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MCU MATERIALS COMPATIBILITY WITH CSSX SOLVENT

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MCU MATERIALS COMPATIBILITY WITH CSSX SOLVENT

Summary
The Modular Caustic-Side Solvent Extraction (CSSX) Unit (MCU) plans to use several new materials of construction not previously used with CSSX solvent. SRNL researchers tested seven materials proposed for service in seal and gasket applications. None of the materials leached detectable amounts of components into the CSSX solvent during 96 hour tests. All are judged acceptable for use based on their effect on the solvent. However, some of the materials adsorbed solvent or changed dimensions during contact with solvent. Consultation with component and material vendors with regard to performance impact and in-use testing of the materials is recommended.

Polyetheretherketone (PEEK), a material selected for use in contactor bearing seals, did not gain weight or change dimensions on contact with CSSX solvent. Analysis of the solvent contacted with this material showed no impurities and the standard dispersion test gave acceptable phase separation results. The material contains a leachable hydrocarbon substance, detectable on exposed surfaces, that did not adversely contaminate the solvent within the limits of the testing. We recommend contacting the vendor to determine the source and purpose of this component, or, alternatively, pursue the infrared analysis of the PEEK in an effort to better define potential impacts.

Experimental

Samples
MCU Design Authority personnel obtained samples of seven materials of construction planned for use in the MCU. Table 1 provides identification information and a description of the samples. In some cases (i.e., ETFE, Grafoil® stem seal and bonnet gasket) an entire piece was leached. In other cases, the samples provided were cut in half (i.e., Simriz®, Grafoil® Grade GTB) or a piece was cut off (i.e., PEEK). The gasket construction includes concentric rings of GTA nuclear grade graphite held together with metal bands. When cut into pieces small enough for leaching, the graphite and metal bands separated. The two portions were leached separately.

Leach Test
In the general procedure, pieces of the materials were soaked, without agitation, in CSSX solvent for 96±1 hours at ambient temperature (23 ± 3 °C). Individual tests used ~ 40 mL of CSSX solvent (archive sample of batch prepared at SRNL, Batch#S2-D1-Yes-BOB-T-WI).[1,2] Table 2 lists the solvent composition. Testing of the Simriz® sample varied from the others. The small size of the Simriz® O-ring necessitated smaller test volumes (~ 15 mL of solvent). In addition, Simriz® pieces were slowly tumbled in a mixture of solvent and an aqueous phase (either 0.05 M nitric acid or simulated waste solution) to more closely simulate the service application. Table 3 lists the composition of the simulated waste solution.[3] The simplified simulated waste did not contain hazardous, transition metal, or organic components.

TABLE 1. Identification Information for Samples

	Material	Source	Application	Shape	Other
1	ETFE (Tefzel®) (ethylene-tetrafluoroethylene copolymer)	McCanna	Valve seat	ring, 4 cm diam	Color: white
2	Grafoil® (flexible graphite)	McCanna	stem seal	ring, 2 cm diam	Color: black, metallic sheen
3	Grafoil®	McCanna	bonnet gasket	ring, 5 cm diam	Color: black, metallic sheen
4	Graphite (GTA nuclear grade) from Garlock Edge™ flex seal gasket	Garlock	piping flange gasket	ring, 13 cm diam	composed of alternating rings of graphite and 304L stainless steel bands
5	Grafoil®, Grade GTB			sheets	Color: black, metallic sheen
6	Simriz®		bearing seal	ring,	
7	PEEK (polyetheretherketone)			disk, 18 cm diam x 2.5 cm thick	Color: light gray

TABLE 2. CSSX Solvent Composition[2]

Component	Concentration (molar)
Extractant	0.007
Modifier	0.75
TOA	0.003
Isopar® L	(remainder)

TABLE 3. Simulated Waste Solution

Component	Concentration (molar)		Component	Concentration (molar)
Na^+	5.6		CO_3^{2-}	0.15
K^+	0.015		Cl^-	0.024
Cs^+	0.00014		F^-	0.028
OH^-	2.06		PO_4^{3-}	0.007
NO_3^-	2.03		oxalate	0.008
NO_2^-	0.50		SiO_3^{2-}	0.03
AlO_2^-	0.28		MoO_4^{2-}	0.00007
SO_4^{2-}	0.14			

Examination Methods

Personnel evaluated the solvent and materials using infrared (IR) spectroscopic analysis, including IR and Raman spectra of the solvent before and after contact with the materials, and surface IR spectra of the materials before and after contact with solvent. Researchers also measured weight and dimensional changes in the materials samples, and recorded visual observations (such as color changes, sample integrity, and solvent transparency).

Dispersion Test Protocol

Using a literature procedure,[4] SRNL researchers performed dispersion tests on combinations of the solvent and simulated waste solution. The tests used graduated cylinders (of 100-mL working volume) with ground glass joints or Teflon ™ cap plugs. The cylinders were physically similar, approximately 190 mm tall and 25.4 mm diameter. Researchers measured break times (t_b, seconds) with a calibrated stopwatch and calculated the dispersion number (**N_{DI}**) using the following equation where **H** is the working height of the graduated cylinder in meters.

$$N_{DI} = \frac{1}{t_b}\sqrt{\frac{H}{9.81}} \qquad \text{Equation 1}$$

The literature procedure indicates that replicate results may vary up to 25%, so we take this value as the experimental uncertainty.

Results

Table 4 summarizes the results of the effects of the materials on the solvent properties. Table 5 summarizes results of the effects of the solvent on the materials samples.

Effects on Solvent

None of the materials imparted color to the solvent or caused the solvent to become hazy. IR analysis detected no impurities in the solvent samples after leaching. Some changes exceeding the nominal error (±25%) occurred in the dispersion numbers. For most materials, (i.e., ETFE, GTA graphite, Grafoil®, and PEEK), the dispersion number increased relative to the controls. An increase in the dispersion number indicates improved separation and is of benefit to the MCU process. Simriz® caused a decrease in the dispersion number relative to the control. However, the decrease to a value of 0.0005 remains within the range considered acceptable for the process (acceptable: > 0.0004).[5] Note that the Simriz® measurements were made using smaller apparatus that may have affected the accuracy of the measurement. Nevertheless, we report the results since the control samples in the small apparatus agreed well with other controls.

The metal bands from the Garlock gasket also reduced the dispersion number. Again, the reduction did not cause the dispersion number to drop below the acceptable value. However, it is not clear why the metal parts caused the change. Researchers noted that the bands contained periodic yellow spots, possibly paint or glue, that did not change in appearance during leaching.

TABLE 4. Effects of Materials on CSSX Solvent

Material	Solvent Color	Solvent Clarity	IR Analysis	Dispersion Number (acceptable range: >0.0004)
ETFE (Tefzel®)	No change	No change	No detectable impurities	0.0013
GTA graphite from Garlock gasket	No change	No change	No detectable impurities	Graphite 0.0012 Metal rings 0.0006
Grafoil® stem seal	No change	No change	No detectable impurities	0.0015
Grafoil® bonnet gasket	No change	No change	No detectable impurities	0.0012
Grafoil® Grade GTB	No change	No change	No detectable impurities	0.0014
Simriz®	No change	No change	No detectable impurities	Strip 0.0005 Waste 0.0005
PEEK	No change	No change	No detectable impurities	0.0014
Controls				Large apparatus 0.0010 ±0.0002 Small apparatus 0.0011 ±0.0001

TABLE 5. Effects of CSSX Solvent on Materials

Material	Color/Integrity	Weight (%)	Dimensions	Surface IR Analysis*
ETFE (Tefzel®)	No change	+ 0.2	ID -3% OD +0.01% Thickness -4%	NA
GTA graphite from Garlock Gasket	No change	+28	Thickness +33%	NA
Grafoil® stem seal	No change	+38	Thickness +39%	NA
Grafoil® bonnet gasket	No change	+39	Thickness +60%	NA
Grafoil® Grade GTB	No change	+46	No change	NA
Simriz®	No change	+ 0.08	Thickness +2%	Surface hydrocarbon removed
PEEK	No change	+ 0.01	No change	Surface hydrocarbon partially removed

* NA indicates not analyzed.

Effects on Samples
Visual examination of the samples showed no changes due to contact with CSSX solvent. Samples maintained their integrity (i.e., did not break down into smaller pieces) and did not change color.

All of the samples showed weight gains. The magnitude of the weight gain (0.01%) for PEEK approximately equaled the error in the weight measurement, and we consider it insignificant. The weight gains for Simriz® and ETFE (Tefzel®) exceeded the measurement errors but are quite small. Weight gains by the GTA graphite (Garlock gasket) and Grafoil® samples proved quite large (28 to 46%). In three cases (GTA graphite, Grafoil® stem seal, and Grafoil® bonnet gasket), researchers noted bubbles of gas evolved over several hours following immersion of the material in CSSX solvent. We suspect the materials are porous and the air bubbles result from displacement of air by the solvent. The large weight gains support this interpretation.

The dimensional changes in the samples follow a pattern similar to the weight changes. PEEK showed no change in dimensions, commensurate with the lack of weight gain. Simriz® measured slightly larger (+2%) in both tests (in 0.05 M nitric acid and in simulated waste solution). ETFE (Tefzel®) unexpectedly measured slightly smaller in two dimensions, although the outside diameter of the O-ring remained constant. The shrinkage in the inside diameter and thickness may reflect measurement uncertainty. The GTA graphite (Garlock gasket), Grafoil® stem seal, and Grafoil® bonnet gasket increased significantly in thickness, reflecting similar changes in weight. The Grafoil® Grade GTB sheet did not measurably increase in thickness, even though it did gain considerably in weight. We recommend evaluating the potential impact on performance of these changes in size and weight. Though often of limited value for specific applications, vendor data (Union Carbide) indicates high compatibility of homogeneous Grafoil® sheet with many hydrocarbons, including kerosene.[6]

The surface IR analysis of the Simriz® and PEEK materials showed CSSX solvent removed hydrocarbons present on the original surfaces. The material removed from the Simriz® may have been oils imparted to the surface during human handling. The PEEK material, however, appear to contain a hydrocarbon on freshly prepared surfaces that were not contaminated during sample preparation. This material was partially removed during the leach test.

Conclusions

None of the materials tested imparted detectable amounts of impurities to the solvent, as evidenced by no visible color changes, no haziness, and no detectable compounds in the IR spectroscopy. These materials will be used sparingly in the MCU process, so the potential for solvent contamination is small just from consideration of the volume of solvent in contact with the limited volume of the materials. Some changes in dispersion number occurred but measured values remain within acceptable limits. From the point of view of impact on solvent, all of the materials are considered acceptable in MCU service.

The results are not as clear from the point of view of the impact of the solvent on the materials. PEEK, Simriz®, and ETFE (Tefzel®) showed the least effects. Weight gains and dimensional changes were non-existent or quite small. However, the GTA graphite and Grafoil® products gained significantly in weight, with corresponding changes in dimensions (with the exception of Grafoil® Grade GTB sheet). Depending on the application, these changes may be acceptable if cracking, softening, stress-relaxation, binding or other forms of degradation that may occur do not cause component failure. Consultation with component and material vendors with regard to performance impact and in-use testing of these materials is recommended.

References

[1] K. Adu-Wusu, D. D. Walker, T. L. White, and S. L. Crump, memorandum to S. D. Fink, "Preparation of Caustic-Side Solvent Extraction (CSSX) Solvent with BOBCalixC6 for Wright Industries - Component Amounts, Analytical and Quality Assurance Results," SRNL-WPT-2005-00134, December 2, 2005.

[2] Systematic names for solvent components are: modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (CS-7SB); extractant, calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6); and TOA, tri-*n*-octyl amine.

[3] R. A. Peterson, "Preparation of Simulated Waste Solutions for Solvent Extraction Testing," WSRC-RP-2000-00361, Rev. 0, May 1, 2000.

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[6] Union Carbide Grafoil® Engineering Design Manual, Volume 1, 1987.

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