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Electrochemical Denitration and Caustic Generation (EDCGe) System: Year One Project Report

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REVIEWS AND APPROVALS

AUTHORS:

DYLAN RODENE (Affiliate) Digitally signed by DYLAN RODENE (Affiliate)
Date: 2025.09.23 22:16:36 -04'00'

D. D. Rodene, Advanced Materials & Process Technology Date

MATTHEW CRAPS (Affiliate) Digitally signed by MATTHEW CRAPS (Affiliate)
Date: 2025.09.24 10:30:27 -04'00'

M. Craps, Advanced Materials & Process Technology Date

TECHNICAL REVIEW:

MARISA MOSS (Affiliate) Digitally signed by MARISA MOSS (Affiliate)
Date: 2025.09.25 10:16:21 -04'00'

M. R. Moss, Advanced Materials & Process Technology Date

APPROVAL:

CHARLES JAMES (Affiliate) Digitally signed by CHARLES JAMES (Affiliate)
Date: 2025.09.25 10:58:41 -04'00'

C.W. James, Advanced Materials & Process Technology, Manager Date

JOSEPH MANNA (Affiliate) Digitally signed by JOSEPH MANNA (Affiliate)
Date: 2025.09.25 11:36:44 -04'00'

J. Manna, Materials Technology & Energy Sciences Division, Director Date

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EXECUTIVE SUMMARY

An advanced electrochemical denitration and caustic generation (EDCGe) system is being developed to process legacy waste through the direct feed high-level waste (DFHLW) flowsheet at Hanford. This system aims to destroy nitrates and organics in DFHLW and potentially DFHLAW feeds, significantly reducing off-gas concerns from both process safety and process flowsheet perspectives. Supported by a multidisciplinary team, this effort includes creating a tandem denitration electrolyzer/off-gas system as part of a broader mission to accelerate waste treatment through fundamental and applied research and development initiatives. The progress for the first year of the three-year program to develop technology for the EDCGe system is described within this document. Some key highlights in year 1 are as follows:

- Proof-of-concept denitration of benchtop electrochemical experiments at a high voltage
- Benchtop electrochemistry within flow cell systems
- The use of polymer-based ion-exchange membranes in the H-type electrochemical cell
- A review of legacy electrochemical work
- The development of ceramic sodium super ion conductive (NaSICON) membranes via 3D printing and tape casting techniques
- The execution of a subcontract for the Electrosynthesis Company to evaluate engineering-scale electrochemical denitration processes
- The identification of a Ru/Al_2O_3 baseline off-gas catalyst for NH_3 abatement
- The development of off-gas evaluation systems
- The use of temporal analysis of products (TAP) reactor for the evaluation of baseline off-gas abatement catalysts
- The synthesis and scale-up to produce testable quantities of initial high entropy alloys (HEAs) on graphene oxide (GO) for the benchtop off-gas systems
- The development of a framework for computational modeling for off-gas catalyst material discovery
- Published a peer-reviewed perspectives review paper on high entropy alloy (HEA) catalysts and drafted a N_2O review article

The accomplishments from year 1 will be the foundation for a successful and productive year 2 for the project.

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LIST OF ABBREVIATIONS

AEM	Anion Exchange Membrane
AMU	Atomic Mass Unit
CFD	Computational Fluid Dynamics
Clemson	Clemson University
CRU	Larger Caustic Recovery Unit
DFHLW	Direct Feed High Level Waste
DFT	Density Functional Theory
DOE-EM	Department Of Energy – Office of Environmental Management
DOS	Density of States
EDCGe	Electrochemical Denitration and Caustic Generation
EIS	Electrochemical Impedance Spectroscopy
fcc	Face-Center Cubic
FIU	Florida International University
GDL	Gas Diffusion Layer
GO	Graphene Oxide
H-cells	H-Type Electrochemical Cells
hcp	Hexagonal Close-Packed
HD	Deuterated Hydrogen
HEA	High Entropy Alloy
HLW	High-Level Waste
IC	Ion Chromatography
INL	Idaho National Laboratory
ILAW	Immobilized Low Activity Waste
LAMMPS	Large-Scale Atomic/Molecular Massively Parallel Simulator
LAW	Low-Activity Waste
LDR	Land Disposal Restriction
MC	Monte Carlo
MCDC	Materials Computation and Data Science Group
MD/MC	Molecular Dynamics/Monte Carlo
MEA	Membrane Electrode Assembly
ML	Machine Learning
MS	Mass Spectrometer
NaSICON	Sodium Super Ionic Conductor
NC A&T	North Carolina Agricultural and Technical State University

NNLEMS	Network of National Laboratories for Environmental Management and Stewardship
NP	Nanoparticle
NTCR	Near-Tank Cesium Removal
PEM	Proton Exchange Membrane
PNNL	Pacific Northwest National Laboratory
PREDICT	PRedict Properties from Existing Database In Complex Alloys Territory
RGA	Residual Gas Analyzer
R&D	Research and Development
rGO	Reduced Graphene Oxide
SCR	Selective Catalytic Reduction
SE	Southeast
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SS	Stainless-Steel
SST	Shear Stress Transport
TAP	Temporal Analysis of Products
td	Time Delay
TDU	Smaller Electrochemical Caustic Recovery Technology Demonstration-Scale Unit
TRL	Technology Readiness Level
USC or UofSC	University of South Carolina
VASP	Vienna Ab-Initio Software Package
WM	Waste Management Symposia
WTP	Hanford Tank Waste Treatment and Immobilization Plant

1.0 Introduction

In 2021, the Department of Energy – Office of Environmental Management (DOE-EM) and the Network of National Laboratories for Environmental Management and Stewardship (NNLEMS) developed a research and development (R&D) roadmap for the Hanford tank waste treatment mission. In 2023, DOE-EM issued a Lab Call for projects supporting the Roadmap to accelerate the waste treatment mission at Hanford and provide tangible returns on investments, as well as supporting the development of fundamental science. The Electrochemical Denitration and Caustic Generation (EDCGe) project was funded by a DOE-EM R&D Roadmap Award. The Hanford Roadmap Award 277996 has been funded for the first year of three years of projected work scope. The work performed in year 1 aligned with the awarded proposal scope to recover competency from legacy reports and in designing the EDCGe system.

The Hanford Tank Waste Treatment and Immobilization Plant (WTP) functions to immobilize both low-activity waste (LAW) and high-level waste (HLW) in borosilicate glass waste forms. Direct feed flowsheets are being pursued for both LAW and HLW. The direct-feed high level waste (DFHLW) flowsheet offers major cost and time savings to the Hanford WTP and stakeholders but presents challenges in process control strategy and off-gas treatment. Namely, the DFHLW process skips the utilization of a waste pretreatment facility and is planned to send the waste directly from the Tank Farms to the vitrification facility. The feed will be rich in nitrites and nitrates, which will produce copious amounts of hazardous NO_x and NH_3 gases from the WTP melter, which may also present regulatory and safety hazards due to permitting limitations. The processing requirements and complexity of the off-gas treatment process can be largely reduced if these nitrite and nitrate compounds are removed prior to vitrification.

Project overview:

- The project supports the roadmap to accelerate the waste treatment mission at Hanford and provide tangible returns on investments. The work scope is supported by a team of scientists and engineers from national labs, academia, and industry and includes fundamental science, technology development, and multiple-scale demonstrations for DOE-EM
- Accelerate the Hanford Mission by developing an EDCGe system to treat nitrates and generate caustic solution
- Understand pretreatment of HLW supernatant simulants to help enable a DFHLW process in the Southeast (SE) quadrant and a secondary waste-form process in West area
- Develop a robust process that includes risk mitigation steps for the destruction of nitrates and organics in tank supernate, including the abatement of process emissions
- Show the viability of an engineering-scale system for the pretreatment of simulated tank supernate

Electrochemical treatment has been selected for development due to its inherent level of safety, selectivity for nitrate and nitrite destruction, ability to produce caustic, and economic viability.[1] Previous work has been conducted, both at Savannah River National Laboratory (SRNL) and elsewhere, to study the feasibility and efficiency of electrochemical processing applications within the waste treatment and disposition flowsheets at the Savannah River Site (SRS) and at Hanford.[2-7] The current work seeks to scale up proof-of-concept technology to propose full-scale integration of a similar system into the DFHLW flowsheet. A nitrate species destruction targeting at least a 50% reduction would be of significant benefit to Hanford. Innovative science and technology development is anticipated for electrode materials, selective membranes, and off-gas abatement catalysts.

2.0 Methodology

Project activities are directed toward three distinct goals, guided by the DOE-EM NNLEMS matrix of investment priorities that are summarized in Table 1.[8] The goals are set to manage NO_x emissions within the HLW vitrification facility by the destruction of nitrate and nitrite species prior to transferring to the facility. The process being developed will target treatment within the tank farms to treat tank waste supernate through destruction of nitrate/nitrite species, destruction of land disposal restriction (LDR) organic species, and development of strategies for at-tank HLW pretreatment implementation.

Table 1. DOE-EM NNLEMS List of Prioritized Investments for Hanford R&D Roadmap.

Priority	Concept	Technical Maturity	R&D Timeframe	Investment Total cost	Estimated Cost Savings	Schedule Acceleration
Top	At-tank pretreatment of HLW Sludge	Prototype	0–5 yrs.	$100–300M	>$25B	>10 yrs.
High	RCRA organics removal from tank supernate	Lab demonstration	0–10 yrs.	$10–50M	>$25B	>10 yrs.
Medium	Sodium nitrate separation or destruction technologies	Pilot, prototype	0–15 yrs.	$10–50M	$0–250M	0–3 yrs.

The project is divided over 3 yrs into 4 overall tasks including:

1. Process evaluation and computational approach of waste tank processing
2. Engineering-scale electrochemical denitration electrolyzer
3. Scoping and development of off-gas system for engineering scale
4. Off-gas catalyst synthesis with focus on high entropy alloy (HEA) and NH_3 decomposition catalysts

The project is a multi-institutional collaboration effort with several key partners that have defined tasks and responsibilities. SRNL is the lead for the team. Table 2 outlines the high-level responsibilities, and associated task leads among each organization. The multi-institutional collaboration enables each team to contribute their expertise and fosters synergy.

Table 2. EDCGe Team Breakdown.

Organization	Principal Investigator(s)	Tasks
SRNL	Dylan Rodene	Lead Principle Investigator for both the EDGCe process and pilot-scale skid development; Team lead for Hanford liaison
SRNL	Junhua Jiang	Electrochemical development support for modification of pilot-scale electrolyzers
SRNL	Matthew Craps	Off-gas treatment and HEA catalyst development
Polykala Technologies, LLC	Maoqi (Mark) Feng	Commercial catalyst development, commercial electrolyzer design development, tank feed filtration
INL	Rebecca Fushimi	SRNL catalyst evaluation, commercial catalyst evaluation, temporal analysis reactor for off-gas study
Clemson University	Jianhua (Josh) Tong	Ceramic separator development, material characterization, durability testing
North Carolina A&T	Aparna Aravelli	Nitrogen species modeling, identification of Hanford water management opportunities, sensing probes for nitrogen species in key process streams
University of South Carolina	Fanglin (Frank) Chen	Small-scale electrolyzer validation, solid oxide fuel cell alternative for gas phase NO_x management or power recycle
Clemson University	Dilpuneet (DP) Aidhy	Machine learning and density functional theory (DFT) modeling to inform HEA catalysts, selection and development for off-gas treatment and electrochemical processes
University of South Carolina	Jochen Lauterbach	Ammonia gas phase testing and decomposition catalyst development, HEA catalyst development assistance, catalyst immobilization

The workflow of the EDCGe team is divided into two main focuses: the electrochemical side Figure 2-1a and the off-gas abatement side Figure 2-1b. The electrochemical side is investigating simulant selection that will feed fundamental electrochemical studies. Insights from these studies will feed into the development and refinement of electrochemical models and the operation of small-scale electrolyzers. The small-scale electrolyzer work will include some analytical development for liquid and gas phase analyte sensing, which informs the intermediate-scale electrolysis work conducted in flow cells. The intermediate-scale electrolyzers contribute to modeling efforts for flow efficiencies and reactor archetypes and provide critical data on off-gas compositions, nitrate conversion efficiencies, scale-up designs, as well as pilot-scale electrolyzer selection. This data is pivotal in determining optimal operating conditions and device configurations. Concurrently, the team is also advancing membrane development studies focused on NaSICON-based materials for electrochemical evaluation.

The off-gas abatement side begins with machine learning and computational design aimed at materials discovery for ammonia decomposition catalysts, with emphasis on material phase and composition. These computational insights guide catalyst design, which influences the synthesis and selection of catalysts. Synthesized catalysts undergo evaluation in various cutting-edge and traditional gas-phase reactor systems. The data collected from these evaluations will generate feedback that is used for further refinement in computational modeling, design, and synthesis. The outcomes of these evaluations will lead to the selection of effective catalysts for the off-gas abatement system, potentially requiring multiple catalytic stages based on electrolyzer outputs. Off-gas catalyst performance will help with engineering and scaling these catalytic strategies, ultimately guiding the design of an off-gas reactor system.

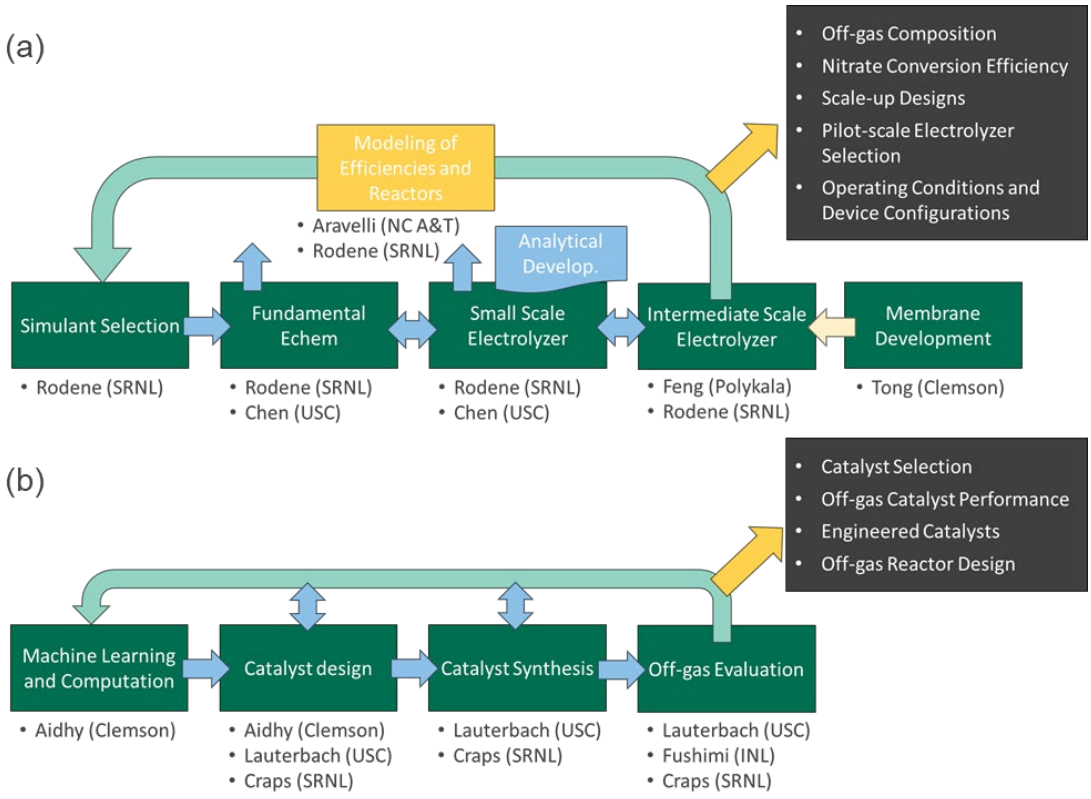

Figure 2-1. Electrochemical denitration flow diagram for the electrochemical (a) and off-gas abatement (b) teams.

2.1 Phase 1

Phase 1 of the EDCGe project is currently underway, and focuses on a review of past research, procurement, scoping tests, design, and proof-of-concept development for an engineering-scale electrochemical denitration and off-gas treatment system. The literature review conducted by SRNL, in tandem with initial scoping tests conducted in H-type electrochemical cells (H-cells), has informed the basis for current and ongoing research. Current baselines for future work include cell membrane materials, electrode materials, and electrolyzer manufacturers. Sodium super ionic conductor (NaSICON) ceramic membranes have been chosen for future study due to their sodium selectivity and minimal transport of contaminants. Organic-based polymer membranes are also being studied as an alternative to NaSICON materials, due to their successful commercialization in the chemical industry and use in previous studies.[2-5] Anode and cathode materials are subject to change as H-cell tests continue, however, nickel has been chosen as the electrode base-case material due to its low susceptibility to corrosion and fouling detailed in previous work.[6, 7] Commercially available electrolyzers have been identified and evaluated based on fitment to proposed process conditions, such as modularity, throughput, construction materials, and the ability to withstand corrosion. ElectroCell A/S and NORAM Electrolysis Systems, Inc. (NESI) have been identified as possible suppliers of electrolyzer units as process development is scaled.

2.2 Phase 2

Phase 2 includes scaling up the electrolyzer system and tailoring the process to produce caustic as a desirable byproduct. Phase 2 will be used to optimize and expand these systems, while also implementing a caustic recycle generator (electrolyzer) to operate downstream of the denitration electrolyzer. Planning for Phase 2 is informed by the literature review and initial Phase 1 experiments. Possible vendors for larger scale electrolyzers have been identified and are being evaluated. Current research and development of sodium-selective ceramic membranes will aid in the production of useable sodium hydroxide as caustic.

The caustic generation electrolyzer will afford a recycle stream of caustic NaOH back to the batching tanks at Hanford to aid in preparation of the waste for WTP.

2.3 Phase 3

Phase 3 of the EDCGe project will focus on optimization of the engineering-scale electrochemical process and facilitate planning for the integration of an EDCGe process into the WTP. This phase involves extended engineering-scale testing with Hanford supernate waste simulants to optimize process parameters. Moreover, Phase 3 will advance the integration of the denitration electrolyzer, caustic generation electrolyzer and tandem off-gas abatement reactor to develop a cohesive system plan. Each respective unit operation (i.e. electrolyzer, off-gas reactor, etc.) will continue to undergo further optimization to enhance process efficiency and material robustness. Additionally, a flowsheet for the implementation in the WTP will be developed.

Task	Tasks Leads	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1: Process evaluation using computational approach of tank waste processing	SRNL FIU												
Task 1.1 Literature review of electrochemical reduction technologies of nitrates	SRNL												
Task 1.2 Evaluation/Scoping (pt.1) studies of engineering scale process	SRNL UofSC												
Task 1.3 Procurement of eng. scale denitration electrolyzer	SRNL UofSC Polykala												
Task 2: Eng. scale electrochemical denitration electrolyzer	SRNL UofSC Polykala												
MS 2.2 Selection of a eng. scale denitration electrolyzer	SRNL Clemson UofSC												
MS 2.1 Provide initial denitration system downselection of membrane and electrode materials	SRNL Clemson UofSC												
MS 2.3 Verification of the eng scale denitration electrolyzer	SRNL Clemson UofSC												
Task 2.1: Develop the selectivity and efficienty of the electrocatalysts for the electrolyzers	SRNL Clemson UofSC												
MS 2.4 Bench scale studies (pt.2) for electrochemical denitration in conjunction with the eng. scale	SRNL UofSC												
MS 2.5 Bench scale (pt.3) studies for the simultaneous denitration and organic destruction	SRNL Clemson UofSC												
MS 2.6 Studies for denitration electrolyzer membrane selection	SRNL Clemson UofSC												
MS 2.7 Selection electrochemical operation conditions for the electrolyzers	SRNL												
Task 2.2: Scoping of additional technologies (pt.4) for the EDCGe system (e.g. solid oxide fuel cell)	SRNL Clemson UofSC												
Task 3: Scoping and development of the off-gas system for the eng. scale	SRNL												
MS 3.1 Selection of an offgas system	SRNL												
MS 3.2 Optimization of the eng. scale apparatus to test and expand upon	SRNL Clemson UofSC												
Task 3.1: Validation and verification of the eng. scale off-gas system using simulated denitration off-	SRNL Clemson UofSC												
Task 3.2: Process evaluation of integrated denitration and off-gas system using simulated Hanford tank streams	SRNL FIU												
Task 4: Offgas catalyst synthesis with focus on HEA and NH3 decomposition catalysts	SRNL Clemson UofSC												
Task 4.1: Temporal Analysis of Products (TAP) reactor catalyst validation	INL												
Task 4.2: Develop simpler alloys database and fundamental understanding of adsorption sites	Clemson												
Task 4.3: ML model development, HEA HT testing feedback	SRNL Clemson UofSC												
MS 4.1 Test commercially available off-gas catalysts	SRNL INL												
MS 4.2 Downselect cats and test down-selected HEAs/cats with TAP reactor	SRNL INL												
Task 4.4: Evaluation of filtering of HLW to feed the EDCGe pretreatment process	SRNL Polykala												
Task 4.5: Evaluation of sensors for measuring nitrates and other species at the tank	SRNL FIU												

Figure 2-2. EDCGe Project schedule (given as accepted in the proposal) for Award 277996.

3.0 Electrochemical Denitration Discussion

This document presents the preliminary results identified for use in the EDCGe system to accelerate the Hanford mission. A literature review combined with the preliminary scoping experiments have shown that an electrochemical denitration system is viable for removal of nitrates and nitrites from waste tank supernate. This satisfies the *Year 1, Go/No-Go Milestone* to "show that an electrochemical system like what will be used at the engineering scale is effective at nitrates destruction." A paper presentation of the legacy technologies from literature and applicability was given at Waste Management Symposia 2025 (WM2025).[9, 10]

3.1 Task 1, Process evaluation and computational approach of waste tank processing:

A thorough literature review of previous research from the national laboratories has been conducted, which is being used to form the basis of initial electrochemical testing.

3.1.1 Literature review

For Task 1 in Figure 2-2, a literature review of legacy reports has shown that an electrochemical denitration system is viable for the removal of nitrates and nitrites from waste tank supernate. A summary of that review and presentation is given below.[9, 10]

3.1.1.1 Denitration Electrolyzer

Work from the Westinghouse Savannah River Company in the 1990's and early 2000's showed promise for electrochemical denitration both at the benchtop- and pilot-scale. In pilot-scale and small-scale tests, the ICI FM21-SP cell (Figure 3-1) and the ICI FM01-LC cell were utilized, respectively. However, neither of the reactors are still commercially available. These series of experiments compared current efficiency between divided and un-divided cell configurations, tested varying electrode materials, and utilized non-radioactive Hanford and SRS liquid waste simulants along with SRS tank waste supernate. Key findings include an increase in efficiency in a divided cell as opposed to an undivided cell,[11] a proof-of-concept at both the benchtop- and pilot-scale[12] with over 99% of nitrates destroyed, and the observation of "induction periods" in which the initial rate of nitrate destruction is low.[11, 13]

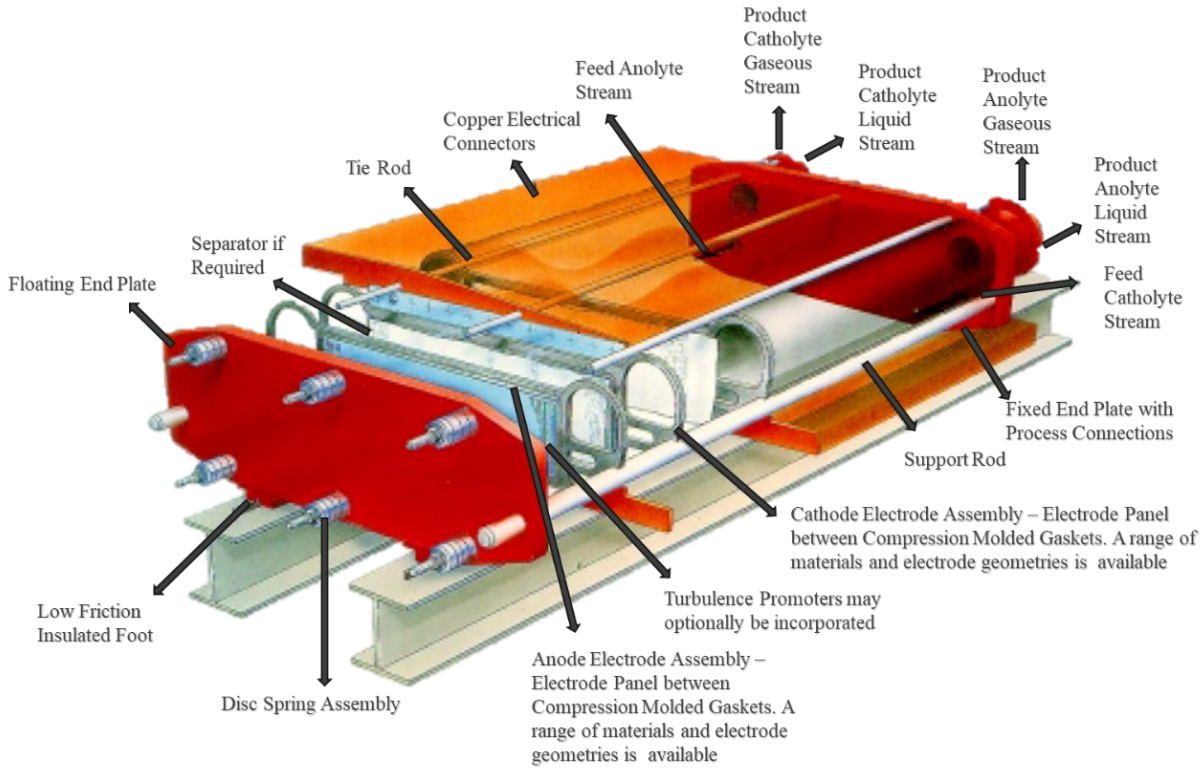

Figure 3-1. ICI FM21-SP Plate and Frame Flow Cell used in pilot-scale demonstration. Image taken from ref. 11.

Work conducted by the Electrosynthesis Co. Inc. focused primarily on scoping tests utilizing various combinations of electrodes, membranes, current density, and temperature, with non-radioactive waste simulants. Significant findings include the identification of lead as an efficient cathode material and the effect of irradiation on selected polymer membranes (Nafion 417 and Nafion 324).[6, 7] Tests show no appreciable difference in efficiency or resistance after exposure to radiation,[6] and that polymer-based membranes could become plugged with precipitates over time.[7]

Furthermore, the Electrosynthesis Co. Inc. utilized both the ElectroCell MP and ICI FM01 LC Electrolyzers in these experiments. The undivided ICI FM01 flow cell with an electrode area of 64 cm^2 showed a slight increase in denitration efficiency (~33% nitrate reduction efficiency) when the current density was almost doubled from 75 to 140 mA cm^{-2} at 50 °C. An ~20% increase in denitration efficiency was further achieved by increasing the temperature to 80 °C and using a Pb-Sn-Ca alloy cathode and a Ni anode. It was also confirmed that divided cells operate at a higher denitration efficiency than undivided cells.[7] Longer term (100 and 1000 h) tests were conducted to study the consequences of corrosive material exposure on anode and cathode materials. The results demonstrate that lead proved to be the most corrosion-resistant cathode material tested, and all anode materials tested exhibited varying degrees of corrosion, etching, or formation of metal oxide layers.[7]

3.1.1.2 Caustic Generator Electrolyzer

The Pacific Northwest National Laboratory (PNNL) focused on testing actual Hanford tank waste and non-radioactive simulated Hanford waste supernate. These experiments aimed to study NaSICON membrane performance and assess the feasibility of a caustic recycle process for sodium recovery (schematic shown in Figure 3-2). This process would supply a NaOH feedstock for other waste treatment processes such as sludge leaching and reduce the total volume of immobilized low activity waste (ILAW) produced. An

ElectroCell MP electrolyzer (Kovar anode and Ni cathode, 100 cm^2) with NaSICON membranes in a large-area configuration (6.1 cm dia. membrane with 13.6 cm^2 active surface area) was used to conduct 5-day benchtop-scale tests of Tank 5 and 6 supernate samples.[2] The 5-day tests resulted in high sodium removal selectivity, high electrical efficiency, and no observation of contaminant transport besides Cs (decontamination factor of 5,717).[2] Further testing conducted on the benchtop-scale with proprietary LANS-GY NaSICON membranes showed an ability to produce 19 M NaOH solution, and a membrane break-in period was identified.[3] Broadly, PNNL research demonstrated the viability of using NaSICON to produce NaOH in an electrolyzer with no observable membrane or electrode degradation.

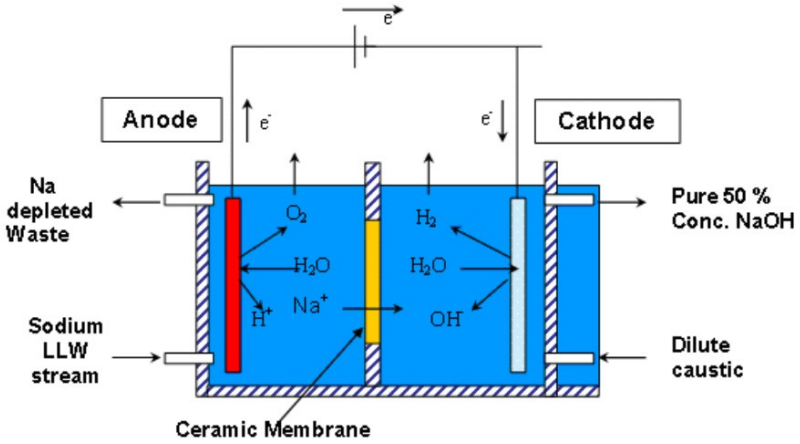

Figure 3-2. Schematic for the electrochemical caustic generator operation with a NaSICON membrane. Image taken from ref. 3.

The PNNL report provided testing results using an Electrocell MP electrolyzer with a Ni cathode and Pt/Ti anode. A circular sodium super ionic conductor (NaSICON) disk (7.62 cm diameter) served as the membrane.[3] Anolytes for the batch tests used a tank waste composite solution of material from AP104, SY101, and AZ101 tanks. Non-radioactive tests used a simulant based on the tank waste composite. The catholyte was either 1 M or 18.6 M NaOH. The solution temperatures were maintained at 40 °C.

Ceramatec Inc. successfully manufactured and operated a prototype electrochemical caustic recovery technology demonstration-scale unit (TDU), consisting of 22 tubular ceramic membranes.[4] A larger, 38 membrane caustic recovery unit (CRU) was then designed and constructed to be a pilot process on a ¼ scale.[5] The ceramic membranes used in both units are a proprietary NaSICON formulation called NaSelect™. The CRU demonstrations were performed with both LAW simulants and actual waste supernate.[4]

The TDU treated 7 L h^{-1} of near-tank cesium removal (NTCR) effluent simulant, and successfully removed 80% of the original sodium concentration to produce 30 wt% NaOH (Figure 3-3).[4] Sodium transport efficiency across the NaSelect™ membranes in the pilot-scale CRU was near 100%, allowing for up to 70% sodium hydroxide removal on the ¼ scale when processing 16.8 L h^{-1} of NTCR effluent.[5] This recycle rate would allow for total LAW volume to be reduced by 39% and would provide a 10 M stream of NaOH of up to 9.3 kg hr^{-1}.[5] The pilot-scale CRU has been evaluated as having a technology readiness level (TRL) of 6.

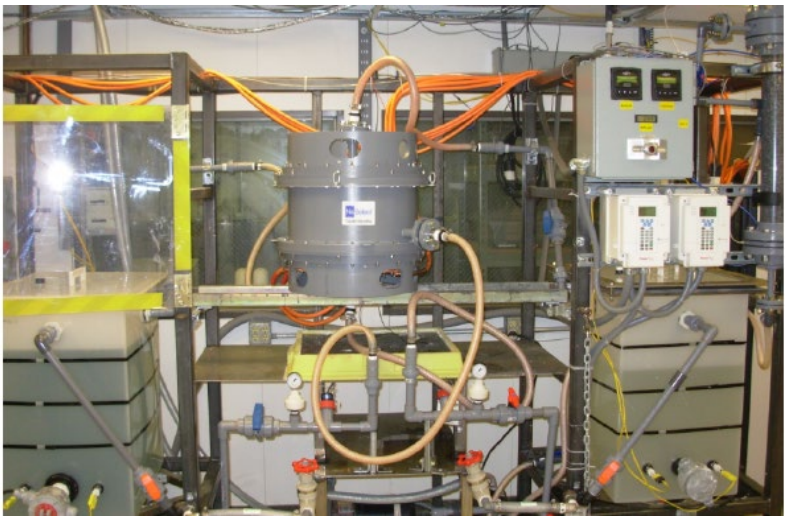

Figure 3-3. The TDU test skid from Ceramatec Inc. Image taken from refs. 4, 14.

The WM2010 report describes testing with a tubular cell design with varying NaOH concentrations.[15] The tubular cells feature a stainless-steel (SS) cathode (grade not specified) and a Kovar (Fe-Ni-Co) anode. No discussion was identified on selection of electrode materials. Performance was very similar to that with the flat disk membrane. Batch tests were carried out with no material additions during testing until aluminum hydroxide solids precipitated from the anolyte (bayerite and gibbsite).

3.1.2 Benchtop-scale electrochemical development

Preliminary scoping experiments have shown that an electrochemical denitration system is viable for the removal of nitrates from waste tank supernate. Benchtop-scale H-cell electrochemical experiments have been initiated to satisfy Figure 2-2, **Task 1.2** (*Evaluation/Scoping (pt.1) studies of engineering scale process*). Electrochemical conversion of nitrates was observed with a variety of electrodes (Ti, Ni, SS, Co, Cu, and Pt) and membranes (PiperION, which we ordered and tested independently, and proprietary membranes received with the flow cells). In-situ aqueous Raman and gaseous mass spectroscopy analytical capabilities are being developed to observe chemical conversion efficiencies and product formation in real-time.

Please note, all data presented is preliminary to provide proof-of-concept findings. The systems and experiments require further optimization that is ongoing in year 2. The –5.0 V operating conditions that SRNL tested were in excess so that a high current density could be achieved to accelerate bulk nitrate reduction in the solution for the benchtop-scale H-cell (8.5 mL of simulant per compartment) with small electrodes (~0.3–2 cm^2). For the future evaluations, the applied electrochemical potentials will be lowered to study selectivity and denitration efficiencies at potentials between –1.2 and –5.0 V.

3.1.2.1 Non-radioactive Tank Waste Simulant development

Non-radioactive supernatant simulant recipes were developed to closely resemble the supernatant for AP-102 (composition based upon the analytes present in 2024). The simulant recipes were utilized in year 1, where the compositions and molarities listed in Table 3 were used to evaluate the electrochemical parameters among the collaborators. Four simulants were developed with increasing levels of complexity. The main components of interest for electrochemical treatment and processing from the waste tanks are accounted for within these simulants. Constituents present in AP-102 that are not included in the initial simulants prepared because they either had negligible concentrations (<0.002 M) or are planned to be included in future experiments.

Table 3. Concentrations and components for the simulants used in year 1.

	Nitrate Simulant (M)	Simulant1 (M)	Simulant2 (M)	Simulant3 (M)
NaOH	1.0	0.826	0.826	0.826
$NaNO_3$	1.0	1.708	1.708	1.708
$NaNO_2$		1.067	1.067	1.067
Na_2CO_3			0.765	0.765
$Na_2C_2O_4$			0.012	0.012
$NaAlOH_4$		0.095	0.095	0.095
NaCl				0.055
NaF				0.042

3.1.2.2 Year 1 electrode materials study:

Proof-of-concept electrochemical screening was performed with commercially available metal foils to show the feasibility of reducing nitrate from a nitrate simulant. The electrochemical denitration of the nitrate simulant was conducted using a BioLogic SP-300 potentiometer. Cathode materials were considered based on commercial availability and use in legacy reports. The cathodes reported include Ti, Ni, SS, Co, Cu, and Pt foils. A two-electrode H-cell setup was employed with an over-dipped graphite-rod anode, nitrate simulant for both electrolytes, and PiperION anion membrane. The systems were run at –5.0 V for 4 h at room temperature. The electrochemical current was collected for each run, and the catholyte solutions were analyzed using ion chromatography (IC) to determine the percentage of nitrate removed, as shown in Table 4. An increase in NO_3^- concentration in the anolyte indicates nitrate transfer from the catholyte to the anolyte via anion exchange membranes (AEM). Table 4 also summarizes the percentage of nitrate transferred across the membrane, as well as the percentage of nitrate reduced at the cathode to form gaseous products. No nitrites were able to be detected in either of the electrolytes after any of the experiment.

Table 4. Summary of electrochemical denitration analytical results.

Electrode Name	Electrode nominal area (cm^2)	Average current density ($mA\ cm^{-2}$)	Energy (Wh)	Power (W)	NO_3^- Removed (%)*	NO_3^- Transferred across the membrane (%)†	NO_3^- Reduced (%)Ø
Ti Foil	0.916	-64.26	1.18	0.29	52.26	31.28	20.98
Ni Foil	0.186	-302.9	1.13	0.28	52.91	27.09	25.82
SS Foil	0.709	-66.59	0.94	0.24	22.10	-1.30	23.40
Co Foil	0.342	-168.9	1.16	0.29	28.39	8.86	19.53
Cu Foil	0.311	-162.2	1.01	0.25	44.50	15.47	29.05
Pt Foil	1.953	-30.08	1.18	0.29	55.00	20.80	34.21

* $\%NO_3^-_{removed} = ([NO_3^-_{initial\ nitrate\ sim.}] - [NO_3^-_{final\ catholyte}]) / [NO_3^-_{initial\ nitrate\ sim.}]$

† $\%NO_3^-_{transferred} = ([NO_3^-_{final\ anolyte}] - [NO_3^-_{initial\ nitrate\ sim.}]) / [NO_3^-_{initial\ nitrate\ sim.}]$

Ø $\%NO_3^-_{reduced} = \%NO_3^-_{removed}] - \%NO_3^-_{transferred}$

The IC anion results indicate that electrochemical removal of nitrate ions from the nitrate simulant solution is feasible. Ni foil achieved the highest current density, suggesting superior overall electrochemical performance with comparable energy and power to the other electrodes. According to the IC anion results, ~53% of the nitrate ions were removed from the catholyte solution. Pt, Ti, and Ni electrodes were the most effective, removing ≥50% of the nitrates from the catholyte. Interestingly, an increase in nitrate ion concentration was observed for most anolyte solutions, except for the SS cathode. Up to 31% of nitrate ions

were transferred from the catholyte to the anolyte due to the use of an AEM. Despite nitrate ions transfer to the anolyte, all cathodes showed at ≥20% nitrate ion reduction after 4 h. More tests are being performed to study nitrate reduction with proton exchange membranes (PEMs) so that nitrate transfer across the membrane does not occur, as well as studying electrodes that are of more consistent areas.

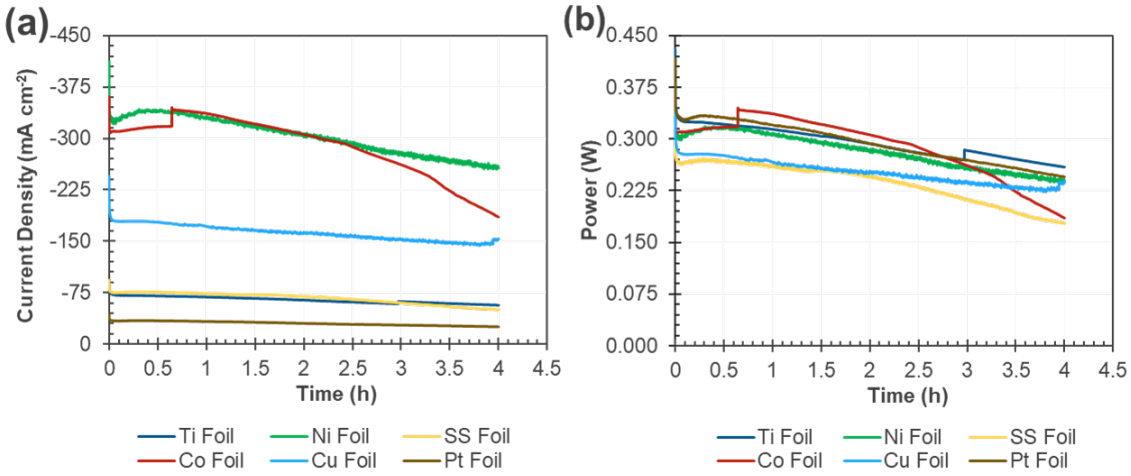

Figure 3-4. Chronoamperometry testing results: current density (a) and power (b) vs. time.

The electrochemical currents collected are shown in Figure 3-4, which displays the current density for each electrode and the power of the system as a function of time. The nominal area of the electrodes varied from 0.1–2.0 cm^2. The differences in electroactive area may play a role in the observed electrochemical results in Figure 3-4a. However, the area of the electrode did not seem to affect the percent denitration for these experiments, considering that electrodes of varying electroactive areas yielded similar percent denitration results. The current is likely facilitating a combination of the following reactions:[16]

Nitrate reduction reactions:

$$NO_3^-(aq) + H_2O(l) + 2e^- \rightarrow NO_2^-(aq) + 2OH^-(aq) \quad (1)$$

$$2NO_2^-(aq) + 3H_2O(l) + 4e^- \rightarrow N_2O(g) + 6OH^-(aq) \quad (2)$$

$$2NO_2^-(aq) + 4H_2O(l) + 6e^- \rightarrow N_2(g) + 8OH^-(aq) \quad (3)$$

$$NO_2^-(aq) + 5H_2O(l) + 6e^- \rightarrow NH_3(g) + 7OH^-(aq) \quad (4)$$

Water splitting competing reaction:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad (5)$$

Hydroxide oxidation:

$$4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^- \quad (6)$$

The selectivity of the system is based on the electrodes, operating conditions, and electrolyte compositions. Interestingly, these initial electrochemical material studies have provided insights into utilizing a polymer-based AEM to separate nitrate species from the feed solution. The use of an AEM may increase the nitrate removal efficiencies from a tank by reducing nitrates at the cathode as well as by transferring a portion of the nitrates to a subsequent stream, offering an alternative method for controlling nitrate concentrations in the waste tank supernatant fed to the WTP facility.

3.1.2.3 Polymer Membrane Discussion:

Polymer-based membranes are commercially available and widely implemented for chloro-alkali and other commercial electrochemical processes. Various membranes that have recently been developed for other

industrial applications are of interest to be studied for viability in denitration and caustic generation electrolyzers with high ionic strength feeds. The PiperION AEM from the Fuel Cell Store was studied the most extensively in year 1 and the results were reported in section 3.1.2.2. The other polymer-based membranes will be studied and reported on more extensively in year 2 of the project.

To use PEMs in an alkaline solution, it should be noted that PEMs require conversion from the protonated form to the Na form prior to use to facilitate Na transport. This can be achieved prior to electrochemical testing through a hydrating activation method, which involves soaking the membrane in either a 2 M NaOH solution for 3 h at 60 °C, a 1 wt% NaOH solution for 3 h at 95 °C, or through in-situ electrochemical Na activation.[17] The polymer membranes will exhibit varying Na transport and electrolyte durability, which will be evaluated in Phase 2, where USC is studying the conductivity of membranes and electrode performance using small-scale electrochemical cells in a membrane electrode assembly (MEA) architecture (shown in Figure 3-5).

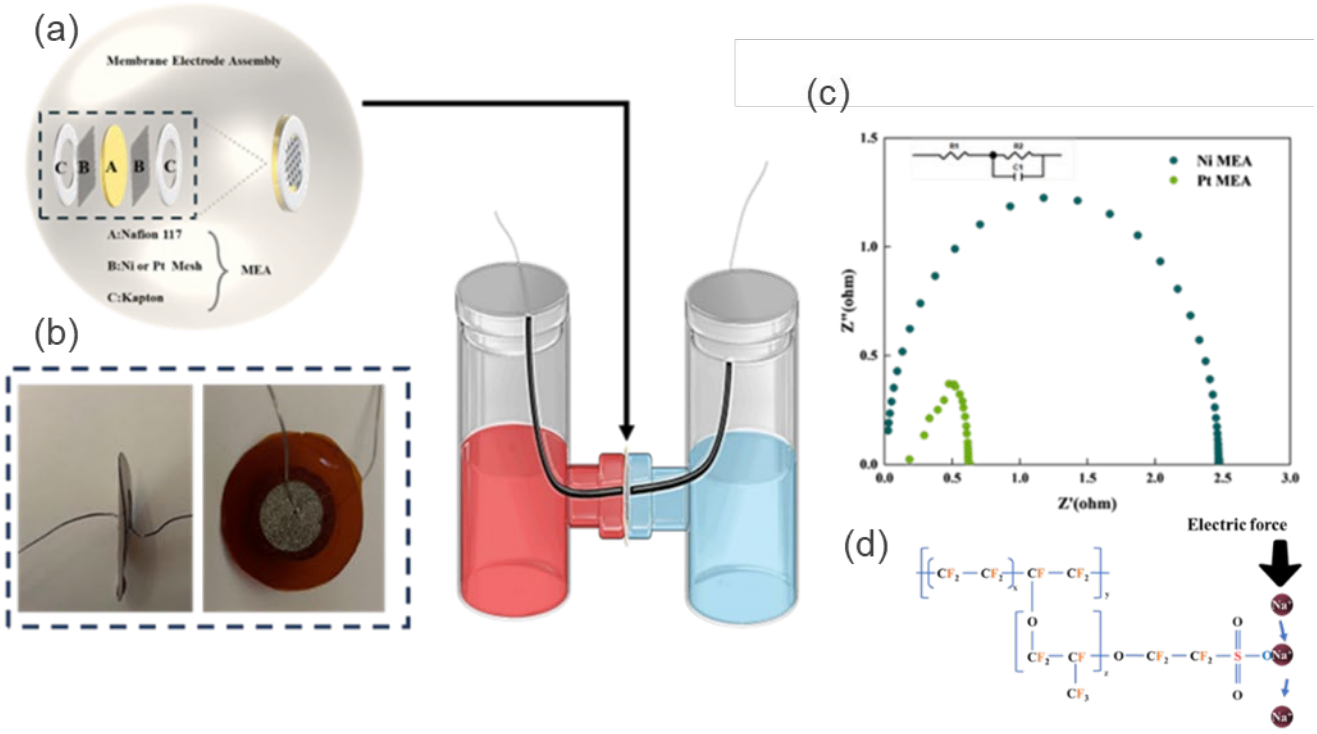

Figure 3-5. (a) Pictorial depiction of MEA structure design and implementation into a small-scale electrochemical cell, (b) real photo of MEA structure, (c) example of electrochemical impedance spectroscopy (EIS) results, and (d) depiction of a Na-activated polymer chain like what would compose a PEM.

3.1.2.4 Development of highly conductive and durable NaSICON electrolyte membranes

At this stage, both polymer and ceramic membranes are viable for the full-scale denitration and caustic generation electrolyzers. Polymer-based membranes have the advantage of commercial availability, while ceramic-based NaSICON membranes represent a newer technology that does not yet have a commercial track record and must be developed. Nafion-based membranes are considered the baseline membrane for this work until another membrane shows more promise or NaSICON is developed to a high enough TRL. NaSICON is of interest due to its high Na selectivity, which prevents contamination of subsequent electrochemical compartments by Cs and other soluble compounds via membrane transfer. The development of NaSICON membrane manufacturing capabilities, material discovery, and processing is being conducted at Clemson.

The overarching goal of NaSICON research is to develop highly conductive and durable NaSICON membranes for efficient caustic recovery from Hanford tank waste liquids. The following three main objectives will be fulfilled during the three phases of performance:

1) Discover NaSICON materials with high Na ion conductivity and specificity
2) Manufacture NaSICON membranes with desired geometries and Na ion permeation
3) Demonstrate high caustic recovery performance for developed NaSICON membranes

During Phase 1, a literature review identified 7 state-of-the-art NaSICON materials include: $Na_3Zr_2Si_2PO_{12}$, $Na_{3.2}Zr_{1.8}Al_{0.2}Si_2PO_{12}$, $Na_{3.2}Zr_{1.8}Fe_{0.2}Si_2PO_{12}$, $Na_{3.2}Zr_{1.8}Y_{0.2}Si_2PO_{12}$, $Na_{3.4}Zr_{1.8}Co_{0.2}Si_2PO_{12}$, $Na_{3.4}Zr_{1.8}Ni_{0.2}Si_2PO_{12}$, and $Na_{3.4}Zr_{1.8}Zn_{0.2}Si_2PO_{12}$.[18] The materials exhibited conductivity from 1.55–7.05 × 10^{-4} S cm^{-2} at 25 °C. The NaSICON material of $Na_3Zr_2Si_2PO_{12}$ was synthesized from the raw materials of Na_2CO_3 (Sigma, >99.5%, nano-sized ZrO_2 (Sigma, 99.9%), SiO_2 (Sigma, 99.8%), and Na_2HPO_4 (Sigma 98–102%) based on a batch size of 0.1 mol. 2 mol% of phosphorus and sodium were used to compensate for volatility loss. After 24 h of ball-milling in isopropyl alcohol solvent with 3 mm YSZ balls, the $Na_3Zr_2Si_2PO_{12}$ precursor powders were pressed into pellets to sinter at 1200 °C for 12 h.

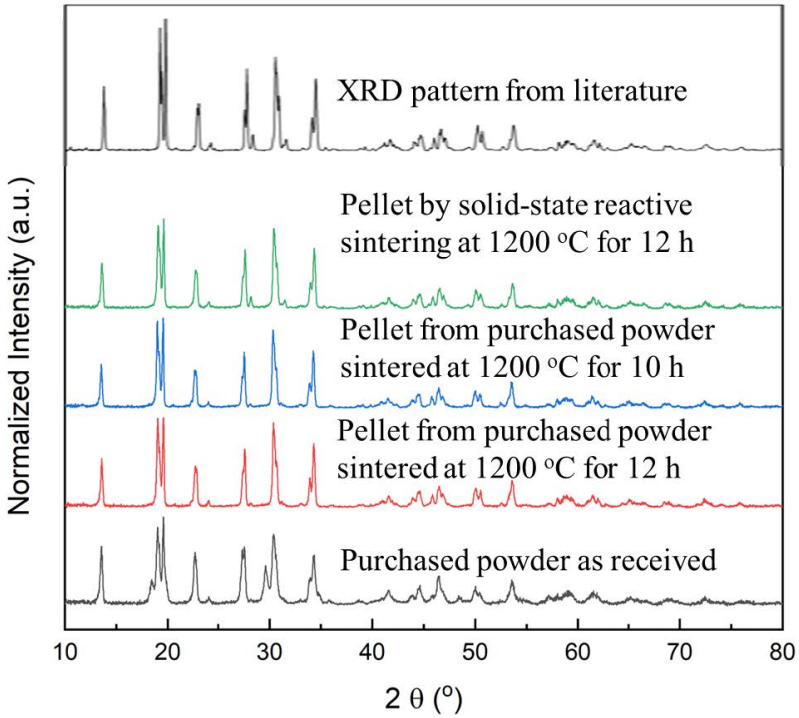

Figure 3-6. Summary of XRD patterns of $Na_3Zr_2Si_2PO_{12}$ samples.

The as-synthesized $Na_3Zr_2Si_2PO_{12}$ pellet shows a crystal structure identical to the one reported in the literature, which was identified as the same crystal structure as the pellet samples prepared from a commercial powder after being sintered at 1200 °C for 10 h and 12 h (Figure 3-6). Figure 3-7a and Figure 3-7b show the SEM micrographs of the sintered $Na_3Zr_2Si_2PO_{12}$ pellets from commercial powders. The pellets did not show any large pores on the surface, indicating the high relative density of the pellets. The pellets were fabricated into symmetrical cells to measure the electrical conductivity.

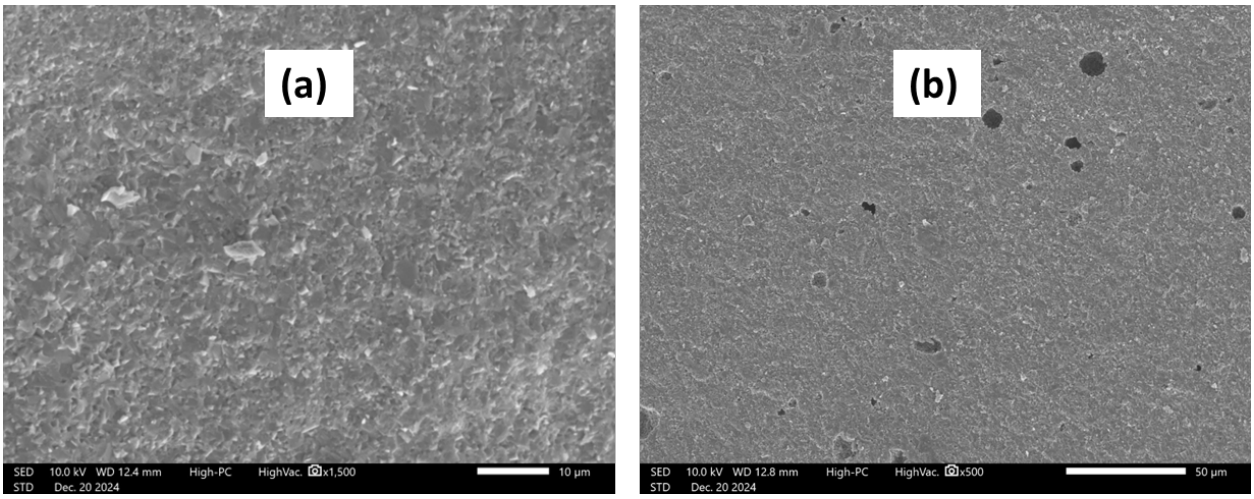

Figure 3-7. SEM micrographs of $Na_3Zr_2Si_2PO_{12}$ pellets fabricated from a developed sintering method (a) and conventional solid-state sintering of commercial phase-pure powder (b).

The electrical conductivity was measured in an argon atmosphere at 20–250 °C for the pellets fabricated from commercial powder and by the direct solid-state reactive sintering method and is shown in Figure 3-8. It can be concluded that total conductivity and the activation energies are close to the values reported in the literature. Therefore, in phase 1, NaSICON materials were successfully synthesized with suitable microstructure and conductivity.

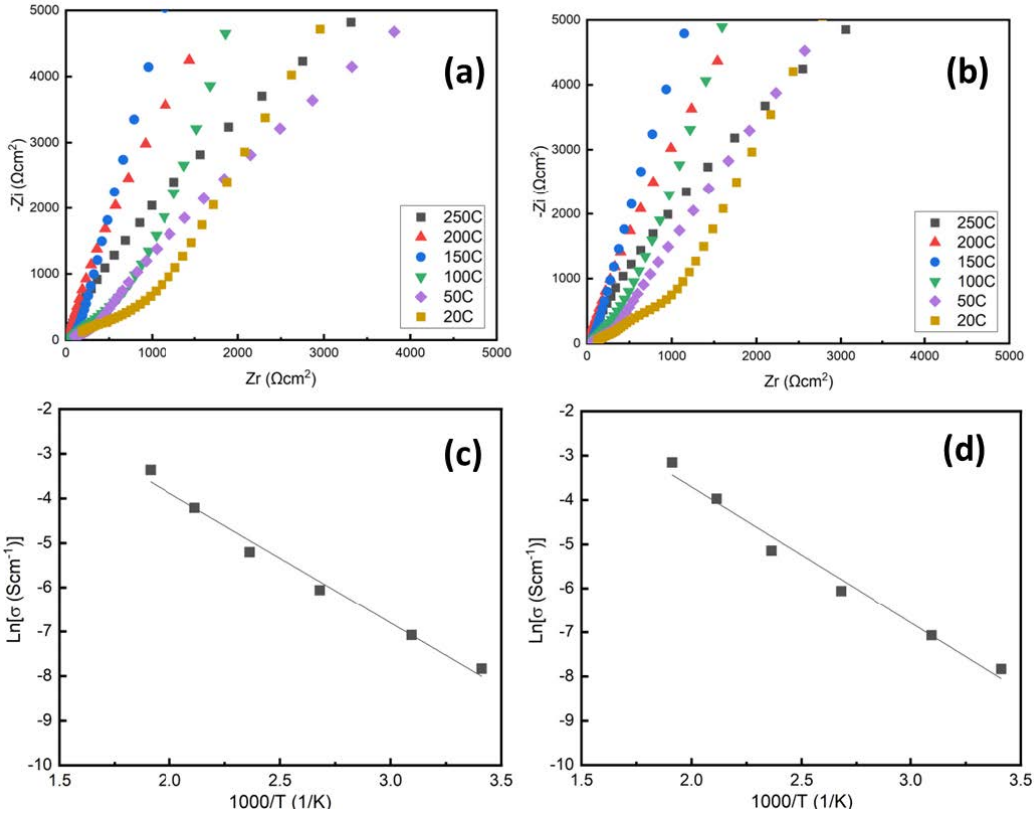

Figure 3-8. Electrical conductivity results (Nyquist and Arrhenius plots) of pellets fabricated by solid-state reactive sintering (a, c) and conventional solid-state sintering from commercial phase-pure powder (b, d).

3.1.3 Computational Modeling of Electrolyzer System

The computational aspect for Figure 2-2, **Task 1** (*Process evaluation using computational approach of tank waste processing*) has been delayed due to the lead modeling collaborator switching institutions from FIU to NC A&T. Both electrochemical modeling and general system impacts are scoped to provide results in year 2. This delay has been communicated to DOE and is not expected to directly affect other aspects of the project. The work will continue to ramp up and produce results in phase 2 of the project now that the collaborator is established at NC A&T university.

For phase 1, the work included design of three spacer-filled channel models using SolidWorks 2023 for the purpose of computational fluid dynamics (CFD) simulations of a filter press electrolyzer. The models comprised of a stand-alone spacer hollow chamber, a hollow chamber with pillars at selective locations, and an internal hollow chamber with a net-like exterior. Each model incorporated an inlet and an outlet to facilitate flow, ensuring dimensions matched those from a reference study.[19] ANSYS Fluent fluid flow analysis was utilized. Fluid regions were defined in each model to determine where the fluid could flow, assigning water (density: 998.2 kg m^{-3}, viscosity: 0.001003 kg $m^{-1}s^{-1}$) for the fluid and aluminum (density: 2719 kg m^{-3}) for the solid domain. Mesh generation used an element size of 1.0 mm for the fluid region, employing quad dominant and sweep methods for sheet and sweepable bodies, respectively, and the tetrahedron method for the fluid region.

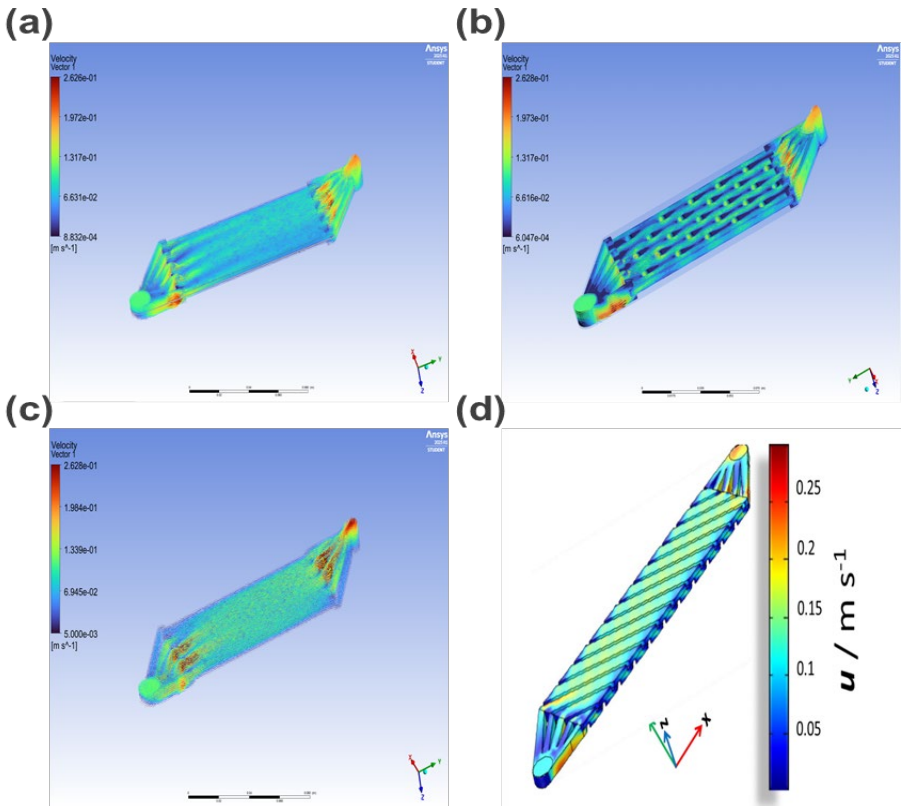

Figure 3-9. CFD simulation (velocity field) for (a) stand-alone hollow chamber, (b), hollow chamber with pillars, (c), internal hollow chamber with net-like exterior and (d) reference CFD simulation (initial velocity of 0.11 m s^{-1}).[19]

The simulation results validated current models by closely matching literature values.[19] Flow fields for the various archetypes are shown in Figure 3-9. Comparisons were made between the three designs using different turbulence models (SST k-Ω and Standard k-ε), showing velocity contours and vectors in ranges akin to those documented in previous studies.[19] Shear stress transport (SST) k-Ω and Standard k-ε models

revealed velocity contours between 0.3518–25.83 cm s^{-1} and 0.04402–27.97 cm s^{-1}, respectively. These findings align closely with literature values ranging from 0.050–0.25 cm s^{-1} at an initial velocity of 0.11 m s^{-1}. The agreement in velocity metrics reinforces the validity of the models for further computational studies in spacer-filled channel design for filter press electrolyzers. This work will further be used to model and optimize novel electrolyzer designs.

3.2 Task 2, Engineering-scale denitration electrolyzer:

3.2.1 Intermediate-scale electrochemical studies

For Task 2, work has begun with the development of benchtop-scale flow electrolyzers led by Polykala Technologies, LLC. Batch parallel-plate electrolyzer tests with two Ru/Ti anodes (3 x 10 cm each) and three Ti cathodes (3 x 10 cm each, with Teflon on the outer two to prevent a mismatch in electrode geometry/efficiency) were studied for the reduction of nitrate and nitrite. The nitrate and nitrite conversions were determined via a UV-Vis method reported in literature.[20]

The parallel-plate electrolyzer results are shown in Table 5, where all but the first experiment used Ru/Ti electrodes for both the anodes and cathodes at 2.0 V and ~0.54 A (initial A, dropping by ~0.1 A at the end) for 4 h. The $NaNO_2$ conversion for a 1.08 M $NaNO_2$ / 0.826 M NaOH feed was 0.767 mg $cm^{-2}min^{-1}A^{-1}$ $NaNO_2$. The activity increased when the plate electrolyzer was configured with two Ru/Ti anodes (3 x 10 cm each) and two Ru/Ti cathodes (3 x 10 cm each) of 1.011 mg $cm^{-2}min^{-1}A^{-1}$ $NaNO_2$. For a 1.71 M $NaNO_3$ / 0.826 M NaOH feed, the $NaNO_3$ conversion was 1.925 mg $cm^{-2}min^{-1}A^{-1}$. For a of 1.71 M $NaNO_3$ / 1.08 M $NaNO_2$ / 0.095 M $NaAl(OH)_4$ / 0.826 M NaOH feed, the $NaNO_2$ and $NaNO_3$ conversion was 0.225 and 0.388 mg $cm^{-2}min^{-1}A^{-1}$, respectively.

Table 5. Parallel-plate electrolyzer testing results.

Voltage (V)	Current (A)	Duration (h)	Feed Composition	Conversion Rate ($NaNO_2$) (mg $cm^{-2}min^{-1}A^{-1}$)	Conversion Rate ($NaNO_3$) (mg $cm^{-2}min^{-1}A^{-1}$)	Configuration
2.0	0.54	4	1.08 M $NaNO_2$ / 0.826 M NaOH	0.767	-	Two Ru/Ti anodes (3 x 10 cm each) and two Ti cathodes (3 x 10 cm each)
2.0	0.54	4	1.08 M $NaNO_2$ / 0.826 M NaOH	1.011	-	Two Ru/Ti anodes (3 x 10 cm each) and two Ru/Ti cathodes (3 x 10 cm each)
2.0	0.54	4	1.71 M $NaNO_3$ / 0.826 M NaOH	-	1.925	Two Ru/Ti anodes (3 x 10 cm each) and two Ru/Ti cathodes (3 x 10 cm each)
2.0	0.54	4	1.71 M $NaNO_3$ / 1.08 M $NaNO_2$ / 0.095 M $NaAl(OH)_4$ / 0.826 M NaOH	0.225	0.388	Two Ru/Ti anodes (3 x 10 cm each) and two Ru/Ti cathodes (3 x 10 cm each)

Flow cell testing was conducted using an assortment of benchtop-scale flow electrolyzers procured by Polykala, including 3 small square (3.5 cm x 3.5 cm), 1 large square (5 cm x 6 cm), 3 large rectangle (3.5 cm x 7.5 cm), and 1 large octagonal flow electrolyzers (Table 6). The square cells, which only have one

inlet and are equipped with a PEM, were found to perform poorly for the denitration task. Testing the larger square flow cell on nitrite reduction with a 1.08 M $NaNO_2$ / 0.826 M NaOH feed at a flow rate of 0.6 mL/min resulted in a $NaNO_2$ conversion of 0.582 mg $cm^{-2}min^{-1}A^{-1}$. For the rectangular flow cells, tested under conditions of 1.9 V, 0.52–0.54 A, and a flow rate of 30–40 mL min^{-1} for 1 h, the $NaNO_3$ and $NaNO_2$ conversion rates were 0.014 and 0.027 mg $cm^{-2}min^{-1}A^{-1}$, respectively (without the presence of sodium aluminate in the feed). Under similar conditions, the small square flow cell (without sodium aluminate in the feed to avoid possible blockage by solids in the feed), had $NaNO_3$ and $NaNO_2$ conversion rates of 0.00 and 0.056 mg $cm^{-2}min^{-1}A^{-1}$, respectively. All the tests were performed in a once-through configuration without recycling, where the feed was flown into the flow cell for 1 h. Further evaluations of operating conditions and flow rates of the various configurations are still ongoing.

Table 6. Commercial flow electrolyzer testing result.

Flow Cell Type	Dimensions	Inlet(s)	Denitration Performance	Feed Comp.	Operating Cond.	$NaNO_2$ Conversion (mg $cm^{-2}min^{-1}A^{-1}$)	$NaNO_3$ Conversion (mg $cm^{-2}min^{-1}A^{-1}$)	Flow Rate (mL/min)
Small square	3.5 cm x 3.5 cm (12.25 cm^2)	1	Poor	1.71 M $NaNO_3$ / 1.08 M $NaNO_2$ / 0.826 M NaOH	1.9 V, 0.20 A, 1 h	0.056	0.00	30
Large square	5 cm x 6 cm (30 cm^2)	1	Average	1.08 M $NaNO_2$ / 0.826 M NaOH	2.2 V, 0.24 A, 1 h	0.582	-	0.6
Large rectangle	3.5 cm x 7.5 cm (26.25 cm^2)	2	Good	1.71 M $NaNO_3$ / 1.08 M $NaNO_2$ / 0.826 M NaOH	1.9 V, 0.52–0.54 A, 1 h	0.027	0.014	30–40
Large octagonal	15.2 cm^2 x 3 (45.6 cm^2)	2	In Progress	-	-	-	-	-

3.2.2 Engineering-scale electrochemical flow cell studies

The procurement of an engineering-scale denitration electrolyzer is no longer scoped for SRNL, instead a subcontract was drafted and submitted for the Electrosynthesis Company (the subcontract has been executed on 08/19/2025) to aid in engineering-scale discovery. The Electrosynthesis Company, Inc. has a proven record of success with electrochemical R&D, process engineering, and scale-up projects. The utilization of a NESI Norscand electrolyzer systems and the Electrosynthesis Company's pilot-scale testing facility satisfies Figure 2-2, **Task 1.3** (*the procurement of an engineering scale electrolyzer*). The Electrosynthesis Company, Inc. will carry out experimental tasks under SRNL guidance and direction. They have worked with many full-scale electrochemical systems and are experienced with the denitration task, considering their contributions and involvement with the legacy testing as collaborators of the Westinghouse Savannah River Company.[6, 7] Future decisions regarding system design will be based on the outcomes of the collaborative effort with the Electrosynthesis Company.

4.0 Off-gas Abatement Discussion

4.1 Task 3, Scoping and development of off-gas system for engineering scale:

The denitration electrolyzer is expected to produce various amounts of gaseous H_2, NH_3, N_2, N_2O, and H_2O products and byproducts as the nitrates and nitrites are removed from the tank supernate. Off-gas catalyst abatement is planned to mitigate release of potentially hazardous gases from the denitration electrolyzers. University of South Carolina (USC), SRNL, and Idaho National Laboratory (INL) have developed benchtop-scale testing systems to evaluate catalyst-based off-gas treatment processes. Initial tests have evaluated commercial catalysts and legacy research catalysts. The electrochemical denitration and benchtop-scale off-gas testing will inform the compositional range for the full-scale off-gas catalytic abatement system. A literature review for abating denitration off-gas byproducts (nitrous oxide) is near completion (SRNL-MS-2025-00225_DRAFT). This work, which will be submitted for publication, and will aid in understanding the necessary catalytic design considerations and possible reactor feed conditions required to have efficient off-gas treatment.

Initial testing with commercially available off-gas catalysts has been performed for Figure 2-2, **MS 4.1,** *Test commercially available off-gas catalysts*. Only a few commercially available off-gas catalysts were identified and selected for the NH_3 decomposition reaction due to NH_3 being a key byproduct from the electrochemical process. A leading commercial catalyst of Ru/Al_2O_3 has been identified as the baseline for the traditional catalytic off-gas reactor systems and TAP analysis for NH_3 decomposition. INL has performed scoping experiments on a commercial power plant catalyst (V_2O_5-WO_3-Al_2O_3) and legacy research catalysts (Ru/Al_2O_3). An HEA sample and baseline material, partially-reduced graphene oxide (rGO), were shipped from SRNL to INL and is currently being evaluated. Additionally, studies on these catalysts will be performed as catalyst testing progresses with additional materials to target key byproducts necessary for abatement targets. Additional studies will also be performed based on feed composition informed by the electrochemical denitration team and the off-gas abatement literature review.

4.1.1 Reactor and off-gas testing

Throughout year 1, USC designed and built a reactor system capable of testing catalysts with N_2O, NH_3, H_2, and O_2 in the feed stream (Figure 4-1). The reactor is a single-channel reactor to allow for the initial screening and long-term testing of catalysts under different operating conditions, such as temperatures, flowrates, pressures, and feed compositions. Reaction progress is currently being analyzed with an FTIR gas-phase cell that will be calibrated to allow for the evaluation of catalytic activity from the concentrations of N_2O and NH_3 in the effluent.

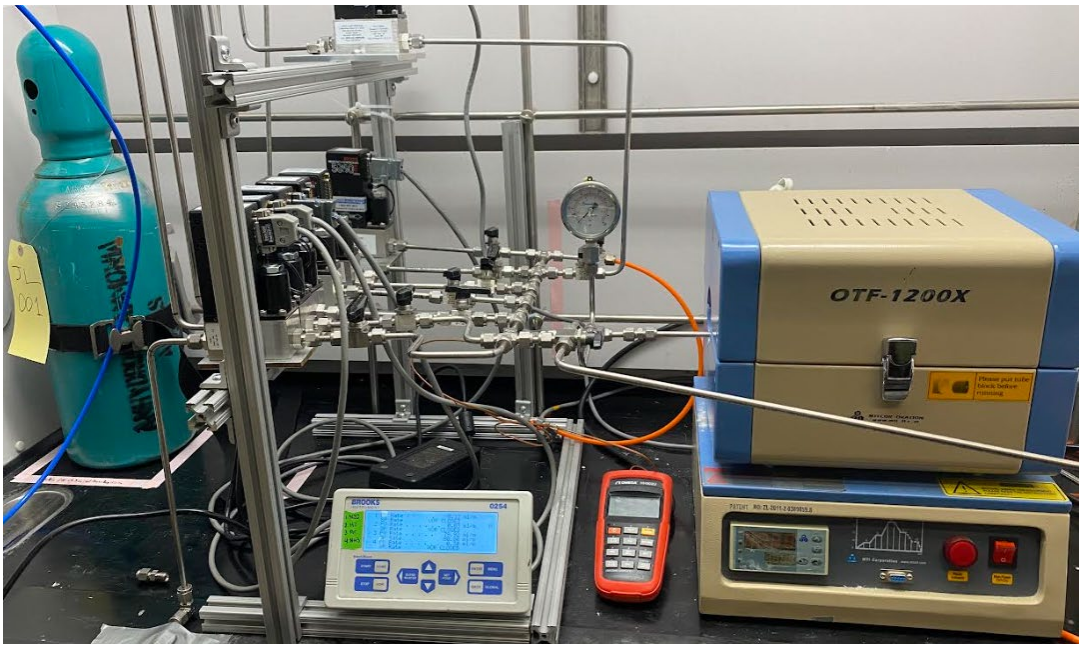

Figure 4-1. Off-gas reactor system at USC showing the gas manifold feeding a tube reactor inside an OTF-1200X furnace.

A system to test catalysts at a range of temperatures, gas flow rates, and gas compositions was built in year 1 at SRNL and is shown in Figure 4-2. The gas manifold feeding the catalyst testing chamber can accommodate seven unique gas inputs and accommodate temperatures up to 550 °C. The system and metrology have been validated by running a standard NH_3 decomposition reaction over the catalyst and the products are measured before being safely vented to the hood.

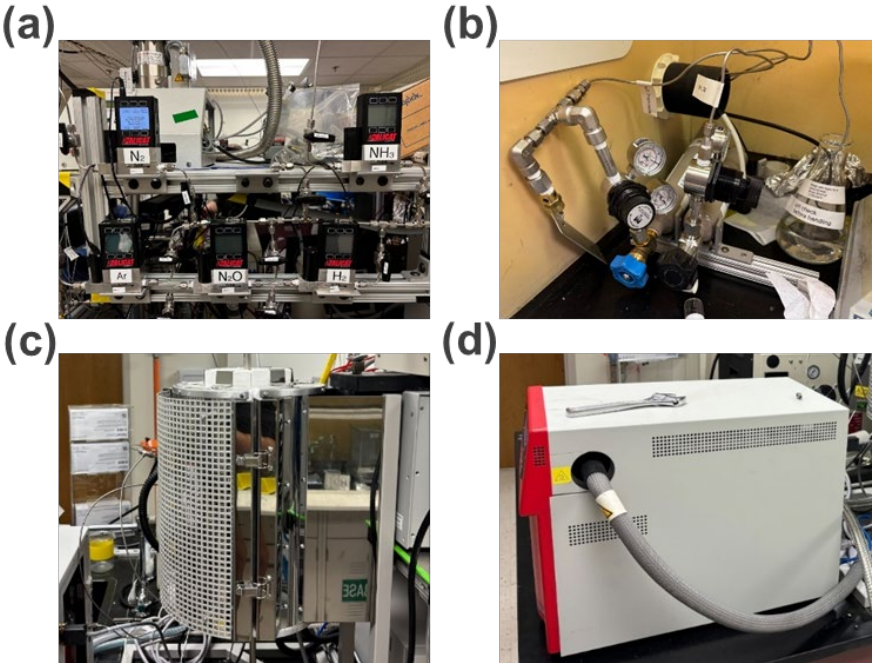

Figure 4-2. Images of reaction apparatus, displaying gas manifold of Ali-Cat flow controllers supplying N_2, NH_3, H_2, N_2O, and H_2 (a), NH_3 and N_2O lecture bottles located in the hood, plus exhaust gas bubbler (b) Conventional clam-shell resistive furnace for off-gas abatement with a stainless reactor mounted inside (c), mass spectrometer for gas analysis (d).

Transient kinetic studies of heterogeneous-catalyzed gas phase reactions in TAP reactors can be effectively utilized to obtain kinetic parameters based on time-dependent interactions between gas molecules and the catalyst surface and offer deeper mechanistic insights into reaction elementary steps (Figure 4-3). A typical TAP reactor setup consists of four major components, including high-speed pulse valves, a packed bed microreactor, and a quadrupole mass spectrometer and high-throughout vacuum system at the exit of the microreactor. The nanomole-sized pulses of gas molecules in the TAP reactor enables the mechanistic study of gas/solid interactions and intrinsic kinetics of the pristine active sites under isothermal conditions. Moreover, minimal catalyst restructuring is controlled in a TAP reactor due to the number of active sites significantly exceeding the number of adsorbed gas molecules in the ultralow pulses.

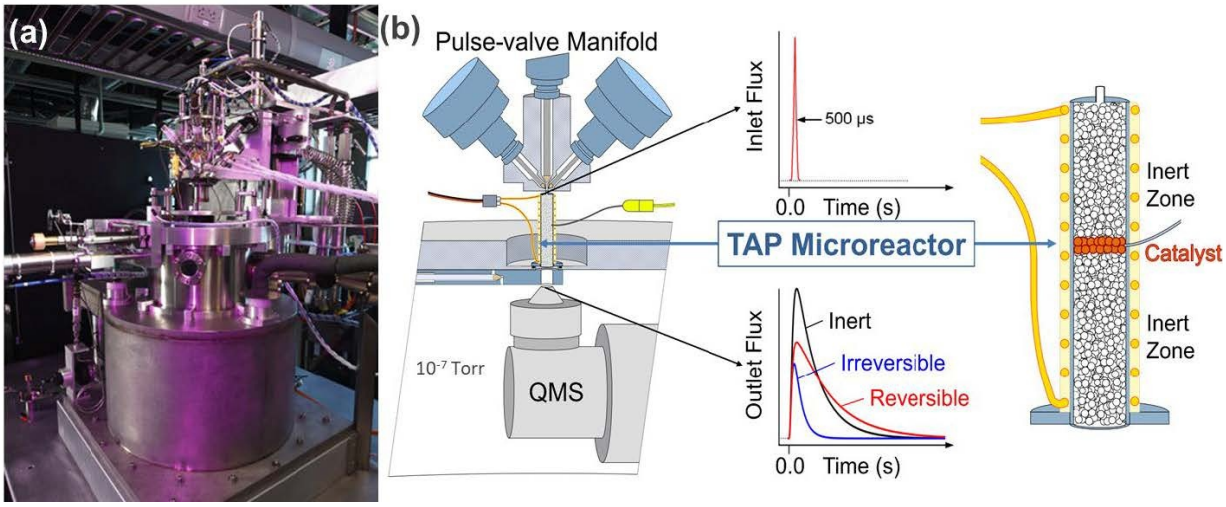

Figure 4-3. Photograph of a TAP-3 reactor system built by Mithra Technologies, Inc. (Photo courtesy of INL) (a), Key components of a TAP pulse response experiment(b). Adapted from ref. 21.

4.1.2 Temporal Analysis of Products (TAP) reactor catalyst validation

Catalyst validation was successfully performed in the TAP reactor to compare ammonia decomposition over Ru/Al_2O_3 and V_2O_5-TiO_2 catalysts at 300–500 °C to satisfy **Task 4.1**, Figure 2-2**.** Ammonia decomposition was selected as the probe reaction to represent the abatement of the off-gas stream from the electrolyzer, as ammonia is a potential nitrogen-containing gas molecule generated from the electrochemical transformation of nitrate/nitrite compounds. The catalytic performance of two catalysts, including Ru/Al_2O_3 (prepared by incipient wetness impregnation at INL) and V_2O_5-TiO_2 (commercial catalyst from USC), were studied and compared by nanomole-size pulse experiments in the TAP reactor.

While Ru-based catalysts are known to be highly active for ammonia decomposition, V_2O_5-TiO_2 is commonly used in commercial applications for selective catalytic reduction (SCR) of NO_x with NH_3 reductant. In pulse experiments, an amount of 5 mg catalyst pellets with particle size ranging from 250-300 microns was sandwiched between quartz particles and loaded in the ¼-in. i.d. quartz tube reactor. Prior to ammonia/argon (50/50) pulses under high vacuum, Ru/Al_2O_3 catalyst was reduced by hydrogen flow at 400°C to generate Ru metal sites, while V_2O_5-TiO_2 catalyst was activated by oxygen flow at 400°C to create V^{5+} active species. Eight different atomic mass units (AMU) were tracked in each pulse cycle, including 2 (H_2), 17 (NH_3), 18 (H_2O), 28 (N_2), 30 (NO), 40 (Ar), 44 (N_2O), and 46 (NO_2) AMU.

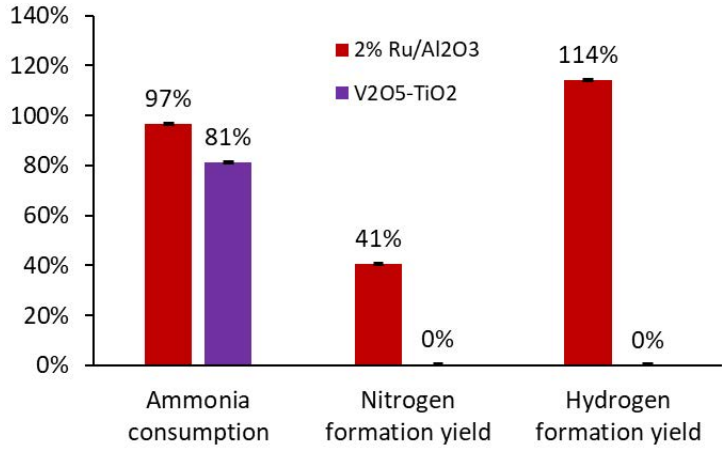

Figure 4-4. Ammonia consumption and product (nitrogen and hydrogen) formation yield in pulse experiments over Ru/Al_2O_3 and V_2O_5-TiO_2 at 400°C. Error bars show the standard deviation of 4 pulse cycles (8 pulses/cycle).

In Figure 4-4, the ammonia consumption and product (nitrogen and hydrogen) formation yield remain stable during the pulse experiments, indicating that the change of catalyst surface properties is negligible under reaction conditions. This result is attributed to the nanomole-size ammonia pulse which is much smaller compared to the number of sites in the catalyst bed. Both Ru/Al_2O_3 and V_2O_5-TiO_2 catalysts show very high ammonia consumption of above 80%. The catalytic decomposition of ammonia to form nitrogen and hydrogen was observed on Ru/Al_2O_3 catalyst. However, it shows in Figure 4-4 that ammonia molecules adsorb irreversibly on V_2O_5-TiO_2 at 400°C without forming decomposition products (nitrogen and hydrogen) in gas phase. These catalytic behaviors of Ru/Al_2O_3 and V_2O_5-TiO_2 catalysts upon interaction with ammonia molecules are further revealed by temperature dependence experiments below.

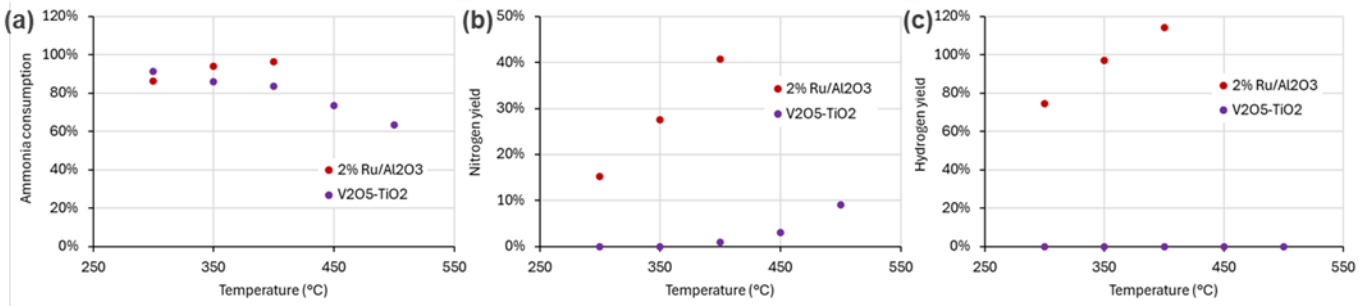

Figure 4-5. Ammonia consumption (a), nitrogen formation yield (b), and hydrogen formation yield (c), in pulse experiments over Ru/Al_2O_3 and V_2O_5-TiO_2 with varying reaction temperature from 300–500°C.

Figure 4-5 shows the trends of ammonia consumption and decomposition product yield over Ru/Al_2O_3 and V_2O_5-TiO_2 catalysts with varying reaction temperature. On Ru/Al_2O_3, the ammonia consumption and decomposition product yields increase with temperature, which follows conventional thermocatalytic principles. This result indicates that the interaction between ammonia molecules and Ru/Al_2O_3 catalyst surface is governed by the catalytic decomposition reaction. On V_2O_5-TiO_2, while the nitrogen product yield increases with temperature due to the catalytic decomposition reaction, the ammonia consumption decreases at higher temperatures. This observation suggests that the dominant process on V_2O_5-TiO_2 catalyst surface is a strong ammonia adsorption, which begins to be outcompeted by the desorption process at increasing temperature. In addition, Figure 4-5 shows that there is no hydrogen observed in the gas phase at reaction temperature up to 500°C during the ammonia pulses on V_2O_5-TiO_2 catalyst. Interestingly, it was

found that the formation of water becomes detectable at high temperatures (Figure 4-6). Therefore, it is speculated that the absence of hydrogen in the gas phase during ammonia pulses on V_2O_5-TiO_2 is due to the recombination of hydrogen atoms from ammonia decomposition with hydroxyl groups on V_2O_5-TiO_2 catalyst surface to form water molecules.

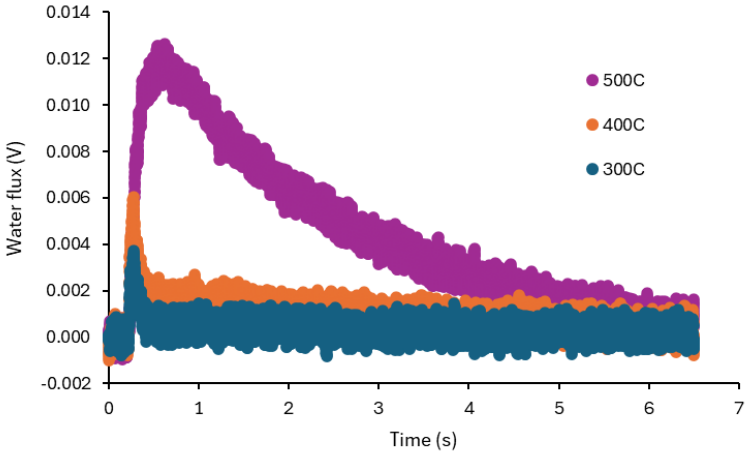

Figure 4-6. Water flux detected by the online quadrupole mass spectrometer in pulse experiments over V_2O_5-TiO_2 at 300–500°C. Signal noise was reduced by Savitzky-Golay smoothing function.

The difference in interaction of ammonia molecules with the catalyst surface between V_2O_5-TiO_2 and Ru/Al_2O_3 catalysts is shown in Figure 47. While ammonia flux is broad and has a long tail from V_2O_5-TiO_2 catalyst results, the pulse shape of ammonia is much sharper for the Ru/Al_2O_3 catalyst. This observation indicates that there is a strong adsorption of ammonia and thus a slow desorption of ammonia molecules on V_2O_5-TiO_2 surface, adding more evidence for the dominant reversible adsorption behavior of ammonia on this catalyst.

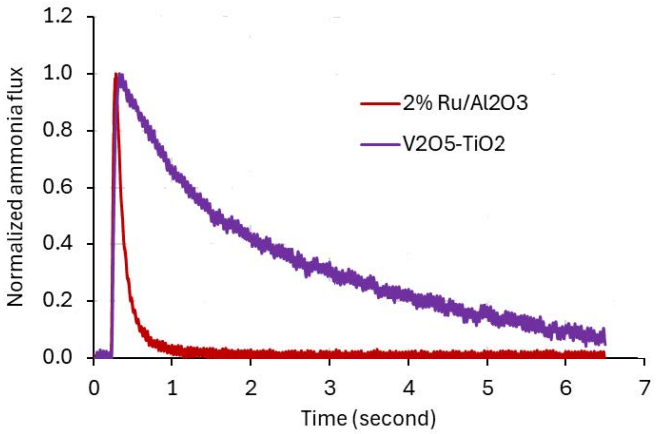

Figure 4-7. Normalized ammonia flux detected by online quadrupole mass spectrometer in ammonia pulses over Ru/Al_2O_3 and V_2O_5-TiO_2 at 400°C. Signal noise was reduced by Savitzky-Golay smoothing function.

4.1.3 Ammonia-deuterium exchange over Ru/Al_2O_3 at 300–400°C in the TAP reactor

Another successful accomplishment for the TAP reactor in year 1 was performing an ammonia-deuterium exchange over the Ru/Al_2O_3 catalyst. The lifetime of key intermediates of ammonia decomposition on Ru/Al_2O_3 catalyst were investigated by ammonia-deuterium pump-probe experiments in the TAP reactor.

Ammonia/helium mixture is the primary (pump) pulse, followed by the secondary deuterium/argon (probe) pulse with varying time delay (td) from 0.2 second to 1.0 second. These pump/probe cycles are repeated >25 times. Different atomic mass units were detected by the online quadrupole mass spectrometer to track the reactant and isotopic products in these experiments, including 2 (H_2), 3 (HD), 4 (D_2), 17 (NH_3), 18 (H_2O), 19 (HDO), 20 (D_2O), 28 (N_2), and 40 (Ar) AMU.

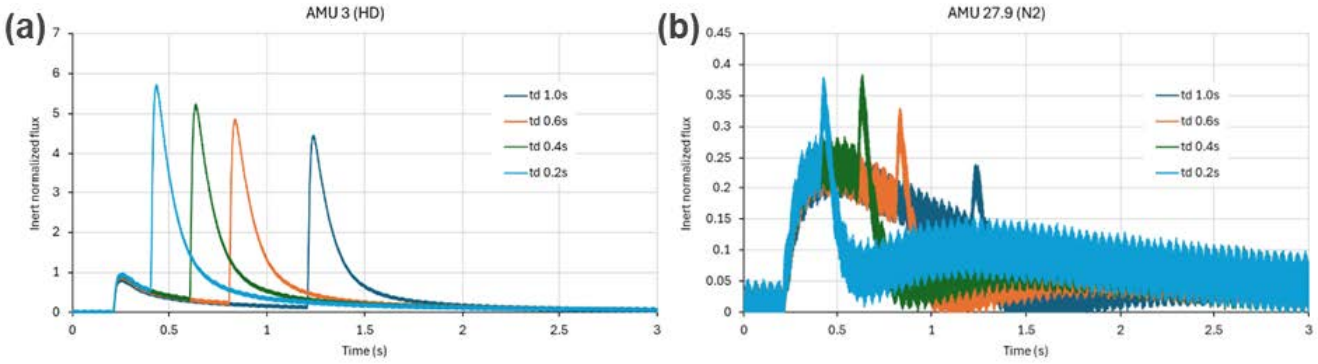

Figure 4-8. Inert normalized flux of HD (a) and inert normalized flux of N_2 (b), detected by online quadrupole mass spectrometer in ammonia/deuterium pulses over Ru/Al_2O_3 300°C with different pump-probe time delays.

Figure 4-8a illustrates the change of the HD (deuterated hydrogen) flux recorded during the deuterium/argon secondary pulses with varying the pump-probe time delay. It shows that with a shorter time delay between ammonia and deuterium more HD is formed. With the ammonia pulse, the decomposition process generates surface H* and NH_x* species. Surface H* species can combine with another H* atom or NH_x* intermediates, decreasing the surface concentration. The secondary D_2 pulse then probes the surface state and liberates H* and NH_x* species as deuterated products that leave the surface. From this data, the rate of the ammonia decomposition step and the lifetime surface species can be determined.

Figure 4-8b indicates that there is a separate flux of nitrogen desorption into the gas phase associated with the deuterium secondary pulses in addition to the nitrogen product flux from ammonia pulses. In fact, this second nitrogen flux in response to deuterium is faster than the main nitrogen flux related to the ammonia primary pulses. As the deuterium pulse increases the surface coverage, it is suggested that this induces the desorption of N_2 and optimum surface coverage can be determined. The formation of isotopic ammonia species such as NH_2D and NHD_2 will be analyzed to determine the competing steps on the catalyst surface related to both forward ammonia decomposition and backward ammonia synthesis.

4.2 Task 4, Off-gas catalyst synthesis with focus on HEA and NH_3 decomposition catalysts:

An HEA microwave synthesis approach has been developed to scale up the HEA synthesis process so that materials can be produced in large enough quantities per batch to be studied at the benchtop-scale within the off-gas reactor systems developed for this work. An initial Pt-Ru-V-Co-Ni HEA catalyst has been synthesized and is being evaluated for activity. Additional catalysts will be prepared, building on the results of the catalyst performance and any new findings and developments from the literature.

4.2.1 Selection and synthesis of traditional catalysts

A perspectives literature review for HEA catalysts was published in Material Letters (SRNL-MS-2025-00214) and was performed to survey catalyst compositions relevant to the project.[22] Additionally, a literature review on N_2O abatement methods is nearing submission, focusing on N_2O decomposition and

SCR of N_2O via NH_3, which is highly relevant to the off-gas abatement methodology for the EDCGe system. The review examined metal-supported, metal oxide, and zeolite-based catalysts under various reactor feed compositions and included studies using various reductants. These extensive literature reviews provide background to decisions on catalyst and alloy compositions that are tailored towards abating non-ideal feeds, like those generated from denitration electrolyzers.

Traditional baseline catalysts for NH_3 and NO_x abatement testing, including commercial catalysts and supports (i.e. gamma alumina and activated carbon) were sourced or synthesized at USC, such as V_2O_5-TiO_2 and Cu-SSZ-13, and Ru/Al_2O_3. These were synthesized and distributed to the team to establish a common baseline across all reactor systems discussed in section 4.1.1. Additional synthesis of traditional catalysts will be performed to aid in informing HEA composition selection in the later phases of the project. Promoted Ru-based catalysts have shown high NH_3 decomposition activity (e.g. $RuYK/Al_2O_3$) in the literature and are of interest to study the off-gas abatement of NH_3 and the expected EDCGe off-gas feed stream compositions.[23, 24]

4.2.2 Synthesis of HEAs Catalysts

Catalysts on rGO were designed and created using the following microwave synthesis procedure.[25] First, appropriate volumes of aqueous metal salt precursors (e.g., chloroplatinic acid, ruthenium (III) chloride hydrate, vanadium (III) chloride, cobalt (II) nitrate hexahydrate, nickel (II) chloride hexahydrate) (commercial, Sigma-Aldrich or similar) were mixed into a graphene oxide (GO) and water slurry (Graphenea, 0.4 and 2.0 wt%, D_{10}=1-2 µm, D_{50}=2-4 µm, D_{90}=5-7 µm, pH 2.2-2.5, monolayer content (measured at 0.05 wt%) is >95%). This mixed dispersion was dried overnight under vacuum at 40 °C. The dried GO films with dried metal salts were transferred to a CEM 10 mL quartz vessel and inserted in a microwave synthesis reactor (CEM Discover 2.0) (Figure 49a) equipped with the CEM 10 mL Flow Cell S-Class (SKU 908910). The tube was flushed with Ar using the continuous gas flow attachment and then heated at 300 W for 30 sec or up to 300 °C, whichever occurred first. The powder was then removed for characterization and testing.

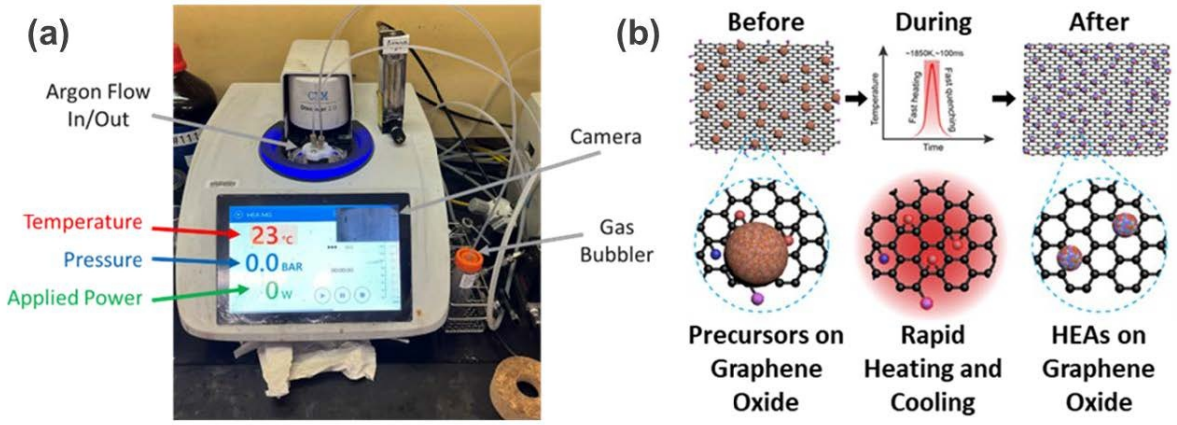

Figure 4-9. (a) Microwave reactor and (b) model of the sample before, during, and after microwave heating. Image (b) taken from ref. 25.

The functional groups on the GO are microwave susceptors, therefore, when irradiate, high temperatures (potentially >1500 K) occur at localized positions under one second (Figure 4-9b).[25] This allows the metals salts in the vicinity to melt, reduce, and aggregate on the then rGO surfaces. This created spherical nanoparticles embedded on the carbon microflakes ~2-5 nm, with individual metal atoms also observed on

the rGO surface. The facile, solvent-free synthesis along with nanoscale morphology produces a material with high atom efficiency.

As a proof-of-concept, Pt-Pd-Fe-Co-Ni HEAs on rGO were synthesized on a small scale (<10 mg total, ~5 wt% loading). Additionally, an equimolar composition of Pt-Ru-V-Co-Ni was synthesized and produced ~3 nm particles (Figure 4-10). The new composition included elements that traditionally favor NH_3 reactions (e.g. Ru) and promoting/adsorption elements (e.g. V). To support the amount of material required in an off-gas reactor system, a significant scale-up (>50x) was necessary. By using a more concentrated GO precursor and larger drying containers individual batches achieved gram-scale quantities at ~5 wt% loading. Monometallic analogs of Pt, Ru, V, Co, and Ni on rGO and metal-free rGO were also prepared for comparison. These samples have been sent to INL for TAP reactor testing.

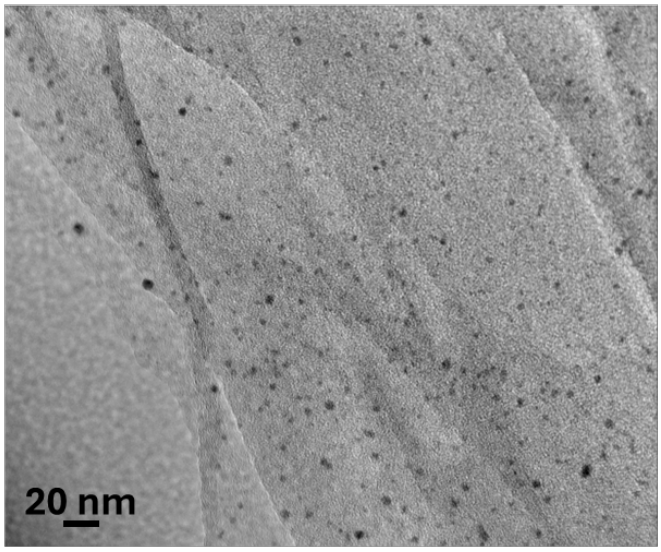

Figure 4-10. Transmission electron micrograph of Pt-Ru-V-Co-Ni HEA catalyst (black particles) on graphene oxide support.

4.2.3 Develop simpler alloys database and fundamental understanding of adsorption sites:

4.2.3.1 Modeling realistic catalyst surfaces

For Task 4.2 in Figure 2-2, the Materials Computation and Data Science group (MCDC) at Clemson University is performing atomistic calculations of surface and catalytic properties in alloys through density functional theory (DFT) calculations. The overall goal of the DFT calculations is to gain an understanding of the catalytic reaction energetics of HEAs to replace expensive Pt and other metals. The first year of the project was devoted to developing a strong foundation for our approach and methodology. Specifically, it involved (1) the determination of surface structures and compositions, and (2) reaction energetics calculations on the surfaces.

An important consideration in the computational modeling of alloy compositions for catalysis is the determination of surface structure and composition. A standard molecular dynamics/Monte Carlo (MD/MC) approach was implemented, where the atoms move based on Newtonian equations of motion with the forces given by an interatomic potential. Subsequent Monte Carlo (MC) swaps between atom positions of different elements are attempted with a Boltzmann acceptance criterion. This procedure was implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code to model the surface segregation of extended surfaces of common face-center cubic (fcc) surface terminations (100, 110, 111) of bimetallic compositions (PtCo, AgAu, AuCu) across a temperature range (300–1100 K). Figure 4-11 shows the starting and ending MD/MC surface composition in the PtCo alloy.

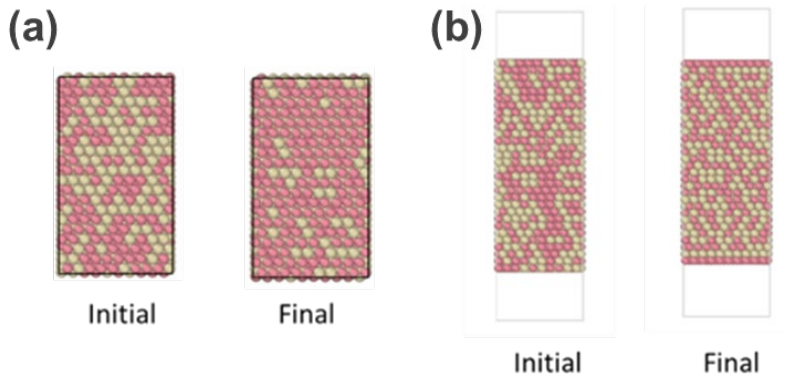

Figure 4-11. Top (a) and side (b) view of the PtCo fcc(111) slab before and after a MD/MC simulation at 1100 K.

After modeling the extended surfaces, nanoparticles (NPs) of the bimetallic alloys were modeled with the Atomsk software, and the modified MD/MC procedure was employed to simulate the cooling of the NPs from their melting temperature to room temperature to determine the nanoparticle configurations of different alloys. Figure 4-12 shows the evolution of the surface composition before and after thermal treatment for three different 4 nm diameter nanoparticles.

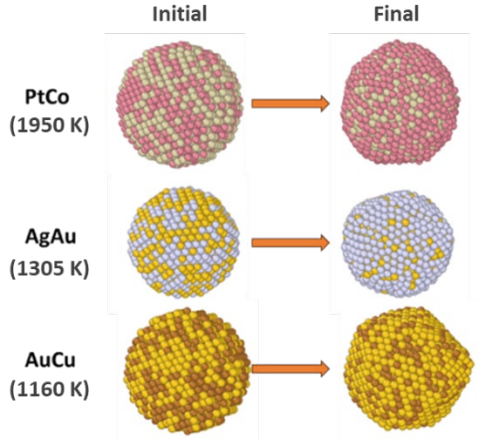

Figure 4-12. Initial and final configuration of 4 nm PtCo (a), AgAu (b) and AuCu (c) NPs that were cooled from melting temperature (1950/1305/1160 K) to 300 K at a rate of 1.3 K ps^{-1}.

Table 7 shows the analysis of the final structures. The core (interior) and shell (surface layer) compositions are within 2% of a literature reference value,[26] illustrating good control over the simulation methodology.

Table 7. Comparison of core and shell compositions for MD/MC simulations performed by Clemson and ref. 26.

Nanoparticle	Surface Composition (A:B)		Core Composition (A:B)	
	This work	Ref.	This work	Ref.
4 nm PtCo	29:71	30:70	60:40	59:41
4 nm AgAu	79:21	78:22	36:64	38:62
4 nm AuCu	68:32	70:30	42:58	42:58

4.2.3.2 Reaction energetics calculations on the surfaces for machine learning model data generation

DFT calculations provide important insights into both the nature of the metallic bonding within the catalysts and the orbital interactions between the catalysts and the adsorbate molecules. The commonly used electronic structure features include the electronic density of states (DOS), from which the d-band center and width can be found, the magnetic moment, and the Bader charge. These features can be calculated for both the pristine catalyst and after the metal alloy has been adsorbed on the surface. To calculate these features, DFT simulations through the Vienna Ab-initio Software Package (VASP), along with post-processing with VASPKIT and Python have been utilized. We were able to get close agreement with our simulation values and a literature reference for the layer-by-layer d-band center position of a Pt slab as shown in Figure 4-13.[27]

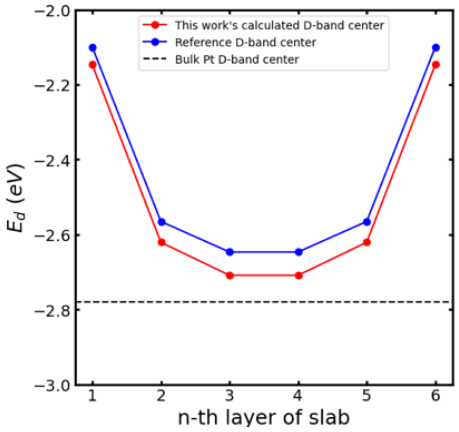

Figure 4-13. Layer-by-layer d-band center position for a Pt(111) slab from reference and our calculations.

Table 8 shows the same comparison in complex bimetallic PtCo system, at three different compositional ratios (1:3 PtCo, 1:1 PtCo, 3:1 PtCo) in ordered and disordered structures, for a total of six different structures.

Table 8. Summary of comparison for calculated values from Clemson and ref. 28.

Structure	d-band center (eV)		Magnetic moment per atom (μ_B)	
	This work	Ref.	This work	Ref.
Pt_3Co $L1_2$	–2.08	–2.06	0.71	0.75
Pt_3Co disordered	–2.18	–2.14	0.64	0.74
PtCo $L1_0$	–1.62	–1.57	1.13	1.16
PtCo disordered	–1.52	–1.68	0.93	1.13
$PtCo_3$ $L1_2$	–1.17	–1.25	1.41	1.45
$PtCo_3$ disordered	–1.22	–1.28	1.29	1.40

Finally, we have calculated the adsorption energy, metal-carbon bond length, and carbon-oxygen bond length for the molecular adsorption of CO and have close agreement with hexagonal close-packed (hcp), fcc, and on-top reference values as shown in Table 9.[29]

Table 9. Comparison of CO adsorption energies from Clemson and ref. 29.

Adsorption Site	Adsorption energy (eV)		M-C bond length (Å)		C-O bond length (Å)	
	This work	Ref.	This work	Ref.	This work	Ref.
hcp hollow site	–2.013	–2.066	2.112	2.107	1.195	1.195
fcc hollow site	–2.123	–2.099	2.108	2.112	1.195	1.195
On-top site	–1.994	–1.960	1.850	1.841	1.157	1.158

Validation of generated DFT simulations for simpler systems is vital for the development of ensuing machine learning (ML) models. The MDMC group has previously developed a ML model, PREDICT (PRedict properties from Existing Database In Complex alloys Territory), to successfully predict elastic constants in ternary, quaternary, and quinary alloys from DFT training data of their binary constituents.[30] The PREDICT approach greatly reduced the computational cost of evaluating the fcc Ni-Cu-Au-Pd-Pt HEA compositional space. This framework can be repurposed from elastic properties to catalytic properties to aid in predicting the energetics of more complex catalysts (e.g. for ternary, quaternary, and quinary alloys).

5.0 Proposed Scope for Year 2

5.1 Year 2 Electrochemical Denitration

5.1.1 Electrodes:

From the literature review, Kovar materials (Fe-Ni-Co) are of interest for initial electrochemical tests. Additional commercially available alloys will be sourced and evaluated. The selectivity and efficiency of the electrodes for the electrolyzer will be evaluated. The objective is to identify electrode compositions that can operate at a desirable current density and selectively reduce the nitrate/nitrite anions to desirable gaseous species (i.e. N_2), while also suppressing the water splitting reaction and other competing side reactions at the cathode. Electrode selection under optimized operating conditions will increase the overall electrochemical efficiency. Electrode discovery will feed into flow cell evaluations. Further optimization of the electrochemical system designs on the benchtop-scale will be performed.

Polykala Technologies LLC will electrodeposit Cu-Fe, Cu-Co and Cu-Ni on gas diffusion layer (GDL) carbon materials and mail the samples to Clemson, SRNL, and USC for characterization and electrochemical testing. Additional electrode coatings will be postulated to include Ru-Cu, Ru-Cu-Ni, Ru-Cu-Co coatings on GDLs by electrodeposition.

5.1.2 Membranes:

Progress towards membrane selection has been made in year 1 and will continue into year 2. From the electrochemical literature review, Nafion organic-polymer membranes are of interest for initial tests. Commercial-grade Nafion and various membranes that have recently been developed for other industrial applications (such as for the chloro-alkali industry) are of interest to be studied for viability in denitration and caustic generation electrolyzers with high ionic strength feeds. The reinforcement and thickness of the membranes may also influence viability for this work and will need to be studied.

The following polymer-based membranes were sourced for year 2 from the respective distributors:

From Chemours:

- Nafion N2050TX (chlor-alkali)
- Nafion 326 (unsure of membrane form)
- Nafion 966WX (chlor-alkali)

- Nafion 424 (sulfonated, single equivalent weight PFSA polymer and reenforced)

From Fuel Cell Store:
- PFSA D50-R ePTFE reinforced PEM
- PiperION Anion Exchange Membrane, (40 μm thickness), self-supporting
- ePTFE Reinforced PFSA Membrane (15 μm thickness) for PEM Fuel Cells

From Electrocell A/S:
- Nafion 117 (not reenforced)
- Nafion 324 (a bilayer membrane comprising two different equivalent weight PFSA polymers)
- Nafion 424 (sulfonated, single equivalent weight PFSA polymer and reenforced)

Nafion 117 is likely still available commercially, but it is not reenforced, and Nafion 324 is no longer commercially available for large-scale applications. Therefore, it is expected that Nafion 424 is a good candidate for scale-up moving forward since it is reinforced and has a lot of the same properties and durability that were proven in the legacy work.

Chemours is the leader in industrial membranes for Nafion and specialty Nafion products. The Fuel Cell Store provides similar membrane alternatives to the Nafion brand. The Electrocell Company has legacy membranes that have been phased out by other currently available products but might be of interest for comparing against the performance shown in the legacy work. These membranes will be evaluated in year 2 of this project.

NaSICON manufacturing capabilities and material discovery will continue in year 2. New NaSICON materials will be synthesized, characterized, and tested for ion-separation performance. This will include membranes with desired geometries and Na-ion permeation. Activities will also include developing a method for manufacturing large-area NaSICON membranes based on either tape-casting and/or 3D printing followed by high-temperature sintering.

5.1.3 Flow Testing:

Flow electrolyzer systems will be studied more in-depth in year 2, focusing on the denitration efficiency and off-gas composition. Polykala will compare the flow cells using lower flow rates. The electrochemical team is looking to confirm likely ranges of off-gas composition for the off-gas team. The off-gas composition is expected to change based on operating conditions and the feed (which varies significantly as it depends on tank waste compositions). The off-gas expected composition is crucial for understanding and managing the off-gases generated during the electrochemical denitration process.

5.1.4 Modeling:

In this project, both COMSOL (with the Electrochemical package) and SolidWorks CFD will be utilized to study a denitration electrolyzer and other unit operations for processing Hanford complex tank waste. Early in year 2, COMSOL will be procured to develop advanced multiphysics models to explore the electrochemical processes involved in converting nitrate and other species into NH_3 and other products. Concurrently, SolidWorks CFD will be employed to study the flow dynamics within the electrolyzer, focusing on gas diffusion and denitration efficiencies. Detailed CFD analyses will inform the design and optimization of the electrolyzer by providing insights into fluid flow and species transport. Using COMSOL, multiphysics models will be developed to simulate the coupled phenomena within the electrochemical reactions, including mass transport, fluid flow, and electrochemical kinetics. If ASPEN is integrated into the project, it will aid in developing processing conditions for the electrolyzers and other related systems, ensuring a comprehensive approach to optimizing and computationally demonstrating the entire electrochemical denitration process.

5.1.5 Scale-up Testing:

The Electrosynthesis Company will assemble two large benchtop electrolyzers. The electrolyzers are the MP cell from Electrocell A/S and the LS-01 from NESI. Both electrolyzers feature a parallel-plate design but with slightly different liquid flow patterns and sealing methods. Both cells will initially test Ni electrodes. This phase of testing will provide direct comparisons on cell performance (e.g. voltages, current density, overall denitration efficiency, and off-gas composition).

A general outline of an accelerated schedule for the Electrosynthesis Company is as follows:

- Phase 1 (project year 2): Revalidate the legacy reports with the current 150 cm^2 electrolyzer available to the company.
- Phase 2 (project year 2): Optimization and expansion of the scope of testing for the electrolyzer systems to achieve processing objectives. Recommendations for the development and improvement of the identified materials, reactions, and devices for the EDCGe system will be made. Electrosynthesis Company will give selection guidance of the materials and the design for the denitration electrolyzer and/or caustic generator electrolyzer system.
- Phase 3 (project year 3): Studies of top candidates for engineering-scale application, including durable materials, viable reactors, and desirable operating conditions for the EDCGe system under a simulated feed at larger-scale conditions. Further integration and optimization of the developed process and targeting the potential additions of process components and technologies to the system (i.e. sensors, etc.) will be considered.

During all three phases, benchtop-scale studies and collaborative efforts will be performed to inform the selection of technologies to be utilized at the engineering scale.

5.2 Year 2 off-gas

5.2.1 Catalyst synthesis year 2

Catalyst synthesis will include a variety of HEA catalysts compositions, as well as binary and ternary catalysts on the same supports the HEAs are synthesized upon. Different supports will be studied to identify the best catalyst motif for abatement reaction and thermocycling evaluations. HEA materials will expand both in composition and in studies related to the phase stability of the catalysts. Pt-Ru on carbon and Ru-V-Pt-W on titania are possible catalysts to be synthesized in year 2. Additional catalysts may include single metal catalysts (Pt/C, Ru/C), bimetallic system (Ru-Pt/C), and additional complex multi-metallic HEA catalysts. USC will also work on synthesizing its own HEA catalysts and perform a study on the different possible combinations of HEA catalysts.

5.2.2 Off-gas reactors testing year 2

USC will work on testing the synthesized catalysts in the reactor system while providing catalytic data to establish an off-gas treatment baseline. They will also verify CO oxidation results from the DFT calculations that are being performed at Clemson. Additionally, SRNL plans to upgrade the mass spectroscopy systems to lower the limit of detection and precision for NH_3/N_2O decomposition species including H_2 and N_2. Concurrent with metrology upgrades, we will continue synthesizing and testing catalysts to treat the gas stream produced by the electrolyzer, targeting high NH_3 and H_2 concentrations. Alongside novel catalyst synthesis, commercially available catalysts will be studied to provide the best recommendation for the full scale off-gas treatment system.

Next steps for the TAP reactor include scoping new materials like Pt-Ru on carbon and Ru-V-Pt-W on titania. Different catalyst samples from USC (Ru/C, Pt/C, Ru-Pt/C) and SRNL (HEA catalysts), along with a variety of additional catalysts not yet identified, will be tested by pulse experiments under high vacuum in the TAP reactor. Ammonia decomposition, nitrous oxide decomposition, and selective catalytic reduction

of nitrous oxide are potential probe reactions to investigate these catalysts. In addition, the catalytic behaviors of reaction intermediates on catalyst surface will be studied by ammonia-deuterium pump-probe experiments with varying time delay.

The thermal redox stability of a larger batch of HEA material will be studied by chemisorption testing and gas phase reactors. For example, thermo-redox cycle experiments on HEA catalysts can proceed through temperature programmed oxidation and reduction experiments, followed by reaction tests in the TAP reactor, to investigate the thermal stability of HEA samples under both oxidizing and reducing environments.

These studies will allow a closer look at surface elementary steps and intrinsic kinetics of reactions relevant to the treatment of the electrolyzer off-gas stream. A systematic investigation will be performed on single metal catalysts (Pt/C, Ru/C), bimetallic system (Ru-Pt/C), and complex multi-metallic HEA materials to gain fundamental understanding of the electronic and geometric effects of the metal-based catalysts. The experimental results in the TAP reactor will be directly compared with DFT and Ab Initio Molecular Dynamics simulations to unravel the underlying reaction mechanisms.

5.2.3 Computational Catalyst Discovery

The team will continue interfacing with our machine learning modeling team to share data to better guide the selection of elemental composition to synthesize and test. In year 2, Clemson will focus on:

1. Expanding simulations (both DFT and MD/MC) from single element and binary systems to ternary, quaternary, and quinary systems
2. Calculate adsorption energies in concentrated alloys

6.0 Summary

This report provides a detailed account of the progress and key advancements towards developing an efficient electrochemical denitration and caustic generation (EDCGe) and off-gas treatment system to process legacy waste at Hanford through the direct feed high-level waste (DFHLW) flowsheet. This project is supported by a multidisciplinary team and leverages advanced electrochemical technologies, machine learning, novel catalysts, and cutting-edge reactor systems. Key highlights from year 1 include proof-of-concept denitration experiments, the use of polymer-based membranes and the development of NaSICON-based membranes, the identification of baseline off-gas catalysts, and the development of a framework for computational modeling for off-gas catalyst material discovery.

The project has successfully accomplished year 1 tasks crucial for developing the EDCGe system, including a comprehensive literature review, benchtop-scale electrochemical development, and building the basics for computational modeling. Initial evaluations of commercially available membranes and electrode materials have built the foundation for improved electroreduction processes and electrolyzer design in the subsequent year. The execution of a subcontract with the Electrosynthesis Company was achieved so that scoping of engineering-scale electrochemical processes can begin in year 2. The year 1 Go/No-Go Milestone (*show that an electrochemical system like what will be used at the engineering scale is effective at nitrates destruction*) criterion has been satisfied based on the work covered in this report and the project is progressing well.

Additional notable achievements include the synthesis of high entropy alloys (HEAs) on graphene oxide (GO) and the development of off-gas abatement strategies have progressed with the synthesis and validation of traditional and advanced catalysts, including detailed testing in the temporal analysis of products (TAP) reactor and the development of off-gas systems. Details for the progress in year 1 with respect to the proposal schedule are shown in Table 10 (only tasks that were scheduled to begin in year 1 are included). Furthermore, year 2 will build on the strong foundation established in the first year and will focus on

optimizing electrodes, membranes, and flow cell performance, alongside enhanced computational modeling efforts to gain deeper insights into larger-scale system functionality and materials discovery. Continuous innovation in catalyst synthesis and off-gas management will further drive the project's success, propelling the EDCGe system towards identifying desirable operating efficiencies and effective waste processing at Hanford.

Table 10. Status for key program tasks completed as well as started in year 1.

Task	Status	Notes
1.1	Complete	Literature review is complete.
1.2	Complete	Initial scoping studies show viability of the system. Further testing is ongoing.
1.3	On track	Electrosynthesis company to use the NESI Norscand electrolyzer systems and pilot scale testing facility.
2.1	Complete	Membranes were considered based on availability and functionality. A variety of full scale and benchtop-scale polymer-based membranes were sourced. Both polymer (Nafion) and ceramic membranes (NaSICON) are viable materials.
2.2	Complete	Electrosynthesis company to use the NESI Norscand electrolyzer systems and pilot scale testing facility.
2.4	On track	Electrosynthesis will conduct this part 2 study after the results from part 1 (Task 1.2) have been summarized and the subcontract is placed.
2.6	On track	Membrane material development and sourcing is underway. This work will continue into year 2.
4.1	On track	Initial testing on commercially available off-gas catalysts has been performed. This work will continue into year 2 and 3.
4.2	On track	This task has begun and is led by Clemson University.

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Distribution:

amy.ramsey@srnl.doe.gov
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