Development of Advanced ISS-WPA Catalysts for Organic Oxidation at Reduced Pressure/Temperature

Ping Yu¹, Tim Nalette²,

Hamilton Sundstrand Space Systems International, Inc., A UTC Aerospace Systems Company, Windsor Locks, CT, 06096

Matthew Kayatin³

NASA Marshall Space Flight Center, Huntsville, AL 35812

The International Space Station (ISS) Water Processor Assembly (WPA) processes a waste stream via multi-filtration beds, where inorganic and non-volatile organic contaminants are removed, and a catalytic reactor, where low molecular weight organics not removed by the adsorption process are oxidized at elevated pressure in the presence of oxygen and at elevated temperature above the normal water boiling point. Operation at an elevated pressure requires a more complex system design compared to a reactor that could operate at ambient pressure. However, catalysts currently available have insufficient activity to achieve complete oxidation of the organic load at a temperature less than the water boiling point and ambient pressure. Therefore, it is highly desirable to develop a more active and efficient catalyst at ambient pressure and a moderate temperature that is less than water boiling temperature. This paper describes our efforts in developing high efficiency water processing catalysts. Different catalyst support structures and coating metals were investigated in subscale reactors and results were compared against the flight WPA catalyst. Detailed improvements achieved on alternate metal catalysts at ambient pressure and 200°F will also be presented in the paper.

Nomenclature

η	Internal Effectiveness Factor
ISS	International Space Station
MSFC	Marshall Space Flight Center
ррт	Part per Million, i.e., mg/L
psia (psig) Pound per Square Inch Absolute Pressure (Gauge Pressure)
sccm	Standard Cubic Centimeters per Minute Flow Rate
SEM	Scanning Electronic Microscopy
TOC	Total Organic Carbon
UTAS	United Technology Aerospace Systems
WPA	Water Processor Assembly

I. Introduction

The ISS Water Processor Assembly (WPA) is designed to produce potable water from several wastewaters, primarily including crew and animal latent, waste hygiene, and urine distillate. A schematic of the WPA is shown in Figure 1. Two main components that provide chemical treatment in WPA are multifiltration beds and catalytic reactor assembly. The multifiltration beds adsorb organic compounds and remove ionic compounds via ion exchange. However, some organic contaminants that are highly soluble in water are not effectively removed by adsorption and these compounds are typically low molecular weight alcohols, ketones, and aldehydes. The primary function of the WPA catalytic reactor assembly is to oxidize these compounds to water, organic acids and CO_2 . The organic acids and CO_2 (as bicarbonate or carbonate) are subsequently removed via ion exchange. The WPA catalyst reactor operates at 265°F and 55 psig with a gaseous oxygen feed to achieve greater than 95% organic conversion efficiency [Ref. 1]. Operation at elevated temperature requires an elevated system pressure to prevent water boiling and the equipment associated with high pressure and temperature adds mass and complexity to the WPA. However, the current ISS state-of-art catalyst does not have sufficient activity to achieve complete oxidation of the organic

¹Research and Development Engineer, Hamilton Sundstrand Space Systems International, Windsor Locks, CT 06096

²Chief of Advanced Systems and Technologies, Hamilton Sundstrand Space Systems International, Windsor Locks, CT 06096

³Aerospace Engineer, Environmental Control Systems, NASA/MSFC, Huntsville, AL 35812

compounds at ambient pressure and a temperature less than the water boiling point. The primary goal of this research was to develop a more active catalyst with sufficient activity at ambient pressure and a temperature close to 200°F.



Figure 1. Schematic of Water Processor Assembly (WPA) at ISS

To develop a more active catalyst, it is first important to understand the multiple impacts of reductions in operating temperature and pressure. The primary impact of temperature reduction will be a corresponding reduction in catalyst activity, *i.e.*, the overall reaction rate, although the temperature decrease will increase oxygen solubility in water. A reduction in operation pressure to near ambient condition may have significant impact as oxygen solubility will be reduced dramatically. As shown in Figure 2 [data were extracted from Ref. 2], the solubility of oxygen at 200°F and ambient pressure is approximately 20% of the current ISS conditions of approximately 55 psig and 265°F. Since any oxidation reaction occurring in the pores of the catalyst results from diffusion of dissolved O₂ from the bulk solution, this reduced O₂ concentration in the bulk solution will have a negative impact on the rate of diffusion of O_2 into the catalyst pores and may have a corresponding negative impact on the rate of oxidation. Additionally, the reduction in pressure will also result in a significant reduction in the rate of O₂ dissolution,





perhaps by a factor of 3 or more, as a result of dropping the O₂ pressure from approximately 55 psia to 14.7 psia,

causing an additional reduction in the overall rate of reaction. Therefore, with both decreases in operating temperature and pressure, the overall reaction rate will be reduced due to reduced catalyst activity and decreased oxygen concentration at catalyst surface.

The surface area of catalyst support plays a noticeable role to overall catalytic reaction as the organic oxidation reaction occurs on available interior catalyst sites. Recent testing of the ISS-WPA flight catalyst at UTAS [Ref. 3] has shown that shifting the particle size from a uniform mixture of 8x14 mesh to 12x14 mesh resulted in a shift in performance of 0.31 ppm TOC to 0.14 ppm TOC in the effluent against the standard contaminant challenge load of approximately 35 ppm TOC. The slightly smaller particle size results in higher catalyst surface area per volume, and a more effective use of the available catalyst area since similar diffusion rates would access more of the available catalyst.

Pore size and distribution, as a characteristic of catalyst support structure, also plays a big role in effectively transporting reactants from bulk solution to the catalyst sites inside pores and transporting reaction products out from inside pores. Small pores limit the accessibility of internal surface because of increased resistance to diffusion of reactants inwards. Diffusion of products outwards is slowed as well. This becomes more dramatic when the reactant concentration in bulk solution is reduced significantly as in the case of operating at ambient pressure and 200°F. In modeling of an early WPA aqueous phase oxidation catalyst, Yang, et al. [Ref. 4] noted that a lower reaction rate resulted from a lower internal effectiveness factor related to intra-particle diffusion, where the internal effectiveness factor η is referred as the following [Ref. 5],

$\eta = \frac{Actual \ overall \ rate \ of \ reaction}{Rate \ of \ reaction \ if \ entire \ interior \ surface \ was \ exposed \ to \ the \ the \ external \ surface \ concentrations}$

Beck and Schultz [Ref. 6] demonstrated that hindered diffusion in pores can be significant when the size of the diffusing molecule is a fraction of the effective pore size. Early work by Akse. et.al. [Ref. 7] also shows that the developed supports with partially ordered interconnected mesopores (5-25 nm) results in a high surface, high pore volume, and reduced diffusion distances for reactants and byproducts to and from interior catalyst sites, which significantly improves the organic oxidation rate at ambient temperature. Based on these works, we propose a novel catalyst support with bimodal pore distribution for overall reaction rate improvement [Ref. 8]. The bimodal catalyst structure is comprised of sub-mesopores and macropores. The sub-mesopores will maintain a high surface area, *i.e.*, a high catalyst area for the oxidation reaction to occur as the conventional catalyst support. The macropores will reduce tortuosity of diffusion channels, diffusion length and diffusion resistance of oxygen reactant and oxidation products/byproducts. Thus the diffusion rate, the internal effectiveness factor, and overall reaction rate can be dramatically increased.

Alternate metal or alloy catalyst developments have been actively pursued to improve organic oxidation rates and organic conversion efficiencies in the past decades [Ref. 1, 7, 9-14]. Based on our previous catalyst development work [Ref. 1, 3, 10], we have identified alternate metal or alloy catalysts to investigate for this application. Detail of development and test results will be presented in the Results Section of this manuscript.

II. Experimental Section

Identified catalysts were prepared using a conventional incipient wetness impregnation procedure and subsequent hydrogen reduction. Their evaluations were conducted in a tubular catalyst reactor either in 36 cc volume or 200 cc volume. The 36 cc reactor was selected for catalyst screening tests, while the 200 cc subscale reactor was selected as it was used for historical development test of the flight WPA catalysts at UTAS. Figure 3 shows a block diagram of catalyst test rig. An organic challenge solution was pre-heated through a regenerable heat-exchanger and a separate heater, and then fed to a catalyst reactor continuously. Each catalyst reactor was tested by flowing an organic challenge through it at 3.6 sccm or 20 sccm flow rate, which gives a residence time of 10 minutes. Ambient or pressurized oxygen gas was fed as a reactant to the reactor at 3 sccm rate for all tests. Reactor effluent containing organic oxidation products passes through the regenerable heat-exchanger to warm the reactor influent before discharged to a drain.

Each catalyst reactor was subjected to one of three types of organic challenge solutions, described as follows, and was evaluated at the sequence of Type I, Type II, and Type III:

Type I challenge is a mixture of ethanol and 2-propanol in volume ratio of 2:1 and with 35-40 ppm total of organic carbon (TOC). It simulates an ersatz solution, with ethanol representing the organics that can be easily oxidized to carbon dioxide and water, and 2-propanol representing the other organics that are difficult to oxidize in the reactor since 2-propanol forms acetone as an intermediate compound during the oxidation process;

Type II is the required Ersatz challenge with compounds identified by MSFC and listed in Table 1. TOC of the challenge is about 35 ppm;

Type III is the goal Ersatz challenge with additional compounds such as formic acid and urea to the required Ersatz compounds. Table 2 lists all organic compounds and their concentrations. TOC of the challenge feed is about 65 ppm.



Figure 3. Block diagram of catalyst test rig.

Performance of each developed catalyst was evaluated in each challenge feed at the conditions in the following sequence:

(1) 265°F, 65 psig; (2) 230°F, 65 psig; (3) 230°F, 30 psig; (4) 200°F, 30 psig; and (5) 200°F, 0 psig.

Each reactor was maintained at one of the aforementioned test conditions for at least 96 hours and one effluent sample was taken in every 24-48 hours. At least 3-4 samples were collected at one test condition and in some cases such as 200°F, 0 psig, more than 6 samples were obtained. All reactors were operated continuously 24 hours a day and 7 days a week until their performances at all the aforementioned test conditions were evaluated. TOCs of the effluent samples were determined using Phoenix 8000 TOC Analyzer. In most cases, if a TOC value is greater than 3 ppm, then the same sample will be further analyzed for its non-ionic TOC value. When tested at Type I challenge, the non-ionic TOC of effluent was determined from the difference of TOC and ionic carbon, *i.e.*, acetate, determined by using Dionex ICS-3000 ion chromatography system. When tested at the Type II or III challenge, the non-ionic TOC was obtained from TOC of an effluent that was pre-treated with Purolite Ultra Clean UCW3600 ion-exchange resin to remove all ionic compounds. TOC performance data present in this paper are average values among the collected samples at each test condition.

Compound	Load (mg/L)	TOC (mg/L)
Acetaldehyde	1.8	0.98
Acetone	4.6	2.85
Ethanol	25.4	13.24
Methanol	5.3	1.99
Propylene Glycol	23.5	11.13
Ethylene Glycol	4.1	1.59
Formaldehyde	3.8	1.52
1-propanol	0.3	0.18
2-propanol	2.7	1.62
1-butanol	1.0	0.65
TOC (ppm)	-	35.75

Table 1. Required Ersatz Feed, Type II Challenge Load

Table 2. Goal Ersatz Feed, Type III Challenge Load

Compound	Load (mg/L)	TOC (mg/L)
Acetaldehyde	2.74	1.49
Acetone	4.4	2.73
Ethanol	39.2	20.44
Methanol	7.94	2.98
Propylene Glycol	35.4	16.76
Ethylene Glycol	5.5	2.13
Formaldehyde	5.9	2.36
1-propanol	0.45	0.27
2-propanol	1.6	0.96
1-butanol	1.5	0.97
Formic acid	49.9	13.02
Urea	3.55	0.71
TOC (ppm)	-	64.82

III Evaluation Results and Discussion

A. Catalyst Support with Bimodal Pore Structure

The WPA catalyst support is granular activated alumina with a particle size of 8x14 mesh. The support is comprised of single pores with a diameter less than 10 nm and total pore volume of 0.5 cc/gram. The catalyst has demonstrated a reasonably high conversion efficiency of organic contaminants, *i.e.*, above 95% at the test condition of 265° F and 55 psig [Ref. 1]. However, its organic contaminant conversion is dramatically reduced at ambient pressure and a temperature close to 200° F. One of factors for the lower conversion, as pointed out in the Introduction, is the decreased oxygen concentration at the catalyst sites due to reduced oxygen solubility by a factor of at least 5 and the reduced dissolution rate by a factor of at least 3. To improve the overall reaction rate, we investigated a bimodal pore structure as an alternate catalyst support to improve diffusion of available oxygen in water stream.

The bimodal pore catalyst support is comprised of pores with diameters from 1 nm to 20 nm and pores with diameters from 100 nm to 1000 nm. The pores with diameters from 1 nm to 20 nm are micropores /mesopores and are of similar size to the conventional catalyst support. They provide a high surface area, *i.e.*, high catalyst area for the oxidation reaction to occur. The pores with diameters of 100 nm to 1000 nm are macrospores, which possesses more open path, less tortuosity, and less diffusion length for oxygen to transport from the water bulk solution to the catalyst surface, and also for organic oxidation products to diffuse from the catalyst sites to the water bulk solution, compared to the conventional micropore structure. Pore size distributions of the supports for HSWPA02 and

HSWPA03 catalysts were characterized with the mercury intrusion porosimetry analysis method per ASTM D4284-12 using the AutoPore IV 9500 instrument from Micromeritics Instrument Corporation. Figure 4 shows their plots of differential intrusion vs. pore size. As shown in the Figure 4, the HSWPA02 support displays two distinct peaks. The first peak falls in the range of 1 nm to 20 nm and the second peak falls in the range of 100 nm to 1000 nm. Percentage of pore volume for the macropores (from 100 to 1000 nm) is estimated to be about 22%. However, the plot of differential intrusion vs. pore size of HSWPA03 support only yields one distinguished peak as shown in Figure 4. This single peak sizes in the range of 1 nm to 20 nm. Therefore, the bimodal pore structure of HSWPA02 support is distinguishable from the single modal structure of HSWPA03 support. With their structure difference, TOC performances of catalysts on these supports were further evaluated in the reactor testing as shown later in this manuscript.



Figure 4. Pore size distributions of the supports for HSWPA02 and HSWPA03 catalysts

Scanning Electronic Microscopy (SEM) pictures of the HSWPA02 and HSWPA03 catalysts were taken using JSM-IT300LV instrument from JEOL and are given in Figure 5. As seen in Figure 5, morphologies of catalysts HSWPA02 and HSWPA03 are similar and they are porous with less-defined grain boundaries. It also noted in the Figure 5 that particle pack density of HSWPA02 appears different from the HSWPA03 catalyst, and the HSWPA03 catalyst seems more intensely packed.



(a)HSWPA02

(b) HSWPA03

Figure 5. SEM pictures of HSWPA02 and HSWPA03 catalysts

Four catalysts on four different supports, *i.e.*, HSWPA01, 02, 03, and baseline ISS-WPA, were evaluated experimentally for TOC conversions. They were prepared with approximately the same percentage of metal loading using the same catalyst preparation procedure. The baseline ISS-WPA is a catalyst with the same metal formulation

and alumina support as the one that is used currently at ISS. The supports for HSWPA01 and 02 catalysts contain bimodal pores while the supports for HSWPA 03 and baseline ISS-WPA catalysts are comprised of single mode pores. BET surface areas of HSWPA01, 02, and 03 catalysts are in the range of 200-275 m²/g, slightly less than the baseline ISS-WPA catalyst of 300 m^2/g . The HSWPA02 and 03 supports are in sphere shape, the HSWPA01 support is pellet, and the baseline ISS-WPA support is granule. Their TOC performances were evaluated in a 36 cc reactor with Type I ethanol/isopropanol challenge (volume ratio = 2:1 and 40 ppm TOC). Figure 6 shows their effluent TOC and non-ionic TOC performances. As seen in the Figure 6, TOC values of all tested four catalysts are less than 0.5 ppm at 265°F, 65 psig and they are reasonably comparable to each other. However, as the test pressure and temperature decreases to 230°F, 30 psig, and to 200°F, 0 psig, the bimodal HSWPA01 and 02 catalysts display lower TOCs and non-ionic TOC values than those of single mode HSWPA03 and baseline ISS-WPA catalysts, and the reduction of TOC and non-ionic TOC by HSWPA02 is more significant than the other catalysts. This impact is more dramatic at lower temperature/pressure such as 200°F, 0 psig, where oxygen concentration is reduced the most and the diffusion effect is more predominant. Repeat tests in the subscale 200 cc reactor also confirm these results (as shown later in Figures 7 and 8). Therefore, a bimodal catalyst structure is proved to be a viable approach to enhance organic contaminant oxidation rate and the removal rate at ambient pressure and lower temperature of 200°F.



Figure 6. TOC and non-ionic TOC performances of catalysts with different supports

B. Alternate Metal or Alloy Catalyst

The other approach we have explored for improvement of organic oxidation rate was to develop alternate metal and alloy catalysts in an aim to increase catalyst activity at lower temperatures. Table 3 lists the catalysts that have been developed and notations of metal or support types. Elements of the alternate metal and alloys are selected from the VIIIB group of Periodic Table. The baseline support in Table 3 is referred to the alumina support for the ISS-WPA catalyst and the alternate support 2 is specified as the support with a bimodal pore distribution as illustrated in Figure 4. The catalysts were prepared via a conventional incipient wetness impregnation procedure and subsequent hydrogen reduction at 500°C. TOC performances of these catalysts were evaluated in 200 cc reactor with challenge feeds in the sequence of Type I - ethanol/isopropanol solution (TOC = 35 ppm), Type II - required Ersatz solution (TOC = 35 ppm), and Type III - goal Ersatz solution (TOC = 65 ppm), and at the test conditions in the sequence of (1) 265°F, 65 psig; (2) 230°F, 65 psig; (3) 230°F, 30 psig; (4) 200°F, 30 psig; and (5) 200°F, 0 psig. Figure 7, 8, and 9 display their performances in both TOCs and non-ionic TOC reductions. It should be noted that non-ionic TOCs were calculated from values of TOC and ionic carbon (*i.e.*, acetate from ionic chromatography) and the negative values of HSWPA02C in Figure 7(b) should be interpreted as below detection limit of our analytical technique. As seen in Figures 7 and 8, the catalyst HSWPA02C loaded on the bimodal support shows lower TOC and non-ionic TOC values than the baseline ISS-WPA catalyst at all tested conditions and at Type I or II challenge feeds. These results are consistent with the test results shown in Figure 6 and further confirm the high oxidation activity of the bimodal pore structure of catalyst support.

Table 3. List of Catalysts Developed.

Catalyst	Catalyst/Support
Baseline ISS-WPA	baseline metal/baseline support
HSWPA02C	baseline metal/alternate support 2
HSWPA12	bimetallic1(metal ratio1)/alternate support 2
HSWPA13	alternate metal1/alternate support 2
HSWPA14	bimetall2/baseline support
HSWPA15	bimetallic1(metal ratio 2)/alternate support 2
HSWPA16	bimetallic1(metal ratio1)/baseline support
HSWPA17	pre-treated bimetallic1(metal ratio1)/baseline support

Figure 7 shows TOC performances of alternate metal or bimetallic catalysts HSWPA12, 13, 14, 15, and 16; the baseline ISS-WPA and HSWPA02C are included for comparison. The HSWPA13 and 14 catalysts don't perform better than the HSWPA12 or 15 at all tested conditions within the test duration. HSWPA12 and 15 are the best catalysts among all alternate metal or alloy catalysts in terms of lowest TOCs after initial higher TOCs. As shown in Figure 7, they have a similar performance trend, *i.e.*, do not perform better than the baseline ISS-WPA catalyst initially at higher pressure/ temperature but out-perform the baseline ISS-WPA at 200°F, 0 psig. Further evaluations of HSWPA 12 and 15 catalysts with Type II - required Ersatz solution (TOC = 35 ppm) in Figure 8, and Type III goal Ersatz solution (TOC = 65 ppm) in Figure 9 show dramatic reductions in both TOCs and non-ionic TOCs, compared to the baseline ISS-WPA or HSWPA02C catalysts. For example, TOC of HSWPA12 was 13 ppm at 200° F, 0 psig and with the required Ersatz feed (TOC = 35 ppm), approximately 50% reduction from the TOC of baseline ISS-WPA at the same test condition. The corresponding non-ionic TOC of HSWPA12 was about 50% less TOC of the baseline ISS-WPA as well, as seen in Figure 8. A similar trend of TOC reduction by HSWPA12 and 15 was also observed at 200° F, 0 psig and with the goal Ersatz feed (TOC = 65 ppm) in Figure 9. Both HSWPA12 and 15 have the same bimetallic elements but in different molar ratios. By margin, HSWPA12 performs slightly better than HSWPA15 catalyst and HSWPA12 catalyst possess the highest activity toward oxidation of the organic challenges.

It is noted in Figure 7(a)-(b) that both HSWPA12 and 15 catalysts demonstrate much higher TOC values at initial testing period from 265°C, 65 psig, 230°F, 65 psig, to 230°F, 30 psig for total test duration of at least two weeks. A similar behavior was also observed on HSWPA16 catalyst, which contains the same type of bimetallic compounds but in different support from HSWPA12 or 15, in Figure 10(a) and 10(b). Although this phenomenon is not fully understood, we believe that it might relate to conditioning of the catalyst surface or metal activation by oxygen. To reduce in-situ conditioning time of the bimetallic catalyst, a duplicate batch to HSWPA16, named as HSWPA17, was pre-treated at 300°C in oxygen atmosphere for 3 hours, and then evaluated in 200 cc reactor with the same protocol as HSWPA16. TOC performance data are given in Figure 10 and the baseline ISS-WPA catalyst was also included for comparison. As seen in Figure 10, TOCs and non-ionic TOCs of HSWPA17 are lower than those of HSWPA16 at initial testing up to 200°C, 30 psig but still higher than the baseline ISS-WPA, suggesting the pre-oxidizing process provides some extent of mitigation to initial higher TOCs. However that mitigation is not significant to off-set HSWPA16's initial TOC spikes and ex-situ pre-oxidizing process does not seem to act the same role as in-situ conditioning.



Figure 7. (a) TOC performances and (b) non-ionic TOC performances of alternate metal or alloy catalysts with Type I Ethanol/isopropanol challenge feed (TOC=35ppm).



Figure 8. (a) TOC performances and (b) non-ionic TOC performances of alternate metal or alloy catalysts with Type II-required Ersatz challenge feed (TOC=35ppm).



Figure 9. (a) TOC performances and (b) non-ionic TOC performances of alternate metal or alloy catalysts with Type IIIgoal Ersatz challenge feed (TOC=65ppm).



Figure 10. Effect of pre-oxidation (in O₂, 300°C) on TOC performances of the bimetallic catalyst.

C. Mechanical Stability of Alternate Catalyst

Mechanical stability of any developed catalyst is an important characteristic to evaluate as any suitable catalyst for the ISS-WPA application should have adequate mechanical strength during mechanical vibration and shock of space flight. To evaluate a mechanical strength of the catalysts developed under this program, we chose to test a catalyst crush strength using CRUSH-BK500 tester provided by Material Technology Inc. Selected catalysts, i.e., the baseline ISS-WPA and HSWPA15 and their supports (i.e., baseline support and alternate support 2, respectively) were evaluated using a standardized testing method per ASTM D7084-4. Figure 11 shows their test results. It is seen in the Figure 11 that the crush strength of baseline support ranges from 250 lb_f to 400 lb_f and increases with decreasing particle size from 8x10 to 12x14 mesh. Crush strength of the baseline ISS-WPA catalyst shows a comparable strength to the baseline support and the catalyst preparation process does not alter its crush strength. On the other hand, alternate support 2 shows comparable crush strength to the baseline support, however, the crush strength of catalyst HSWPA15 noticeably reduces to 290 lb_f from 390 lb_f of the alternate support 2. It should be noted that both baseline ISS-WPA and HSWPA15 have been previously tested in reactors through the conditions of 265°F, 65 psig; 230°F, 65 psig; 230°F, 30 psig; 200°F, 30 psig; and 200°F, 0 psig at three feed stocks, and the total test duration is approximately seven weeks. HSWPA15's decreased crush strength implies that the catalyst preparation process or in-cell testing at high temperature/pressure affects the mechanical strength of alternate Figure 11 also shows crush strengths of two samples on alternate support 2, HSWPA02C with support 2. uncontrolled drying and HSWPA15 with controlled drying. The controlled dry catalyst HSWPA15 shows double the crush strength of uncontrolled dry catalyst HSWPA02C. Future evaluation will focus on their abrasion losses and examine their robustness against the baseline support.



Figure 11. Crush strengths of selected catalysts and their supports

IV. Conclusions

Advanced ISS-WPA catalysts were developed in an aim to improve oxidation of the organic load at a temperature less than the water boiling point and ambient pressure. A novel catalyst support with bimodal pore distribution was first investigated for improvement of organic oxidation rate. The innovation was to utilize macropore structure of the support to facilitate mass transfer of oxygen reactant and oxidation byproducts by reducing tortuosity of diffusion channel, diffusion length, and diffusion resistance. Testing in both 36 cc reactor and 200 cc reactor confirms the improvements of TOC and non-ionic TOC conversions by the bimodal catalyst support. Alternate metal and alloy catalysts were also investigated and further performance enhancement has been achieved on the bimetallic HSWPA12 catalyst, which shows about 6 ppm TOC and 3.4 ppm non-ionic TOC at 200°F, 30 psig with the required Ersatz challenge, as much as 50% less than the baseline ISS-WPA catalyst. This development work implies that operating the WPA reactor at a reduced pressure, *i.e.*, 30 psig and 200°F temperature with less than 3 ppm non-ionic TOC of effluent is technically possible through advanced developments in both support and metal alloy.

Acknowledgements

This work was supported by the National Aeronautics and Space Administration's Marshall Space Flight Center, Huntsville, Alabama, under the contract NNM14AA16C. The authors would like to thank Layne Carter at MSFC for helpful technical discussion and support during this development work.

References

¹Nalette, T., J. Bedard, and L. Carter, "Catalyst Development for the Space Station Water Processor Assembly", 32nd International Conference on Environmental Systems, Paper No. AIAA 2002-2362, San Antonio, TX, July 2002.

²Duan, Z. H. and R. Sun, "An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar", *Chem. Geology*, Vol. 193, 2003, pp 253-271.

³United Technologies Aerospace Systems, "Thermal Catalysts for use in MSFC Development Test", Final Report, NASA Marshall Space Flight Center, NNM10AC10P, October, 2010.

⁴Yang, J., D. Hand, D. Hokanson, J. Crittenden, and E. Oman, "Catalytic Wet Oxidation: Mat0hematical Modeling of Multicompound Destruction", *Water Environment Research*, Vol. 75, No. 2, 2003, pp.180-189.

⁵Fogler, H.S. "Elements of Chemical Reaction engineering", Prentice-Hall International, Inc., Englewood Cliffs, New Jersey, 1992.

⁶Beck, R. and J. Schultz, "Hindered Diffusion in Microporous Membranes with Known Pore Geometry", *Science*, 170, 1970, pp.1302-1305.

⁷Akse, J.R., J. T. Holtsnider, and L. Carter, "Advanced Aqueous Phase Catalyst Development Using Combinatorial Methods", 41st International Conference on Environmental Systems, Paper No. AIAA 2011-5195, Portland, OR, July 2011.

⁸Yu, P. and T. Nalette, US Patent Application 14/954,153, filed Nov. 2015.

⁹Akse, J. R. and C. D. Jolly, "Catalyst oxidation for treatment of ECLSS&PMMS waste streams", 21st

International Conference on Environmental Systems, Paper No. AIAA 1991-911539, San Francisco, CA, July 1991.

¹⁰Birbara, P.J. and J.E. Genovese, "Catalytic oxidation of aqueous organic contaminants", US5234584 (A) (1993).

¹¹Bhargava, S. K, J. Tardio, J. Prasad, K. Folger, D. Akolekar, and S. Grocott, "Wet Oxidation and Catalytic Wet Oxidation", *Ind. Eng. Chem. Res.*, Vol. 45, 2006, pp. 1221-1258.

¹²Lopes, R. and R. M. Quinta-Ferreira, "Manganese and Copper catalyst for phenolic wastewaters remediation by catalytic wet air oxidation", International Journal of Chemical Reactor Engineering, Vol. 6, A116, 2008.

¹³Lei, Y., S. Zhang, J. He, J. Wu, and Y. Yang, "Ruthenium Catalyst for Treatment of Water Containing Concentrated Organic Waste", *Platinum Metals Rev*, Vol.49, No.2, 2005, pp. 91-97.

¹⁴Levec, J. and A. Pintar, "Catalytic wet-air oxidation processes: A review", *Catalysis Today*, Vol.124, 2007, pp.172–184.