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Solidified Organics Testing

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Isotope and Fuel Cycle Technology Division

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1. INTRODUCTION

The Radiochemical Engineering Development Center currently has plutonium-containing liquid organic waste that must be solidified before final disposal as solid debris waste. The documented safety analysis for the Radiochemical Engineering Development Center limits the amount of plutonium that can be released from solid debris waste forms during a fire scenario, which is less than 10^{-4} airborne release fraction. Experimental results for plutonium release fractions from burning various materials has been compiled by the Department of Energy [DOE, 1994]. Combustion of organic liquids gave an average airborne release fraction of 6×10^{-3} and combustion of surface-contaminated solids (paper, plastic, etc.) gave an average airborne release fraction of 5×10^{-4}. Burning of 30% tri-*n*-butyl phosphate (TBP) in kerosene gave cerium release fractions of $5.6–7.7 \times 10^{-3}$[Mishima and Schwendiman, 1973].

Earlier testing had evaluated many different grout-based formulations to solidify plutonium-containing organic waste liquids, and the ones used in these tests were shown to produce monolithic, fairly homogeneous solids. Each of the waste forms tested would meet the waste acceptance criteria for disposal at the Waste Isolation Pilot Plant as transuranic waste, but there were questions about whether they would meet the plutonium release criteria during a fire. The purpose of the work described here was to quantify the airborne release fraction for cerium, as a surrogate for plutonium, in these proposed waste forms. Cerium is often used as a simulant for plutonium in bench-scale testing, and cerium nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$] was added to the organic solutions that were solidified to prepare the surrogate waste forms for these tests. The waste forms were subjected to the designated fire scenario of 600ºC for 1 hour, and any cerium in the off-gas was trapped using a quartz filter followed by a scrubber containing 0.1 *M* NaOH, which is the same as used by Mishima and Schwendiman, [1973].

2. MATERIALS AND METHODS

Solutions of 1 *M* Di-(2-ethylhexyl) phosphoric acid (HDEHP) in Exxon Exxsol D60, 2 *M* HDEHP in D60, and 30% tri-*n*-butyl phosphate (TBP) in D60 were prepared, and cerium nitrate was added at near the maximum solubility limit. The resulting solutions were translucent, and the concentration of cerium in the three simulants is shown in Table 1 below. The Radiochemical Engineering Development Center uses 30% TBP in D60 to extract plutonium from dissolved targets and uses 1 *M* HDEHP in D60 to reduce the amount of plutonium in aqueous waste solutions. The D60 can evaporate from the used extractant solutions during storage before disposal, so a 2 *M* HDEHP solution was also tested as a worst-case scenario for HDEHP concentration.

Table 1. Cerium simulant concentrations.

Simulant	[Ce] in mg/L
1 *M* HDEHP-Ce	10,100
2 *M* HDEHP-Ce	8,000
30% TBP-Ce	23,000

The process for solidifying a surrogate 1 *M* solution of HDEHP in a cementitious matrix has been established in previous work. Because the solvent is not miscible with water, the direct addition of the liquid waste to the cement paste does not produce a homogeneous mixture. It was found that neutralizing the HDEHP-containing simulants with an excess of $Ca(OH)_2$ above the stochiometric value rendered the solidification possible.

The cerium-loaded HDEHP simulants were first neutralized with calcium hydroxide. The reaction is exothermic, and the resulting slurry was allowed to cool before being added to the cement paste. The calcium hydroxide neutralization did not work for the 30% TBP simulant, so it was absorbed into an organoclay, Tixogel VZ (BYK USA Inc.), before being mixed with the cement paste. A Type III Portland cement (LafargeHolcim Ltd.) was used as the main constituent of the mix. A high-water reducer, Glenium 7700 (BASF), was used to decrease the water needed for hydration. The mixing was done manually, and the composition of the waste forms is shown in Table 2.

Table 2. Grouted waste form compositions.

Simulant	**1 *M* HDEHP-Ce**		**2 *M* HDEHP-Ce**		**30% TBP-Ce**	
	Weight (g)	**Weight (%)**	**Weight (g)**	**Weight (%)**	**Weight (g)**	**Weight (%)**
Simulant	108.2	19.8	101.1	21.5	97.5	26.5
Ca(OH)	97.2	17.8	78.3	16.7	—	—
Tixogel VZ	—	—	—	—	28.9	7.8
Ordinary Portland cement Type III	216.4	39.7	203.8	43.4	171.4	46.5
Water	117.3	21.5	72.7	15.5	69.8	18.9
Glenium 7700	1.5	0.3	1.7	0.4	1.0	0.3
Perlite	4.9	0.9	12.3	2.6	—	—

A paste was prepared by adding the water and water reducer to the cement. The pretreated simulants were then added to the cement paste. All the mixes were thick and casted in covered plastic containers during curing. Several specimens were prepared with each mix. The samples were cured at room temperature for 16 days before testing.

The HDEHP cerium-loaded simulants were also solidified using PM-199 Organoclay® (Cetco), which is a granular solid. The PM-199 is simply poured into the organic liquids until there is a dry layer on top of the sample, which would be much easier to perform inside a hot cell than the grouting. Two samples were prepared for each simulant, and two blanks were prepared using 1 *M* HDEHP in Exxsol D60 with no cerium nitrate. The Organoclay samples were prepared by adding 25 mL of simulant, followed by 40.5 g of sorbent—just enough to cover the liquid—to a stainless-steel cup. The samples were stored uncovered for 7 days before testing.

The fire scenario testing was performed by placing a solidified organic sample under a 3 in. × 1 in. bell reducer in a stainless-steel pan. The bell reducer was connected to an off-gas system and was held about 1 in. up from the pan to provide an airflow path. The building vacuum system was used to pull air through the gap beneath the bell reducer, past the sample, and then through a filter assembly, scrubber, and rotameter, to capture any cerium that was volatilized during testing. The desired air flow rate was 1 ft^3/min; however, soot buildup on the quartz filter sometimes reduced the flow rate. Figure 1 shows the system used to test the Ce release fraction from the solidified organic samples. The furnace was turned on at a setpoint of 600°C, and once the furnace had reached the setpoint, the test was run for an additional hour.

Figure 1(a). Furnace, filter assembly, scrubber and rotameter.

Figure 1(b). Rotameter and scrubber.

Figure 1(c). Bell reducer inside furnace.

After each test, the quartz filter(s) from the filter assembly were removed and leached with 70% HNO_3 and rinsed several times with deionized H_2O to recover the cerium captured by the filter. This diluted nitric solution was then added to the 0.1 *M* NaOH solution used for the scrubber. The resulting solution was analyzed at the ORNL Radioactive Materials Analysis Laboratory to determine the amount of cerium collected in the off-gas system. This was compared to the amount of cerium originally in the starting sample to determine the release fraction. Several samples of the liquid organic solutions were tested to determine the effectiveness of the solidification processes in reducing cerium release. During runs, a thermocouple was used to determine the temperature just above the sample, and the furnace temperature was also monitored. The flow rate of the off gas was also monitored to ensure that the off-gas was being captured. Temperature and flow data for each run can be found in Appendix A.

3. RESULTS

The release fractions obtained from these tests indicate that these sorbents would be effective in mitigating risks associated with plutonium release during a fire. Release fractions for runs performed using the solidified samples were typically on the order of 10^{-5} to 10^{-6}, which would be an acceptable release fraction to meet the documented safety analysis. As expected, the sorbent had a significant impact on release fraction. Release fractions for runs performed on the liquid extractant solutions were about an order of magnitude higher than those performed using solidified samples. The cerium release fraction for the Exxsol D60 sample that contained cerium was about an order of magnitude higher than for the liquid samples containing the extractants (HDEHP or TBP). It is important to note that cerium was also measured in the off-gas from the liquid and solidified samples that did not contain cerium (Runs 1 and 2). These two runs were performed before any Ce-containing samples were used in the test system, so residual contamination in the off-gas system could not be the source. The results listed for Runs 1A and 2A are a reanalysis of the combined scrubber solution and acid leach for Runs 1 and 2. This could indicate that the actual release fraction reported for sorbent runs may be lower than calculated. Runs 13 and 14 are repeats of runs 3 and 6, respectively. The results for all runs are summarized in Table 3.

Table 3. Bell reducer inside furnace.

Run no.	**Solution**	**Sorbent**	**[Ce] in solution (ug/L)**	**Release fraction**
1	1 *M* HDEHP, no Ce	Not applicable (NA)	0.0028	NA
2	1 *M* HDEHP, no Ce	Organoclay	0.0042	NA
3	1 *M* HDEHP+Ce(NO$_3$)3	Organoclay	0.0003	1.08E-06
4	2 *M* HDEHP+Ce(NO$_3$)3	Organoclay	0.0010	3.83E-06
5	30% TBP+Ce(NO$_3$)3	Organoclay	0.0184	2.69E-05
6	1 *M* HDEHP+Ce(NO$_3$)	Grouted	0.0079	5.00E-06
7	2 *M* HDEHP+Ce(NO$_3$)3	Grouted	0.0516	4.53E-05
8	30% TBP+Ce(NO$_3$)3	Grouted	0.1800	5.99E-05
9	Exxsol D60+Ce(NO$_3$)3	NA	0.7830	5.87E-03
10	1 *M* HDEHP+Ce(NO$_3$)3	NA	0.2200	6.98E-04
11	2 *M* HDEHP+Ce(NO$_3$)3	NA	0.1220	4.71E-04
12	30% TBP+Ce(NO$_3$)3	NA	0.0868	1.27E-04
13	1 *M* HDEHP+Ce(NO$_3$)3	Organoclay	0.00393	1.25E-05
14	1 *M* HDEHP+Ce(NO$_3$)3	Grouted	0.00953	6.01E-06
1A	1 *M* HDEHP, no Ce	NA	0.00179	NA
2A	1 *M* HDEHP, no Ce	Organoclay	0.00958	NA

4. REFERENCES

US Department of Energy. Airborne Release Fractions/Rates and Respirable Fractions for Nonreactor Nuclear Facilities, Report no. DOE-HDBK-3010-94, US Department of Energy, Washington, DC, 1994.

Mishima, J. and L. C. Schwendiman, “Some Experimental Measurements of Airborne Uranium (Representing Plutonium) during Burning of Contaminated Wastes,” Report no. BNWL-1730, Pacific Northwest Laboratory, Richland, WA, June 1973.

APPENDIX A. FLOW RATE AND TEMPERATURE DATA FOR EACH RUN

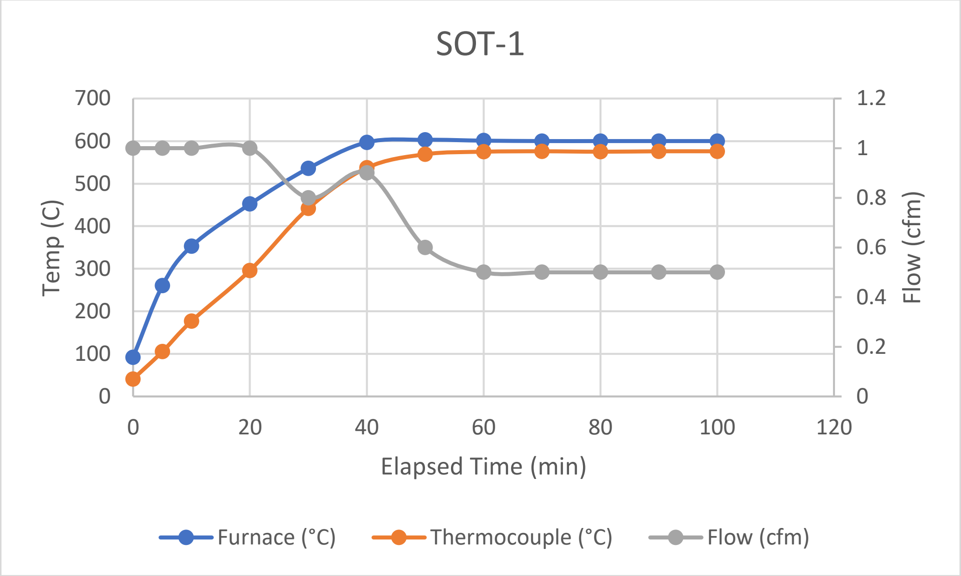

Figure A-1. Temperature and flow data for run #1.

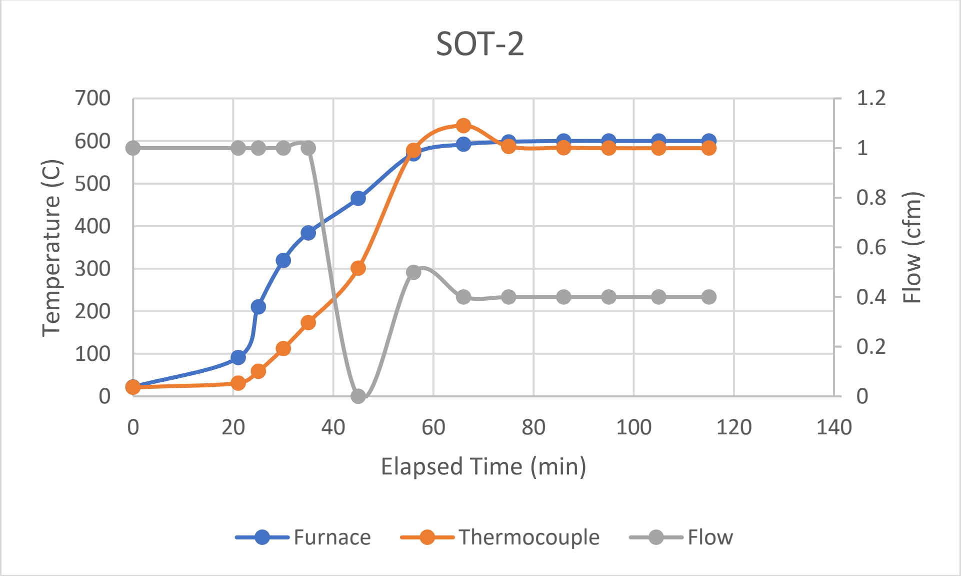

Figure A-2. Temperature and flow data for run #2.

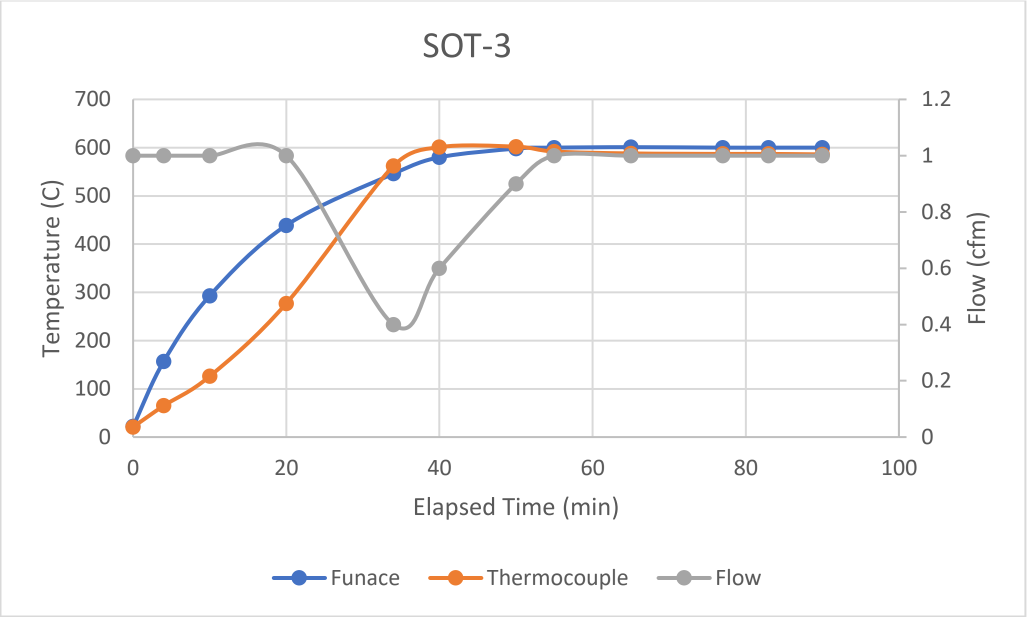

Figure A-3. Temperature and flow data for run #3.

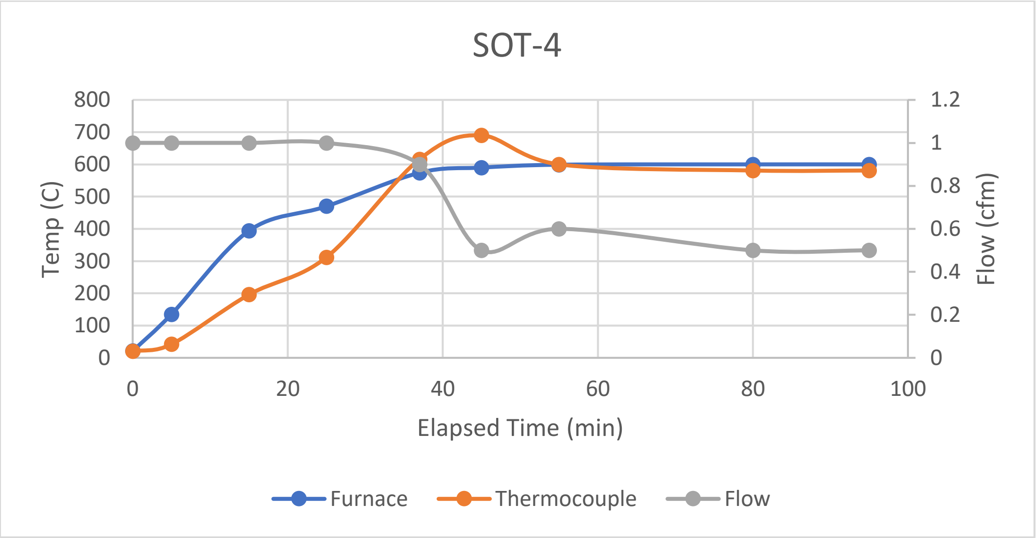

Figure A-4: Temperature and flow data for run #4

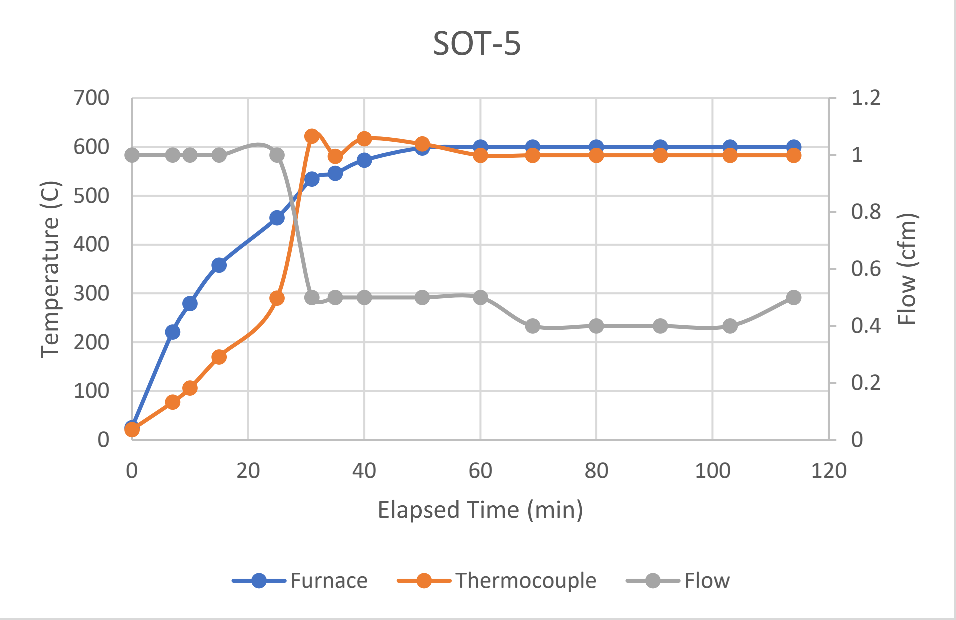

Figure A-5. Temperature and flow data for run #5.

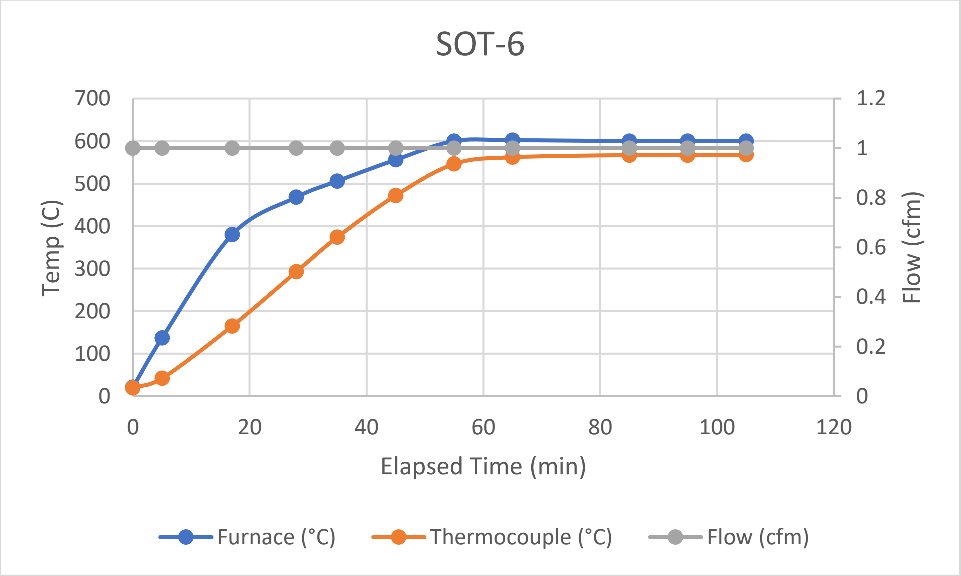

Figure A-6. Temperature and flow data for run #6.

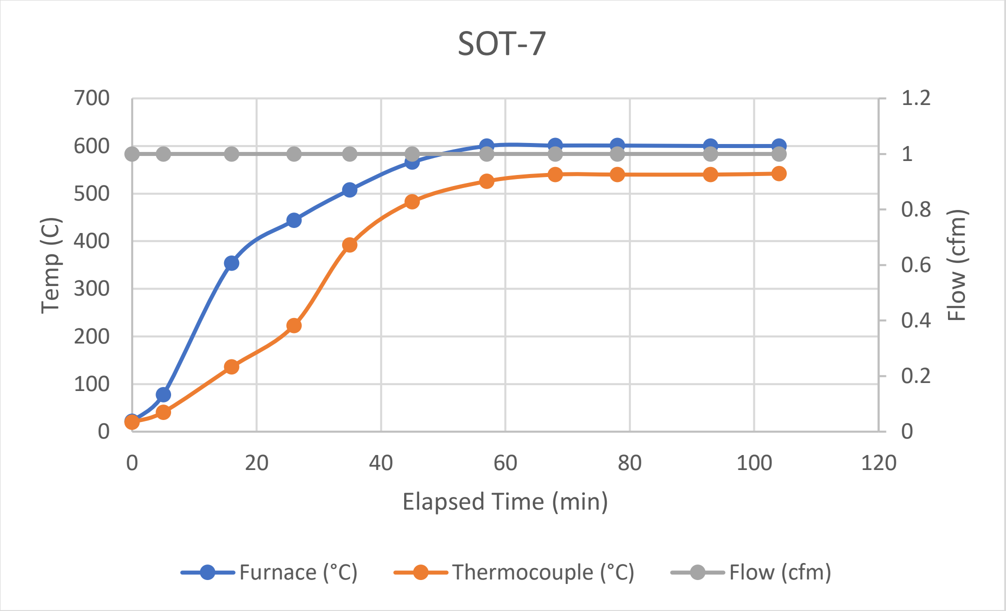

Figure A-7. Temperature and flow data for run #7.

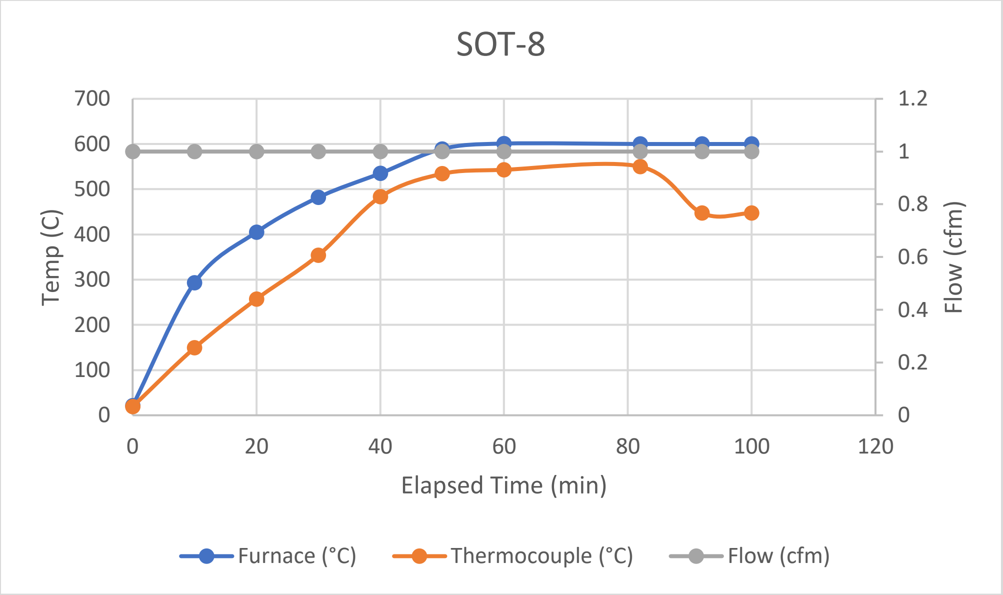

Figure A-8: Temperature and flow data for run #8

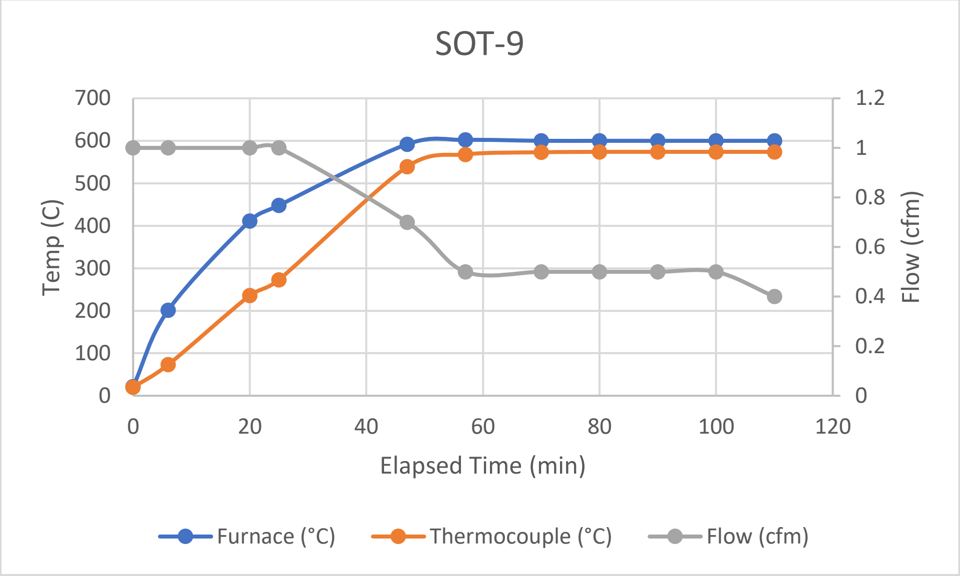

Figure A-9. Temperature and flow data for run #9.

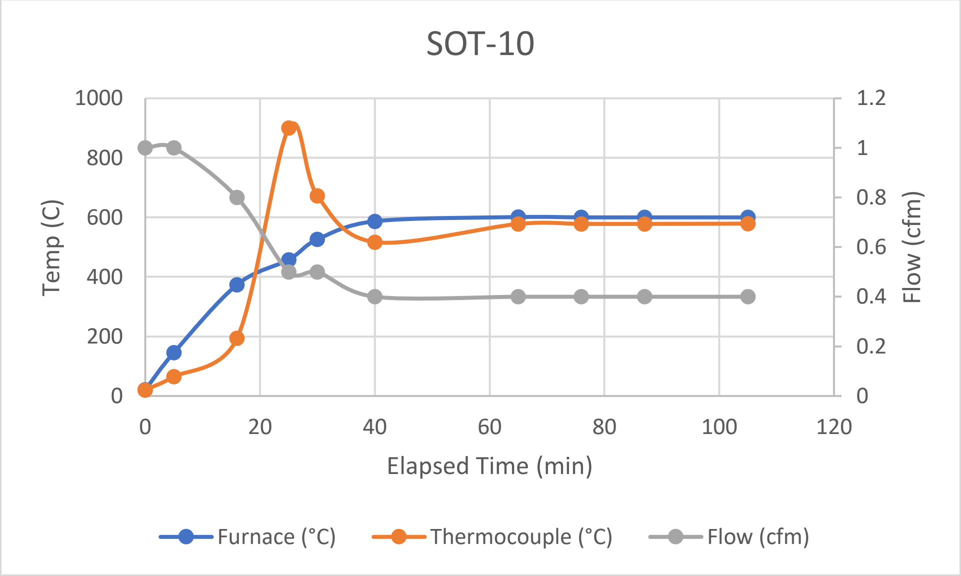

Figure A-10. Temperature and flow data for run #10.

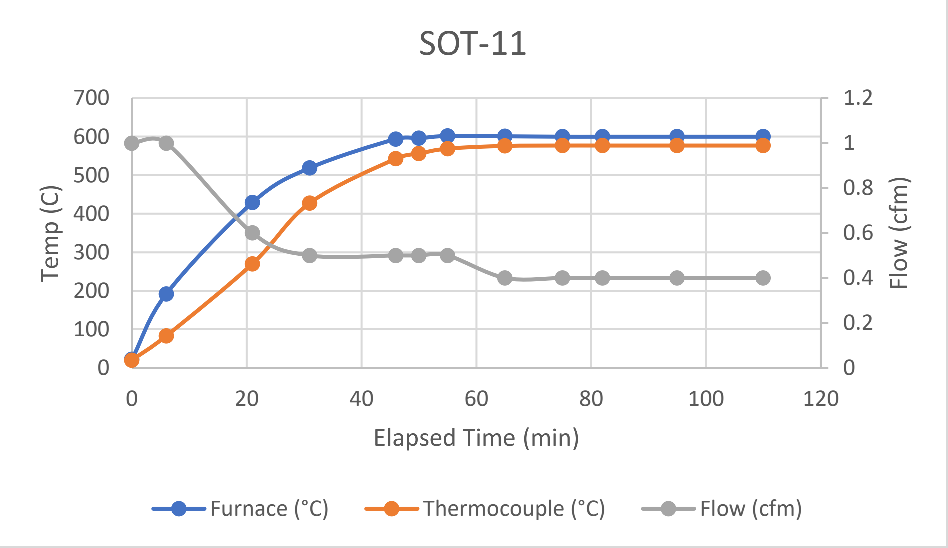

Figure A-11. Temperature and flow data for run #11.

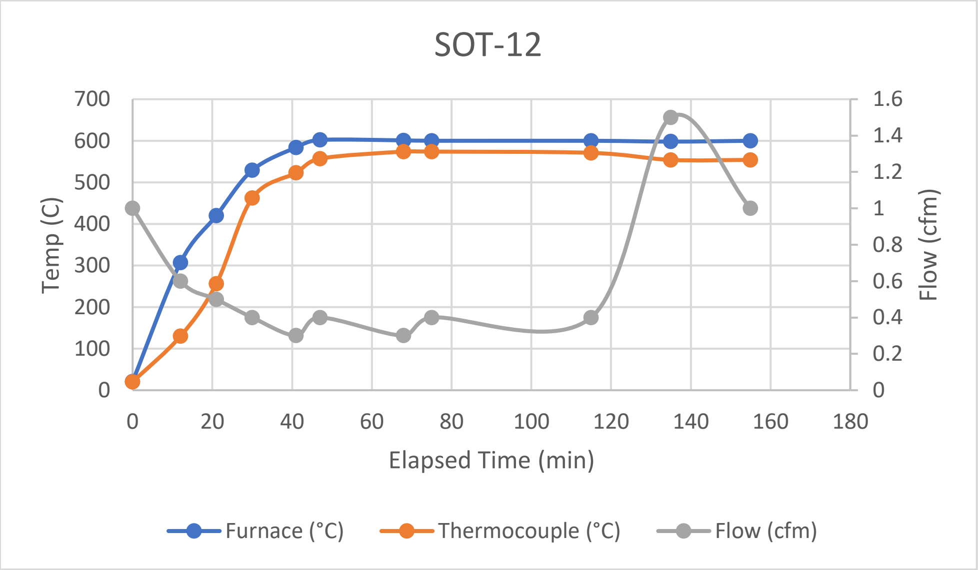

Figure A-12. Temperature and flow data for run #12.

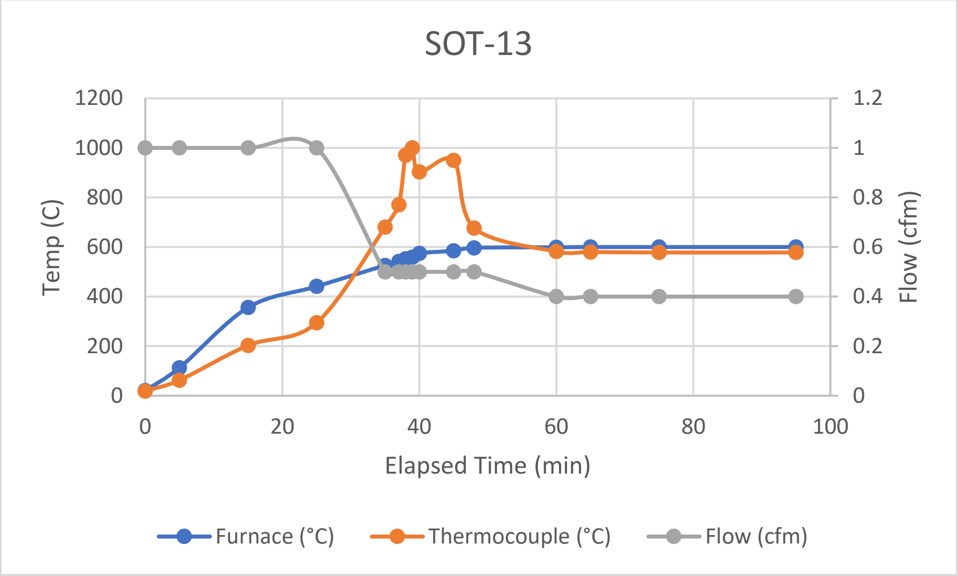

Figure A-13. Temperature and flow data for run #13.

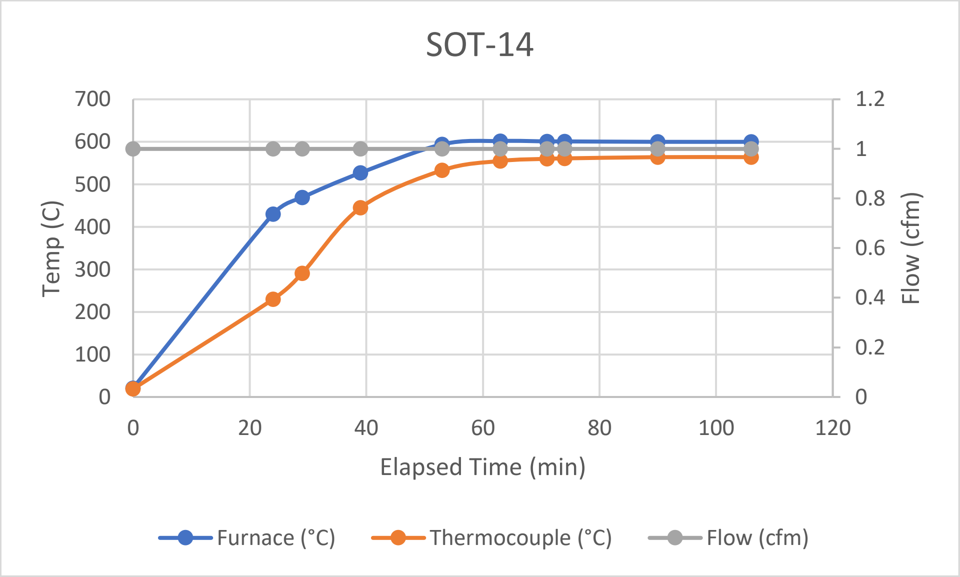

Figure A-14. Temperature and flow data for run #14.