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Simultaneous Thermal Analysis of Anion and Cation Exchange Resins

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Nuclear Energy and Fuel Cycle Division

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CONTENTS

LIST OF FIGURES

ABSTRACT

The decomposition reactions of one anion exchange resin (Bio-Rad AG MP-1) and one cerium-loaded cation exchange resin (DOWEX 50W-X8), both in nitrate form, were analyzed using simultaneous thermal analysis methods. Thermogravimetric analysis, dynamic scanning calorimetry, and evolved gas analysis were deployed in combination to probe the temperature profiles, reaction enthalpies, and off-gases from these resins under process-relevant temperature ranges. Analysis indicates that both resins undergo three clear phases during heating. The first is a dehydration step with prominent off-gassing of water, the second is a decomposition step with evolution of several gaseous species, and lastly is a combustion step with a large release of CO_2. The temperature at which combustion ends varies slightly between AG MP-1 and DOWEX 50W: combustion completed at ~690°C and ~810°C, respectively. For the DOWEX cation resin, the combustion reaction showed greater sensitivity to the availability of oxygen under the test conditions. Both resins displayed broad exotherms during the combustion step of the decomposition, but the DOWEX cation resin demonstrated a 4.5 times higher specific enthalpy than that of the AG MP-1.

1. INTRODUCTION

Deep space exploration requires reliable and specialized sources of thermal power to meet ongoing NASA mission needs. Radioisotope thermoelectric generators (RTGs), which rely on the decay heat of the radioisotope ^{238}Pu to produce power, are a current technology used to meet these requirements and are crucial for the future of deep space exploration. The simplified process scheme for ^{238}Pu production involves fabrication of ^{237}Np targets, including purification of ^{237}Np and synthesis of ceramic–metallic target materials, irradiation of ^{237}Np targets to produce ^{238}Pu, postirradiation processing of targets to purify ^{238}Pu from ^{237}Np and associated fission products, and postirradiation processing to extract and recycle ^{237}Np [1]. Chemical processing plays a key role throughout these steps, including initial purification of ^{237}Np as well as postirradiation separations of ^{237}Np, ^{238}Pu, and fission products into individual streams [2, 3].

Anion and cation exchange resins are routinely used in the ^{238}Pu production flowsheet for chemical purification of actinide solutions. Resins that are currently utilized in processing at the Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory (ORNL) are the Bio-Rad AG MP-1 anion exchange resin and the DOWEX 50W-X8 cation exchange resin. In ORNL's ^{238}Pu flowsheet, anion exchange resin is used to purify recycled aqueous streams of ^{237}Np. Specifically, this technique can be used to remove Na and fission products from recycled ^{237}Np solutions and then elute ^{237}Np, ^{238}Pu, and Th separately [4]. Anion exchange was also introduced into the flowsheet for removal of P, Th, and ^{237}Np from ^{238}Pu as a preprocessing step before cation exchange [5]. Cation exchange resin is utilized for ^{238}Pu purification and oxide conversion within the flowsheet. After target irradiation and dissolution, ^{238}Pu must be separated from ^{237}Np and fission products. A cation exchange column for separation is used to retain ^{238}Pu while eluting other byproducts. The ^{238}Pu loaded resin column can then be decomposed in a furnace to produce $^{238}PuO_2$ product [4]. Cation exchange resin has also been considered for removal of Th, ^{238}Pu, and Pa from ^{237}Np for purification of initial aqueous ^{237}Np solutions [5].

Both types of ion exchange resins can be thermally treated after their use to decompose the styrene divinylbenzene copolymer that constitutes the framework of the resin, allowing for the recovery of actinide products as needed and the reduction of total waste volume of spent resins. As described above, cation exchange resins loaded with ^{238}Pu are decomposed to eliminate the resin and produce the desired $^{238}PuO_2$ product through calcination. The decomposition of anion exchange resins is desired for overall reduction of waste throughout the ^{238}Pu flowsheet, given that resins cannot be reused indefinitely.

Thermal degradation of anion and cation exchange resins has been of interest to the actinide chemistry community for decades because of the ubiquity of ion exchange resins in many kinds of radiochemical separations. Interest in thermal degradation of resins has focused on the safety and stability of resins during storage [6-8], as well as synthesis of actinide microspheres from thermal degradation of resin [9-12]. Study of pure resins has found that thermal degradation of these classes of resins is typically complete by 800°C and includes three stages of decomposition—dehydration, depolymerization, and structural decomposition of resin—and the release of an array of volatile organic compounds (VOCs) [6]. Other studies involving resins with sorbed cations, such as uranium [9], neodymium [11, 12], and curium [10], indicate that higher temperatures (900–1400°C) are required to complete the degradation of the resin to an oxide phase. Although the literature provides evidence for mechanisms of thermal degradation of resins, targeted studies of the resins utilized in the ^{238}Pu production flowsheet in relevant conditions are still lacking. Specifically, high-fidelity thermochemical data and evolved gas analysis are needed to verify reactions of resins so that the findings can be extrapolated to larger-scale systems, namely, hot cell operations.

To evaluate the thermal destruction of these resins and the feasibility of thermal destruction on a large scale within the hot cells, detailed data on the reaction mechanisms were obtained. This work leveraged simultaneous thermal analysis (STA), which is a combination of thermogravimetric analysis (TGA), dynamic scanning calorimetry (DSC), and evolved gas analysis (EGA), to investigate the temperature profiles, reaction enthalpies, and off-gases from these resins across process-relevant temperature ranges. Specifically, the application of state-of-the-art STA analysis can help improve confidence in process development and scale-up.

2. MATERIALS AND METHODS

2.1 RESINS

The anion exchange resin tested was the commercially available Bio-Rad AG MP-1 resin. AG MP-1 is an anion exchange resin with ammonium functional groups on a styrene divinylbenzene copolymer. For these experiments, the AG MP-1 resin was converted from the as-received chloride form to the nitrate form, which is representative of application.

The cation exchange resin tested was the DOWEX 50W-X8, which is a cation exchange resin with sulfonate (SO_3) functional groups on a styrene divinylbenzene copolymer. This resin was also tested in the nitrate form but was additionally loaded with Ce^{4+} nitrate in support of a separate study. A 90g/L solution of Ce^{4+} (as ceric ammonium nitrate) in 0.5M HNO_3 was prepared. Then, 550 mL of DOWEX 50W-X8 was prepped by washing the resin with DI H_2O and by subsequently washing the resin with 0.5M HNO_3 to prepare it for loading with Ce. The resin was then contacted with 550 mL of the 90g/L Ce^{4+} solution for 2 h to ensure sufficient interaction with the DOWEX 50W-X8 resin. After the 2 h, the solution was decanted from the resin, in which a yellow solution, likely containing residual Ce in solution, was obtained. This solution was collected and analyzed via inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine the quantity of Ce that did not sorb to the resin. The loaded DOWEX 50W-X8 resin was then transferred to a 1 L glass crystallization dish and left to dry overnight in a fume hood.

2.2 SIMULTANEOUS THERMAL ANALYSIS

Simultaneous thermal analysis (STA) was performed on a Netzsch STA 449 F1 Jupiter equipped with an Aëolos quadrupole mass spectrometer (QMS) for evolved gas analysis. Analysis was performed with a

TG-DSC sample carrier and Type-S thermocouple. Samples were placed in an 85 µL alumina crucible with a lid containing a pinhole opening for controlled off-gas release. Samples were measured under air (Airgas, ultra zero grade) purge gas (50 mL/min) and argon (Airgas, ultra-high-purity) gas protective flow (20 mL/min). Buoyancy effects were corrected by measuring the empty crucible under the same measurement conditions used for the samples and applying the appropriate corrections via the Netzsch software. Temperature was increased at a rate of 10°C/min to a final temperature of 800 or 1400°C for anion or cation resin, respectively, and evolved gases were transferred to the Aëolos QMS via a heated (200°C) transfer line. Mass spectra were scanned in the range of 1–80 amu. TG, DSC, and QMS data were analyzed and visualized using Netzsch Proteus Thermal Analysis 8.0. For QMS data, masses of background gases (air, argon) were subtracted from the spectra, and only masses with signal-to-noise ratios greater than 1 were considered for analysis.

3. RESULTS AND DISCUSSION

3.1 ANION EXCHANGE RESIN

Combined STA data of the AG MP-1 resin in nitrate form indicate that three mechanisms occur during the heating profile (Figure 1). The first reaction occurs at approximately 100°C, with changes to the sample mass corresponding to an endothermic measurement in DSC and a large spike in evolved gas (Figure 1). Second, continued, gradual mass changes occur in the 200–500°C range, which correspond to multiple, smaller exothermic reactions and gas evolution. Lastly, a larger exothermic excursion occurs at approximately 570°C, which corresponds to a mass loss in the sample as well.

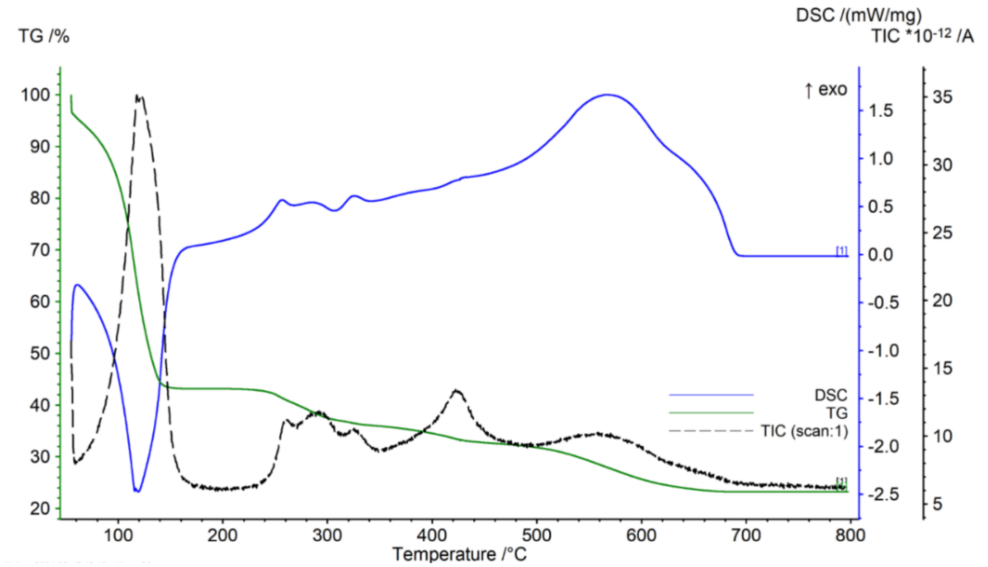

Figure 1. Combined simultaneous thermal analysis (STA) of the AG MP-1 resin, including TG data (green), DSC data (blue), and total ion counts (black).

3.1.1 Dehydration

The dehydration of the resin begins at approximately 100°C, resulting in a significant mass loss of just over 50% of the original sample, as shown in Appendix A, Figure A-1. This process is accompanied by an endothermic event between 98 and 148°C, which corresponds to a specific enthalpy change of −1012 J/g (Figure 4). Simultaneously, a large spike in evolved gas is observed, with the majority of this gas corresponding to a peak in the mass spectra at m = 18 (Figure 2), clearly indicating the release of water. Notably, m = 18 was the only recorded mass in the full range of 0–100 amu that had registered a signal-to-noise ratio greater than 1 in the temperature range of 0–200°C.

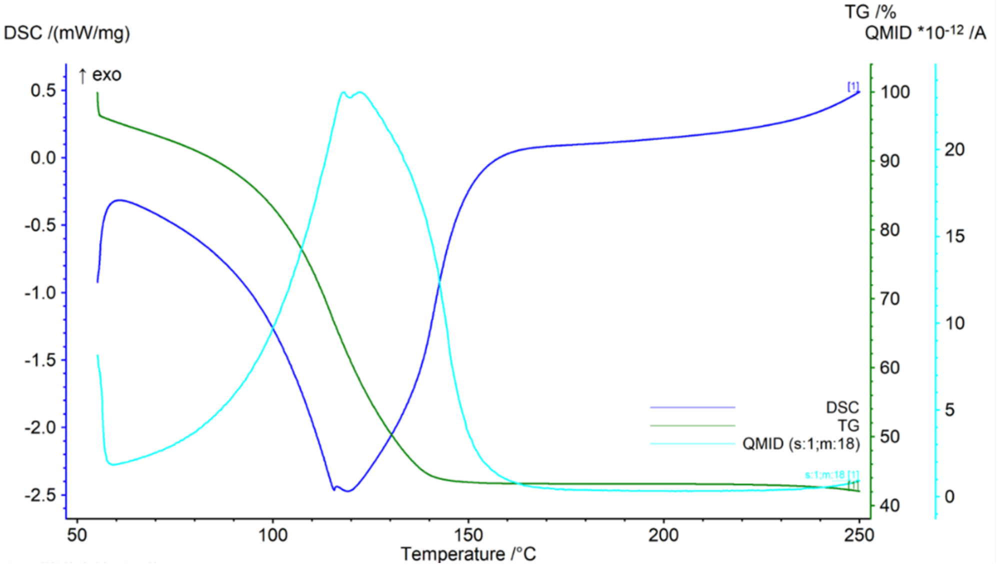

Figure 2. Combined plot of TG (green), DSC (dark blue), and evolved gas data (light blue) from the AG MP-1 resin as a function of temperature from 60 to 200°C.

3.1.2 Decomposition

Decomposition continues in a series of continued, gradual mass changes between 200°C and 500°C (Figure 1) that correspond to two small exothermic events that occur between 239°C and 339°C (Figure 4). Evolved gas analysis in this temperature regime is more complex: observed masses of interest with peaks in this temperature range include m = 12, 18, 30, 34, 36, and 44 (Figure 3). Interestingly, additional dehydration (m = 18) occurs in the 200–700°C range (Figure 3). The off-gases from m = 30, 34, and 36 do not have a clear source. However, this resin is composed of styrene-divinylbenzene ($C_6H_4(CH\text{-}CH_2)_2$) and trimethylammonium methylide ($CH_2N^+(CH_3)_3$) and is nitrate-loaded, so some expected degradation products could include hydrocarbons or nitrogen species. Particularly, m = 30 may be due to the presence of NO, a degradation product of nitrate species.

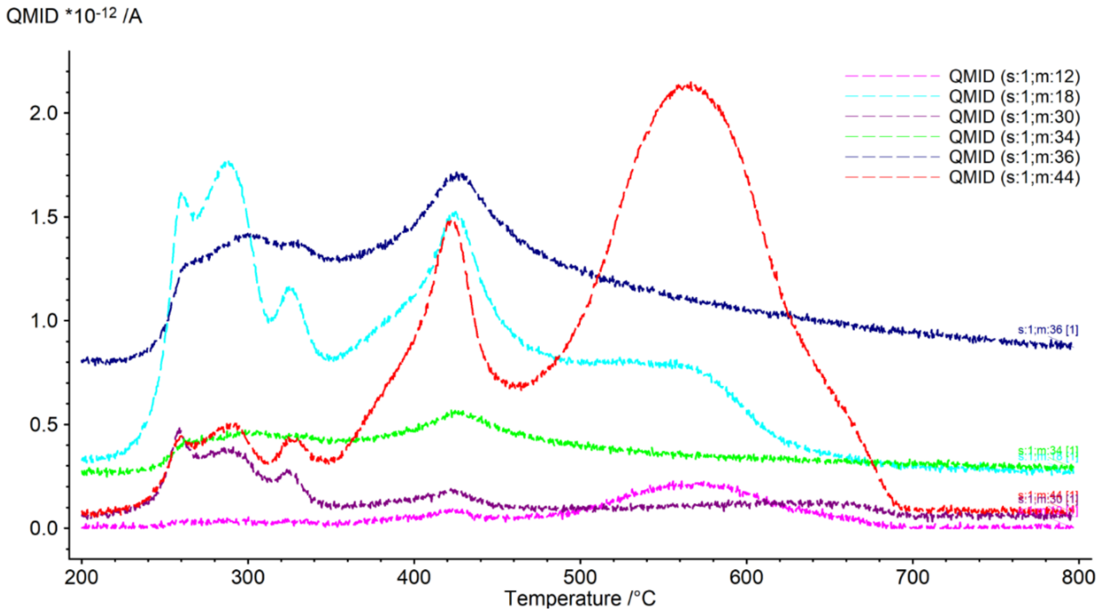

Figure 3. Recorded masses in the off-gas from the AG MP-1 resin as a function of temperature from 200°C to 800°C.

3.1.3 Combustion

The combustion reaction of the resin can be observed above 500°C. The reaction begins at 500°C and continues to 688°C, corresponding to a large exothermic excursion that peaks at around 578°C (Figure 4). This exotherm is associated with release of CO_2 off-gas, seen in the m = 44 peak in EGA data (Figure 3). There is additional influence from m = 12, which is attributable to the release of elemental C associated with CO_2 combustion.

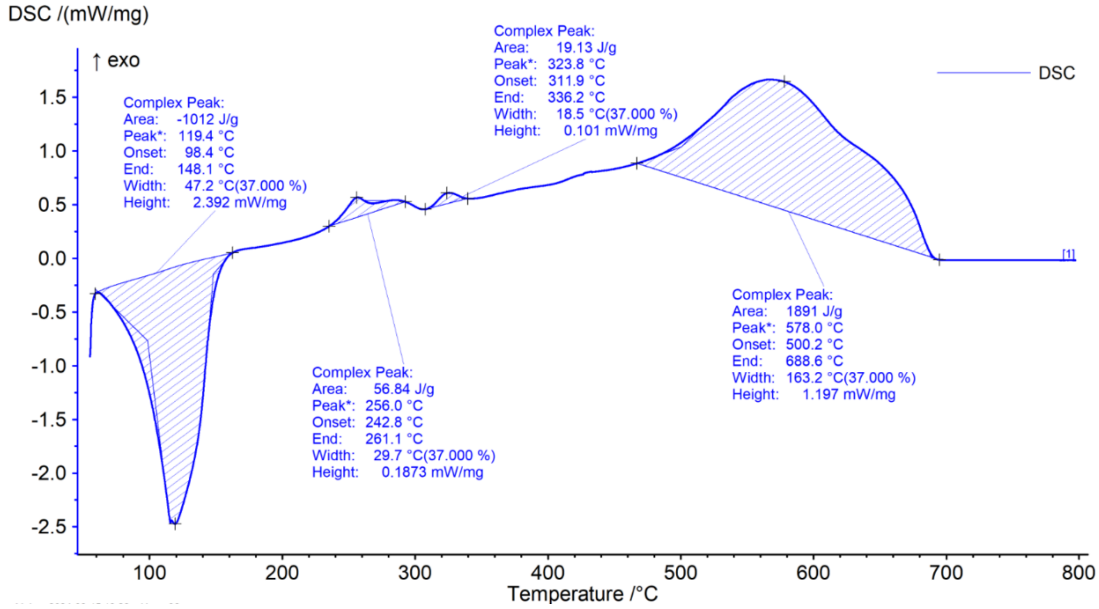

Figure 4. Dynamic scanning calorimetry (DSC) for the AG MP-1 resin.

3.2 CATION EXCHANGE RESIN

3.2.1 Dehydration

Combined STA data of the DOWEX 50W-X8 resin loaded with cerium nitrate show that the first reaction occurs below 200°C, with changes to the sample mass corresponding to an endothermic measurement in DSC and a large spike in evolved gas (Figure 5). The dehydration reaction occurring below 200°C is confirmed through presence of m = 18, corresponding to water (Appendix A, Figure A-2).

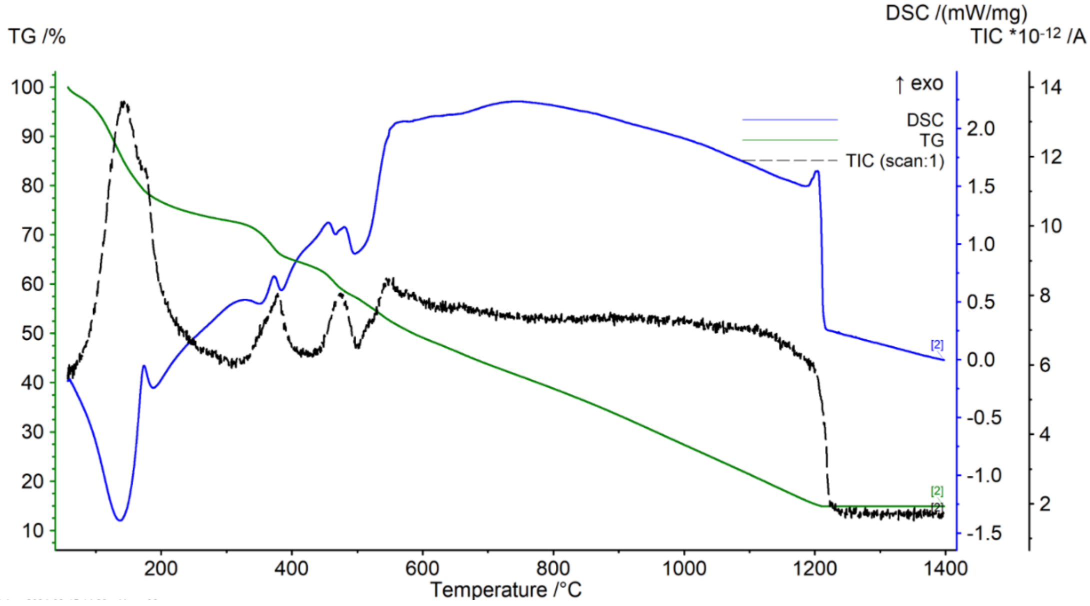

Figure 5. Combined simultaneous thermal analysis (STA) of the Dowex 50W resin, including TG data (green), DSC data (blue), and total ion counts (black).

3.2.2 Decomposition

Further decomposition of the resin is observed between 300°C and 500°C as part of a series of gradual mass changes (Figure 5). These mass changes are associated with two peaks in off-gas measurement as well as two smaller exotherms (Figure 5). The evolved gas analysis in the range of 200–500°C indicates continued water loss (Figure 6), but there is also evidence of smaller contributions in this temperature regime from m = 30, 48, and 64 (Appendix A, Figure A-3). As previously stated, the off-gas from m = 30 may be due to the presence of NO, a degradation product of nitrate species. The contributions from m = 48 and m = 64 could be attributed to sulfur-bearing species such as SO, SO_2, or S_2, all of which could result from degradation of the sulfonate groups on the DOWEX resin. These results indicate that resin decomposition is occurring in this temperature range.

3.2.3 Combustion

The main combustion reaction of the resin begins at approximately 500°C and continues to nearly 1200°C. The mass changes between 300°C and 1200°C are associated with a broad exotherm and gas evolution (Figure 5). Within the broad exotherm of 500–1200°C, the greatest contribution within evolved gases is m = 44 (Figure 6), which can be attributed to CO_2 off-gas. The presence of CO_2 off-gas confirms the expected combustion reaction in this temperature regime. Many smaller contributions are also observed (Appendix A, Figure A-3), including m = 12, 30, 48, and 64. Influence from m = 12 is attributable to the release of elemental C associated with CO_2 combustion, whereas other off-gases are similar to those of the decomposition reactions above and are likely attributable to sulfur-bearing species.

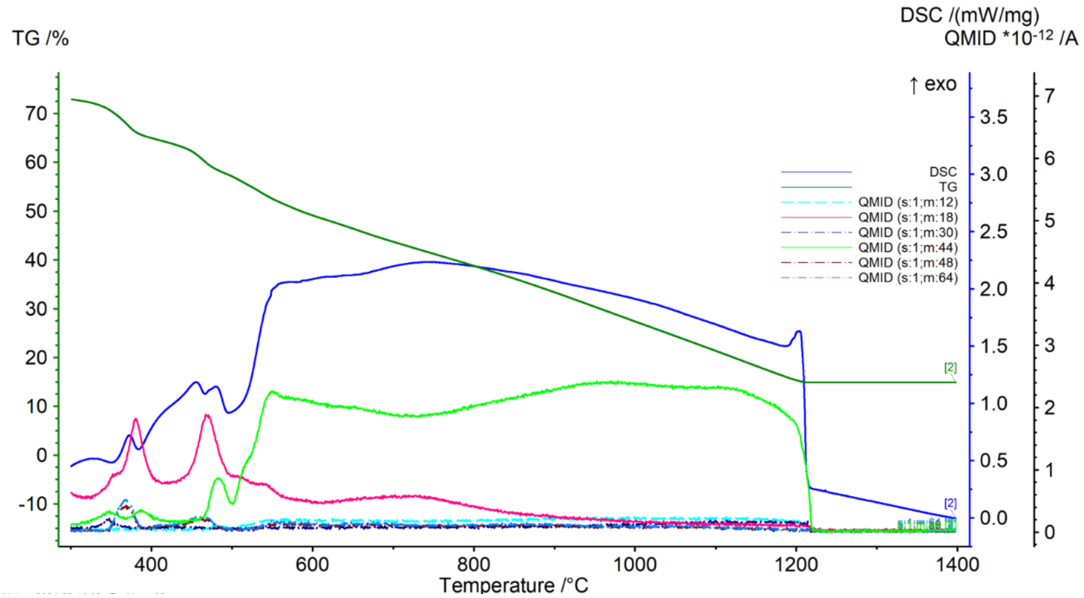

Figure 6. Combined plot of TG (green), DSC (dark blue) and evolved gas data from the Dowex 50W resin as a function of temperature from 300 to 1400°C.

3.2.4 Effect of Oxygen on Combustion of DOWEX Resin

The prolonged profile and controlled slope of decomposition observed in Figure 5 and Figure 6 raised questions about the effect of sample mass and the associated interaction of oxygen with the sample during decomposition, motivating additional studies of the DOWEX 50W-X8 resin. It was hypothesized that the reaction was oxygen-limited at high sample masses used in the first test (70 mg), which prevented the combustion of the resin. To test this hypothesis, several samples of decreasing sample mass were analyzed using the same techniques. The decomposition profile, particularly the end of the final decomposition step, was found to be a function of sample mass. For the 70 mg sample, decomposition continued up to 1200°C, whereas decomposition was complete at 972°C and 810°C for the 38 mg and 13 mg samples, respectively (Figure 7). Interestingly, the onset of this reaction is relatively invariant as a function of mass, with all samples having onset between 500°C and 520°C.

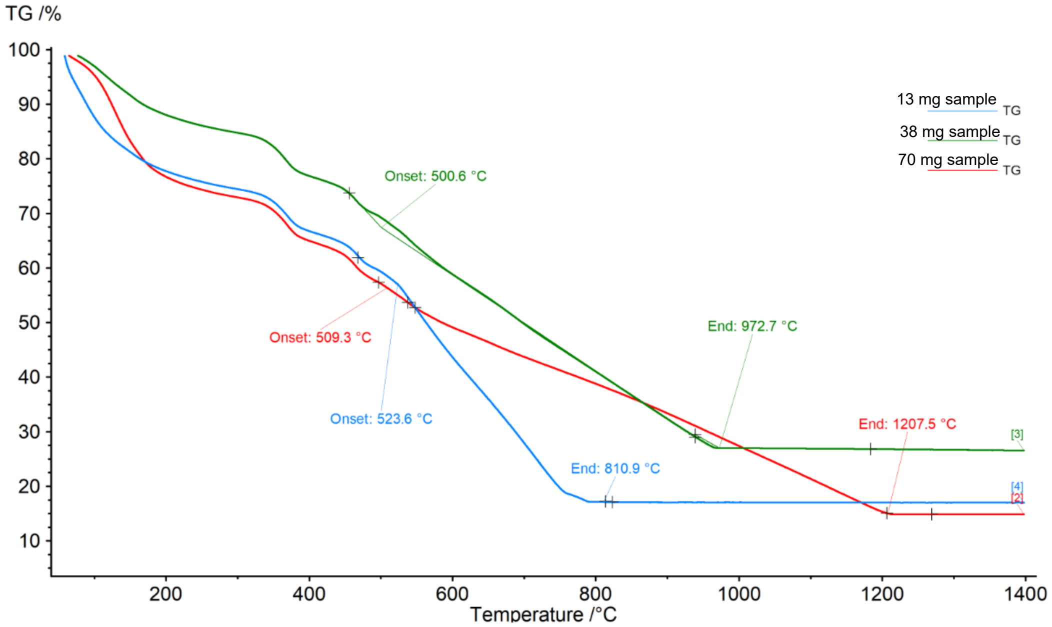

Figure 7. Thermogravimetric analysis of the Dowex 50W resin as a function of initial sample mass, including calculated onset and end of final decomposition step.

The trends as a function of sample mass extend to the energy generation of the primary decomposition reaction. As sample mass increases, the exotherm becomes increasingly broad and decreases in energy, in J/g (Figure 8). The influence of sample mass on both decomposition temperatures and system energetics suggests that oxygen is a key parameter for completion of the resin combustion reaction and that a lack of available oxygen during the combustion reaction will prevent complete combustion. Based on assumptions of the volume that resin samples occupy in the TGA crucibles, it is estimated that the volume of oxygen in the crucible decreases by more than an order of magnitude from the 13 mg to the 70 mg resin sample. Further consideration should be given to oxygen availability in reactions to prevent incomplete or prolonged combustion.

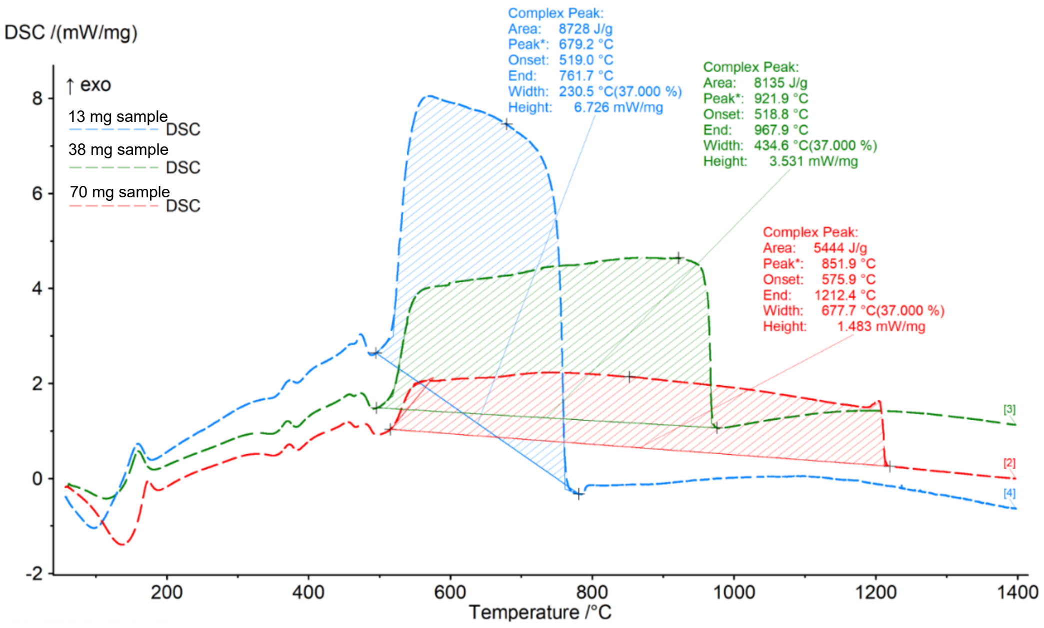

Figure 8. DSC measurement of the Dowex 50W resin over time and peak area calculation as a function of initial sample mass.

3.3 COMPARISON OF ANION AND CATION EXCHANGE RESIN

3.3.1 Comparative Dehydration

Direct comparison of the anion and cation exchange resin dehydration steps is complicated by the different initial hydration states of the resins. Both resins undergo dehydration below 200°C, as evidenced by endothermic reactions coupled with water in the evolved gas (Figure 2, **Error! Reference source not found.**). The magnitude of mass loss varies due to differences in initial hydration of the resin.

3.3.2 Comparative Decomposition

The initial decomposition steps for both anion and cation exchange resins consist of a series of gradual mass changes in multiple, exothermic steps across similar temperature ranges. Both resins display decomposition between 200°C and 500°C associated with multiple, small exotherms (Figure 1, Figure 5). The nature of the evolved gas measured varies based on the resin type, with the ammonium-functionalized anion resin showing off-gases assumed to be associated with N-bearing species (Figure 3) and the sulfonate-functionalized cation resin showing S-bearing species (**Error! Reference source not found.**).

3.3.3 Comparative Combustion

Direct comparison of anion and cation exchange resin data indicates differences in decomposition temperatures and energetics of combustion. The AG MP-1 cation anion exchange resin completed decomposition by 688°C, whereas the Dowex 50W-X8 cation exchange resin did not completely decompose until 810°C (Figure 9) in a system that was presumed not to be oxygen limited (see the discussion in Section 3.2 regarding the impact of oxygen limitation on combustion). Although both combustion reactions are exothermic, the specific enthalpy of the two reactions varies. The specific enthalpy of the combustion of Dowex 50W is 4.5 times greater than the specific enthalpy of AG MP-1 (Figure 9).

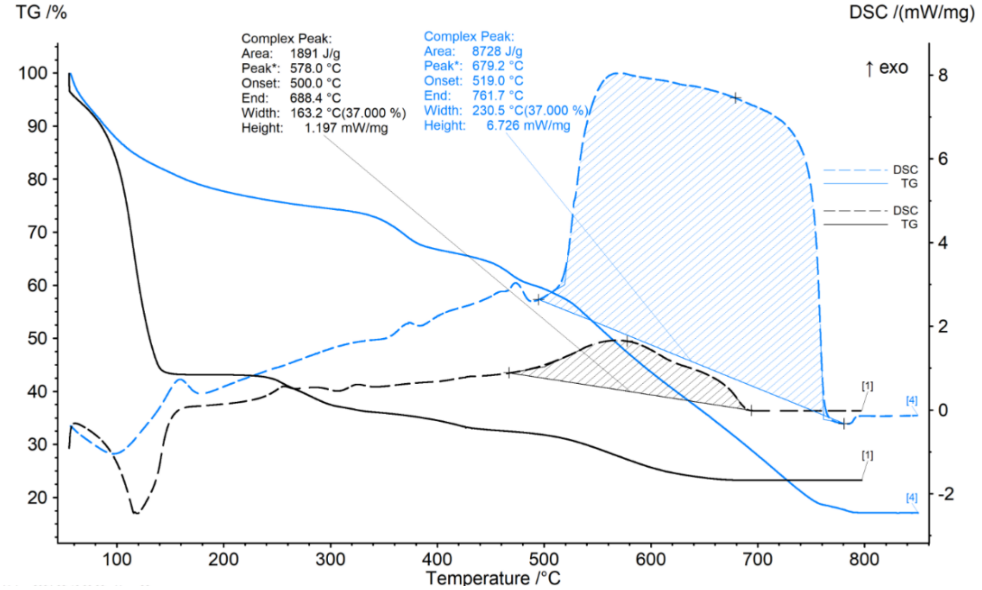

Figure 9. Comparison of TGA and DSC data from the Dowex 50W cation resin (blue) and AG MP-1 anion resin (black) up to 800°C.

4. CONCLUSIONS

The decomposition of two common anion and cation exchange resins—Bio-Rad AG MP-1 and DOWEX 50W-X8, respectively—was analyzed using simultaneous thermal analysis. In its nitrate form, the AG MP-1 resin was found to decompose by 680°C. Although there are approximately five reaction steps, the two main steps include an endothermic dehydration step below 200°C and an exothermic combustion step between 500°C 650°C. The decomposition of the DOWEX resin follows a similar path, characterized by a dehydration and combustion step. The combustion reaction of the DOWEX resin has a significantly larger specific enthalpy than the AG MP-1. The combustion reaction of the DOWEX resin was also found to be dependent on available oxygen: incomplete combustion was recorded when the volume of oxygen was limited compared to the mass of sample.

This work applied high-fidelity analytical techniques to determine the decomposition reactions of the anion and cation exchange resins, including analysis of key decomposition temperatures, reaction energetics, and off-gas products. This evidence is important to provide foundational chemical data for process development but is not the only data stream required for adequate process development. This data set is particularly limited in that the masses used are extremely small compared to the real masses of resin used in production. Therefore, there is a key need to perform resin testing at scale to assess how the observed chemical phenomena change. Specifically, the oxygen limitation of the cation exchange resin combustion should be evaluated to determine the appropriate masses of resin and air flow rates.

ACKNOWLEDGMENTS

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Aeronautics and Space Administration and administered by the US Department of Energy, Office of Nuclear Energy, under contract DEAC05-00OR22725.

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APPENDIX A. ADDITIONAL FIGURES

APPENDIX A. ADDITIONAL FIGURES

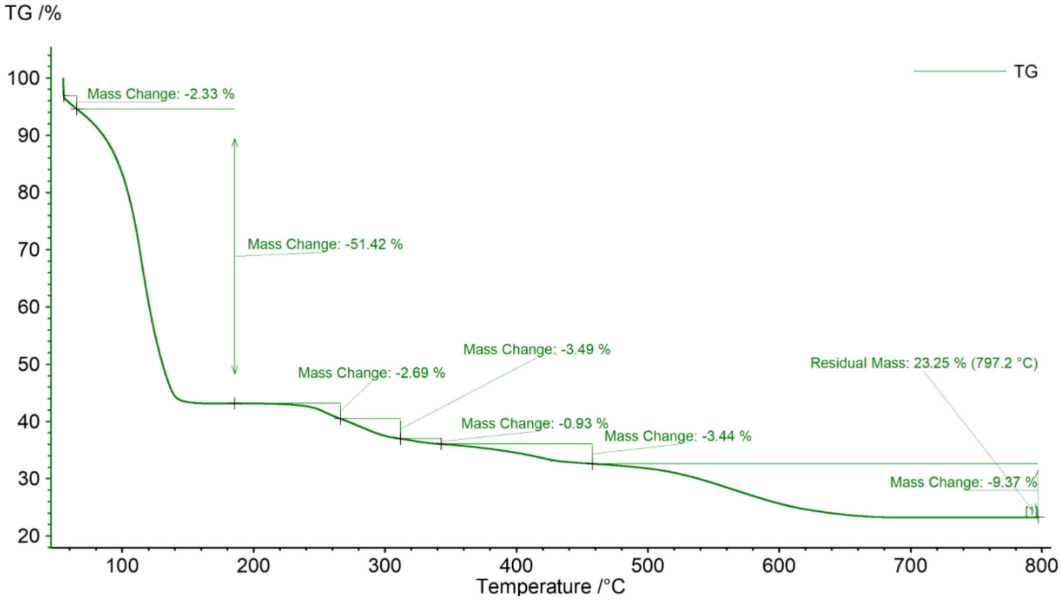

Figure A-1. Thermogravimetric analysis (TG) of AG MP-1 resin, including calculated mass losses.

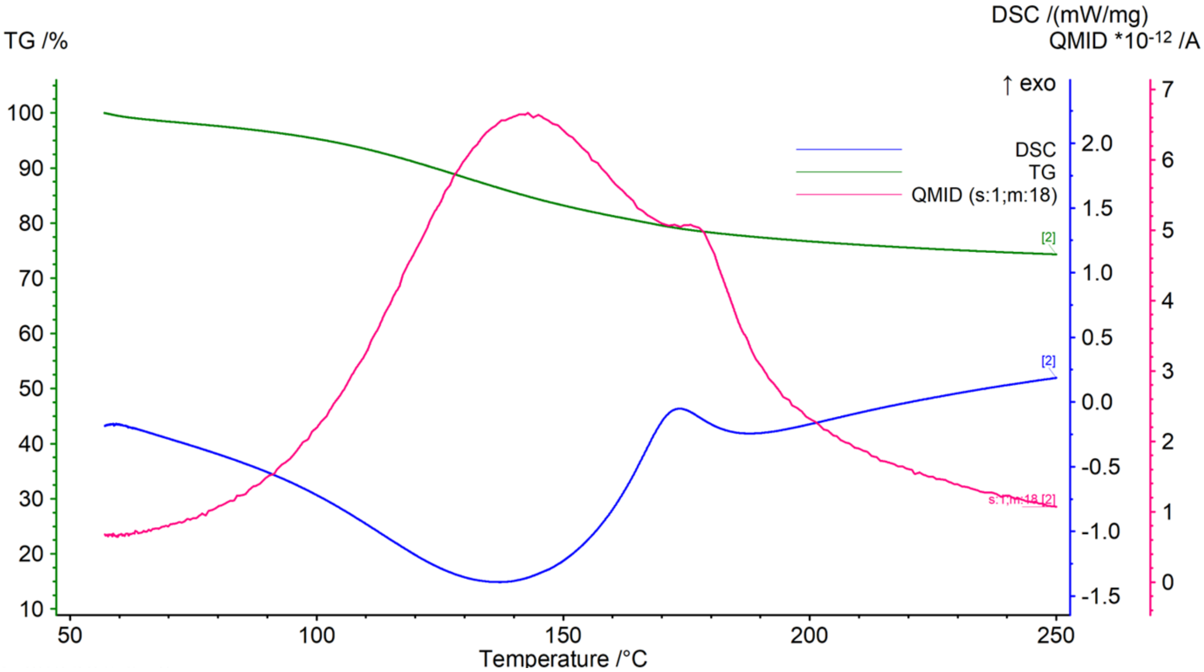

Figure A-2. Combined plot of TG (green), DSC (blue) and evolved gas data from Dowex 50W resin as a function of temperature from 50 to 1250°C.

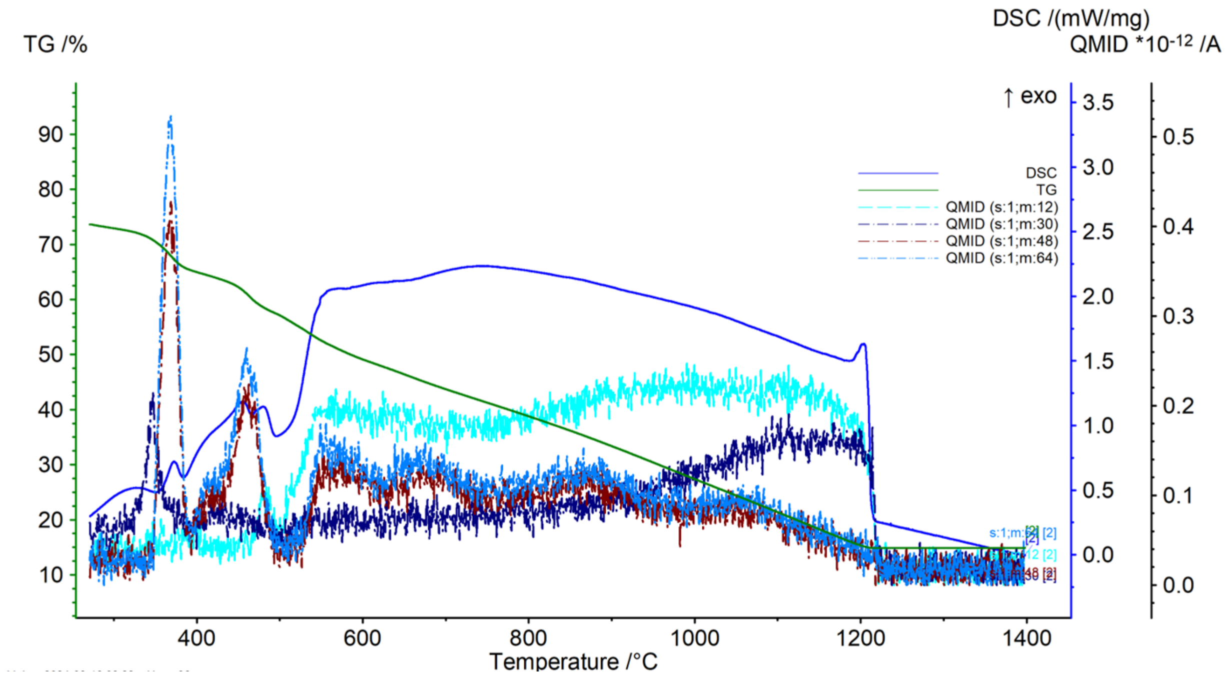

Figure A-3. Combined plot of TG (green), DSC (dark blue) and evolved gas data from Dowex 50W resin as a function of temperature from 300 to 1400°C.