

Poisoning Evaluation of On-Orbit Sabatier Assembly

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The on-orbit Sabatier Assembly (SA) was designed by Collins Aerospace to partially close the life support loop on ISS by reacting two waste gases (carbon dioxide and hydrogen) to produce water (and waste methane). Waste CO₂ gas is recovered from cabin air by the Carbon Dioxide Recovery Assembly (CDRA) and waste H₂ comes from the Oxygen Generation System (OGS). By recycling these waste gases, the Sabatier Assembly produces water and reduces the need to launch water from ground, which is costly. The SA was successfully launched in 2010 and was in operation from June 2011 through October 2017. In late 2016, the Sabatier unit began to show significant signs of degradation in the reactor and did not produce water while in Process mode. The unit was returned to Collins Aerospace in 2018 for TT&E (Test, Teardown and Evaluation) with the goal of providing an upgraded system to support Exploration demonstration hardware on ISS. This paper reports the TT&E evaluation results.

Nomenclature

<i>BET</i>	=	Brunauer-Emmett-Teller
<i>CDRA</i>	=	carbon dioxide removal assembly
<i>CV</i>	=	check valve
<i>DMSD</i>	=	dimethylsilanediol
<i>DMSO₂</i>	=	dimethylsulfone
<i>DP</i>	=	differential pressure
<i>EDS</i>	=	energy dispersive X-ray spectroscopy
<i>FTIR</i>	=	fourier transform infrared spectroscopy
<i>ISS</i>	=	International Space Station
<i>ITCS MLP</i>	=	internal thermal control system moderate temperature loop
<i>NDE</i>	=	non-destructive examination
<i>OGA</i>	=	oxygen generation assembly
<i>PDMS</i>	=	polydimethylsiloxane

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<i>QD</i>	=	quick disconnect
<i>SEM</i>	=	scanning electronic microscopy
<i>SA</i>	=	Sabatier assembly
<i>TGA</i>	=	thermogravimetric analysis
<i>TT&E</i>	=	test, teardown and evaluation
<i>UPA</i>	=	urine processor assembly
<i>WPA</i>	=	water processor assembly

I. Introduction

THE Sabatier process was first discovered by the French chemists Paul Sabatier and Jean-Baptiste Senderens in 1897. It involves a reaction of hydrogen with carbon dioxide at elevated temperatures and pressures in the presence of a metal catalyst to produce methane and water. The process was not commercialized until more than a half-century later. From 1990-2000, Collins Aerospace (formerly known as Hamilton Sundstrand) designed a Sabatier Assembly (SA) which would allow this process to be incorporated aboard the International Space Stations (ISS). The SA was launched in 2010 and remained in operation until 2017. Over this period of time the SA spent twenty thousand hours in the process state and produced 1081 liters of water by recycling waste gases. The SA supports NASA's goal of closing the life support loop on station while saving money by reducing the need to launch additional water from ground. This is critical for ISS and for future exploration missions. The SA schematic can be found in Figure 1.

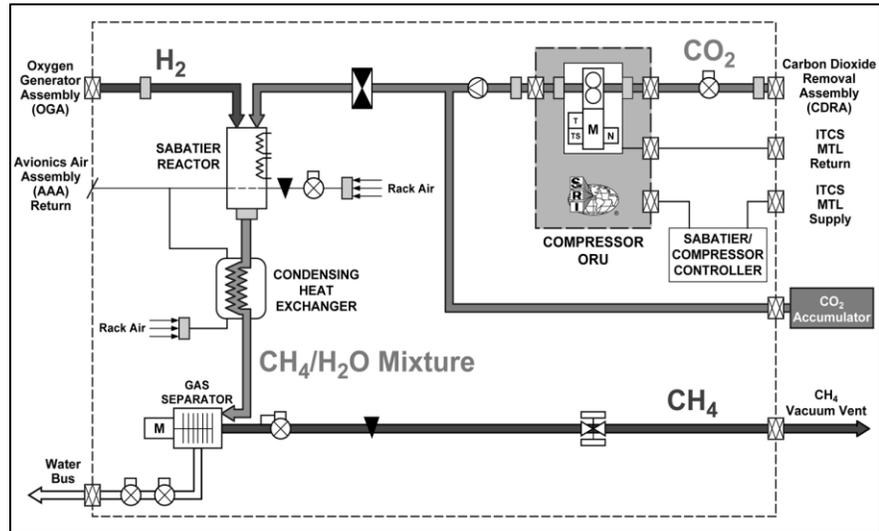


Figure 1. Sabatier simplified schematic.

In late 2016, the Sabatier assembly began to show sign of performance degradation with inlet of reactor not reaching reaction temperature and gradually it stopped producing water while in PROCESS mode from early 2017. Additionally, both the gas-liquid separator and liquid sensor had increased (nuisance) shutdowns. To keep the system operating, increasingly involved procedures were required to restart the reactor after a shutdown and it still could not produce a nominal amount of water at the nominal reactant gas flows. Eventually, the decision was made to shut down the SA and to return it to Collins Aerospace for test, teardown and evaluation (TT&E). This report intends to present some contamination findings of major components in the SA.

II. TT&E (Test, Teardown and Evaluation)

The purpose of TT&E was to investigate the cause of the degradation in performance of the flight Sabatier Assembly. During TT&E the SA was subjected to as-received testing, disassembly, visual inspection and material evaluation. All examinations were non-destructive with much care taken to avoid any changes to material physical conditions and properties presented at ISS. Detailed examination results are given in the following:

A. Carbon Dioxide Filter

The CO₂ inlet filter is the first component within Sabatier that is exposed to the incoming CO₂ from CDRA. The CO₂ filter is designed to provide protection to the compressor from any incoming particulate in the CO₂ Stream. On-orbit, the CO₂ filter did not show any signs of failure or increased pressure drop. However, after the external housing was removed exposing the internal filter during disassembly, white particulate was noticed on the inlet path of the filter, as well as within the filter housing (reference Figure 2). Swab samples of the particulate were taken and a SEM/EDS analysis was performed on the sample. It was concluded that the particulate was comprised of alumino-

silicates. It is believed that possible sources of this contaminate was from CDRA which includes silica gel (SiO₂) and zeolites (alumino-silicates). Additionally, from a hardware perspective the CO₂ filter performed its function in capturing particulate above 10 micron. However, microscope images revealed that the incoming gas contained particulates down in the submicron range.

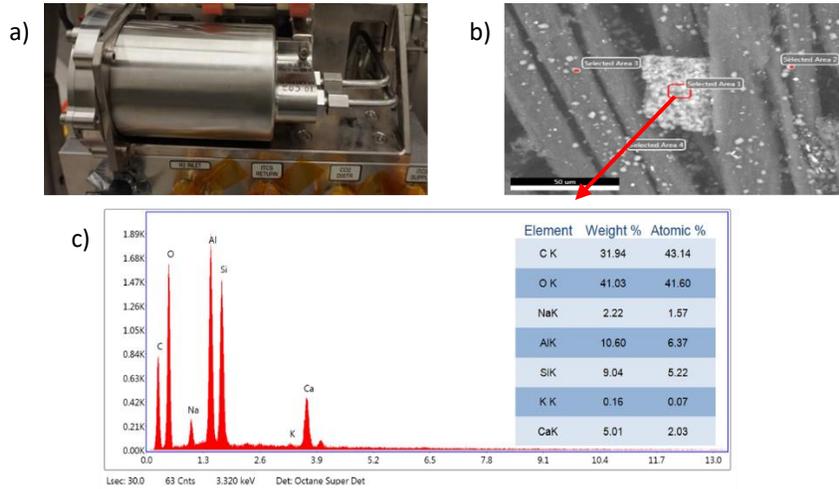


Figure 2. (a) Photo and (b) SEM image of CO₂ inlet filter, and (c) EDS profile of the selected area with white residue shown in (b).

B. Compressor Manifold

Downstream of the CO₂ filter, resides the compressor manifold assembly. The compressor manifold assembly consists of various valves and sensors which are used for fault detection, protection and isolation. On-orbit, the sensors and valves within the compressor manifold did not show signs of performance degradation. As-received testing (range check, functional check, leak check) was performed on the sensors, valves, and manifold. Results indicated that the components operated nominally with no signs of issues.

Next, the compressor manifold assembly was completely disassembled and a visual inspection was performed. A significant amount of “white film” contamination was noticed throughout the internal flow passages of the valves, and the corresponding manifold bores (Reference Figure 3(a)). Swab samples were taken and an EDS analysis was performed. The EDS analysis revealed that the majority of the contamination was comprised of alumino-silicates. (1:1 Al to Si ratio indicates primarily zeolites (alumino-silicates) from CDRA (See Figure 3(c)). The EDS analysis also revealed a high O content and F content (most likely source is Braycote 601EF from the O-rings on the valves and sensors). It is thought that Braycote may have been introduced during the sample collection.

C. Compressor Suction Filter

Downstream of the compressor manifold, and internal to the compressor, is the 2 micron absolute compressor suction filter. The function of this filter is to provide protection to the compressor by preventing any upstream contaminants from entering the compressor. During TT&E it was noticed that a significant amount of zeolite/alumino-silicate had made it past the CO₂ inlet filter, and contaminated the compressor manifold. The suction filter was visually examined. On the inlet side of the suction filter a “brown” contamination was noticed and a swab sample was obtained. EDS analysis revealed the presence of zeolite (alumino-silicates) on the inlet side of the suction filter. A visual of the contamination and SEM/EDS results can be found in Figure 4. Additionally, the SEM/EDS analysis identified Fe-Ni-Cr with the presence of Ti and Mo. It is believed that this could be from CRES A-286, which is the makeup of the manifold. Lastly, the outlet side of the suction filter was examined and appeared to be much cleaner than the inlet side, and no longer indicating the heavy presence of zeolite.

D. Compressor Discharge Filter

Internal to the compressor on the discharge side resides a 2 micron absolute compressor discharge filter. The function of this filter is to provide protection to the sensors and valves downstream of the compressor from compressor interface particles. During TT&E, the outlet side of the filter was visually examined. A slight brown film was noticed

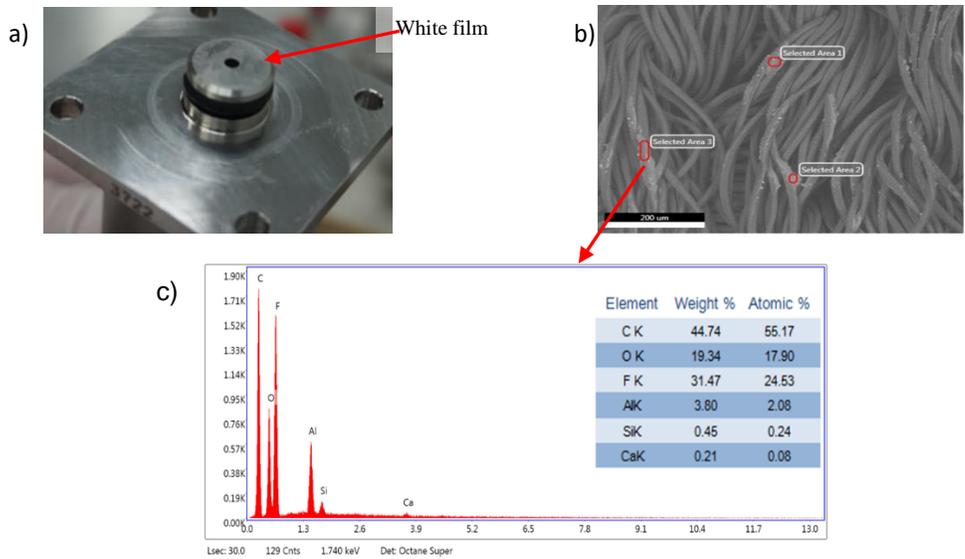


Figure 3. (a) Photo and (b) SEM image of compressor manifold bore, and (c) EDS profile of the selected area from (b).

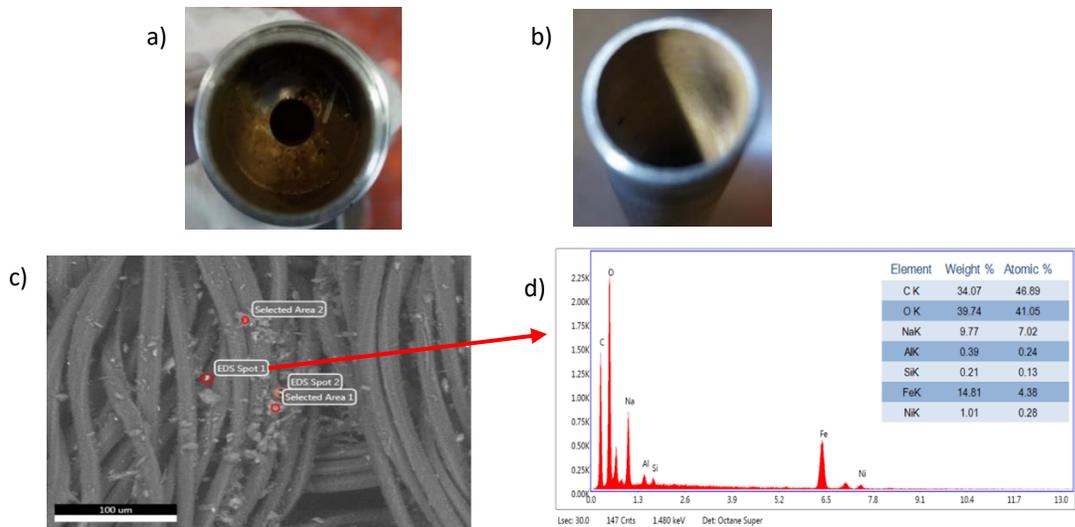


Figure 4. Photo of suction filter (a) inlet and (b) outlet, (c) SEM image of brown swab residue, and (d) EDS of selected area in (c).

on the filter and swab samples were obtained. EDS analysis revealed that the primary sources of contamination was 6000 series aluminum and fluorine. Other elements found were sulfur, calcium, and chlorine (Reference Figure 5).

Upon completion of the TT&E it was concluded that the presence of the aluminum particle contamination was the result of the CO₂ Storage tanks which had corroded. These particles were also seen in a water sample collected from the CO₂ tank in 2014. Unfortunately, return of the CO₂ Storage Tanks for examination was not possible due to the way the tanks were built into the on-orbit rack. It would have taken an unreasonable amount of rack disassembly to return even one tank. The tanks have been abandon in place with the intent to not use them again.

The fluorine was likely from the Niflor coating on the Quick Disconnects (QDs), and Rulon® seal rings within the compressor. Overall, the 2 micron filter performed its function in preventing the majority of the interface particles within the compressor from working its way further downstream.

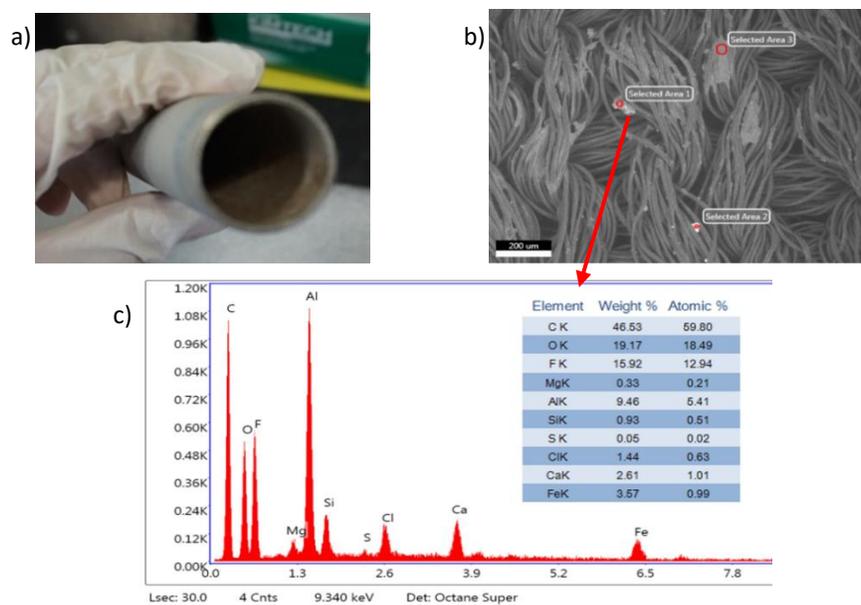


Figure 5. (a) Photo of compressor filter inlet; (b) SEM image of brown swab; (c)EDS of selected area in (b).

E. Reactor Manifold

Downstream of the compressor resides the reactor manifold. The reactor manifold receives the incoming H_2 from OGA and controls the flowrate of CO_2 into the reactor. On the CO_2 flow path, the manifold contains sensors and valves which provide fault detection, protection, and isolation.

As-received testing (range check, functional check, leak check) was performed on the sensors, valves, and manifold. Results indicated that the components operated nominally with no signs of issues. Next, reactor manifold assembly was completely disassembled and a visual inspection was performed. A significant amount of “beige/yellowish” contamination was noticed throughout the valves, sensors and corresponding manifold bores (Photos in Figure 6). Swab samples were carefully taken and an EDS analysis was performed. Results revealed that the primary contaminants were nickel based corrosion (possible sources - corroded nickel plated component in the compressor and Niflor from QDs) and aluminum corrosion products (possible source - 6000 series aluminum).



Figure 6. Contamination on manifold sensor/bore.

F. Reactor Filter

Directly upstream of the reactor resides the 10 micron reactor filter. The function of this component is to prevent fines/contamination from reaching the reactor. To examine the filter the outer housing was removed. Once exposed, significant signs of “greenish” contamination were noticed throughout (reference Figure 7). This contamination was sampled and sent for SEM, EDS, and XPS analyses. The results revealed the presence of fluorine, (which is believed to be from the Braycote that is applied to the O-rings on the valves and sensors or from degraded Niflor present in upstream QDs), traces of Fe, Mg, Mn, Cr, P (possible source - 6000 series aluminum), Nickel (Possible sources - present as nickel oxide corrosion products from nickel plated component in the compressor or degradation of Niflor coated QDs), silicon and sulfur traces (possible sources - The most likely source for sulfur is Dimethylsulfone ($DMSO_2$) from crew urine, other possible sources include byproducts of the Nafion[®] membrane from the OGA cell stack, and carbon disulfide passed from CDRA).²

G. Reactor

The core of the Sabatier system is the SA Reactor. The Sabatier Reactor combines waste carbon dioxide and hydrogen to produce water and methane using a proprietary Collins’ developed catalyst. In 2017 the reactor on-orbit

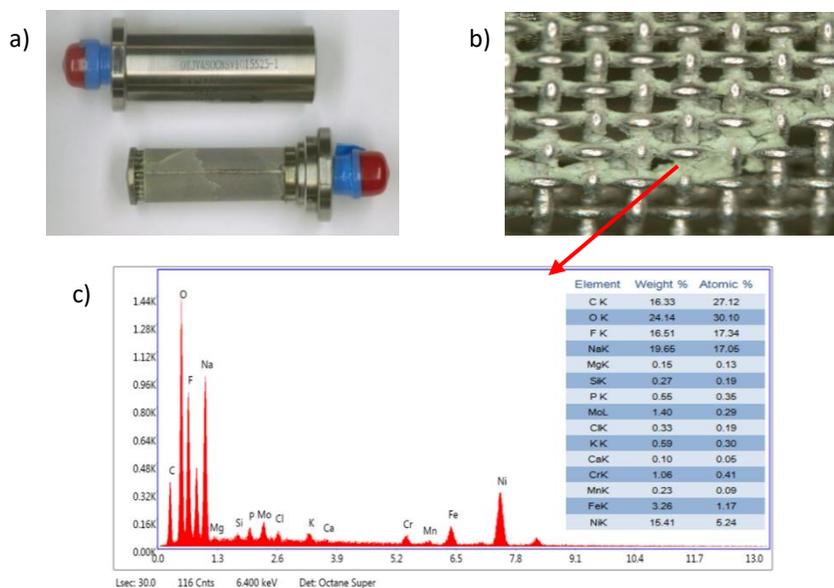


Figure 7. (a) Photo of reactor filter; (b) SEM image of “greenish” contamination on filter screen; (c)EDS results from the “greenish” residue in figure 7(b).

began to show significant signs of degradation through temperature changes indicating the front of the bed was deactivating. It was unclear as to what the cause was; whether it was from a combination of aging, contamination from the introduced H_2/CO_2 gases, or a byproduct of the reaction.

Prior to disassembly, non-destructive examination (NDE) via X-ray scans were taken to assess the spring load, location and to examine the packed bed for non-uniformity. No evidence was seen in the X-ray scans indicating breakage of the catalyst particles, clogging by small pieces, potential flow channels developed through the bed after use, or any additional abnormalities within the bed. Upon review of the NDE, it was confirmed that the spring and retaining cup remained properly aligned. The packed catalyst bed did not show any signs of channeling. Flow passages in the cooling fins were clear of debris.

Next disassembly of the reactor was performed. First the outermost layer (the heat shield and insulation- thermal blankets) of the reactor was removed. The heat shield and exterior layers of the thermal blanket appeared intact, however, the innermost layer of the thermal blanket showed signs of flaking. Once the insulation layers were completely removed, the reactor body became exposed. The exterior metal of the reactor body ranged in color reflecting the various temperatures achieved in the different zones within the reactor. After review of the materials condition, it was concluded that the variation in color of the metal was not abnormal.

Next, the reactor catalyst material was unloaded from the reactor body and the bed was split into seven sections. Sample #1 was collected from the exit of the reactor; Sample #7 was collected from the inlet. Each section of catalyst was evaluated using several test techniques as listed in Table 1. The light-off testing and space velocity challenge tests were conducted in a subscale tubular reactor with 30 cc catalyst volume to evaluate catalyst activity. Physical characterizations were performed at United Technology Research Center to examine catalyst conditions.

The first test to be performed was the “Light-off Test”. During the light-off testing, reactant gases (H_2 and CO_2) were introduced

Type	Purpose description
Light-off test	catalyst is active or not upon initial heating of catalyst reactor
Flow challenge test	distinguish catalyst activity level at different flow rate
TGA (thermogravimetric analysis)	weight loss as f (rate of temperature increase)
BET (Brunauer-Emmett-Teller)	physical surface area
SEM (scanning electron microscope)	high magnification photos
EDS (energy dispersive X-ray spectroscopy)	elemental analysis
XPS (X-ray photoelectron spectroscopy)	near-surface (< 10 nm) elemental analysis
FTIR (Fourier Transform infrared spectroscopy)	organic species
XRD (X-ray diffraction)	crystalline structure

into a catalyst bed heated above the reaction initiation temperature. If the catalyst bed temperature increases, this indicates an exothermal reaction occurs and the sample is declared active. Figure 8(a) shows the temperature profiles/results of each catalyst sample. Results show that only sample #2 and #3 were able to light off with sustainable temperature, although sample #3 was slightly unstable, compared to sample #2. The other samples did not light off, indicating they are inactive to Sabatier reaction.

The next test performed was the “Flow Challenge Test”. During the challenge test, the reactant gases were fed to sample #2 and #3 (the active catalyst) in the same subscale reactor at increasing flowrates (decreasing residence time) to check catalyst conversion efficiency as an activity indicator. In order to distinguish activity levels between catalyst samples unused pristine catalyst was tested as a reference. Data in Figure 8(b) show that samples #2 and #3 have similar methane conversion efficiencies as the unused catalyst in activity. Overall, the light-off and space velocity testing indicate that at the end of life, water production was supported by only 30% of the bed (only 2 of 7 samples were active).

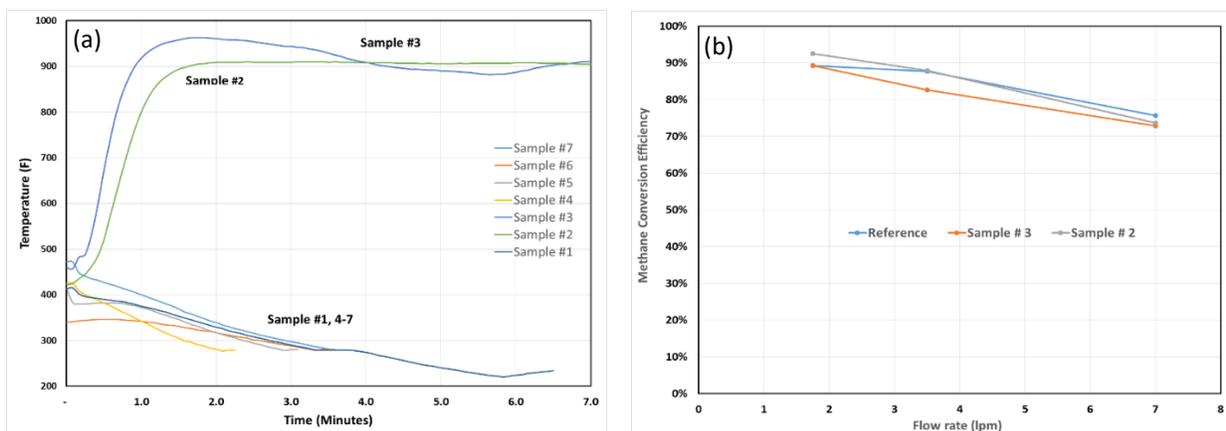


Figure 8. (a)Reactor light-off test results; (b)Flow challenge test results. Samples were taken from seven split sections from reactor inlet to outlet in the order: 7, 6, 5, 4, 3, 2, and 1. The reference sample is unused pristine catalyst.

Upon completion of the light off and space velocity challenge test, the remaining tests (TGA, BET, SEM, EDS, XPS, FTIR, XRD) were performed on the seven catalyst samples. A summary of results from this test can be found in Table 2 and 3. For comparison, the unused catalyst and catalyst support were characterized in the same setting to reveal what has changed, and what has not. In the tables, the green highlight means that character of the used catalyst is comparable to the unused one (nominal). The red and yellow colors indicate they are different (off-nominal) from what the unused “normal” catalyst should be, and the “red” is more far off than “yellow”.

After reviewing all the data, the following findings have been obtained:

1) Sulfur and silicon appeared to be present in the front of the bed. This result is consistent with no light-off in samples #4-7 catalyst, suggesting that most likely they are the catalyst poisons. XPS analysis indicates sulfates and sulfides are the sulfur compounds, siloxanes and silicon sub-oxides are the most likely silicon compounds. The lack of detected sulfur and silicon on the surface of samples #2 and #3 by XPS seems consistent with both samples showing activity through the light off and flow challenge tests.

2) Although chlorine was not detected in front of bed, fluorine was noted throughout the bed. Low amount of fluorine was also detected in the unused catalyst by XPS, which is suspected to be background noise. However, both fluorine and chlorine were noted in higher concentration at the rear of the bed in sample #1 and #2. It is also noted that sample #2 was active while sample #1 was not. XPS indicates that fluorine content in sample #1 is much higher than in sample #2, although the chlorine contents are comparable in both samples. This implies fluorine most likely caused the inactivity of sample #1. XPS indicates metal fluoride is predominant fluorine compound and there is no indication of organic fluorides.

3) After further examining the reactor, it was noticed that the Teflon seal located on the outlet end of the bed had “flowed”(reference Figure 9). This seal is primarily comprised of fluorine. Its distortion can occur at higher pressures or temperatures. It’s our believe that the reactor Teflon seal distortion may have been caused by higher than expected temperatures at the seal caused by the shift in the hot zone, excess fluorine worked its way into the back end of the

Table 1: Characterization of Catalyst Samples Results

	This test characterizes:	Identified	Inlet							Exit		Unused catalyst 'Reference'	Support
			7	6	5	4	3	2	1				
	Physical characteristic during removal		Loose flowing, some statical cling	Loose flowing	Loose flowing	Loose flowing	Loose flowing	Hard packed top layer, then loose	Very Hard packed	Very Hard packed	Free flowing	Free flowing	
Bench test	Performance	Activity level change with space velocity	No light-off	No light-off	No light-off	No light-off	Near normal activity	Near normal activity	No light-off	Active	n/a		
BET	Physical surface area (dominated by the support)	BET surface area (m ² /g)/support (m ² /g)	0.31				0.31		0.24	0.6	1		
		Average pore volume (cm ³ /g) / support (cm ³ /g)	0.72				0.74		0.66	0.62	1		
		Average pore size (nm)/reference (nm)	1.9				2		2.4	1	n/a		
XPS	Near surface (<10 nm) elemental analysis, information on bonding (qualitative) Samples mounted on C tape	F (%) (consistent with metal fluorides, no indication of organic fluorides)	0.4	0.5	1.2	0.8	0.6	2.6	5.75	0.5			
		Cl (%)	0	0	0	0	0	0.3	0.3	0.2			
		S (%) (sulfate (more abundant) and sulfide)	0.9	1.2	1	0.8	0	0	0	0			
		Si (%) (siloxanes & silicon sub-oxides)	3.9	2.7	0	0	0	0	0	0			
		Catalyst (metallic), no other metals identified (%) / reference (%) ratio'd to reference =1	1.4	2.3	2.2	1.1	0.95	0.16	0.18	1	n/a		
TGA	Weight loss over temperature range	Test performed with both N ₂ and Ar, similar/same results	-5%				-3%		-13% wt loss; peaks @ 100°C, 300°C, & 500°C (largest peak)	-13% wt loss; peaks @ 100°C, 300°C	Weight loss profile similar to 2011 sample		

Table 2: Characterization of Catalyst Samples Results

	This test characterizes:	Identified	Inlet							Exit		Unused catalyst 'Reference'	Support
			7	6	5	4	3	2	1				
	Physical characteristic during removal		Loose flowing, some statical cling	Loose flowing	Loose flowing	Loose flowing	Loose flowing	Hard packed top layer, then loose	Very Hard packed	Very Hard packed	Free flowing	Free flowing	
Bench test	Performance	Activity level change with space velocity	No light-off	No light-off	No light-off	No light-off	Near normal activity	Near normal activity	No light-off	Active	n/a		
FTIR	Organic species; additionally other combs will have (broad) IR response	No organic species	spectra may indicate hydrate/water, sulfate					spectra may indicate hydrate/water		between baseline sample and #3	similar to baseline sample	baseline sample	
SEM/EDS	High magnification photos and elemental analysis	Particles potted and cross-sections examined	tighter packed particulates with less porosity	----->					looser packed particulates with more porosity		different from support; reference material has larger structural features	baseline sample	
		F (%)	0	0	0	0	0	0.8	0.6-0.7	0	0		
		Cl (%)	0	0	0	0	0	0.2	0.2-0.3	0	0, 0, 0.1		
		Si (%)	0.2-0.3	0-0.2	0	0.2-0.3	0	0.2	0-0.2	0.1-0.2	0, 0, 0.1, 0		
		S (%)	0.3-0.4	0.4	0.4	0.3	0	0	0	0	0, 0, 0.1		
		Catalyst (%) / Reference (%)	0.74	0.92	0.90	0.92	0.90	0.90	1.0	1	0		
		Al (%)	21.57	21.75	21.5	21.9	20	21.2	20.8	20.45	14		
XRD	Crystalline structure	Support		Al ₂ O ₃ (1.33 not fully stoichiometric; more consistent with a gamma alumina					boehmite	Al(OH) ₃	largely boehmite alumina-oxy-hydroxide, amorphous AlO(OH)		
		Catalyst		catalyst present as metal					catalyst present as metal	catalyst present as metal oxide and metal	n/a		

catalyst causing significant poisoning in sample #1.
4) No metal poisons were detected through the reactor bed. Also no carbon deposit was detected on the catalyst surface, even after hot zone shifting to the rear of reactor during late attempts to activate the reactor. These results suggest non-catalyst metals or carbon did not contribute to the inactive catalyst sections in the Sabatier reactor.

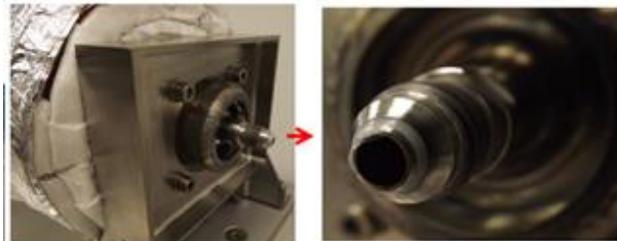


Figure 9. Distorted Teflon seal on the reactor outlet.

H. Heat exchanger

The condensing heat exchanger reduces the temperature of the product gas stream coming from the reactor to condense the maximum amount of water. On-orbit the heat exchanger performed as expected. During disassembly, the nickel plated fins were observed to be in good condition; however a slight brown film was noticed at the air inlet. Material samples were taken, and the EDS analysis showed the presence of chloride and sodium, likely introduced with the cooling air.

I. Separator

The gas-liquid separator receives two phase fluid from the outlet of condensing heat exchanger, separates the liquid water from the waste gases, delivers waste reactant gases and product methane through the vent line to space vacuum. When the separator fill level meets criteria for water delivery, it spins at a higher rpm to deliver the water above the pressure of the waste water bus to the bus. On-orbit, the separator began to experience faults during extended periods of Standby at 900 rpm. A work-around was developed to operate at 1100 rpm; no further faults were obtained with the higher nominal rpm.

Prior to disassembly, an X-ray examination was performed to assess the internal condition of the separator for any signs of wear, disengagement, buildup or anything abnormal. Results were nominal. Upon completion, it was concluded that mechanically the internals of the separator appeared to be in good condition. No significant observations were recorded.

On-orbit the separator failed during extended standby operation (several hours) at 900 rpm. There were no issues seen during process at 900 rpm on the ground, and the faulting during extended standby operation was something only seen during on-orbit operation. During ground testing several conditions were run on the Separator in an attempt to duplicate the on-orbit failure. Conditions were run at both 900 and 1000 rpm, varying the inlet and exit pressures, water fill levels as well as the orientation. However, the team was unable to duplicate the on orbit failure. No issues were identified in any test with the separator's performance. However, in all tests, there were observations of gas bubbles developing in the differential pressure (DP) sensor's high pressure line and water moving in/out of separator during testing.

J. Separator Manifold

The separator manifold consists of multiple pressure sensors and valves, used to monitor and provide feedback to the separator to control delivery of water to the waste water bus and gas flow to the system backpressure regulator and valves leading to vacuum. On-orbit the separator manifold, sensors and valves did not show any signs of performance degradation. One valve initially failed internal leakage during ground testing but upon cycling performed nominally. A visual examination on the separator manifold was performed. During disassembly, each check valve, and pressure sensor was carefully removed. The removed valves, sensors and corresponding manifold bores were examined and "white" tightly held contamination was noticed throughout. Subsequent EDS analysis identified calcium and sulfur on the manifold by the separator DP sensors and iron and fluorine were identified on the back pressure regulator swab sample.

K. Water Sampling

During the disassembly of the Sabatier System, water samples were collected in several locations including separator and lines leading to the waste water bus (WWB). Table 4 shows the analysis results. As illustrated in the Tables, F, Cl, SO_4^{2-} , Na^+ , K^+ , Ca^{2+} , Ni, Si were all presented with noticeable amounts in the DP sensor, separator line, separator exit line to WWB, line of WWB to check valve (CV), and then to QD. These results are consistent with other TT&E results mentioned above in each individual component, further confirming contamination of the SA unit.

		2014 sample	2018 Sabatier TT&E Samples					
		Water purged from CO2 tank 2014:352	Separator Water 8/1/18 (post all ground testing)	Water from Separator EXT Test (as-received)	Separator exit Line to Waste Water Bus (ID#1)	DP Sensor High Leg (ID#2)	Line between WWB and CV (ID #3)	Sample from waste H2O QD removal (ID #4)
TOC (ppm)		250		9.8		ND	20.1	49
F (ppm)		2	0.31	0.2	1.43	1.84	2.1	<5
Cl (ppm)		7.6	1.41	1.01	<0.05	0.39	<0.5	<5
NO ₂ ⁻ (ppm)		<0.05	0.21	<0.05	<0.05	<0.05	<0.5	<5
SO ₄ ²⁻ (ppm)		1.4	11	6.41	0.07	0.1	1.1	8.2
NO ₃ ⁻ (ppm)		<0.05	0.98	<0.05	<0.05	<0.05	<0.5	9.8
PO ₄ ³⁻ (ppm)		<0.05	<0.5	<0.05	<0.05	<0.05	5.3	23
Li ⁺ (ppm)		<0.05	<0.5	<0.05	<0.05	<0.05	<0.5	<5
Na ⁺ (ppm)		10	2.67	0.8	<0.05	0.09	15.7	30.7
NH ₄ ⁺ (ppm)		21	2.02	4	6.64	17.4	6.5	6.2
K ⁺ (ppm)		2.9	0.77	0.81	<0.05	<0.05	1.82	<5
Mg ²⁺ (ppm)		<0.05	0.51	0.14	<0.05	0.07	0.21	<5
Ca ²⁺ (ppm)		<0.05	0.76	0.41	<0.05	0.11	0.42	<5
Aluminum (ppm)	Total	0.27	<0.01	0.02	0.04	0.02	0.03	<1
Chromium (ppm)	Total	0.14	<0.01	<0.01	<0.01	<0.01	<0.1	<1
Iron (ppm)	Total	2.7	<0.01	0.02	0.01	0.29	0.1	<1
Nickel (ppm)	Total	116	1.14	0.95	0.01	0.09	3.6	11
Silicon (ppm)	Total	11	2.29	1.29	0.18	0.65	<0.1	6.4
Zinc (ppm)	Total	1.3		0.15	<0.01	<0.01	0.15	
DMSD (ug/L)					<625			
MMST (ug/L)					<1000			

III. Results and Discussion

Throughout the TT&E as the system was disassembled, about 70 swab samples were collected for analysis of the contamination found in the SA. Figure 10 displays the contaminant trace throughout the system. Overall, the three major compounds found were aluminosilicates/zeolites, silica, and trace contaminants from 6000 series aluminum (these compounds are listed as arrows in the figure). The stars indicate additional elements of concern identified through this TT&E.

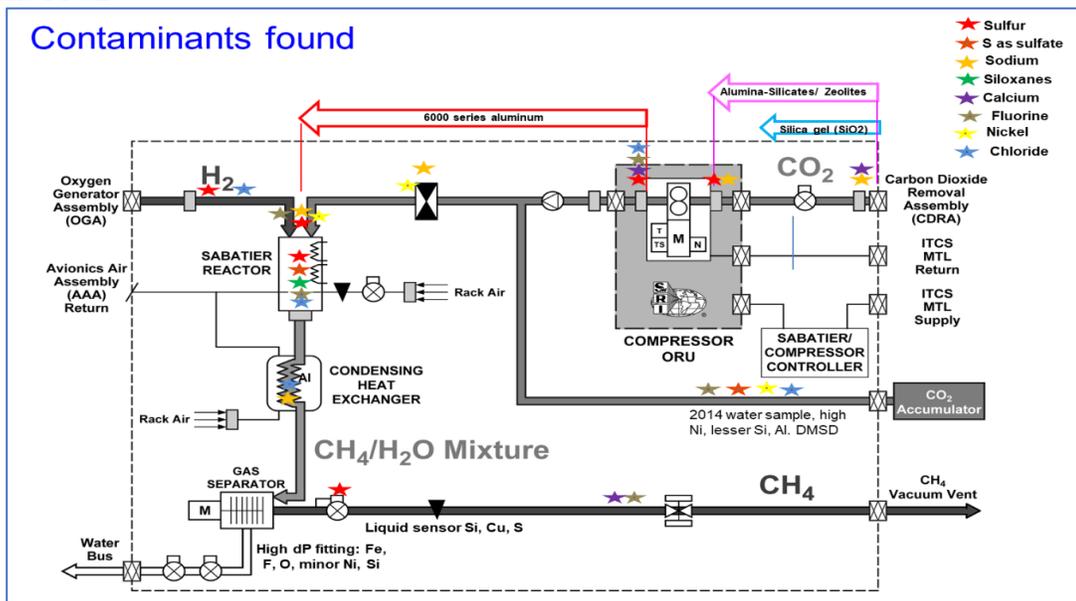


Figure 10. Contamination trace in the Sabatier assembly.

The predominant contaminants to the Sabatier catalytic reactor are sulfur, silicon, fluorine, and chlorine; all of which are well known catalyst poisons.¹ To understand which contaminant is the “worst” compound to the catalyst, total mass amount of silicon, sulfur, fluorine, and chlorine in each section were estimated from the EDS data and was

plotted in Figure 11. The light-off testing results are also included to correlate the results. It is noted that sections #4-7, with sulfur/silicon present, do not light off even though the total poison mass (between 0.2-0.4 grams) is less than sections #1 and #2 (about 0.65 grams) near the outlet. Section #5 with only sulfur presents does not light off. Section #2 with silicon/fluorine/chlorine present lights off while section #1 does not. Overall, the contaminant “worst” order is estimated to be sulfur \geq silicon > fluorine, chlorine.

During the Sabatier operation on orbit, contaminants of S/Si/F/Cl worked through several upstream filters (i.e., CO₂ filter, compressor suction filter/discharge filter, and reactor filter) even at down to 2 micron size and then deposited onto the catalyst surface. This result implies that those contaminants were likely not in the form of fine shattered power such as zeolite, instead, most likely in the form of gas compounds. To identify possible sources for them, both hydrogen and CO₂ gas streams to the Sabatier were evaluated by NASA/Boeing.²⁻⁴

The analysis indicates that DMSO₂ is the most likely compound for sulfur.² DMSO₂ originates from crew urine and has been found in WPA waste water sample and OGA recycle water loop.² It was reported as a component of the urine distillate produced by the Urine Processor Assembly and present at low concentration (median concentration is 120 $\mu\text{g/L}$) in the product water.³ DMSO₂ concentrates in the OGA recirculation loop where it has been measured at concentrations as high as 49 mg/L.⁴ It is a volatile compound, likely partitions between the water phase and the H₂ vapor phase in the OGA rotary separator assembly and travels with H₂ to the Sabatier.² DMSO₂ is also reported in humidity condensate at an average 142 mg/l which corresponds a cabin concentration of approximately 0.05 mg/m³ in equilibrium with water⁵, and thus it can also pass through the CO₂ stream to Sabatier.

The most likely source for silicon is polydimethylsiloxane (PDMS) in ISS cabin air. PDMS originates from crew hygiene products, silicone components/tubing, lubricants/adhesive etc.⁶ PDMS in the cabin atmosphere can pass on to Sabatier through CO₂ stream, it can also degrade and hydrolyze over time to produce smaller molecules of methyl siloxanes such as dimethylsilanediol (DMSD),⁶ which is volatile and dissolves in water condensate from heat exchanger and then passes on through WPA water to OGA H₂ stream and to Sabatier.

As shown in Table 2, fluorine and chlorine are present mainly in the rear sections of reactor. Reactor Teflon seal is considered the most likely source for fluorine. Teflon seal distortion was observed due to a higher than expected temperatures at the seal related to a shift in the hot zone, excess fluorine worked its way into the back end of the catalyst. It is unclear how chlorine presented in the rear sections, as no chlorine was identified from the Teflon seal. One hypothesis is that dichloromethane as the most predominant halogen from cabin air passed through CO₂ stream to Sabatier, and was pushed toward the rear section when siloxanes or DMSO₂ kicked in. A similar behavior can also be possible that refrigerants such as R-218, R134a as fluorine compounds passed on to Sabatier from cabin air, and be pushed toward the rear section by adsorption of S/Si compounds.

The results from this Sabatier TT&E provide valuable information about conditions of major components, which will help future design of more robust Sabatier system regarding material selection and operation conditions. In term of contaminant prevention, several mitigation strategies should be considered on addressing the sources (cabin air, product water) and within Sabatier system:

(1) Alumino-silicate particles

These particles create a risk for sensors and valves. The existing 2 micron filter within the CO₂ compressor worked well in capturing the alumino-silicate particles. Recommendation is to retain 2 micron filter on the CO₂ delivery line.

(2) Corrosion products

The CO₂ compressor has a nickel plated component which corroded when water condensed inside the compressor. The QDs in the CO₂ system were selected for operation with gases and Niflor is present on some of the QD internals, which provides a source of nickel. The CO₂ accumulator tank is made of 6000 series aluminum and it was never passivated. Aluminum based corrosion particles were seen downstream of the aluminum accumulator tank from

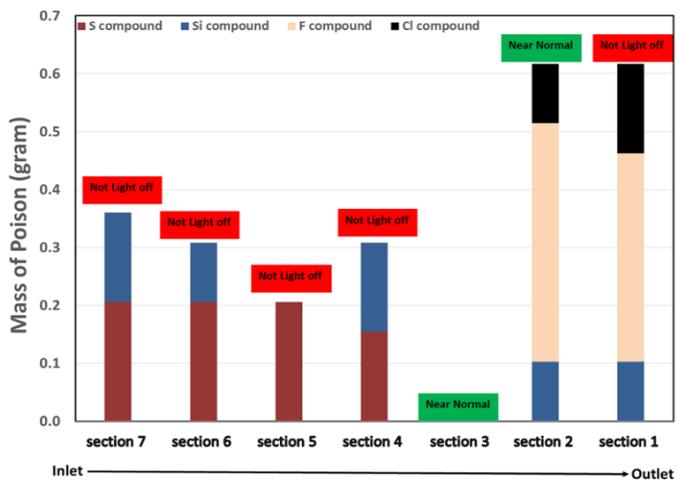


Figure 11. Estimated contaminant mass in each section of Sabatier reactor. The split sections are in the order: 7, 6, 5, 4, 3, 2, and 1 from reactor inlet to outlet, respectively.

previous water exposure and could continue to make their way downstream to the reactor manifold. While there were no valve or sensor failures in the reactor manifold, the concern remains if there are residual corrosion products in the existing tanks which could eventually enter a rebuilt Sabatier system.

The recommendation is to replace aluminum accumulator tank and eliminate water condensation by maintaining a low dew-point in the inlet CO₂. This would address the nickel corrosion in compressor and QD hardware, and aluminum corrosion. If tank replacement is not feasible, other risk mitigation needs to be pursued, e.g. development of replaceable/maintainable filtration with a tighter micron rating. However, some of pressure drop issue across the filter need to be addressed ensure a minimum risk of an unacceptable pressure increase if condensed water was present in the filter. QDs without Niflor is highly recommended in case of CO₂ feed with a level of humidity. Any new compressor should include review of materials and discussion of ways to make the system robust to an off-nominal input of humid gas.

(3) Sulfur, silicon and halogen poisons

Sabatier is downstream of other life support systems CDRA, UPA/WPA/OGA and any trace of contaminants in upstream H₂ and CO₂ from air and waste water/humidity condensate could pass on to Sabatier if not treated. NASA has been actively pursuing research, development, and implementation of new control approaches in the ISS. In the past few years, the activated carbon/HEPA filter replacements for the ISS Bacteria Filter Elements are distributed at the cabin ventilation duct inlets in each U.S. Segment module, which shows a capability to remove siloxanes in cabin air.⁷⁻⁸ Also regular flushing of the OGA recirculation loop would be a robust mitigation approach to remove all contaminants from hydrogen stream to Sabatier. In addition, Collins is currently working with NASA to develop a Sabatier guard bed to be placed upstream of Sabatier reactor to protect it from identified trace S/Si/F/Cl contaminants. The ultimate goal is to extend life of Sabatier reactor on-orbit and in future missions.

IV. Conclusions

Sabatier Assembly degraded on-orbit after being operated for about 20,000 hours and produced over 1000 liters water. Extensive TT&E was conducted on the ground on major components. The results reveal that there are three major contaminant compounds, i.e., alumino-silicates/zeolites, silica, and trace contaminates from corrosion of 6000 series aluminum in CO₂ accumulator and nickel plated compressor/Niflor coating. The Sabatier catalyst reactor was contaminated by sulfur/silicon/fluorine/chlorine, resulting in about 70% catalyst becoming inactive. Sulfur/silicon appears to be the “worst” poisons to catalyst among others. In order to extend Sabatier operation life, several mitigation strategies including material replacement in compressor/accumulator/QDs, low humidity operation in CO₂ feed, installation of siloxane scrubber filter, flushing of OGA recirculation loop, and Sabatier guard bed are considered to be effective.

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