Polymer Compositions in Critical Experiments: Possibly Not What You Think

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INTRODUCTION

The Chlorine Worth Study (CWS) Experiment was performed at the National Criticality Experiments Research Center (NCERC) in December 2021. Its goal was to provide a validation benchmark experiment with chlorine and plutonium in the thermal neutron spectrum. This purpose is necessary to reduce the margin of subcriticality in aqueous chloride operations at the Los Alamos National Laboratory Plutonium Facility (PF-4). Reducing the margin of subcriticality will enable higher throughput, required to meet NNSA mission needs.

The experiment used layers of plutonium plates, polyethylene (HDPE), aluminum, and polyvinyl chloride (PVC) or chlorinated polyvinyl chloride (CPVC). They were optimized to match plutonium-chloride solutions of 30 g/L, 300 g/L, and 600 g/L. Upon completion of the experiment, a International Criticality Safety Benchmark Evaluation Program (ICSBEP) [1] report was immediately started. The compositions of all materials were assumed pure unless additional information was known (such as for the plutonium plates).

During the benchmark analysis, the assumed CPVC composition was questioned. The follow-on work led to lessons learned on compositions in benchmarks. Materials, and specifically polymers, are often much more complex than a basic chemical formula. The CWS experiment is used as an example in this paper to document the lessons learned.

BACKGROUND

The design of the CWS experiments was requested of the LANL Critical Experiments Team in June 2020 as the need for thermal chlorine validation experiments became increasingly pressing and other efforts were not proceeding. The request also followed the successful ARCHIMEDES project [2], which demonstrated use of machine learning (ML) in critical experiment design to optimally match user-specified nuclear data sensitivities via similarity coefficients that include covariance data. For CWS, the ^{35}Cl (n,gamma) was matched. In a first of its kind effort, the design was directly sponsored by the PF-4 program, NA191. The initial design included a wide range of chlorine containing compounds- organics, inorganics, and salts. [3] Many chlorine compounds are unstable or very hazardous. Three configurations with PVC and CPVC were determined to best match application sensitivity profile. These configurations all used plutonium in the form of thin (≈0.125 in.) plates known as the Plutonium Aluminum No Nickel (PANN) plates. [4] Details of the unit definition for the three configurations are given in Figure 2. The third configuration, shown in Figure 3, contained CPVC. The material was procured at high quality with certification paperwork stating it met ASTM Standards.

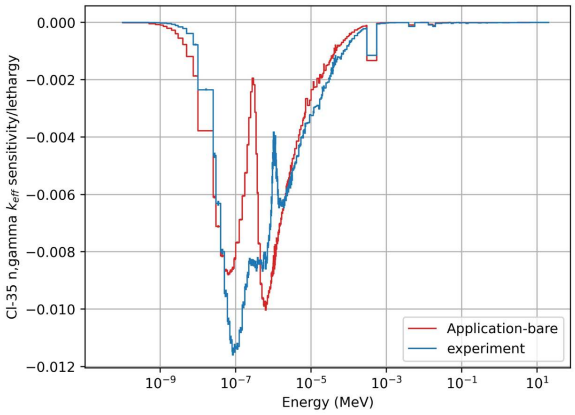

Fig. 1. Sensitivity Profile for the CPVC-containing Configuration Model with the Application Model

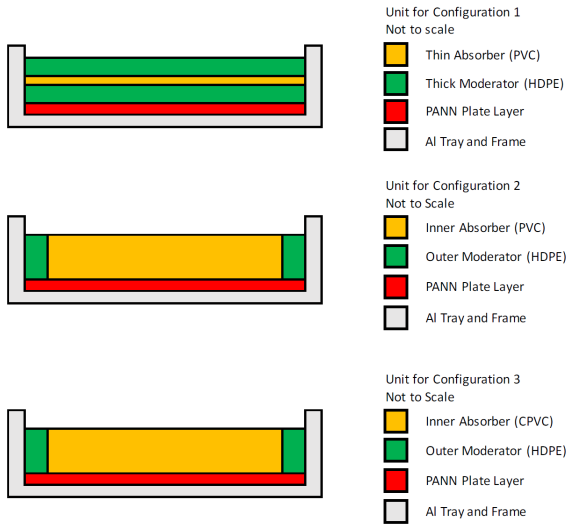

Fig. 2. Unit Details for the CWS Experiments

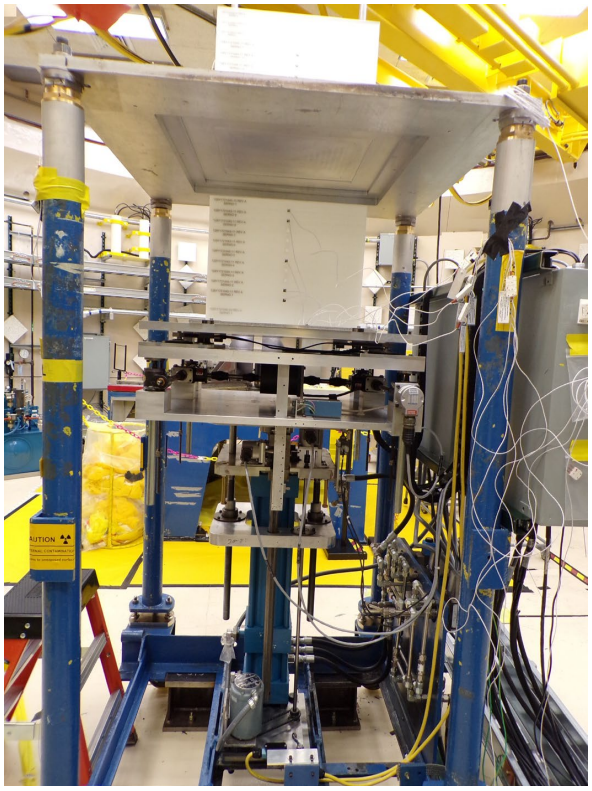

Fig. 3. CWS experiment Configuration with CPVC

Detailed models were made for the experimental configurations and preliminary uncertainties were evaluated, leading to a focused set of physical measurements for each configuration. For aspects such as material composition, sample pieces were requested from the manufacturer so that they could be sent for chemical analysis. These results were used for drafting the benchmark report.

The sample analysis results were used for determining polymer composition for benchmark-level uncertainties. It was quite challenging. The results from the process used for CWS apply broadly to all plastics and potentially to all materials that contain additives and fixatives, which are proprietary.

METHODOLOGY

The CWS experiment was planned for the ICSBEP. These benchmarks have four main sections and require in-depth knowledge of every aspect of the experiment, both numerical values and their uncertainties. The first section documents the experiment and all known information; the second section evaluates all uncertainties other than nuclear data; the third section develops a benchmark model; and the fourth section gives sample results.

In writing the second section and thus evaluating uncertainties, it was realized that the CPVC composition was not fully constrained by the ASTM standard for CPVC materials, D1784-20, and the chemical impurity results. Specifically, the chemical impurity results did not adequately narrow the range of Cl wt.% in the CPVC (57-69 wt.%). The k_{eff}uncertainty is determined using this via parametrics. The resulting k_{eff}uncertainty from the chlorine content had bounds (> 300 pcm) that were too large. Additionally, the chemical impurity results did not include carbon, oxygen or hydrogen. C, H, and O content can be determined via combustion analysis. Samples were sent to two labs for combustion analysis. Unfortunately, the results between the two labs varied widely and did not match expected values from the combination of ASTM Standard and chemical impurity analysis. Literature points to this issue. [5] These elements could not be ignored or approximated because they are known to be in polymer binders. Upon further review of the results and methods, CPVC and PVC are susceptible to issues with combustion analysis, under representing key element proportion.

Given the difficulties in using combustion analysis and the ASTM standard, the manufacturer and material supplier were contacted regarding the composition. The exact composition is proprietary so only Cl, C, H, and O weight percent with ten-percent uncertainty bounds were requested. This information was received. The remaining composition was assumed to be scaled values from the initial chemical impurity analysis.

These results were presented to the ICSBEP Technical Review Group but were met with confusion due to conflicting information provided by the manufacturer. Additional characterization methods were suggested for the CPVC.

Samples were sent for X-ray photoelectron spectroscopy (XPS) analysis, specifically targeting Cl, C, H, and O. XPS analyzes surface chemistry and is known for its ability to determine elemental composition. The company performing the analysis had difficulty quantifying H content, thus leading to large uncertainties in the other elemental content. The results did not match any of the previous results.

Additional techniques were looked into, and samples were submitted using multiple types of analysis methods. The results have not yet been received.

RESULTS

The benchmark models, created in MCNP version 6.3 [6] with ENDF/B-VIII.0 [7] cross sections, were updated each time new information on the composition was received. This effort was completed for both CPVC and PVC compositions. The variation in $k_{\text{eff}}$with the progression of information is given in Table I.

TABLE I. The keff of the configuration with CPVC varied widely with the assumed CPVC composition. This table shows those results with everything else in the model held constant. The manufacturer and XPS compositions have no impurities, while the other two include impurities from ICP-MS.

CPVC Composition Basis	k_{eff}	Δk_{eff}
pure	1.00274 ± 0.00002	
Manufacturer	1.00883 ± 0.00002	0.00609
O from Unterzaucher Method, Cl from Schoniger Method	1.01136 ± 0.00002	0.00862
C, H, Cl from XPS	1.04285 ± 0.00007	0.04011

The issues with the methods used, as well as others investigated are summarized in Table II. Some methods can analyze for a wider range of elements but struggle with chlorine specifically. Halogens and volatile compounds are very

challenging to quantify via analysis. Overall, polymer chains of varying lengths and structures lead to larger than expected variations in composition throughout a part. The binders and additives contain short polymers and other compounds with the same elements as the main molecule, which causes issues in analysis.

CONCLUSIONS AND FUTURE WORK

The CWS experiment was designed to validate chlorine nuclear data in a thermal neutron spectrum. This is needed to reduce the margin of subcriticality for PF-4 operations and hopefully improve throughput. The ICSBEP benchmark evaluation has been drafted.

Challenges in determining the CPVC composition have provided useful insight into how polymers are treated in modeling and benchmarks. They are likely much less well known that assumed and depending on the exact composition assumed, yield widely varying k_{eff}results. In using existing benchmarks, care should be taken to acknowledge what polymers are included and realize that the uncertainty quantification for these is likely incomplete. For future experiments, as well as criticality safety analyzes, care should be taken in assessing heterogeneity and incomplete knowledge of composition. polymers in particular have non-insignificant percentages of stabilizers and additives with a range of elements including C and H.

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TABLE II. Chlorine Analysis Methods and Issues

Analysis Method	**Elements Scanned**	**Issues**
ICP-MS	Cl and metals	does not capture elements bound in polymer chains
C,H,N,O	C,H,N,O	off-gasing with halides
XPS	Cl,O	H cannot be quantified and Cl suffers from confusion with other halogens
XRF	Cl,O	highly dependent on reference sample
Schoniger Combustion	Cl	interference from other halogens; issues with volatiles