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Processing and Characterization of Sol-Gel Cerium Oxide Microspheres

September 2016

ZD McClure
C Padilla-Cintron

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

Of interest to space exploration and power generation, Radioisotope Thermoelectric Generators (RTGs) can provide long-term power to remote electronic systems without the need for refueling or replacement. Plutonium-238 (Pu-238) remains one of the more promising materials for thermoelectric power generation due to its high power density, long half-life, and low gamma emissions. Traditional methods for processing Pu-238 include ball milling irregular precipitated powders before pressing and sintering into a dense pellet. The resulting submicron particulates of Pu-238 quickly accumulate and contaminate glove boxes. An alternative and dust-free method for Pu-238 processing is internal gelation via sol-gel techniques. Sol-gel methodology creates monodisperse and uniform microspheres that can be packed and pressed into a pellet. For this study cerium oxide microspheres were produced as a surrogate to Pu-238. The similar electronic orbitals between cerium and plutonium make cerium an ideal choice for non-radioactive work. Before the microspheres can be sintered and pressed they must be washed to remove the processing oil and any unreacted substituents. An investigation was performed on the washing step to find an appropriate wash solution that reduced waste and flammable risk. Cerium oxide microspheres were processed, washed, and characterized to determine the effectiveness of the new wash solution.

Acknowledgments

National Security Directorate

National Security Internship Program

Dean Paxton (TGM)

Alex Stephan (TTL)

Christine Noonan (Formal Mentor)

Jeff Katalenich (Pu-238 Microsphere Project Lead)

Lab Colleagues – Cristina Padilla-Cintron & Paul Pierson

Acronyms and Abbreviations

DOE – Department of Energy
NASA – National Aeronautical & Space Administration
NSIP – National Security Internship Program
RTG – Radioisotope Thermoelectric Generator
CeO_2 – Cerium Dioxide
^{238}Pu – Plutonium 238
UO_2 – Uranium Dioxide
Sol-Gel – Solution Gelation
HMTA – Hexamethylenetetramine
TCE – Trichloroethylene
IPA – Isopropyl Alcohol
NH_4OH – Ammonium Hydroxide
B.P. – Boiling Point
D.I. – De-Ionized
TGA – Thermal Gravimetric Analysis

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Introduction

Radioisotope thermoelectric generators (RTGs) have given space and terrestrial applications the necessary power needed to succeed in remote missions. Rather than rely on wind, hydro, solar, or fossil fuel power sources, RTGs harness the heat emitted from the nuclear decay of radioactive material in the form of a pellet. The extended half-life of select radioactive elements allows for long-term deployment in critical environments. Continued space exploration faces an unavoidable barrier to continued success: readily available fuel sources. Materials of interest include ^{238}Plutonium, ^{90}Strontium, ^{210}Polonium, and ^{241}Americium. Of the four, ^{238}Pu remains the most promising for continued use in RTGs. ^{238}Pu boasts a high power density relative to its mass, low gamma emissions, and a half-life of approximately 87 years (Vaidya 2008).

Working with radioactive contamination is an embedded risk when processing ^{238}Pu. An increased risk is associated with fine particulate contamination from ball-milling. The traditional process for ^{238}Pu production involves the precipitation of irregular particles, subsequent ball-milling into submicron powder, and then pressing the material into a pellet. The submicron powders quickly contaminate glove boxes and create potential exposure hazards (Burney et al. 1982). To mitigate this risk, an alternative method for the processing of ^{238}Pu is introduced: internal gelation sol-gel. Internal gelation sol-gel techniques create homogenous, monodisperse microspheres with diameters generally ranging from 50-1000 µm. Since the method is a wet-chemistry technique, there is little if any accumulation during the process. The uniform shape and size distribution of the spheres assist with efficient packing and pellet pressing steps. Previous studies have shown that sol-gel processes are successful and have been demonstrated with UO_2 microsphere production (Brugghen et al. 1970). To further lower the health risks and financial costs associated with handling radioactive material cerium is used as a plutonium surrogate. Similar electronic structures, specific heat, and thermodynamic stability make cerium an acceptable surrogate for non-radiological work (Katalenich 2014).

The general schematic for the internal gelation sol-gel production of ceramics is shown in Figure 1. A metal nitrate solution is mixed with an appropriate ratio of HMTA/urea. The reagent ratios are highly dependent on the nitrate species and will vary between different metal nitrate feeds. The solution is chilled to approximately 0 ^{o}C before being fed to a heated column of silicone oil. As the reagents are being dispensed into the column as droplets, they begin to gel when activated by heat. After the microspheres have been collected, any unreacted reagents and silicone oil must be removed prior to drying and sintering. Traditional washing techniques involve trichloroethylene (TCE) and dilute ammonium hydroxide (NH_4OH). Non-oxide impurities remaining on or within the

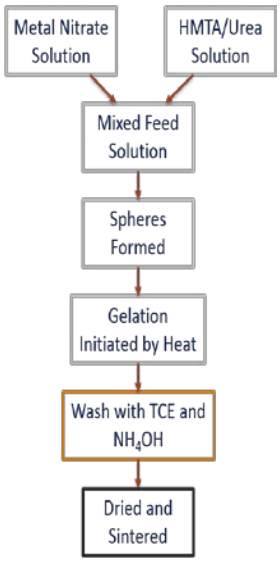

Figure 1: Schematic of sol-gel processing steps

spheres can give rise to cracking and irregularities during the drying and sintering steps. The success of heat treating microspheres is directly dependent on the effectiveness of the solvent in the washing process.

Solvents commonly used in literature such as ethers, isopropyl alcohol (IPA), and methanol are excellent candidates for the removal of silicone oil. However, due to the low air turnover rate in glove boxes, further precautions must be taken to mitigate the risk of flammable vapors. A high vapor pressure and low flash point are indicators of a solvent that could potentially pose a flammability hazard in the glove box. Another consideration with solvent choice is miscibility. If immiscible compounds interact with each other, the spheres will agglomerate and there will remain unreacted reagents or silicone oil locked within the packed spheres.

A comparison of different solvents found in literature is provided in Table 1. Included is the Turco 5948 DPM, which was selected for comparison experimentation. Turco is an aircraft cleaner produced by the Henkel Corporation. In addition to high boiling and flash points, Turco has two active components that make it an ideal choice for unreacted reagent removal. To disperse the microspheres and prevent agglomeration during washing, nonylphenol ethoxylate is present as an emulsifier. For oil removal, dipropylene glycol monomethyl ether is an active component that works in conjunction with the emulsifier. The Turco compound is miscible in water and dilutions can be made to determine an ideal experimental concentration.

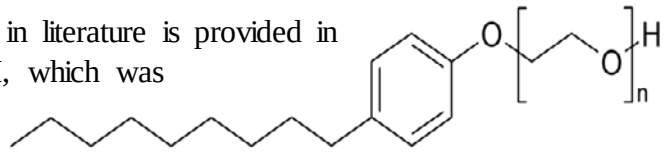

Figure 2: Nonylphenol ethoxylate. An emulsifier.

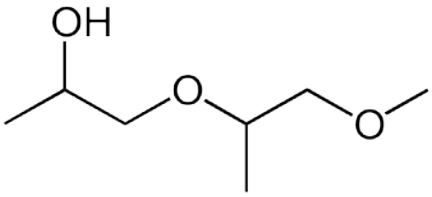

Figure 3: Dipropylene glycol monomethyl ether. For oil removal.

Table 1: Literature solvent comparison of boiling point, flash point, and vapor pressure.

Washing Agents	B.P. [°C]	Flash point [°C]	Vapor Pressure [kPa]
Petroleum Ether	42-62	<0	31
Trichloroethylene(TCE)	87.2	89.6	7.73
Kerosene	149	38	0.1
Carbon Tetrachloride (CTC)	76.72	Non-Flammable	11.94
Dowanol PM (Glycol Ether)	120	31	1.13
Isopropyl Alcohol	82.6	11.7	5.33
Methanol	64.7	12	13.02
Turco	**>93.3**	**>93.3**	**N/A**

Methods

To determine the effectiveness of the Turco cleaner, an experiment was designed to process and characterize cerium oxide microspheres produced on 04/12/2016 and 07/05/2016. Current batch size production of CeO_2 microspheres is limited and two different batches were needed to complete testing. Concentrations of 5, 10, 15, 20, 25, 50, 75, and 100% Turco diluted in water were prepared in 50 mL vials. Three identical samples were prepared at each concentration for statistical significance. The conductivity of the solutions was measured with a dual pH/conductivity probe. The conductivity of the DI water used and the Turco+water solutions were recorded to correct for a baseline measurement. After baseline conductivity measurements were taken, approximately 3g of oily cerium oxide microspheres were added to the vials. The spheres were mixed and washed for 10 minutes. After washing, the conductivity of the supernatant was measured and recorded. The supernatant was then decanted leaving only microspheres and a negligible amount of liquid behind in the vials. Identical concentrations of Turco were prepared for 2nd and 3rd washes of the microspheres. Conductivity measurements were taken after each wash with the exception of the 3rd wash for concentrations 5-20%.

After completing the conductivity measurements, the spheres were prepared for Thermalgravimetric Analysis (TGA). The three replicate vials for each concentration were combined into a single vial for Turco removal. Once combined, the vials were filled with 40 mL of water, mixed for five minutes, and then decanted to remove the remaining Turco solution. The spheres were treated with repeat washes of water until the blue color of the Turco was no longer present and the soap bubbles on the top of the liquid diminished. Once sufficiently clean, the spheres were allowed to dry in an aluminum foil dish for one week. 30-35mg of spheres from each of the Turco concentration experiments were used for the TGA. The microspheres were treated in an air atmosphere with a 10 °C ramp rate to a maximum of 800 °C.

Experimental Results

Figure 4 reports the relative conductivities of each experimental Turco concentration. The data shown has been adjusted from the measurement that was directly recorded. First, the conductivity measured was corrected by subtracting the initial conductivity of the Turco+water mixture. Since the mass of spheres added to the vials differed slightly between each iteration the conductivity was further divided by the mass of the spheres added. Standard units of conductivity are in [mS/cm] and the reported numbers in Figure 4 are [mS/g•cm] (see Appendix B for sample calculations). The first wash reported the highest relative conductivity value while the second and third washes were very similar to each other. Third wash conductivity values for 0-20% Turco were not deemed necessary for the experiment due to the similarity in the 2nd and 3rd washes of the 25-100% samples.

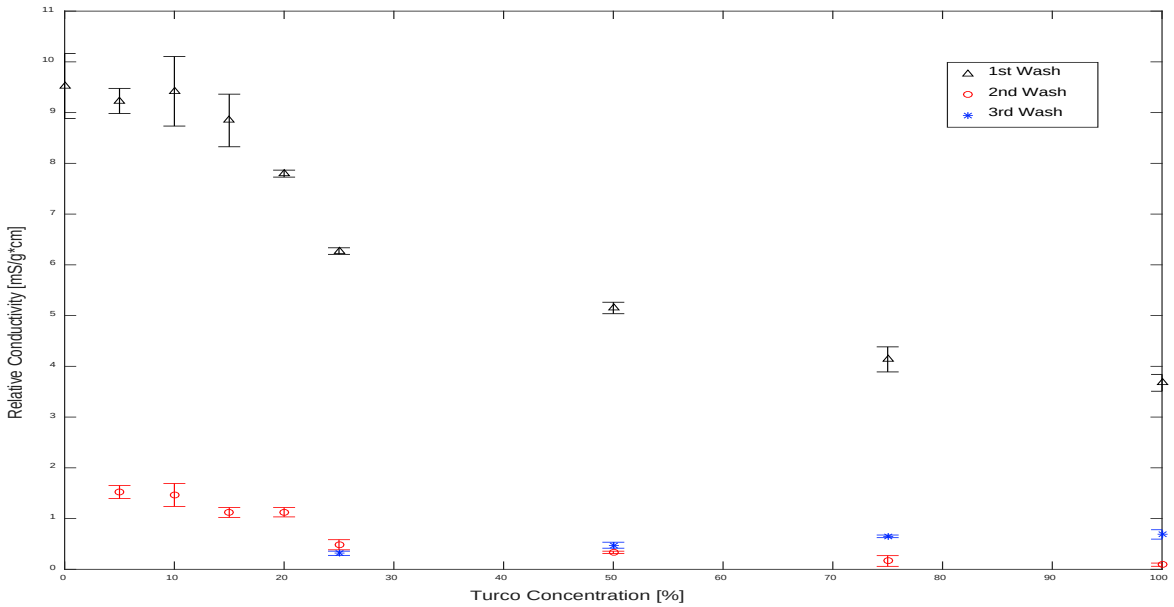

Figure 4: Relative Conductivity vs. Turco Concentration. Conductivity was measured after each washing of cerium oxide microspheres to quantify the removal of silicone oil and unreacted HMTA/urea from spheres.

TGA data was collected for each Turco concentration of washed microspheres after all the conductivity measurements were made. Figure 5 reports the %mass of the original sample vs. the temperature of the system. In the 200-300 °C range, the largest changes in mass were reported. The higher concentrations of Turco spheres did not go through the same rapid change in mass as the lower percentages in the same regime. The higher percentage Turco samples instead show a much more gradual loss of material over the heating cycle instead of a rapid descent. Figure 6 shows the heat flow into the system as the TGA was being performed. The large peaks in the 200-300 °C regime correspond the exothermic off-gas of compounds. The lower concentrations of Turco washed spheres have much higher heat flow spikes than the higher concentration of Turco washed spheres.

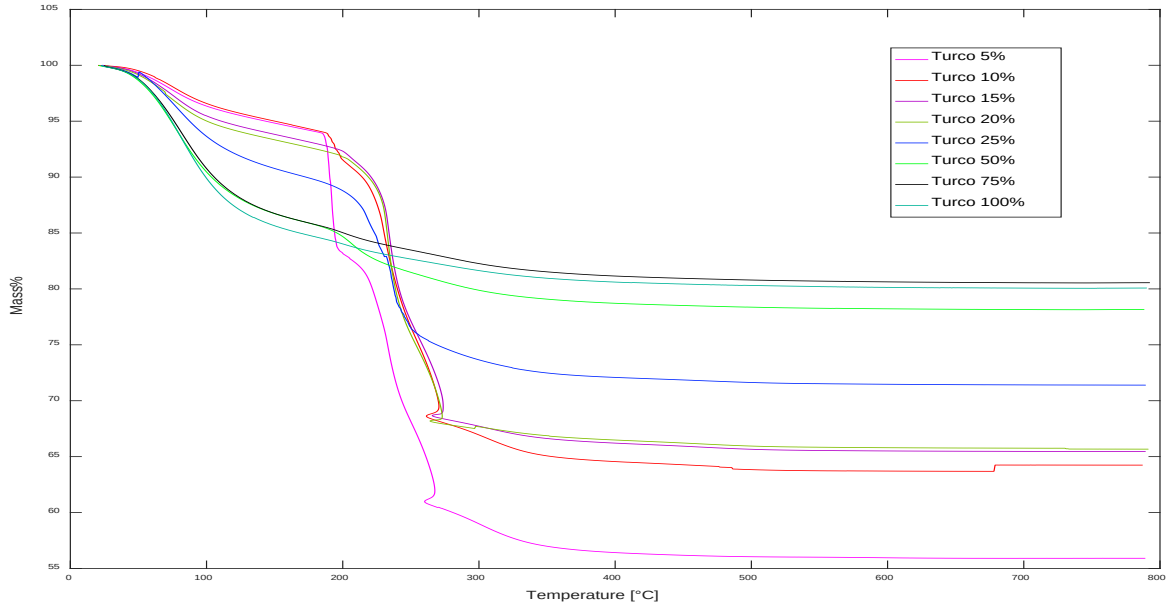

Figure 5: Mass % vs. Temperature. TGA analysis of cerium oxide microspheres was performed on Turco washed microspheres.

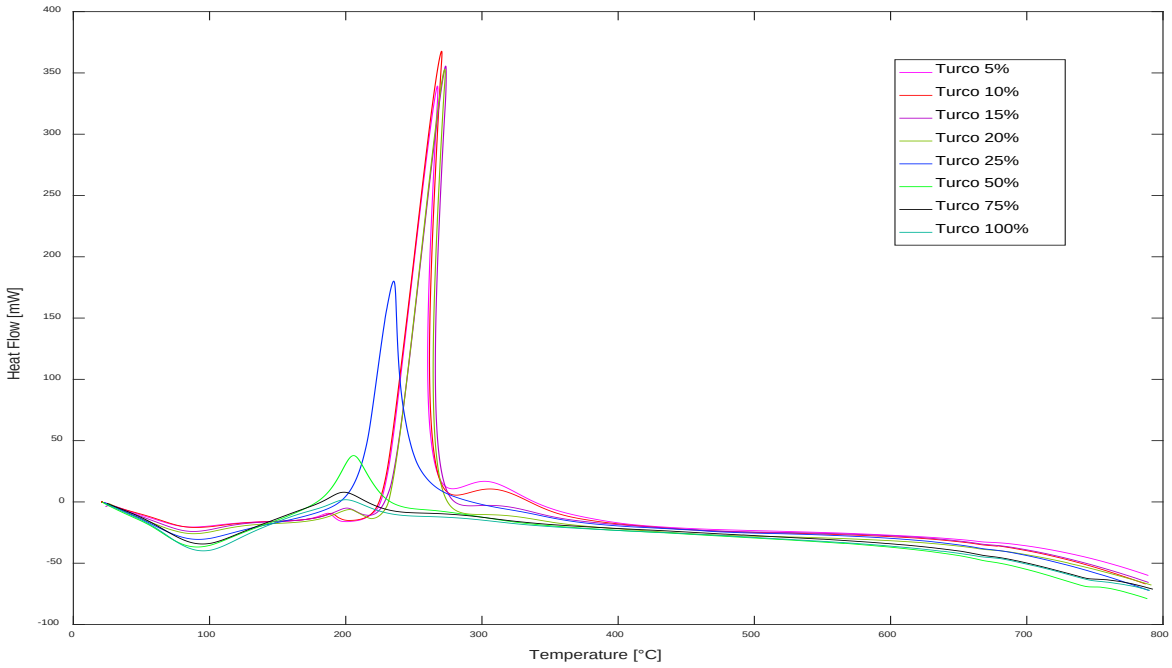

Figure 6: Heat Flow vs. Temperature. During TGA analysis of cerium oxide microspheres heat flow was recorded.

Discussion

From the conductivity data, it can be concluded that with the given mass of spheres/Turco volume ratio a single wash can be sufficient in removing oil and reagent impurities from the microspheres. Qualitatively measuring the amount of dissociated ions in the solution provides a strong trend for the relationship between Turco concentration and relative conductivity. It should be noted that two outlier conductivity values were removed in the presentation of the data (See Table 2, Appendix A). These values were considerable higher than any recorded values. The numbers are similar in value which leads to the suggestion that there was a contamination from the last 10% Turco reading to the first 15% Turco reading. A Q-test for removing outliers was performed on vial #9 of the 10% and vial #10 of the 15% Turco. Vial #9 was able to be removed by statistical significance, but vial #10 could not be removed based on statistical significance. The value was kept for thoroughness, but was not presented in the conductivity plot. The third wash on the 25-100% Turco concentrations reported such similar conductivity values compared to the second wash it was concluded that the additional washing had little effect. If material is removed from the spheres during Turco washing it is likely that the majority of mass is lost during the first washing step. For scaling of production this will be useful to consider when finalizing washing concentrations. It may be more beneficial to have a larger volume of wash solution if it means fewer intermediate steps. If the experiment were to be repeated, it is recommended that a single batch of microspheres be used in the washing. Given the limitations of resources, this experiment was forced to use two separate batches.

Assessing the TGA data provides more insight into the actual effect the Turco has on removing non-cerium oxide impurities. The 50, 75, and 100% Turco concentration experiments showed the least mass lost during the heat treatment. Figure 5 shows that the loss of mass in the three samples is much more gradual over time than the lower percentage experiments. In comparison, the lower percentage samples all showed a sharp mass loss in the 200-300 °C regime. Urea decomposes around 150 °C and HMTA sublimes around 280 °C. While the individual TGA of urea and HMTA are not present, and the coupling of compounds will affect the kinetics of the mass loss, it is highly suggested that the loss of mass in the 200-300 °C range is due to the removal of unreacted HMTA and urea. Figure 6 further supports the claim that the HMTA and urea are being forced out of the system in the 200-300 °C range. Assuming that the specific heat of the sample does not change drastically over a temperature range, the heat flow to a system should be constant when increasing the system temperature. The spikes in heat flow to the system suggest that a phase change occurred. To continue heating at the same speed of 10 °C/min the system compensates for the latent heat needed to promote a liquid to a gaseous state. The heat must be applied sharply to continue with the given ramp rate. From the data, deeper quantitative knowledge can be derived such as phase change and kinetic behavior. Further investigation is being conducted on the curvature of the individual Turco concentration TGA data sets to gain better insight to the physical happenings during the testing.

Conclusion

Assessing the conductivity and TGA results leaves Turco a promising candidate for continued research in the washing of sol-gel microspheres. Traditional literature washing methods involve a binary chemical system where a two-step process must be deployed for oil and unreacted reagent removal. Many of the chemicals that may be considered for silicone oil removal introduce flammable hazards that must be mitigated in a glove box environment. Turco has the potential to remove silicone oil while alleviating flammability concerns. The improvement in worker safety make it a likely choice for the washing step of ^{238}Pu microspheres. Further investigation into producing a reagent grade Turco creates an avenue for improving the efficiency of the washing steps. Since Turco is not a reagent grade chemical it is likely that impurities are present in the washing solution. Additional experimentation with BET, SEM, and mass spectrometry will further quantify the levels of success with the processing steps after washing.

Beyond sol-gel microsphere processing, Turco provides an interesting avenue for alternative washing techniques in a variety of wet-chemistry laboratories. It is common practice to have intermediate solvents between processing steps due to low miscibility of one compound in another. If further research can be promoted for Turco, or compounds similar in nature to Turco, there is the chance for improvement on larger scale chemical processes outside of nuclear fuel fabrication. Of interest to the DOE would be increased efficiency in chemical cycles, decreased waste in production, less hazardous chemical waste, and reduced hazards associated with chemical handling. Further investigation into high flash point solvents will help glove box processing chemistry push forward.

Appendix A: Data Tables

Table 2: Raw Mass and Conductivity Data for 1st Wash of cerium oxide microspheres with Turco

Vial #	Description	Experimental microspheres mass ((± 0.001) g)	Conductivity σ [mS/cm]	Conductivity/ Mass (σ/g) [mS/(g*cm)]	Corrected Conductivity [mS/cm]	Corrected Conductivity/ Mass
1	0% Turco	2.167	23.270	10.738	22.240	10.263
2		2.443	23.450	9.599	22.420	9.177
3		2.390	22.850	9.561	21.820	9.130
4	5% Turco	2.397	21.830	9.107	21.503	8.971
5		2.005	18.880	9.418	18.546	9.252
6		2.251	21.690	9.635	21.307	9.465
7	10% Turco	2.336	21.500	9.202	20.876	8.935
8		2.154	21.920	10.176	21.332	9.903
9		2.468	**29.850**	12.095	**29.250**	11.852
10	15% Turco	2.225	**30.600**	13.753	**29.773**	13.381
11		2.408	21.210	8.808	20.416	8.478
12		2.336	22.310	9.551	21.518	9.211
13	20% Turco	2.837	22.980	8.100	22.002	7.755
14		2.953	24.340	8.242	23.260	7.877
15		2.411	19.770	8.200	18.710	7.760
1	25 % Turco	3.098	20.270	6.544	19.193	6.196
2		3.922	25.810	6.582	24.737	6.308
3		3.151	20.980	6.659	19.876	6.309
4	50 % Turco	3.886	21.640	5.569	19.844	5.107
5		3.361	18.820	5.600	17.020	5.064
6		3.066	17.940	5.852	16.180	5.278
7	75 % Turco	3.115	14.240	4.572	11.996	3.852
8		3.247	16.130	4.967	13.882	4.275
9		3.079	15.420	5.008	13.189	4.283
10	100 % Turco	3.057	13.530	4.426	11.019	3.605
11		3.874	16.270	4.200	13.776	3.556
12		3.257	15.090	4.633	12.589	3.865

Table 3: Raw Mass and Conductivity Data for 2nd Wash of cerium oxide microspheres with Turco

Vial #	Description	Experimental microspheres mass ((± 0.001) g)	Conductivity σ [mS/cm]	Conductivity/ Mass (σ/g) [mS/(g*cm)]	Corrected Conductivity	Corrected Conductivity/ Mass
1	0% Turco	2.167	0.000	0.000	0.000	0.000
2		2.443	0.000	0.000	0.000	0.000
3		2.390	0.000	0.000	0.000	0.000
4	5% Turco	2.397	3.630	1.514	3.303	1.378
5		2.005	3.590	1.791	3.256	1.624
6		2.251	3.900	1.732	3.517	1.562
7	10% Turco	2.336	3.590	1.537	2.966	1.269
8		2.154	4.280	1.987	3.692	1.714
9		2.468	4.090	1.657	3.490	1.414
10	15% Turco	2.225	3.070	1.380	2.243	1.008
11		2.408	3.610	1.499	2.816	1.169
12		2.336	3.560	1.524	2.768	1.185
13	20% Turco	2.837	4.400	1.551	3.422	1.206
14		2.953	4.460	1.510	3.380	1.145
15		2.411	3.530	1.464	2.470	1.024
1	25 % Turco	3.098	2.470	0.797	1.393	0.450
2		3.922	2.664	0.679	1.591	0.406
3		3.151	2.982	0.946	1.878	0.596
4	50 % Turco	3.886	3.120	0.803	1.324	0.341
5		3.361	2.986	0.889	1.186	0.353
6		3.066	2.705	0.882	0.945	0.308
7	75 % Turco	3.115	2.515	0.807	0.271	0.087
8		3.247	3.170	0.976	0.922	0.284
9		3.079	2.600	0.844	0.369	0.120
10	100 % Turco	3.057	2.681	0.877	0.170	0.056
11		3.874	2.947	0.761	0.453	0.117
12		3.257	2.827	0.868	0.326	0.100

Table 4: Raw Mass and Conductivity Data for 3rd Wash of cerium oxide microspheres with Turco

Vial #	Description	Experimental microspheres mass ((± 0.001) g)	Conductivity σ [mS/cm]	Conductivity/ Mass (σ/g) [mS/(g*cm)]
1	25 % Turco	3.098	1.053	0.340
2		3.922	1.050	0.268
3		3.151	1.070	0.340
4	50 % Turco	3.886	1.604	0.413
5		3.361	1.617	0.481
6		3.066	1.626	0.530
7	75 % Turco	3.115	2.049	0.658
8		3.247	2.014	0.620
9		3.079	2.063	0.670
10	100 % Turco	3.057	2.346	0.768
11		3.874	2.271	0.586
12		3.257	2.305	0.708

Table 5: Initial Conductivity of DI Water + Turco

Vial #	Description	Conductivity σ [mS/cm]
1	0% Turco	0.001
2		0.001
3		0.001
4	5% Turco	0.327
5		0.334
6		0.383
7	10% Turco	0.624
8		0.588
9		0.600
10	15% Turco	0.827
11		0.794
12		0.792
13	20% Turco	0.978
14		1.080
15		1.060
1	25 % Turco	1.077
2		1.073
3		1.104
4	50 % Turco	1.796
5		1.800
6		1.760
7	75 % Turco	2.244
8		2.248
9		2.231
10	100 % Turco	2.511
11		2.494
12		2.501

Appendix B: Sample Calculations

Corrected Conductivity

[Measured Conductivity w/spheres – Initial (Turco+Water) Conductivity]
Example Calculation:
-12th Vial—100% Turco 1st Wash
-Measured Conductivity = 15.090 mS/cm
-Initial Conductivity = 2.501 mS/cm

$$Corrected\ Conductivity = 15.090\,\frac{mS}{cm} - 2.501\,\frac{mS}{cm} = \mathbf{12.589\ mS/cm}$$

Corrected Conductivity/Mass

[Corrected Conductivity/Mass of Washed Spheres]
Example Calculation:
-12th Vial—100% Turco 1st Wash
-Corrected Conductivity = 12.589 mS/cm
-Experimental Mass of Microspheres = 3.257 g

$$\frac{Corrected\ Conductivity}{Mass} = \frac{12.589\ mS/cm}{3.257\ g} = \mathbf{3.865\,\frac{mS}{cm * g}}$$

Q-Test

[Rejection of Outliers in Conductivity]
Example Calculation:
-10% Turco

$$Q = \frac{Gap}{Range} = \frac{29.850 - 21.920}{29.850 - 21.50} = 0.9497$$

For 3 Samples:
If Q > 0.941 reject the outlier
Q = 0.9497 > 0.94

References

Brugghen, FWvd, et al. 1970. *Sol-Gel Processes and Reactor Fuel Cycles*. Oak Ridge National Laboratory.

Katalenich, JA. 2014. *Production of Monodisperse, Crack-Free Cerium Oxide Microspheres by Internal Gelation Sol-Gel Methods*. Doctor of Philosophy Thesis. University of Michigan.

Vaidya, VN. 2008. *Status of Sol–Gel Process for Nuclear Fuels*. Journal of Sol-Gel Science and Technology. 46. 3. 369-81

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