the results can be found in Table 1.

	Iron	Chromium	Nickel
Blank (no disc)	8.22	0.11	0.26
Bare disc	85.7	3.44	11.0
Dursan	2.34	0.14	0.23
Silcolloy	1.55	0.07	0.22
RD5-SiN	15.2	0.22	1.24

Table 1: ICP-MS results of sintered discs soaked in methanol for one month. All values are in PPB.

The uncoated sintered disc showed a significant increase in the amount of metal ions that have leached into the solution. It should be noted that the metal content in the Dursan and Silcolloy coated discs appear to be lower than the blank, and the RD5-SiN appears to be higher than blank levels. These values may seem odd since it appears that Dursan and Silcolloy have an adsorptive property to them when it comes to some metal ions. Nothing in our previous testing indicates this to be true. Additionally, it suggests that RD5-SiN is the worst barrier to corrosion. This is counter to all other corrosion measurements that we have done to this point which indicate that RD5-SiN is currently the champion coating at SilcoTek for corrosion.

It is important to keep in mind two things when considering these numbers. First, the sample preparation process was not perfect. Used glassware, a non-cleanroom environment, and sample transfer could all lead to minor variances in metal ion contaminants. Second, the level of metal contamination is low enough that sample to sample variation is just noise in the experiment. All three coatings are close enough to the blank's level of metal ions to say that the coating was successful in blocking metal ions from leaching into the solution. A bare stainless steel disc created at least an order of magnitude greater metal signal in all three elements of interest after the one month immersion time in methanol.

Conclusion

Over the course of a one-month immersion in pure methanol, a stainless steel sintered disc contaminates the methanol with about 80 ppb of iron, 3 ppb of chromium, and 10 ppb of nickel. These values are only semi-quantitative as sample preparation may lead to minor contaminations. Applying a CVD coating to the metal samples creates a sufficient barrier to stop the metal ion leaching into the solvent. Since methanol causes ion leaching to a greater extent with titanium substrates, it is worthwhile to repeat this experiment with a titanium substrate rather than stainless steel. These results also show that repeating Mel Euerby's experiments will be of interest to the HPLC community. The ability to maintain the mechanical robustness of metal components, but have a metal-free analytical flow path is a game changing technology for the liquid chromatography community.

Protection Against Metal Ion Leaching due to Organic Solvent Exposure:
Titanium and Stainless Steel Re-examination

Technical Insight

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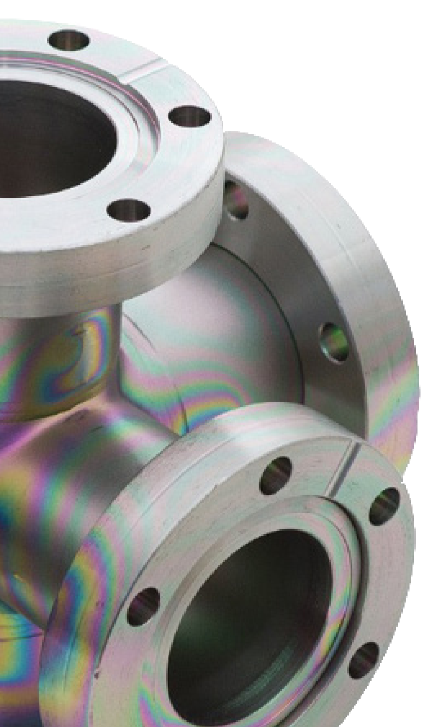

Background

A previous Technical Insight discussed the issues involved with using pure organic solvent in contact with metal alloys such as stainless steel and titanium. In that study, 316 SS sintered discs were exposed to pure methanol for one month. The resulting solution was then examined via ICP-MS for metal ions contamination. The results showed that Silcolloy®, Dursan®, and RD5-SiN were all suitable coatings to protect the substrate from the methanol. In this study titanium is investigated as a substrate for SilcoTek's coatings. Titanium is commonly used as an alternative to stainless steel due to it being lighter, strong, and biocompatible. We find that Silcolloy performs well as a barrier, but Dursan and RD5-SiN do not provide adequate protection.

Data and Discussion

Porous grade 2 titanium discs with 10 µm nominal pore sizes were purchased from VICI Precision Sampling. They were coated with Dursan, Silcolloy, and RD5-SiN. After coating, the frits were placed in 50 mL of HPLC grade methanol and sealed. An uncoated disc as well as a container with no frit were also filled with methanol and sealed to act as a baseline and a blank. After one month of soak time, the porous disks were removed from the methanol and the samples were delivered to the Energy and Environmental Sustainability Laboratories at Penn State University. Samples were then prepared by evaporating 10 mL of the methanol in a PTFA vial. The remains were dissolved in mL of dilute nitric acid which was then analyzed using a Thermo Fisher iCap RQ ICP-MS.

Figure 1 shows the detected titanium from the solution of each container. The blank represents how much titanium was in the methanol bottle. The bare disc represents how much titanium is leached into the methanol without any processing at SilcoTek Corporation.

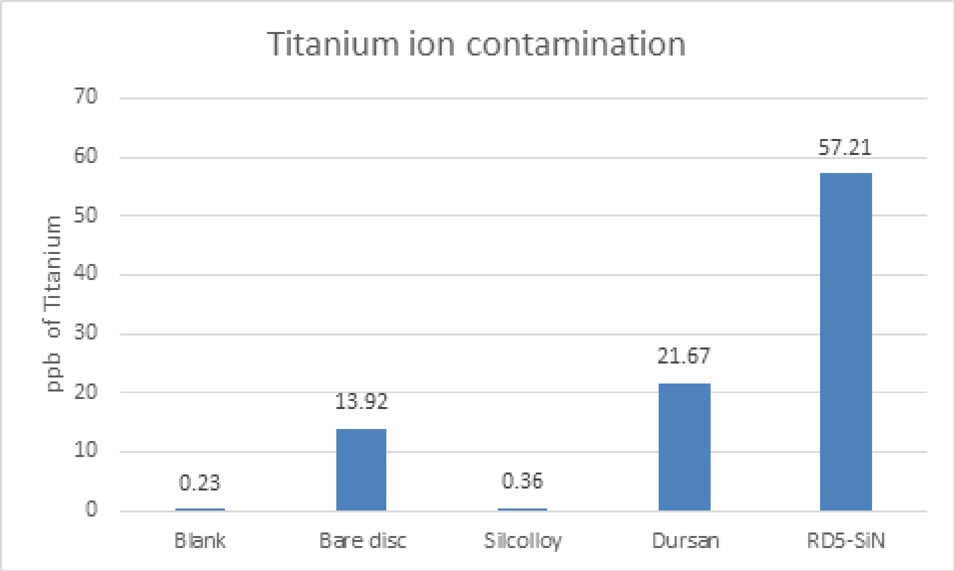

Figure 1: ICP-MS results of the methanol solution after one month of soaking.

Silcolloy provides adequate protection to the titanium substrate from the methanol solution. It is nearly at baseline levels of titanium. The Dursan and RD5-SiN samples show significant titanium contamination of the methanol solution. This is likely due to the oxidative resistance of Silcolloy. Titanium is highly susceptible to oxidation, especially at high temperatures. Part of the Dursan and RD5-SiN processes, there are oxidations steps that are performed to create a more stable coating. These oxidation steps are performed at high temperatures and likely cause titanium, an element that is well known for diffusion at high temperatures, to come to the surface of the coating and become available to dissolve into the methanol during the soak. RD5-SiN is oxidized at a much higher temperature than Dursan. This causes a higher amount of titanium to diffuse through the coating.

As a part of this study, stainless steel discs were also tested as a follow up experiment to a previous Technical Insight. Figure 2 and 3 show the results from the previous study and this study, respectively.

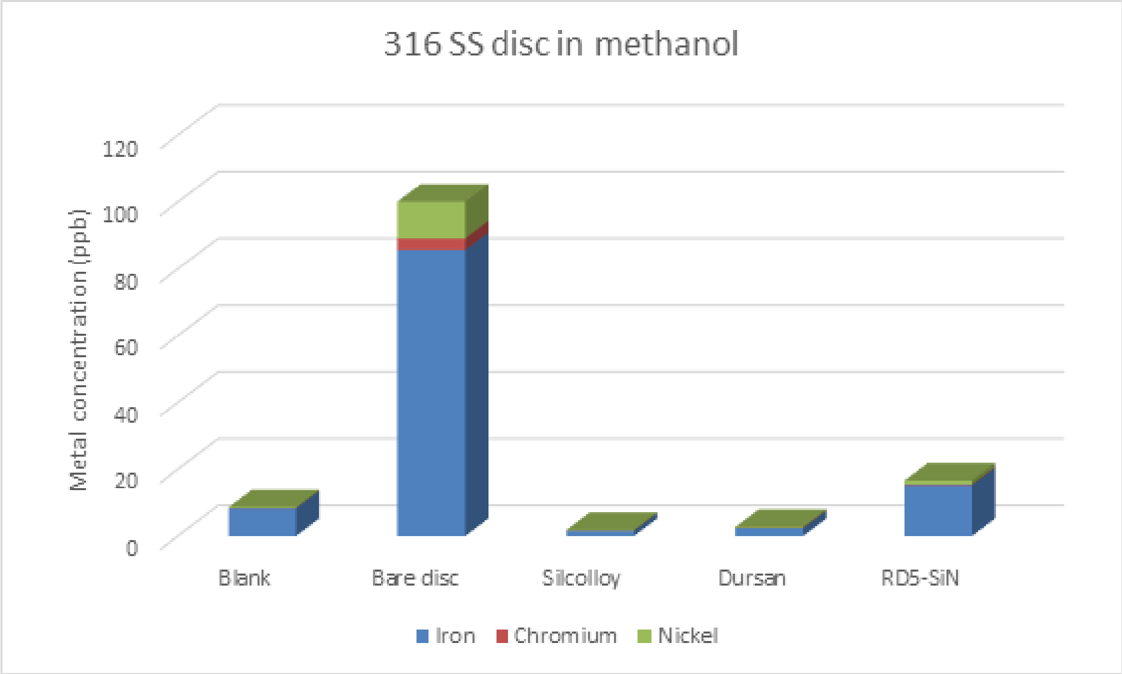

Figure 2: 316 stainless steel porous disc soaked in methanol for 1 month from TI 08-23-19.

It was noted in that TI, sample preparation may have been an issue causing contamination in the blank and RD5 samples. It seemed highly unlikely that Silcolloy and Dursan would have significantly lower concentrations of metals in the solution than the blank, which was run without any disc in the solution. Upon re-examination with more care taken in sample preparation (fresh gloves between samples and more care in resealing the containers after opening), the values look more reasonable as seen in Figure 3.

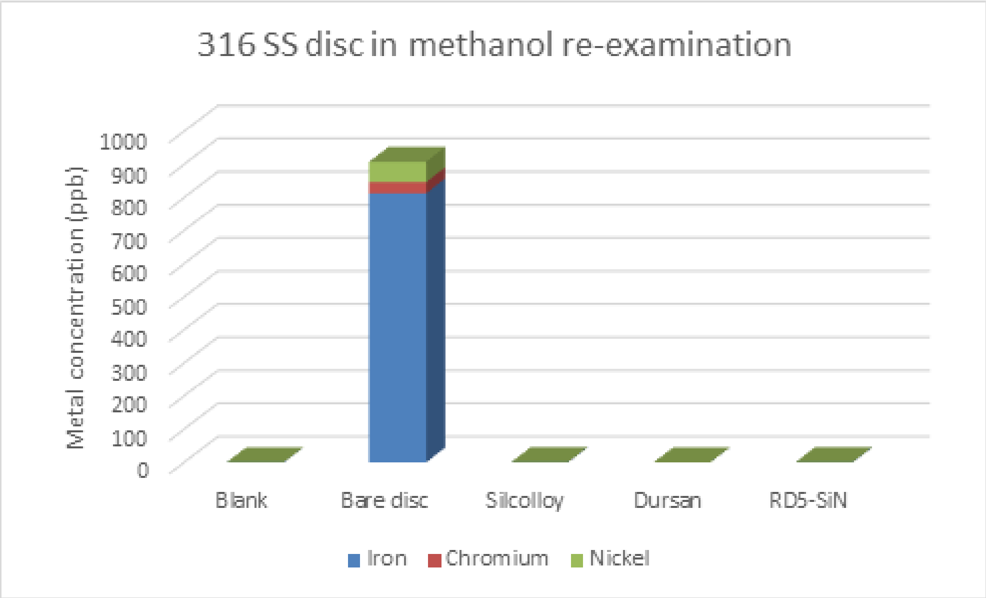

Figure 3: 316 stainless steel porous disc soaked in methanol for 1 month with more care taken in sample preparation.

It is unclear as to why the bare disc in this study is an order of magnitude higher in total metal leaching into the methanol, compared to the original data illustrated in Figure 2. Some things that may affect this are things like temperature of the lab through the test, perturbation of the sealed containers during the 1-month exposure, variation in disc substrate or quality (see here for an example), or some other overlooked factor.

Due to the bare disc total metal value being so high, Figure 4 shows the blank solution as compared to the three coated discs. It should be noted that these values are very close to the detection limits of the ICP-MS for these elements (0.1-0.5 ppb) and are significantly lower than the total metal contamination from the uncoated disc, 908 ppb.

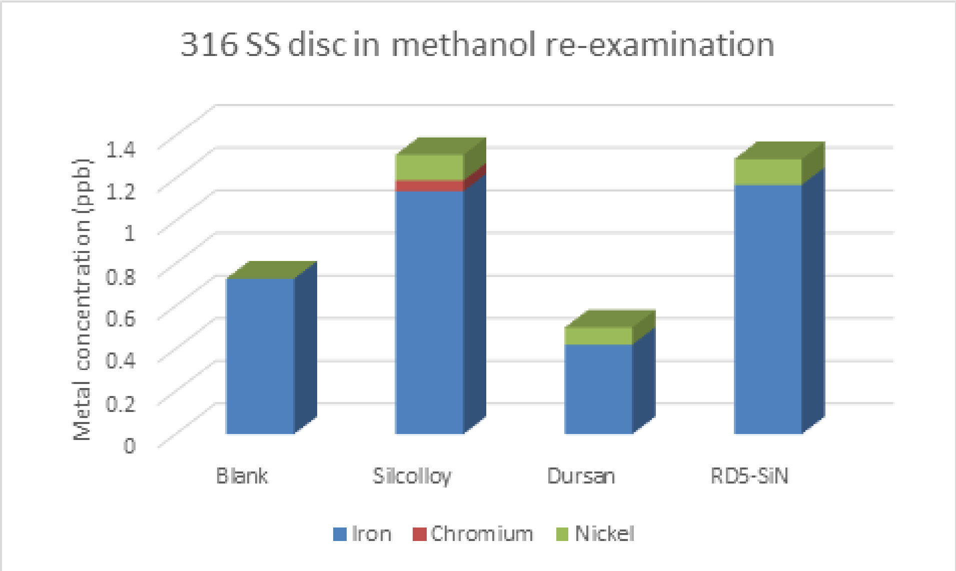

Figure 4: Stainless steel data without the bare disc for comparative purposes. The values are close enough to the blank to consider the metal ion contamination to be zero.

Conclusion

Silcolloy provides great protection of titanium substrates from organic solvent attack of the underlying substrate. Dursan and RD5-SiN do not provide the same benefit as the high temperature oxidation step in both coatings likely cause diffusion of the titanium into the coating which can then be dissolved easily into the methanol when soaking. All three coatings are capable of providing the necessary protection for stainless steel.

Metal ion leaching study in pure methanol part 3: C-22 Hastelloy

Technical Insight

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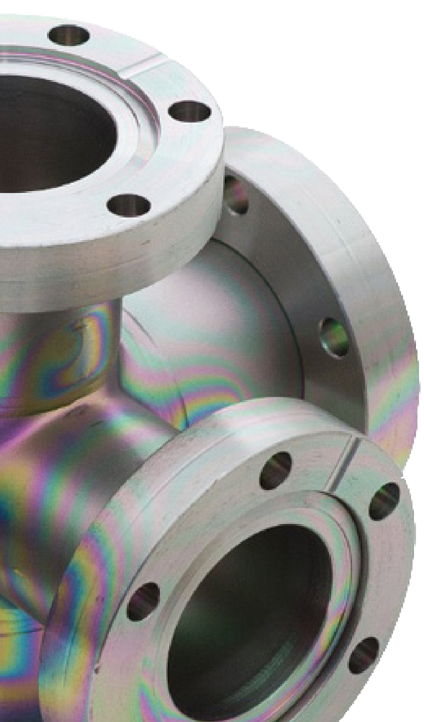
Synopsis

Corrosion encompasses a large variety of material degradation. It can be large enough to see visually such as the numerous examples in harsh acids or salt fog chamber experiments that SilcoTek has performed, or corrosion can be at trace levels that are not detected visually or by weight loss. We previously investigated both Titanium and 316 Stainless Steel in pure methanol and monitored their corrosion via ICP-MS. Exotic alloys, such as Hastelloy, are often used for harsh corrosion conditions. In this TI we investigate the corrosion of C-22 in pure methanol and the impact that SilcoTek's coating portfolio can have on this corrosion.

Background

Two previous Technical Insights (seen here for the initial study of stainless steel and here for the follow up study on stainless steel and an investigation into titanium) discussed the issues involved with using pure organic solvent in contact with metal alloys such as stainless steel and titanium. In those studies, 316 SS and titanium sintered discs were exposed to pure methanol for one month. The resulting solution was then examined via ICP-MS for metal ion contamination. The results showed that Silcolloy, Dursan, and RD5-SiN were all suitable coatings to protect stainless steel from the methanol attack, while only Silcolloy effectively stopped titanium ions from being leached into solution. In this study Hastelloy (specifically C-22) is similarly investigated as a substrate for SilcoTek's coatings.

Hastelloy alloys were developed for severe corrosion conditions. These high nickel exotic alloys typically work well to battle halide and other acid corrosion. They also have great resistance to oxidation which make them an appealing substrate for semiconductor, aerospace, and oil and natural gas industries. There is a wealth of literature supporting their use for visual or severe corrosion conditions, but when it comes to trace levels of corrosion, very little is known.



Here we find that a bare C-22 sintered disc when exposed to pure methanol can leach over 1 ppm total metal into solution, where the same discs coated with Silcolloy, Dursan, and RD5-SiN showed no measurable loss of metal ions, indicating only baseline levels of leaching relative to experimental controls.

Data and Discussion

Porous C-22 Hastelloy discs with 10 µm nominal pore sizes were purchased from Mott Corporation. They were coated with Dursan, Silcolloy, and RD5-SiN. After coating, the discs were placed in 50 mL of HPLC grade methanol and sealed. An uncoated disc as well as a container with no disc (a solvent blank to establish baseline response) were also filled with methanol and sealed. After one month of soak time, the porous disks were removed from the methanol and the samples were delivered to the Energy and Environmental Sustainability Laboratories at Penn State University. Samples were then prepared by evaporating 10 mL of the methanol in a PTFA vial. The remains were dissolved in 5 mL of dilute nitric acid which was then analyzed using a Thermo Fisher iCap RQ ICP-MS.

Figure 1 shows the total metal ion concentrations from the solution of each container. The blank represents the level of metal ions in the methanol bottle, leached from the sealed container, sample preparation, or absorbed via environmental sources. The bare disc represents the level of metal ions leached into the methanol without any coating protection provided by processing at SilcoTek Corporation. Table 1 shows the raw values from each sample along with the total metal ion content. For reference, Table 2 is the composition of C-22 Hastelloy from Haynes International, the producer of Hastelloy materials.

Due to the bare disc total metal ion value being so high, Figure 2 shows the blank solution as compared to the three coated discs. It should be noted that these values are very close to the detection limits of the ICP-MS for these elements (0.1-0.5 ppb) and are significantly lower than the total metal contamination from the uncoated disc, 1235 ppb.

Sample	Ni	Cr	Mo	Fe	W	Co	Cu	Mn	V	Total metal content
Blank (methanol only)	0.5	0.01	0.03	0.66	0.05	0.00	0.14	0.14	0.01	1.54
Bare disc	902.54	151.16	49.88	101.04	3.46	0.60	24.53	1.36	1.00	1235.57
Dursan	0.32	0.02	0.08	0.91	0.03	0.01	0.32	0.23	0.02	2.02
RD5-SiN	0.91	0.02	0.15	0.33	0.03	0.01	0.34	0.21	0.01	2.01
Silcolloy	0.15	0.02	0.05	0.83	0.11	0.01	0.15	0.16	0.18	1.66

Table 1: Metal content in methanol measured via ICP-MS. All units are ppb.

Element	Weight %
Nickel	56% (balance)
Chromium	22%
Molybdenum	13%
Iron	3%
Tungsten	3%
Cobalt	2.5% max
Copper	0.5% max
Manganese	0.5% max
Vanadium	0.35% max
Silicon	0.08% max
Carbon	0.01% max

Table 2: Composition of C-22 Hastelloy according to Haynes International.

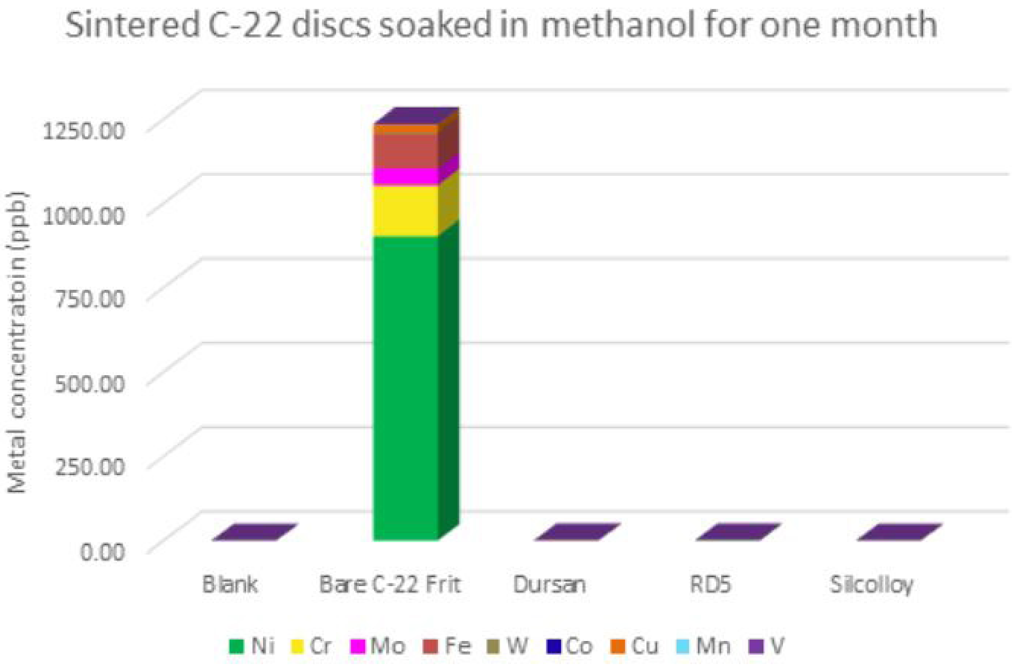


Figure 1: Metal ion concentrations in methanol. The blank is methanol from the bottle with no disc. The four others are a bare disc, and three SilcoTek corrosion coatings on a C-22 disc soaked in methanol for 1 month at room temperature.

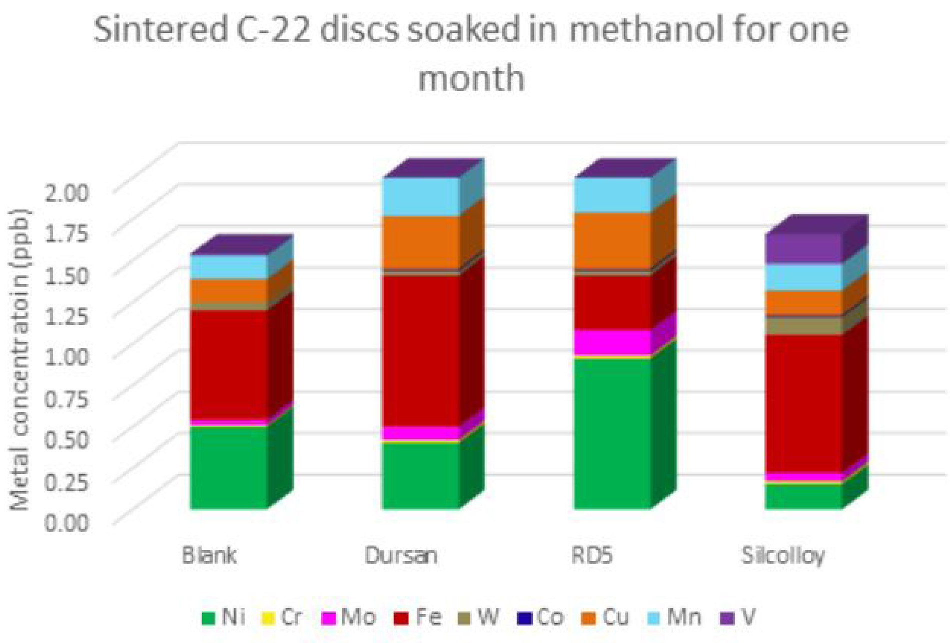


Figure 2: This is data transposed from Figure 1, but with the bare disc removed for better resolution of the coated discs.

Conclusion

All three coatings (Dursan, RD5-SiN, and Silcolloy) provided sufficient protection against metal ions leaching into the methanol during a one-month exposure at room temperature. It should be noted that while these sintered discs are often used for filtering solvents and will experience solvent flow, this experiment was done under static conditions. The metal ionic states as well as the solubility limits of those metal ions in methanol are not readily available through our experiments nor in the literature. It is possible that utilizing these uncoated porous discs for their intended purpose will result in larger quantities of metal ions leached into flow paths as they provide a constant supply of uncontaminated solvent and are in flow conditions rather than static.

Metal ion leaching study part 4: Ultrapure DI water corrosion.

Technical Insight

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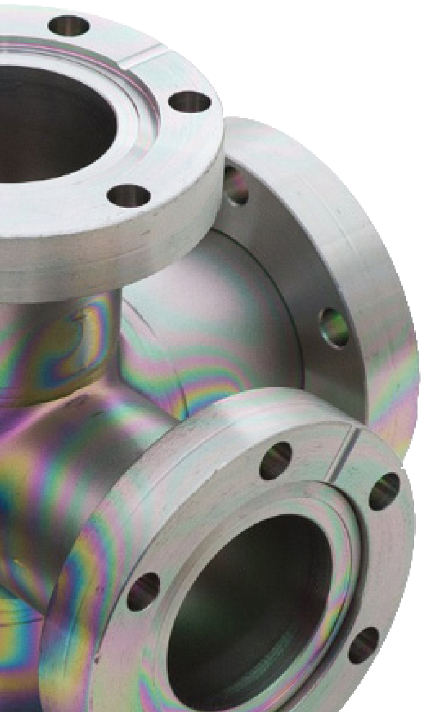
Synopsis

Corrosion encompasses a large variety of material degradation. It can be large enough to see visually such as the numerous examples in harsh acids or salt fog chamber experiments that SilcoTek has performed, or corrosion can be at trace levels that are not detected visually or by weight loss. We previously investigated Titanium, 316 Stainless Steel, and C-22 Hastelloy in pure methanol and monitored their corrosion via ICP-MS. Here we look at ultrapure DI water to see if the corrosion patterns follow the methanol studies.

Background

Previous Technical Insights (seen here for the initial study of stainless steel, here for the follow up study on stainless steel and an investigation into titanium, and here for part 3: Hastelloy) discussed the issues involved with using pure methanol when in contact with titanium, stainless steel, and C-22 Hastelloy. In those studies, sintered discs made of the various alloys were exposed to pure methanol for one month. The resulting solution was then examined via ICP-MS for metal ion contamination. The results showed that all three coatings provided by SilcoTek were able to stop metal ion contamination for 316 SS and C-22 alloys. Only Silcolloy was able to provide protection for titanium ion leaching. The reasons for that were discussed in part 2 of this series.

Here we use the same experimental set-up to investigate DI water's impact on these three alloys. Among numerous other uses, DI water is commonly used as a solvent for HPLC analysis, in food and drug production, and as a precursor in semiconductor applications. Here we show that titanium alloys do not suffer metal ion leaching in DI water, while both stainless steel and Hastelloy show large amounts of metal ion leaching, specifically an abnormally large amount of nickel leached into DI water when compared to the methanol leaching studies.



Data and Discussion

Porous 316 Stainless Steel and C-22 Hastelloy porous discs were purchased from Mott Corporation. Titanium porous discs were purchased from VICI precision sampling. All porous metal discs used in this study have a nominal pore size of 10 µm. One disc of each alloy type was coated with Dursan, Silcolloy, and RD5-SiN. Each coated disc and a bare disc were placed in separate polypropylene containers with 50 mL of UHPLC grade DI water purchased from MilliporeSigma. Additionally, one polypropylene container was filled with 50 mL of water with no disc in it to act as a blank or control for the study. After one month of soak time, the porous disks were removed from the water and the samples were delivered to the Energy and Environmental Sustainability Laboratories at Penn State University. Samples were then prepared by addition of nitric acid to achieve the correct pH and were then analyzed using a Thermo Fisher iCap RQ ICP-MS.

The results for the titanium discs can be seen in Figure 1. All values were within the detection limit of the instrument for titanium (0.2 ppb) showing that in ultrapure DI water, no titanium ions leach into the solution. This is strikingly different than the methanol study where 14 ppb of titanium were leached into the methanol. Dursan and RD5-SiN seemed to exacerbate these result (21ppb and 57 ppb respectively). Previous studies have shown that if titanium has access to water, it will passivate the surface and not allow the pitting of the titanium surface and the release of ions into the solution.1 This also explains observations of De Pra and his group at Thermo Fisher Scientific where they investigated titanium contamination of their HPLC system.2 They found that the silica bed in the column can be poisoned with titanium if using pure methanol and a titanium sintered filter in the solvent bottle. Switching the solvent from pure methanol to just 5% water was sufficient to prevent the metal ion leaching into their system.

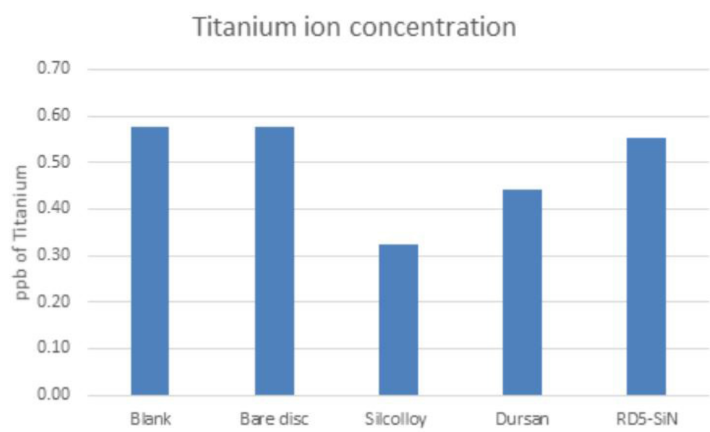


Figure 1: Titanium ion leaching in pure DI water. Blank refers to no sintered disc placed in the liquid to act as a control. All samples showed no titanium ion leaching into solution.

The 316 stainless steel disc results can be seen in Figure 2. It is obvious that the coatings on the sintered metal discs blocks the metal ions from leaching into solution. While there was substantial metal ion leaching into the solution, it was far less than experienced in the previous studies using methanol. Specifically, the iron and chromium levels were roughly an order of magnitude lower, as shown in Table 1. The nickel concentration is relatively unaffected by the solvent choice. The surface of 316 stainless steel has an oxide layer, largely consisting of chromium oxide, but also containing iron and nickel oxides. This layer provides a protective surface and is often self-healing when there is an oxygen source, such as air or water. In this case, it can be concluded that the comparatively low levels of chromium leached into the water indicates less damage to the protective oxide layer when compared to pure methanol. With less damage to the oxide layer, there is less access to the iron to leach into solution.

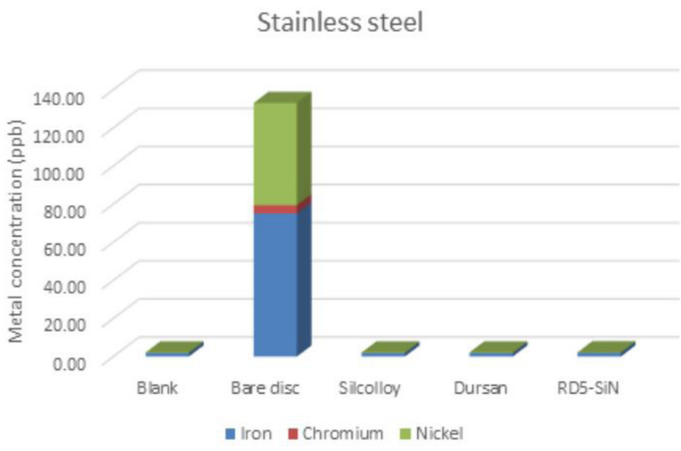


Figure 2: Stainless steel metal ion leaching into ultrapure water.

	Iron	Chromium	Nickel
Methanol extraction	812.81 ppb	33.55 ppb	61.488 ppb
Water extraction	75.13 ppb	4.34 ppb	53.62 ppb

Table 1: Metal ions extracted from an uncoated frit into solution after 30 days of soaking in methanol and water.

What remains unclear is to whether the nickel and iron metal contamination is a passivation effect or if it is truly corrosion of the material. The nickel and iron, along with their respective oxides, are much more easily extracted compared to the chromium oxide in the passive layer.3 It is possible that the contamination seen here is simply the removal of the nickel and iron from the passive layer, and no underlying metal was attacked, leaving a purer chromium oxide surface. Subsequent studies will be necessary to evaluate which mechanism is at play in this situation.

The results from the C-22 Hastelloy can be seen in Figure 3. Once again, the coated discs showed no evidence of metal ions leaching into solution. All three coatings provide sufficient protection from the DI water. Molybdenum and nickel were the major components of the metal ions in solution. It should be noted that the level of contamination was quite high compared to methanol. Table 2 is a comparison between the methanol and water contamination. Once again, the metal ions from chromium and iron are much lower in water when compared to the methanol experiment. Counter to what was seen in the 316 stainless steel alloy, there was a dramatic increase in the corrosion of other metals in the alloy. Most notably, nickel and molybdenum leached ppm levels of metal ions into solution. C-22 Hastelloy's oxide surface is composed largely of nickel, chromium, and molybdenum oxides. Chromium is clearly more stable in water where nickel and molybdenum suffer in water when compared to methanol. Just as with 316 Stainless Steel, it is unclear if this is a passivation effect or if this corrosion will continue with more time. Future studies are planned to determine this.

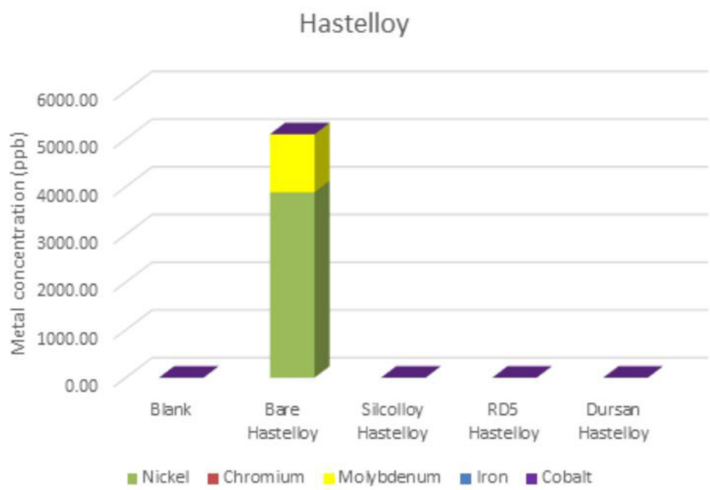


Figure 3: Metal ion contamination of ultrapure water from sintered C-22 Hastelloy discs.

	Nickel	Chromium	Molybdenum	Iron	Cobalt
Methanol	902.54 ppb	151.16 ppb	49.88 ppb	101.04 ppb	0.6 ppb
Water	3881.53 ppb	3.62 ppb	1216.41 ppb	1.99 ppb	1.32 ppb

Table 2: Metal ions extracted into solution after 30 days of soaking in methanol and water.

Conclusion

UHPLC grade DI water has shown it can cause corrosion events on 316 stainless steel and C-22 Hastelloy sintered metal discs. It did not corrode titanium discs, which was expected based on previous literature. In the case of 316 stainless steel and C-22 Hastelloy, chromium and iron corrode in water at a much slower rate than was seen in methanol studies. Nickel corrosion depended on the substrate. For 316 stainless steel, the corrosion seemed comparable to the methanol studies; however, for C-22 Hastelloy, both nickel and molybdenum experience exacerbated corrosion in the DI water. In all cases, the three coatings provided protection to the sintered metal discs from any corrosion event.

Future studies will investigate acetonitrile, which is often used as a solvent in HPLC analysis. An alloy that is growing in popularity in the medical industry, MP35N, a nickel-cobalt-chromium-molybdenum alloy, will be investigated as well. Additionally, the exacerbation of nickel and molybdenum corrosion in DI water will be further investigated to determine the mechanism of corrosion.

References

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3. Menon GR, “Rough and Its Removal from High-Purity Water Systems,” BioPharm 7 (1990) 40—43.

Metal Ion Leaching Study Part 5: Acetonitrile

Technical Insight

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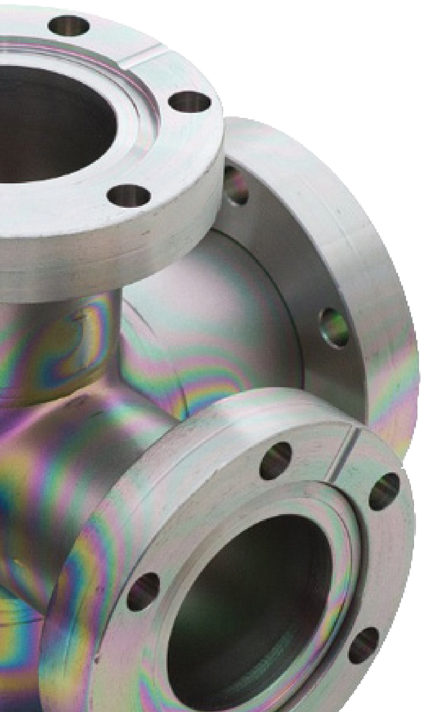

Synopsis

Corrosion encompasses a large variety of material degradation. It can be large enough to see visually such as the numerous examples in harsh acids or salt fog chamber experiments that SilcoTek has performed, or corrosion can be at trace levels that are not detected visually or by weight loss. We previously investigated Titanium, 316 Stainless Steel, and C-22 Hastelloy in pure methanol and DI water. We monitored their corrosion via ICP-MS. Here we look at HPLC grade acetonitrile to see how it may compare to other typical solvents.

Background

Previous Technical Insights have investigated a corrosion phenomenon on common alloys for HPLC and other applications and pure solvent systems. So far, we have investigated water and methanol's impact on stainless steel, titanium, and Hastelloy. Part one through four of this study can be found here:

- Part 1: Stainless steel in methanol
- Part 2: Stainless steel re-examination and titanium in methanol
- Part 3: Hastelloy in methanol
- Part 4: Stainless steel, titanium, and Hastelloy in DI water

In this TI, we investigate acetonitrile's impact on all three metal alloys both with and without our coatings. HPLC systems commonly have two solvents running at a single time. One is typically aqueous (DI water) and the other is typically organic. Methanol and acetonitrile are the two most common organic solvents that are used. Water was more aggressive with Hastelloy and methanol was the most aggressive solvent for titanium and stainless steel. Here we show that acetonitrile is the most benign of the trio. Aside from showing no impact to titanium (similar to water), there are still trace levels of metal ions that leach into the solution which can impact a variety of analyses. ambient atmosphere.

Data and Discussion

Porous 316 Stainless Steel and C-22 Hastelloy porous discs were purchased from Mott Corporation. Titanium porous discs were purchased from VICI precision sampling. All porous metal discs used in this study have a nominal pore size of 10 µm. One disc of each alloy type was coated with Dursan, Silcolloy, and RD5-SiN. Each coated disc and a bare disc were placed in separate polypropylene containers with 50 mL of HPLC grade acetonitrile purchased from MilliporeSigma. Additionally, one polypropylene container was filled with 50 mL of acetonitrile with no disc in it to act as a blank or control for the study. After one month of soak time, the porous disks were removed from the acetonitrile and the samples were delivered to the Energy and Environmental Sustainability Laboratories at Penn State University. Samples were then prepared by evaporating the acetonitrile and redissolving the remnants in dilute nitric acid. This was then analyzed using a Thermo Fisher iCap RQ ICP-MS.

Acetonitrile showed no corrosion or leaching of titanium ions into solution. All values for coated and uncoated tests were within the detection limit of the instrument (0.2 ppb) to the blank showing that no titanium ions leach into the solution. Our previous studies showed that leaching occurred in methanol (14 ppb on a bare frit) but not in water. This was supported by the literature which shows water can create a passivated oxide surface on titanium, thus not allowing corrosion to occur. Others have shown that while methanol solutions with hydrochloric acid will corrode titanium, acetonitrile solutions will not.1 They theorize that the nitrogen on the acetonitrile bonds to the titanium surface creating a passivation layer.

The 316 stainless steel disc results can be seen in Figure 1. It is obvious that the coatings on the sintered metal discs blocks the metal ions from leaching into solution. While there was metal ion leaching into the solution, it was far less than experienced in the previous studies using methanol and water. The results look similar to the water results where iron and nickel were on the same order of magnitude and chromium leaching was much less significant, as seen in Table 1.

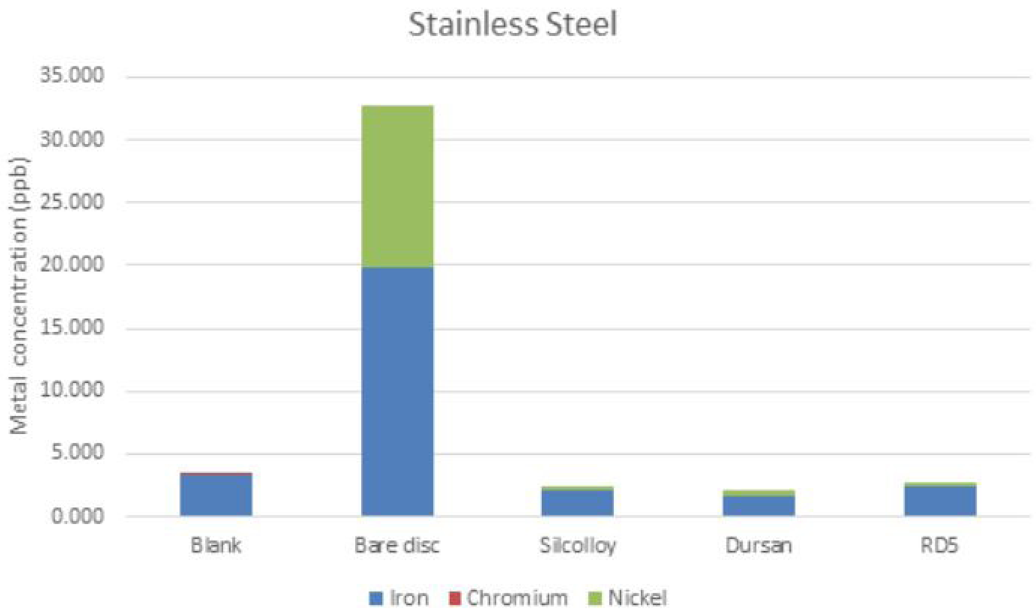

Figure 2: Stainless steel metal ion leaching into ultra-pure acetonitrile.

	Iron	Chromium	Nickel
Methanol extraction	812.81 ppb	33.55 ppb	61.48 ppb
Water extraction	75.13 ppb	4.34 ppb	53.62 ppb
Acetonitrile extraction	19.80 ppb	0.02 ppb	12.96 ppb

Table 1: Metal ions extracted from an uncoated frit into solution after 30 days of soaking in methanol, water, and acetonitrile.

These results are counter to the results seen in previous studies on stainless steel with acetonitrile and methanol.2 In a study by Mowery, it was found that acetonitrile was more aggressive with stainless steel. There are some key differences between that study and this one. In their study, the acetonitrile was under high pressure and was constantly flowing. Here the acetonitrile is static and at atmospheric pressures. The high and low pressures allowed for an electrochemical difference which encourages corrosion. It is unclear what leads to the corrosion in our experiment and why it is different from theirs.

The results from the C-22 Hastelloy can be seen in Figure 2. Once again, the coated discs showed no evidence of metal ions leaching into solution. All three coatings provide sufficient protection from the acetonitrile. Nickel was the main contaminant in the acetonitrile along with a small amount of iron. Table 2 is a comparison between the methanol, water, and acetonitrile. As was the case with stainless steel, acetonitrile is the least aggressive solvent when it comes to the leaching of metal ions into solution. Hastelloy C was investigated by Mowery, and it was shown to be comparable to stainless steel in their high pressure tests. Here, C-22 Hastelloy is by far the worst metal ion leaching substrate that was tested.

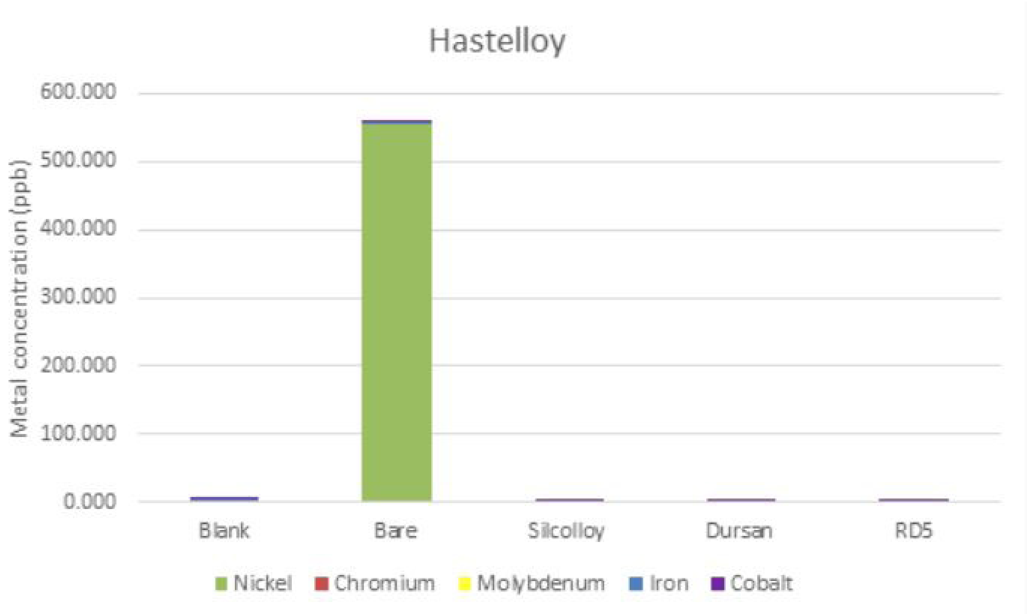

Figure 3: Metal ion contamination of ultrapure acetonitrile from sintered C-22 Hastelloy discs.

	Nickel	Chromium	Molybdenum	Iron	Cobalt
Methanol	902.54 ppb	151.16 ppb	49.88 ppb	101.04 ppb	0.6 ppb
Water	3881.53 ppb	3.62 ppb	1216.41 ppb	1.99 ppb	1.32 ppb
Acetonitrile	554.58 ppb	0.21 ppb	0.03 ppb	3.81 ppb	0.31 ppb

Table 2: Metal ions extracted into solution after 30 days of soaking in methanol, water, and acetonitrile.

Conclusion

HPLC grade acetonitrile has shown it can cause corrosion events on 316 stainless steel and C-22 Hastelloy sintered metal discs. It did not corrode titanium discs. The titanium results were expected based on literature, but the stainless steel and Hastelloy results seem to contrast what is readily available in the literature. While the experiments were not identical, the inverse relationship of methanol to acetonitrile results from Mowery warrants further investigation.

The next round of experiments will investigate the three solvent's effect on MP35N, a Nickel-Cobalt based alloy that is increasing in use for HPLC and medical components due to its bio-compatible properties.

References

1. Ramgopal, T. NACE CORROSION conference 2004, Paper number: NACE-04237, Published March 28, 2004.
2. Mowery, R.A. "The Corrosion of 316 Stainless Steel in Process Liquid Chromatography with Acetonitrile or Methanol Carriers". Journal of Chromatographic Science, Volume 23, Issue 1, January 1985, Pages 22-29.

Metal Ion Leaching Study Part 6: MP35N

Technical Insight

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Synopsis

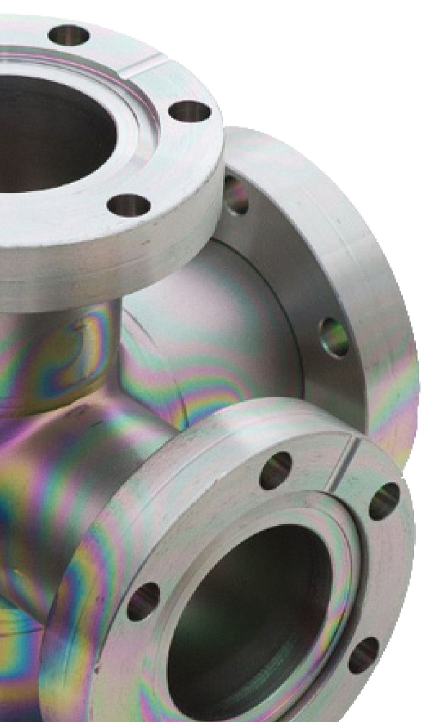
MP35N is an alloy that is increasing in popularity among the medical diagnostic and HPLC community. It is often used as a bio-inert solution for replacing stainless steel as its iron content is very low. While it may be bio-inert in the sense of it does not have any cytotoxic or deleterious effects on biological analytes, it is still made of metal. More and more HPLC users are finding that bio-inertness by replacing one metal alloy with another does not fix their issue of metal ion leaching into their flow path. Here we investigate the metal ion leaching of MP35N in pure methanol, water, and acetonitrile.

Background

Previous Technical Insights have investigated a corrosion phenomenon on common alloys for HPLC and other applications and pure solvent systems. So far, we have investigated water, acetonitrile, and methanol's impact on stainless steel, titanium, and Hastelloy. Part one through five of this study can be found here:

- Part 1: Stainless steel in methanol
- Part 2: Stainless steel re-examination and titanium in methanol
- Part 3: Hastelloy in methanol
- Part 4: Stainless steel, titanium, and Hastelloy in DI water
- Part 5: Stainless steel, titanium, and Hastelloy in acetonitrile

In this TI, we investigate MP35N exposed to ultrapure HPLC grade methanol, acetonitrile, and DI water. MP35N is a nickel-cobalt based alloy (see Table 1 for the composition of this alloy) which has been growing in popularity among HPLC and medical instrument OEMs. It is marketed for the alloy's high strength, corrosion resistance, and biocompatibility. Here we investigate metal ion leaching in the three most common solvents used in HPLC applications: methanol, acetonitrile, and water. As seen in Part 5 of this series, acetonitrile is the most benign solvent. Additionally, the MP35N seems to follow the trend of another nickel based alloy, Hastelloy, in that water shows the most metal ion leaching of any solvent.



	Nickel	Cobalt	Chromium	Molybdenum	Others
MP35N Weight %	33-37	Balance (29-36.5)	19-21	9-10.5	2.5 max

Table 1: Weight percentage of MP35N alloy. “Other” elements include iron, titanium, silicon, and manganese.

Data and Discussion

Previous experiments were done with sintered discs due to the high surface area of a porous material. After checking with numerous sintered filtration companies, it seems as though MP35N sintered materials are not common or available yet. Since sintered discs were not available, MP35N bolts were purchased and cut into half inch cylinders. The sectioned pieces were cleaned via SilcoTek’s standard surface preparation process. The pieces were then left bare or coated with Dursan, Silcolloy, or RD5-SiN. Each coated and bare cylinder were placed in separate polypropylene containers with 50 mL of HPLC grade methanol, acetonitrile, or DI water purchased from MilliporeSigma. After one month of soak time, the cylinders were removed from the solvents and those liquid samples were delivered to the Energy and Environmental Sustainability Laboratories at Penn State University. Methanol and acetonitrile samples were then prepared by evaporating the solvent and redissolving the remnants in dilute nitric acid. The water samples simply had nitric acid added to the correct pH for analysis. These samples were then analyzed using a Thermo Fisher iCap RQ ICP-MS.

The metal ion content leached into methanol can be seen in Figure 1. Roughly 12 ppb of metal ions were released into the methanol after one month of the coupons soaking in solution. Nickel and cobalt were the major contributors to these contaminants. The coated versions all showed low counts, all on similar levels to the methanol from the bottle itself. For instance, Silcolloy, Dursan, and RD5 showed 0.796 ppb, 0.815 ppb, and 0.988 ppb of nickel, respectively. The methanol with no coupon soaked in it for a month showed 0.824 ppb. This shows that all three coatings block the corrosion of MP35N in methanol.

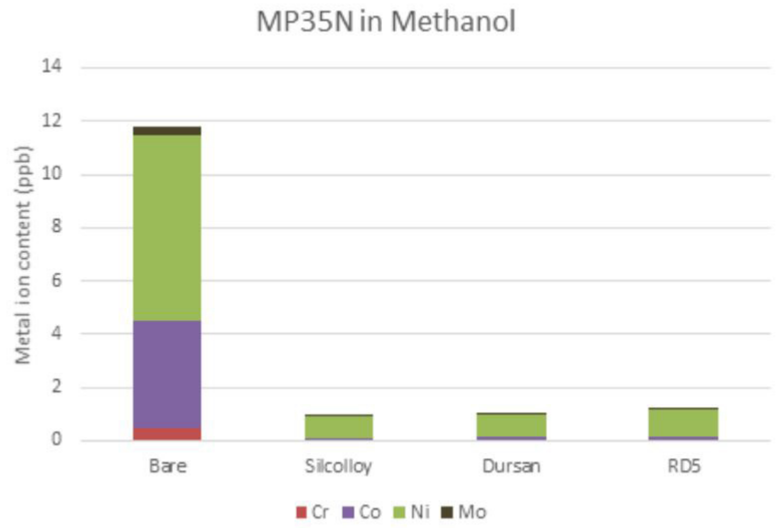


Figure 1: Metal ions leached into methanol solution after one month of soak time. The coated samples were all at or near baseline levels of the methanol in the bottle.

Table 2 shows a comparison of the four alloys that have been tested to this point in methanol. The alloys were all different sizes, weights, and the MP35N samples were solid materials rather than porous material. Most corrosion calculations take surface area into consideration (see ASTM G31 guidelines for immersion corrosion). The higher amount of surface that interacts with the liquid, the more likely a corrosion event is to take place. The last column of the table is total metal ions adjusted for surface area of the samples.

Table 2: Concentration of metal ions leached into methanol among the four different alloys tested. Blank boxes were either not measured or not detected. The final column is adjusted for surface area of the samples that were tested. All values are in ppb.

Alloy	Fe	Ni	Cr	Mo	Co	Ti	Total metal per m^2
Stainless Steel	812.81	61.48	33.55	-	-	-	1011
Titanium	-	-	-	-	-	13.92	696
Hastelloy	101.04	902.54	151.16	49.88	0.6	-	8031
M35N	-	6.969	0.474	0.363	4.005	-	100255

The results in acetonitrile can be found in Figure 2. There was a total of 1.73 ppb of metals leached into the acetonitrile solution. Compared to both methanol and water, acetonitrile appears to be the most benign solvent toward the alloys tested. Once again, the three coatings all provided sufficient protections against the leaching of metal ions into acetonitrile. All coated values were at the same level as the acetonitrile blank from the bottle.

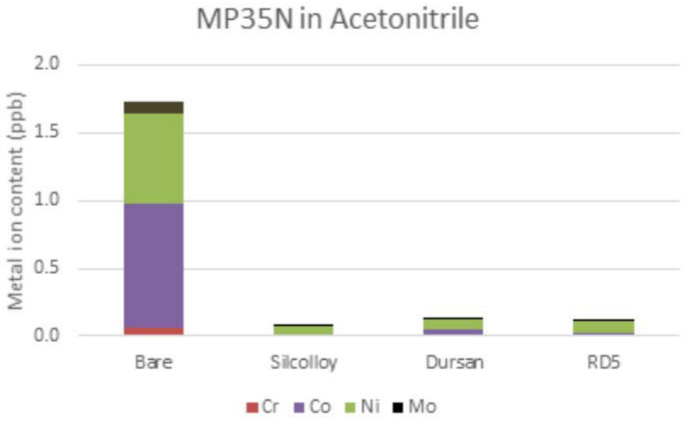


Figure 2: Metal ions leached into methanol solution after one month of soak time. The coated samples were all at or near baseline levels of the methanol in the bottle.

Table 3 shows a comparison between the four different alloys tested in this series. Once again, the last column is adjusted for the surface area of the sample in the acetonitrile. While the total metal content is much lower in acetonitrile than it is for methanol, the pattern among the four alloys is the same. Titanium shows the least amount of metal ion contamination followed by stainless steel. Both of these alloys are capable of creating stable oxides on the surface of the alloy (titanium oxide for titanium and chromium oxide for stainless steel). Oddly enough, nickel-based alloys, which are marketed as having superior corrosion resistance, follow with Hastelloy and finally MP35N showing the most metal ion leaching when compensating for surface area.

Table 3: Concentration of metal ions leached into acetonitrile among the four different alloys tested. Blank boxes were either not measured or not detected. The final column is adjusted for surface area of the samples that were tested. All values are in ppb.

Alloy	Fe	Ni	Cr	Mo	Co	Ti	Total metal per m^2
Stainless Steel	19.8	12.96	-	-	-	-	134
Titanium	-	-	-	-	-	0.159	8
Hastelloy	3.8	554.58	0.2	0.03	0.3	-	3715
M35N	-	0.67	0.06	0.08	0.91	-	14333

The results for water can be seen in Figure 3. The total metal concentration is 667 ppb. This is much more than what was leached in both methanol and acetonitrile. A similar pattern was seen for Hastelloy which is also a nickel-based alloy. As was the case for the first two solvents, the coatings were able to block all metal ion leaching into the water.

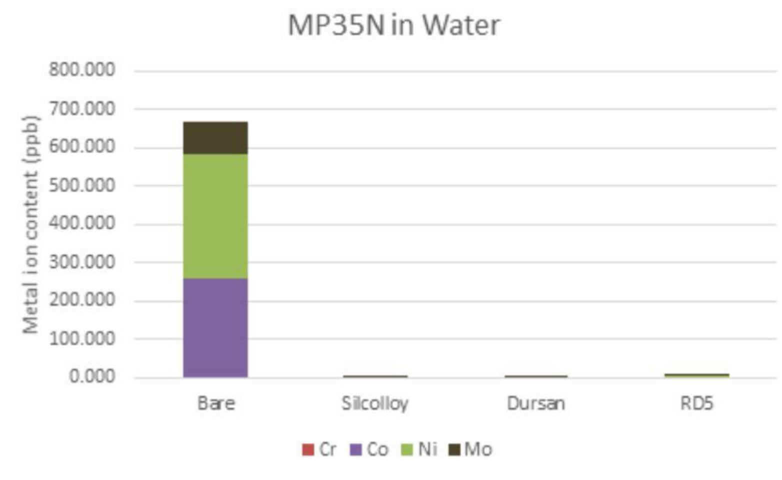


Figure 3: Metal ions leached into methanol solution after one month of soak time. The coated samples were all at or near baseline levels of the water in the bottle.

Table 4 shows the comparison between all four alloys soaked in water for one month. The adjusted column for surface area shows just how different the nickel-based alloys are from titanium and stainless steel for this type of trace level corrosion. The MP35N sample, when adjusted for surface area, leaches 0.55% per m2. This amount of leaching is surprisingly high. It is possibly a reason why the sales of high surface area materials, such as frits/sintered filter media, is not currently available.

Table 4: Concentration of metal ions leached into DI water among the four different alloys tested. Blank boxes were either not measured or not detected. The final column is adjusted for surface area of the samples that were tested. All values are in ppb.

Alloy	Fe	Ni	Cr	Mo	Co	Ti	Total metal per m^2
Stainless Steel	75.1	53.62	4.34	7.7	-	-	574
Titanium	-	-	-	-	-	0.58	29
Hastelloy	1.99	3881.53	3.62	1216.41	-	-	33929
M35N	-	324.5	0.49	81.44	260.44	-	5557250

Conclusion

MP35N is a corrosion resistant, high strength metal alloy that is commonly used in HPLC and the medical industry for its biocompatibility. Here we see that when adjusted for surface area, it leaches the most metal ions of any alloy tested thus far in methanol, acetonitrile, and water. Also, this is the first alloy that has been tested that leaches appreciable amounts of cobalt into solution.

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