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The following report, Surfactant/Extractant Verification Report, by Power Environmental Energy Research Institute marks the completion Task 2 – Identify the Optimized Surfactants and Extractants for their Electric Program Investment Charge's agreement EPC-24-048 with the California Energy Commission (CEC). This agreement was approved at the CEC's April 10, 2025 Business Meeting as part of GFO-23-304 - Geothermal Energy Operations and Lithium Innovation (GEO/LI) where CEC made a commitment to post project reports to the Lithium Valley Vision Docket.

For more information on this project please see the backup materials from this Business Meeting.

If further questions, please reach out to the Energy Research and Development Division (ERDD@energy.ca.gov) or the Office of the Public Advisor (publicadvisor@energy.ca.gov).

Surfactant/Extractant Verification Report (Final)

EPC-24-048

Task 2 – Identify the Optimized Surfactants and Extractants

Table of Contents

List of Figures

List of Tables

1. Introduction

This report is submitted under EPC-24-048 (Task 2 - Identify the Optimized Surfactants and Extractants). Per the Scope of Work, the project objective is to develop a sustainable and energy-efficient process to selectively recover zinc (Zn) and manganese (Mn) from Salton Sea geothermal brines, while managing co-occurring iron (Fe) when present, using surfactant/extractant-enabled foam fractionation and related bubble-contacting approaches. While conventional foam fractionation served as the initial baseline, Task 2 results indicate that a diluent-free micro-/nano-bubble dispersion approach—operated with minimal or no surfactant—can improve hydrodynamic stability in high-salinity brine and reduce chemical inputs. Both approaches are carried forward into Task 3 for semi-continuous apparatus validation.

Task 2 focuses on screening, verification, and down-selecting of commercially available chemical reagents capable of operating under extreme high-salinity conditions. This document serves as the Task 2 Verification Report and is organized as follows: Section 2 defines the objectives and verification scope. Section 3 presents the benchtop test methods and results for speciation modeling, liquid-liquid extraction (LLE) screening, and stripping using proxy brines. Section 4 validates the selected extractant's performance against actual Salton Sea field brine. Section 5 reviews the initial foam extraction trials. Section 6 details the comprehensive screening for diluent-free emulsion stability and the project's strategic pivot toward mechanical dispersion optimization. Finally, Section 7 summarizes the overall conclusions, confirms the final extractant selection and establishes two engineering pathways for the upcoming Task 3 apparatus design.

2. Objectives and Verification Scope

2.1 Task 2 Objectives

Task 2 aims to identify surfactants and extractants that enable efficient Zn and Mn separation under Salton Sea geothermal brine conditions. Work is executed via a verification plan and benchtop testing, culminating in this Verification Report, which documents procedures and results, test methods, technical issues, and lessons learned. The down-selected reagents will inform the foam/bubble

fractionation process design to achieve high-purity recovery of the target metals from the brine.

2.2 Scope Covered in This Report

This draft report summarizes the following verification elements conducted to date:

1. Speciation Modeling: Brine chemistry simulation of Zn speciation, comparing low-salinity conditions with high-salinity proxy brine. [Section 3.1]
2. Baseline Proxy Brine Screening: Liquid-liquid extraction (LLE) screening of anionic, neutral, and cationic extractants; evaluation of Zn selectivity relative to Mn/Ca/Na; and baseline stripping/regeneration feasibility. [Sections 3.2 - 3.3]
3. Field Brine Verification: Validation of LLE extraction efficiency, Zn selectivity, and stripping performance using actual, modified Salton Sea geothermal field brine. [Section 4]
4. Foam Extraction Trials: Evaluation of conventional foaming architectures using dual surfactant/extractant combinations (e.g., NE-1 + SF-2; Alkyl phosphate(AP)) acting as bulk brine foaming agents. [Section 5]
5. Diluent-Free Emulsion Screening: Comprehensive stability screening of 12 surfactant candidates across varying volume fractions to establish an emulsion-assisted pathway for mitigating the high viscosity of neat extractant. [Sections 6.1 - 6.3]
6. Mechanical Dispersion & Final Pathways: Optimization of semi-continuous, surfactant-free mechanical bubble dispersion, establishing the definitive chemical and operational pathways for Task 3 apparatus design. [Sections 6.4 and 7]

3. Test Methods and Results

3.1 Brine Chemistry Simulation

Purpose: Determine dominant aqueous Zn species as a function of pH and brine salinity to guide extractant selection.

We simulated two distinct scenarios to evaluate Zn aqueous speciation under low- and high-salinity conditions:

- Scenario A: Simple baseline (low salinity)

- Composition: A simple mixture containing only Zn (500 ppm) and Mn (1,000 ppm) in water.
- Result: Figure 1 shows the molar fractions of Zn species in the low-salinity environment. Zn exists primarily as the free divalent cation Zn^{2+}, consistent with standard Zn behavior in fresh water and generally amenable to conventional cation-targeting extraction approaches.

- Scenario B: Proxy brine (high salinity)
  - Composition: A complex, high-salinity mixture mimicking geothermal brines:
    - Zn: ~500 ppm
    - Mn: ~1,000 ppm
    - Ca: ~30,000 ppm
    - Na: ~50,000 ppm
    - K: ~1,000 ppm
  - Result: Figure 2 shows the modeled Zn speciation in the proxy brine. The simulation indicates a pronounced chemistry shift: in the presence of high chloride activity (associated with the Ca/Na salt matrix), Zn is no longer predominantly present as free Zn^{2+}. Instead, Zn forms anionic Zn–Cl complexes, dominated by $(ZnCl_4)^{2-}$ over the modeled pH range. This speciation shift fundamentally changes the extraction mechanism required and explains the poor performance of cation-exchange extractants in high-salinity brines.

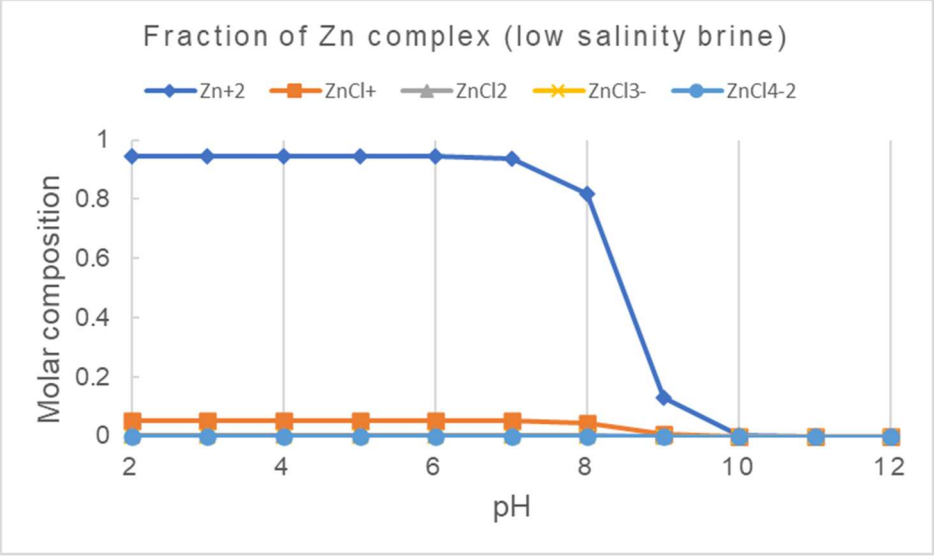


Figure 1. Molar composition of zinc speciation vs pH in low-salinity brine

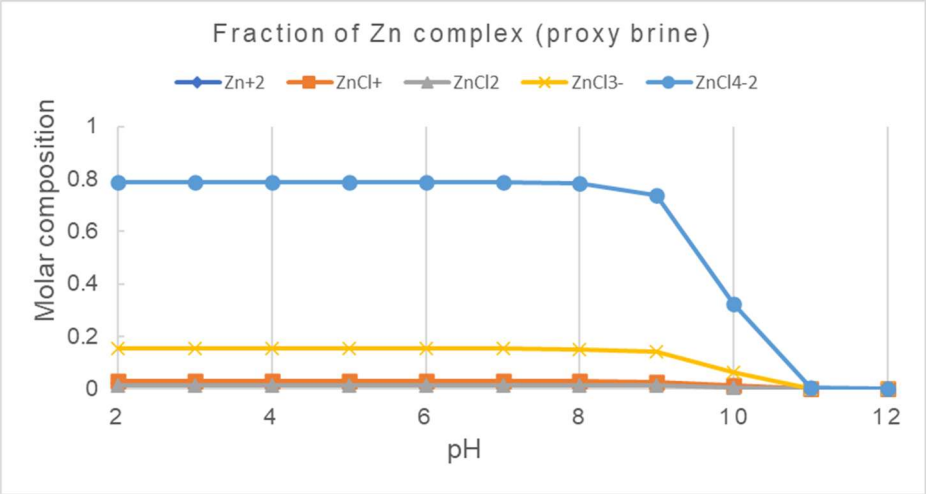


Figure 2. Molar composition of zinc speciation vs pH in proxy brine

This simulation indicates that, in proxy brine, Zn speciation shifts from predominantly free Zn^{2+} (low salinity) to anionic Zn-Cl complexes, dominated by $(ZnCl_4)^{2-}$. This speciation shift explains the poor performance of conventional cation-targeting extractants in high-salinity brines. It also supports our selection of a neutral solvating extractant (NE-1), which is better suited for extracting Zn from chloride-rich systems where Zn is not present primarily as Zn^{2+}.

3.2 Liquid-Liquid Extraction (LLE) Screening

Purpose: Screen extractant classes to identify candidates that provide (i) high Zn extraction efficiency from proxy brine and (ii) strong selectivity over other metal ions such as Mn/Ca/Na. The down-selected extractant(s) will then be advanced to foam extraction and bubble-contacting verification tests.

3.2.1 Acidic Organophosphorus Extractants (Initial Screen)

Extractants tested: AE-1, AE-2, AE-3.

The extractant is a critical component of the separation process because it provides the selective chemical interaction needed to capture the target metal-in this case, zinc (Zn)-from a high-salinity matrix. To identify a suitable extractant for Zn recovery, multiple candidates were screened. PHREEQC modeling indicates that Zn in proxy brine is predominantly present as an anionic Zn-Cl complex, rather than as free Zn^{2+}. Therefore, conventional acidic (anionic) organophosphorus extractants-including AE-1, AE-3, and AE-2-were evaluated as baseline candidates and were expected to exhibit limited performance under these conditions. For this screening, a Zn to extractant molar ratio of 1:2 was

used to approximate the stoichiometric requirement for complexation in the simplified screening design.

The Zn extraction efficiencies of these extractants are shown in Figure 3.

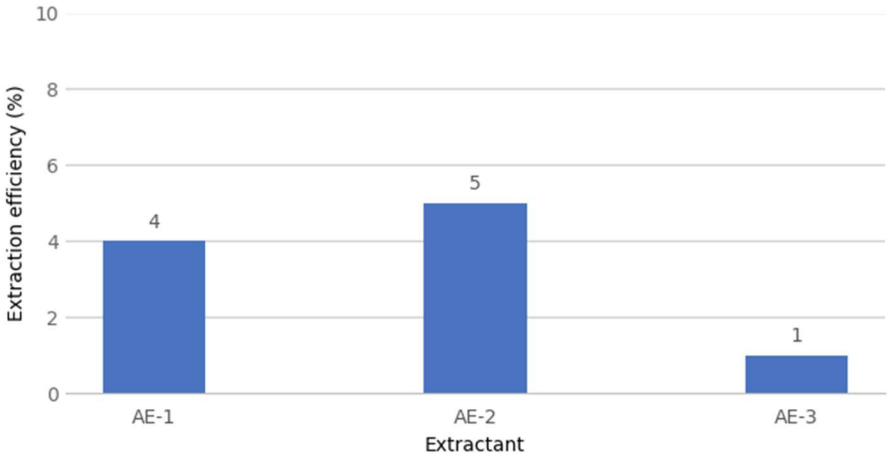


Figure 3. Zinc extraction efficiencies of anionic extractants

The speciation modeling provided a critical insight: across pH 1–8, Zn in the proxy brine exists predominantly as the anionic chloro-complex $(ZnCl_4)^{2-}$, rather than as free Zn^{2+}. The acidic organophosphorus extractants evaluated in this screening set (e.g., AE-1, AE-3, and AE-2) rely primarily on cation-exchange interactions and therefore exhibit limited affinity for Zn when it is present predominantly as an anionic chloro-complex. This speciation–mechanism mismatch is consistent with the low Zn extraction efficiencies observed. Consequently, neutral solvating extractants and cationic extractants were selected for further evaluation, as these classes are more suitable for extracting Zn from chloride-rich systems where Zn is present mainly as an anionic complex under the conditions tested.

3.2.2 Neutral and Cationic Extractants (Follow-on Screen)

The neutral and cationic extractants evaluated in this screening are listed in Table 1 .

Table 1. Neutral and cationic extractants evaluated in LLE screening

Neutral extractants	NE-2
	NE-1
	NE-3
	NE-4
Cationic extractants	NE-3 (at pH=2 and pH=0)

	CE-1

The Zn extraction efficiencies for the neutral and cationic extractants are shown in Figure 4.

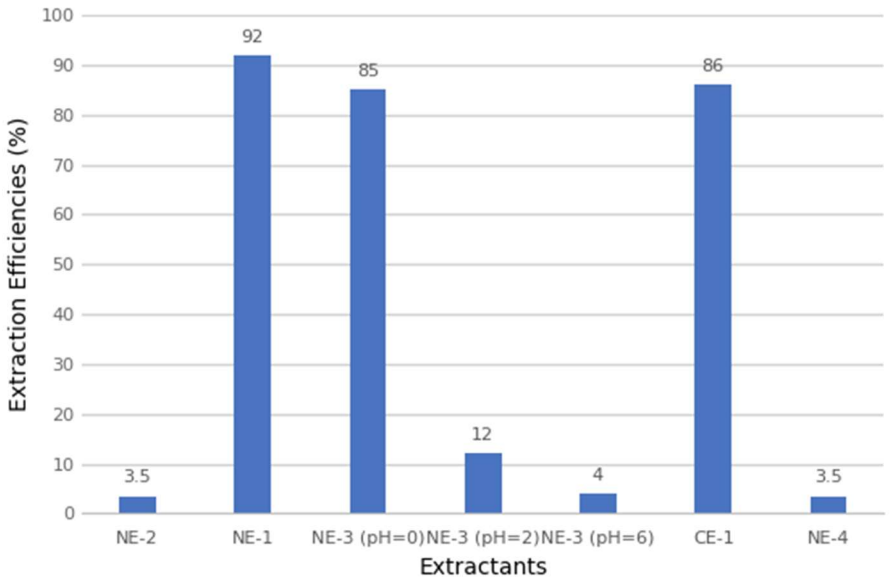


Figure 4. Extraction efficiencies of neutral and cationic extractants

Based on Figure 4, NE-1 and CE-1 show the highest Zn extraction efficiencies among the neutral/cationic candidates tested. Using the ICP results, we calculated the selectivity of each extractant for Zn relative to Mn, Ca, and Na. The selectivity results for NE-1 and CE-1 are presented in Figure 5 and Figure 6, respectively. Both NE-1 and CE-1 exhibit excellent selectivity for Zn over Mn, Ca, and Na under the proxy brine conditions tested. In addition to extraction, stripping is a critical step in the overall recovery process because it transfers Zn from the loaded organic phase back into an aqueous phase for downstream recovery and purification. Efficient stripping is therefore essential for achieving high overall Zn recovery and enabling extractant regeneration and reuse.

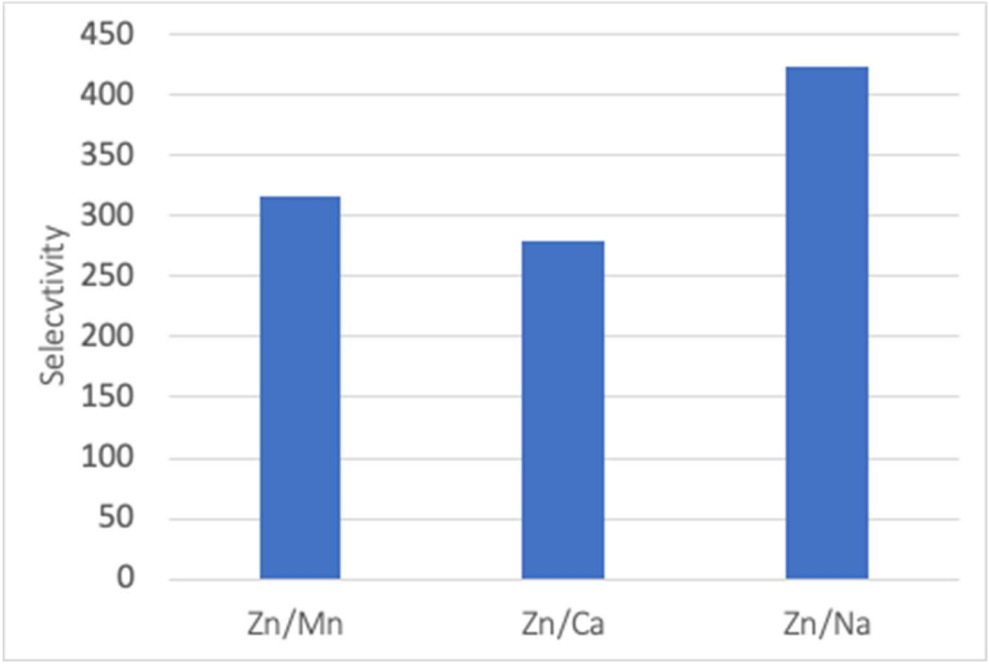


Figure 5. Selectivity of Zn with respect to other metals for NE-1

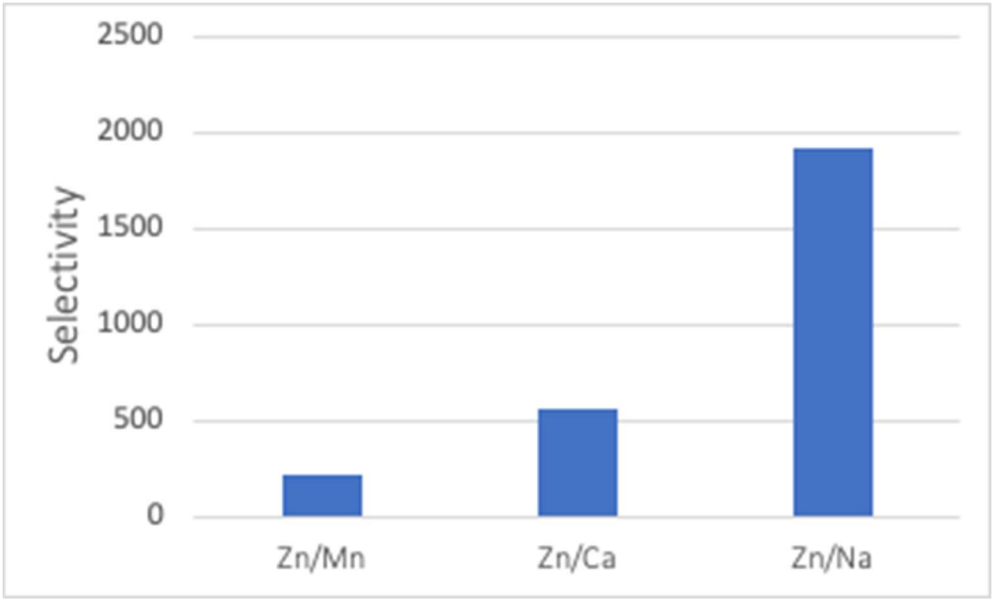


Figure 6. Selectivity of Zn with respect to other metals for CE-1

3.3 Stripping Studies

Purpose: Verify that extracted Zn can be efficiently stripped from the organic phase into an aqueous phase to enable downstream metal recovery and extractant regeneration/recycling.

3.3.1 NE-1 Stripping

For stripping of NE-1, deionized (DI) water and 1.2 M ammonium hydroxide (NH_4OH) were evaluated as stripping agents. The stripping efficiencies are shown below.

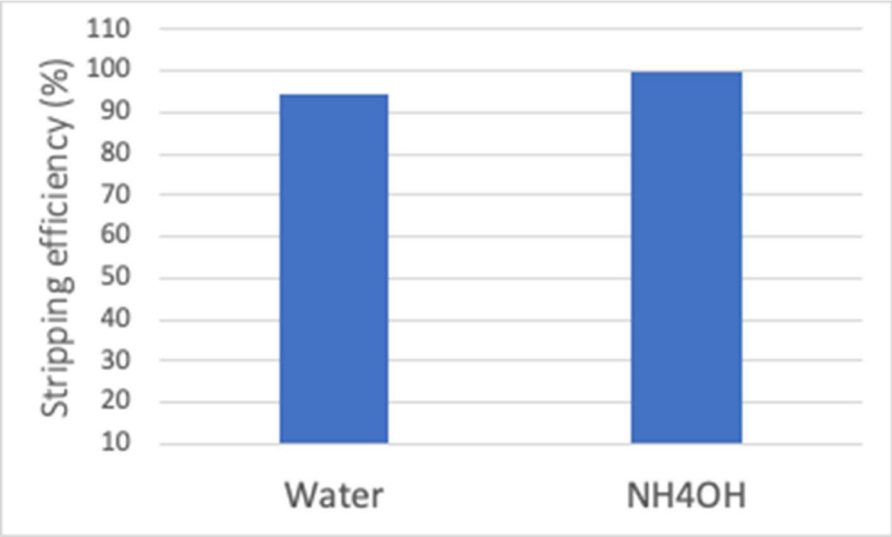


Figure 7. Stripping efficiency of DI water and NH_4OH for NE-1

As shown in Figure 7, NH_4OH and DI water exhibited comparable stripping efficiencies. Therefore, DI water was selected as the preferred stripping agent for NE-1 due to comparable performance and simpler handling in the extractant recycle loop.

3.3.2 CE-1 Stripping

For CE-1, multiple stripping reagents-including DI water, NH_4OH, HCl, H_2SO_4, and NaOH-were evaluated; however, none achieved stripping efficiencies greater than 5% under the conditions tested. Consequently, based on overall extraction performance, selectivity, and-critically-practical stripping/regeneration feasibility, NE-1 was selected as the current candidate extractant for subsequent foam and bubble-contacting evaluation tests.

4. Verification in Field Brine vs. Proxy Brine

Purpose: To verify that the extraction chemistry, kinetics, and selectivity of the selected extractant established using laboratory-synthesized proxy brines, remain robust and effective when applied to a highly complex, real-world geothermal field brine matrix.

4.1 Objective and Field Brine Preparation

Purpose: Establish and document the preparation of the CTR field brine (including spiking to proxy targets) to enable an apples-to-apples comparison with proxy brine performance.

Initial Liquid-Liquid Extraction (LLE) and stripping performance metrics were established using a laboratory-synthesized proxy brine. To verify that the extraction chemistry of NE-1 remains robust in a real-world, complex chemical matrix, comparative validation tests were conducted using actual field brine sourced from Controlled Thermal Resources Holdings Inc. (CTR).

Because the raw field brine may be depleted in target minerals depending on the sampling point, the field brine was modified and replenished with zinc (Zn) and manganese (Mn) to match the baseline target concentrations of the proxy brine. This standardized the thermodynamic driving force, allowing for a direct performance comparison. The ICP analysis of the raw brine collected from the CTR is presented below along with the modified (spiked) brine composition.

Table 2. Elemental composition of the as-received CTR brine and the modified (spiked) brine, illustrating the targeted replenishment of Zn and Mn to match field brine concentrations.

Elements (mg/kg)	CTR Brine	Spiked CTR Brine
S	383.2	412.5
Zn	14.6	510.1
Pb	2.1	-2.8
B	363.5	531.7
Mn	63.7	1549.6
Mg	15.2	15.9
Ca	34825.7	34188.0
Sr	475.6	462.5
Ba	35.0	33.7
Li	231.6	222.0
K	18343.9	17584.6
Na	59804.0	56899.9

4.2 Extraction Performance Comparison

Purpose: Compare Zn extraction efficiency and selectivity of the down-selected extractant(s) in proxy brine versus spiked CTR field brine to confirm performance translation in a real geothermal matrix.

Comparative LLE tests were conducted using neat NE-1.

- **Proxy Brine Extraction:** In the synthetic proxy matrix, the baseline Zn extraction efficiency was 97.82% with high selectivity relative to Mn.
- **Field Brine Extraction:** In the modified field brine, the Zn extraction efficiency was 94.65%.

Table 3. Zn percentage extraction with NE-1 and AE-2 on proxy brine and spiked CTR brine.

	% Extraction by NE-1		
	Zn	Mn	Ca
Proxy Brine	97.82	3.24	1.04
Field Brine	94.65	5.38	0.51
	% Extraction by AE-2		
Proxy Brine	4.6	0.421	0.78
Field brine	2.1	0.13	0.29

The comparative extraction data presented in Table 3 demonstrate a strong translation of performance from the synthetic proxy baseline to the CTR brine. Utilizing NE-1, the system achieved a highly efficient 94.65% zinc extraction in the complex CTR brine matrix, closely mirroring the 97.82% baseline established in the proxy brine. While the CTR brine matrix resulted in a nominal increase in manganese co-extraction (rising from 3.24% to 5.38%), the overall selectivity for zinc remains strongly favorable under the conditions tested. Calcium co-extraction decreased marginally, further confirming the robustness of the complexation mechanism. Furthermore, the poor performance of the industry-standard AE-2 (achieving <5% zinc extraction in either matrix) is consistent with Zn-Cl speciation in the chloride-rich brines and supports selection of NE-1 for this extreme-salinity geothermal application.

4.3 Stripping Performance Comparison

Purpose: Compare single-stage stripping performance of the loaded organic phase from proxy brine versus spiked CTR field brine to assess recovery feasibility and identify any matrix-driven stripping limitations.

Following extraction, the loaded organic phases from both the proxy and field brine trials were subjected to identical stripping protocols to recover the zinc.

Table 4. Zn percentage stripping from NE-1 with water

	% Stripping for NE-1		
	Zn	Mn	Ca
Proxy Brine	82.21	17.98	0.00
Field Brine	54.86	76.48	69.94

- **Proxy Brine Stripping:** The loaded extractant required a 1:1 organic to aqueous phase ratio to achieve 82% Zn recovery in a single contact.
- **Field Brine Stripping:** The extractant loaded from the field brine required 1:1 organic to aqueous phase ratio to achieve 55% Zn recovery.

The stripping profiles indicate that while zinc recovery is feasible, the efficiency of a single-stage strip is noticeably impacted by the complex field brine matrix. Under identical stripping protocols, the proxy brine baseline achieved 82% Zn recovery, whereas the field brine achieved 55% recovery. This partial reversibility in a single contact suggests that matrix components (e.g., competing ions and/or organic matter) in the field brine increase the stability of the loaded NE-1 complex. Consequently, these data support a Task 3 engineering objective to design and implement multi-stage stripping configurations to drive higher overall zinc recovery.

While the extraction kinetics proved highly robust, the stripping data (Table 4) reveals the distinct matrix effect of the CTR brine. Utilizing a single-stage water strip at a 1:1 organic to aqueous phase ratio, the proxy-loaded organic achieved 82.21% zinc recovery. In contrast, the extractant loaded from the CTR brine yielded only 54.86% zinc recovery. Notably, this single-stage water strip of the CTR brine also removed a large fraction of the co-extracted Mn and Ca, stripping 76.48% of the Manganese and 69.94% of the Calcium. This suggests that the CTR brine matrix (e.g., competing ions and/or other dissolved constituents) increase the stability of the loaded Zn-NE-1 complex, such that higher overall Zn recovery may require additional stripping stages and/or optimized strip conditions.

4.4 Conclusion of Field Brine Verification

Validation studies conducted on both the synthetic proxy and the actual CTR field brine confirm that the high zinc selectivity and overall extraction efficiency of NE-1 successfully translate to real-world geothermal matrices. While the complex field matrix appears to increase the stability of the loaded Zn-complex (resulting in a lower single-stage stripping recovery rate of ~55%), this is partially offset by a critical chemical advantage: NE-1 requires only water to reverse the complexation. Unlike alternative extractant candidates that require harsh, concentrated acidic or basic conditions to strip the metals, this water-only mechanism aligns well with the project's strict environmental and reduced-waste mandates.

5. Foam Extraction Verification (Procedure and Results)

5.1 Foam Extraction with NE-1 + SF-2 Surfactant

Purpose: Verify whether the selected extractant (NE-1) can be integrated into foam fractionation with a foaming agent (SF-2) to enrich Zn into the foamate with improved selectivity relative to Mn/Ca/Na, while maintaining stable foam formation and acceptable phase behavior. Based on prior surfactant screening performed per the Surfactant/Extractant Verification Plan, SF-2 was selected as the primary foaming agent based on overall foam stability and handling performance under the tested conditions.

The concentrations of Zn, Mn, Ca, and Na in the foamate samples collected over time are shown in Figure 8 and Figure 9.

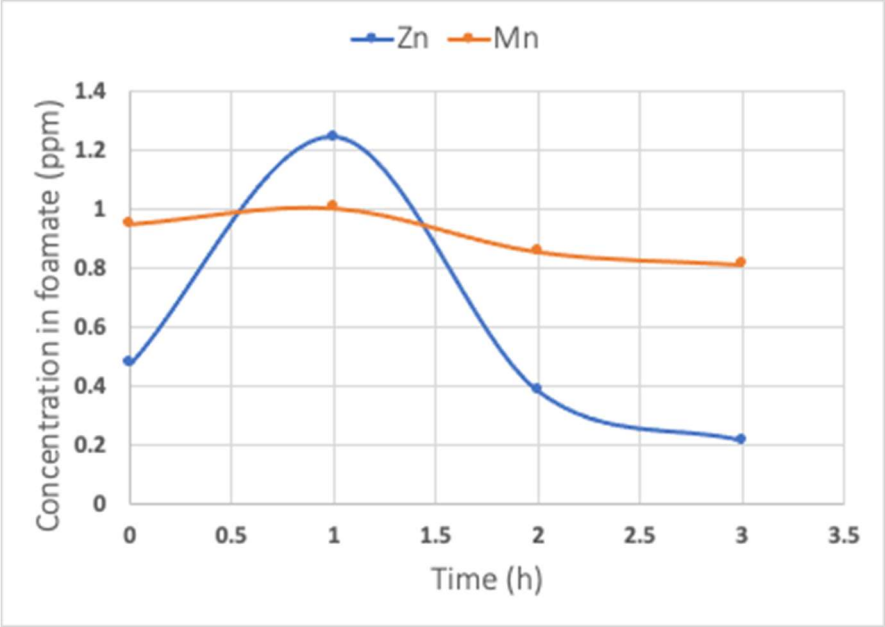


Figure 8. Foamate concentrations of Zn and Mn vs. time

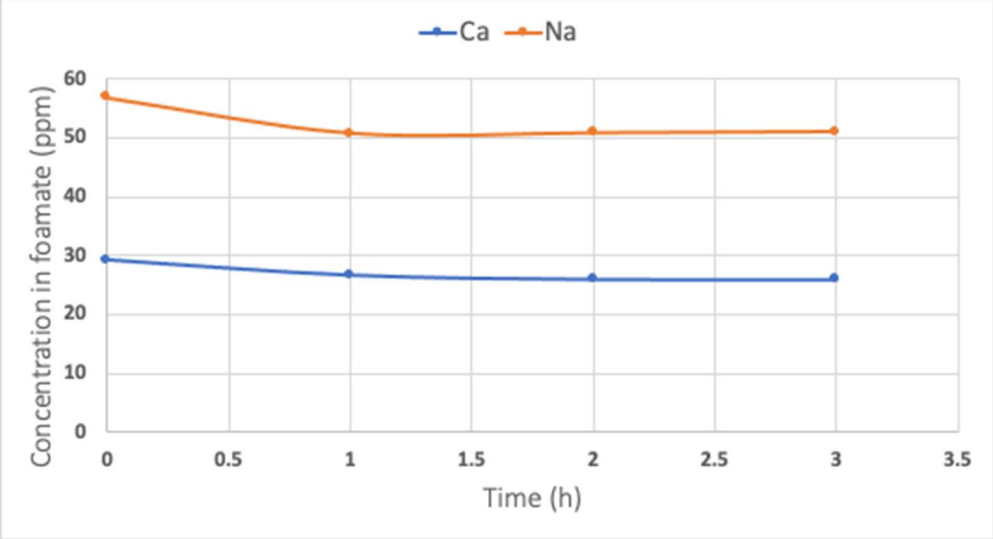


Figure 9. Foamate concentrations of Na and Ca vs. time

As shown in Figure 8, Zn exhibits only a modest enrichment in the foamate during the first hour; however, the Zn concentration decreases over the subsequent two hours. In addition, Figure 8 and Figure 9 show that substantial amounts of Mn, Ca, and Na are present in all foamate samples. Overall, these results indicate that while limited Zn enrichment occurs initially, the foam extraction process demonstrates poor selectivity for Zn over Mn, Ca, and Na under the conditions tested.

These results suggest that the surfactant (SF-2) is not compatible with the extractant (NE-1) under the tested conditions, leading to non-selective entrainment and poor Zn selectivity over Mn, Ca, and Na in the foamate. Accordingly, additional surfactant candidates are being screened to identify formulations that are compatible with NE-1, maintain stable foam/bubble contacting, and improve Zn selectivity in the foamate.

5.2 Extraction with Alkyl Phosphate (Dual Surfactant/Extractant)

Purpose: Evaluate Alkyl phosphate (AP) as a dual-function reagent that may provide both foam generation and Zn extraction and assess whether it can enrich Zn into the foamate with improved selectivity over Mn/Ca/Na under the proxy brine conditions tested.

AP is an organophosphorus extractant with a chemical structure similar to AE-3 and has been reported to exhibit both metal-extraction and foaming behavior. Accordingly, it was evaluated as a dual-function surfactant/extractant in this brine system. During preliminary testing, AP exhibited increased solubility in the brine at pH=2; therefore, the brine pH was adjusted to pH=2 prior to the foam extraction experiments to maintain appropriate phase behavior during testing.

The Zn to extractant/surfactant molar ratio was maintained at 1:4. The gas flow rate through the solution was set at 60 cc/min. The experiment was conducted for a total duration of 6 hours, and foamate samples were collected at 1-hour intervals. Foamate concentrations of Zn, Mn, and P were quantified by ICP analysis, as shown in Figure 10. The results indicate enrichment of phosphorus in the foamate, confirming that AP partitions into (or is carried by) the foaming phase; however, no meaningful selectivity for Zn over Mn was observed. A similar lack of selectivity was also observed relative to Ca and Na. Overall, these findings indicate that AP does not provide sufficient Zn selectivity over Mn/Ca/Na under the conditions tested and therefore does not meet the surfactant/extractant verification criteria for selective Zn foam extraction in this system.

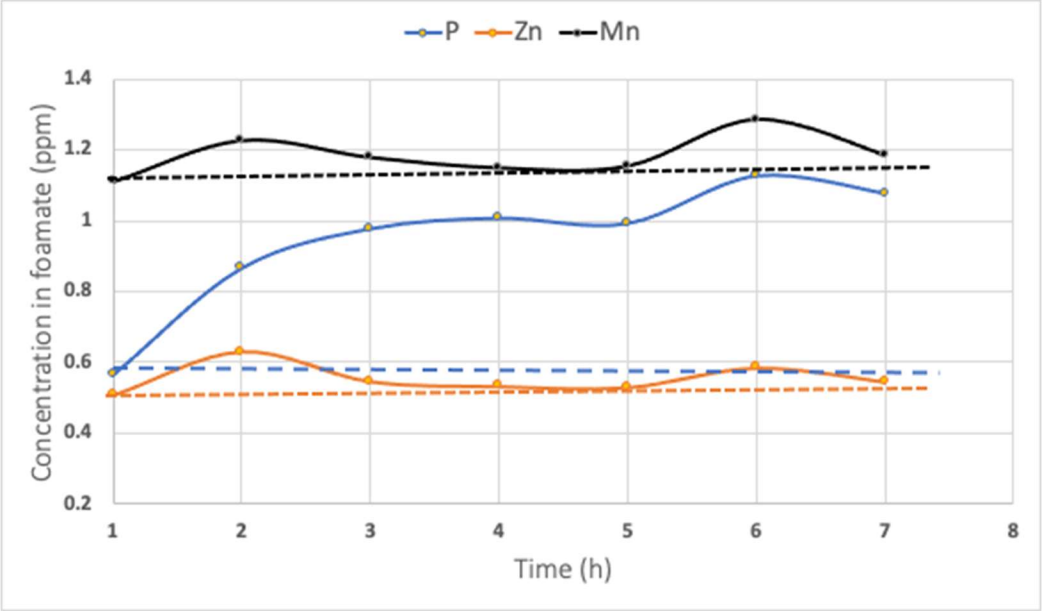
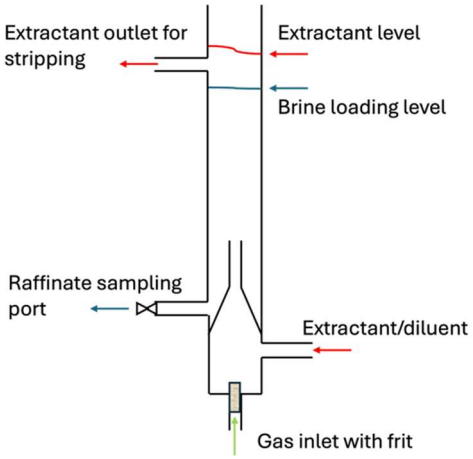


Figure 10. Foamate concentrations of P, Zn, and Mn vs. time

5.3 Supplemental Verification: Semi-Continuous Bubble-Dispersion Column Extraction

Purpose: The primary objective of this project is to develop a sustainable and energy-efficient method for extracting Zn from complex saltwater mixtures (brines). This study investigates a micro-/nano-bubble contacting approach designed to selectively extract Zn while minimizing or eliminating reliance on surfactants for bulk foam formation. This section summarizes the performance of two key experiments conducted to optimize the kinetics (extraction rate) and overall efficiency of the process.

To evaluate the extraction kinetics under dynamic conditions, the system was operated as a semi-continuous bubble-dispersion column shown in Figure 11. In each experiment, a predetermined volume of the target brine was preloaded into the column to establish a static aqueous phase. Rather than utilizing a traditional counter-current liquid flow, the extractant was continuously injected directly into the bottom of the column alongside a pressurized stream of gas. This co-injection generated a rising column of gas bubbles that mechanically dispersed the extractant, providing the necessary high-shear agitation and interfacial surface area for zinc mass transfer as the extractant droplets migrated upward through the preloaded brine.



A) Schematic of experimental setup

B) photograph of the extraction experiment

Figure 11. A) Schematic of the semi-continuous bubble-contacting column for Zn extraction; B) photograph of the column during operation

Two operating conditions were tested:

- Low-rate: gas flow = 60 cc/min; extractant flow = 1 cc/min.
- High-rate: gas flow = 180 cc/min; extractant flow = 3 cc/min.

This section summarizes Zn depletion kinetics by tracking how quickly the Zn concentration decreased from the initial value toward complete depletion under each operating condition.

- Low-rate experiment:
  - 50% removal: ~80 minutes
  - 90% removal: ~150 minutes
  - Final status: after 3.5 hours (210 minutes), ~5% of the initial Zn remained in solution, indicating effective but slower extraction kinetics.
- High-rate experiment:
  - 50% removal: ~20 minutes
  - 90% removal: ~50 minutes
  - Final status: 100% Zn removal was achieved in ~2 hours (120 minutes).

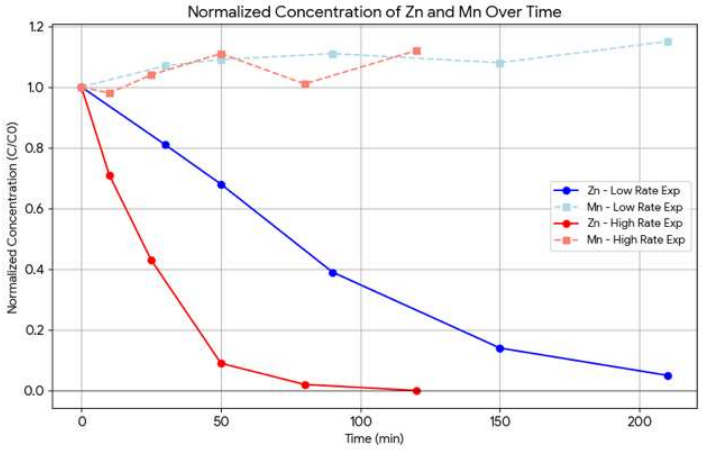


Figure 12. Zn depletion kinetics (normalized raffinate concentration vs. time) for low-rate and high-rate column conditions

Figure 12 compares the normalized Zn concentration in the brine raffinate over time for the low-rate and high-rate operating conditions. The high-rate experiment achieves Zn depletion significantly faster, reaching ~90% removal in ~50 minutes and complete depletion (~0% remaining) in ~2 hours (120 minutes). In contrast, the low-rate experiment reaches ~90% removal in ~150 minutes and does not reach complete depletion within the 3.5-hour test window (~5% Zn remaining at 210 minutes). Overall, increasing the gas and extractant flow rates accelerated Zn removal by approximately 3-4 times based on the time required to reach comparable removal levels (e.g., 50% and 90%).

Table 5. Overall performance comparison of the low-rate and high-rate column extraction experiments

Metric	Low-rate	High-rate
Gas flow rate	60 cc/min	180 cc/min
Extractant flow rate	1 cc/min	3 cc/min
Time to 90% Zn removal	~150 min	~50 min
Total Zn removal	94.4% (210 min)	100% (120 min)
Product purity	>99%	>98%
Physical recovery	67.4%	59.8%

Table 5 summarizes the final performance metrics for both operating conditions. The results highlight a clear trade-off between extraction kinetics and overall recovery balance:

- Speed vs. product quality: Increasing the operating rates accelerated Zn removal by ~3–4 times without compromising product purity. NE-1

maintained high selectivity, yielding >98% purity under high-rate conditions.

- Throughput: The high-rate condition enables higher throughput, achieving 100% Zn removal in ~2 hours (120 min), whereas the low-rate condition reached 94.4% removal after 3.5 hours (210 min) within the test window.
- Recovery bottleneck: Although Zn removal from the brine was highly effective, physical recovery decreased in the high-rate mode (59.8% vs 67.4%, Table 5). This suggests that downstream stripping/recovery capacity (i.e., transferring Zn back out of the loaded organic phase) became the limiting step at higher throughput and should be prioritized for process optimization.

The semi-continuous column extraction process, utilizing the selected neutral solvating extractant (NE-1), demonstrated rapid and selective Zn removal from proxy brine. Under the high-rate operating condition, the system achieved complete Zn depletion (~100% removal) in ~2 hours (120 minutes), establishing a practical high-throughput operating window for subsequent optimization and scale-up.

6. Diluent-Free Emulsion Stability Screening.

Purpose: To evaluate the feasibility of utilizing surfactant-stabilized emulsions to overcome the high bulk viscosity of neat diluent-free extractant, and to establish the optimal physical dispersion method for continuous column operation.

6.1 The Diluent-Free Objective and the Viscosity Challenge

Purpose: To define the project's sustainability goals regarding the elimination of organic diluents and to identify the resulting hydrodynamic challenge of neat extractant viscosity.

To minimize environmental impact, improve process safety, and align with the project’s reduced-waste objectives, the team committed to a diluent-free extraction approach utilizing neat extractant. Eliminating conventional toxic organic solvents (e.g., kerosene) significantly alters the physical dynamics of the extraction system. Most notably, the neat extractant possesses a high inherent viscosity, which initially presented severe hydraulic challenges for maintaining a high gas-liquid interfacial area and sufficient mass transfer kinetics during dispersion.

6.2 Comprehensive Evaluation of Surfactant-Stabilized Emulsions

Purpose: To systematically screen a diverse range of surfactant candidates aimed at mitigating extractant viscosity, and to evaluate their performance across varying operating volume fractions.

To mitigate the high viscosity of the neat extractant, the team hypothesized that formulating an extractant-in-water emulsion using targeted surfactants could improve hydrodynamics. A comprehensive screening of 12 surfactant candidates across multiple chemical classes (linear/branched nonionics, anionics, and aromatics) was conducted at a minimal dosage of 30 ppm.

Crucially, because continuous extraction columns can operate at widely varying organic phase holdup ratios (extractant volumetric content), the surfactant candidates were rigorously evaluated across a spectrum of extractant volume fractions, specifically testing low-volume (10% to 20%) and high-volume (~50%) scenarios.

6.2.1 Emulsion Design Criteria

To replace the conventional organic phase (e.g., kerosene) and operate purely with neat NE-1, an emulsion-assisted extraction approach was explored. In this method, the highly viscous extractant is dispersed in the aqueous brine with the aid of a surfactant. To be viable for the continuous process, the extractant–water–surfactant system must form an emulsion that best satisfies the following criteria:

1. Uniformity: Enables uniform distribution and high interfacial area of the extractant within the aqueous phase.
2. Viscosity Reduction: Significantly reduces the effective bulk viscosity of the extractant to ensure adequate fluid mechanics and mass transfer.
3. Metastability: Remains stable enough for extraction but metastable enough to subsequently separate into distinct phases-allowing for the clean recovery of neat extractant, stripped brine, and surfactant post-extraction.

6.2.2 Rapid 5-Minute Screening Procedure

To identify a surfactant that satisfies all three criteria, the team developed a standardized, rapid 5-minute screening test under static conditions. The procedure was executed as follows:

1. Prepare a premixed solution of the target surfactant in proxy brine at a minimal dosage of ~30–50 ppm.
2. Add the undiluted (neat) extractant to the premixed aqueous solution at volume fractions ranging between 2.5% and 50% to simulate various column holdup scenarios.
3. Homogenize the mixture using high-shear mechanical blending for 30 seconds to initiate the emulsion.
4. Observe the emulsion over a 5-minute static period, rigorously monitoring the meniscus for phase separation and coalescence behavior.
5. After 5 minutes, centrifuge the aqueous phase and analyze it to determine the concentration of any extractant lost or permanently distributed into the aqueous phase.

6.2.3 Surfactant Candidate Matrix

A broad and comprehensive matrix of 12 distinct surfactants, representing various chemical classes and hydrophilic-lipophilic balances (HLB), was evaluated using this rapid screening method:

- Nonionic (Linear Ethylene Oxide / EO Groups): SF-3, SF-4, SF-5, SF-6
- Nonionic (Branched Alkyl Chains with EO Groups): SF-7 (EO=3), SF-8 (EO=5)
- Nonionic (Aromatic Nonylphenol / NP Groups): SF-9 (EO=6), SF-10 (EO=11)
- Anionic: Alkyl sulfonate (sulfonate), Alkyl sulfate (sulfate)
- Cationic: SF-11
- Amphoteric (Zwitterionic): SF-2

6.3 Visual Phase-Separation Analysis and Emulsion Down-Selection

Purpose: To critically evaluate the stability of the formulated emulsions and identify the optimal surfactant candidates based on specific phase-ratio operating conditions.

Figure 13 displays the visual phase-separation behavior of a selected pool of surfactant candidates after 5 minutes of static settling. We summarize the observations regarding HLB values and volume fractions as follows:

- Anionic and Aromatic Behavior: Candidates from the aromatic classes (e.g., SF-9, SF-10) and high EO nonionic surfactants (e.g., SF-6) exhibited rapid phase separation. Anionic surfactants (e.g., sulfonate and sulfate)

showed relatively good short-term visual dispersion in the 5-minute screen; however, follow-on extraction/stripping tests indicated incompatibility with the high-salinity brine/extractant system, including poor phase clarity and formation of gel-like or precipitated material. Accordingly, they were not carried forward.

- Low Extractant Volume (10-20%): At lower organic fractions, a slightly higher HLB is required to stabilize the dispersed extractant in the large continuous aqueous phase. Under these conditions, SF-5 demonstrated the highest relative performance, significantly delaying coalescence compared to other candidates.
- High Extractant Volume (~50%): At high organic fractions, the stabilization requirement shifts, demanding a more lipophilic surfactant to stabilize the crowded extractant interface. Under these conditions, the lower-HLB SF-3 emerged as the optimal candidate.

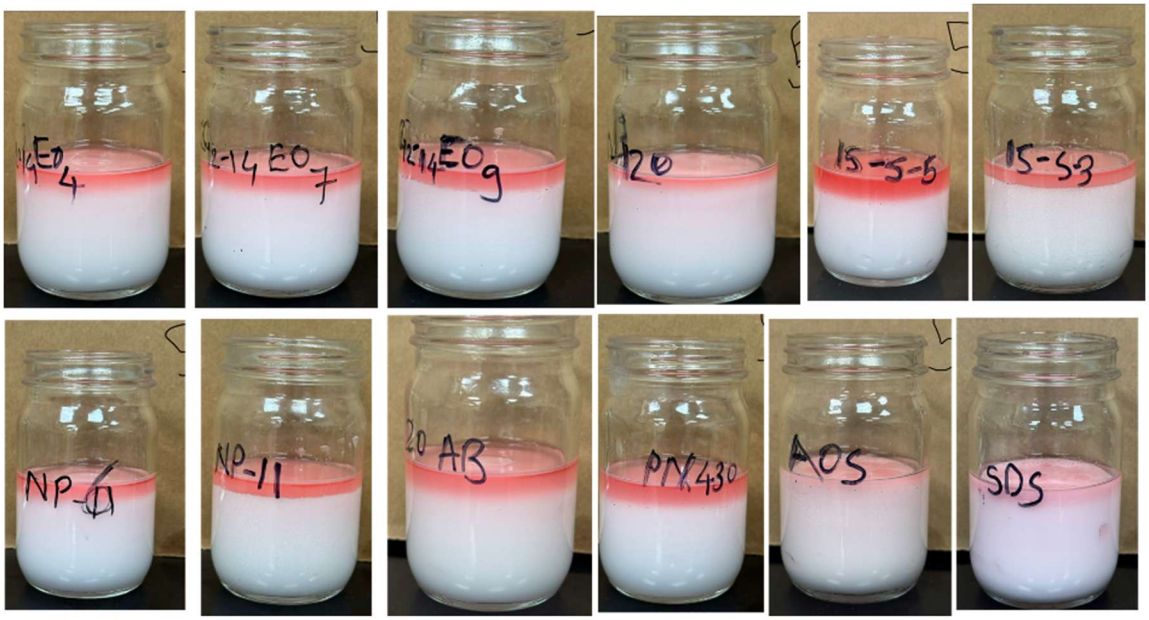


Figure 13. 5-Minute static emulsion stability screening test. Visual phase-separation comparison of 12 surfactant candidates (30 ppm dosage) evaluated at 20% extractant volume fraction. The samples are arranged as follows: Top Row (Left to Right): SF-3, SF-4, SF-5, SF-6, SF-8, SF-7. Bottom Row (Left to Right): SF-9, SF-10, SF-2, SF-11, sulfonate, sulfate

As can be seen from the images, the most stable dispersions at 20% extractant volume fraction were observed for the following surfactants:

- SF-5
- sulfonate
- sulfate

Among the three surfactants, sulfonate was selected for preliminary batch testing. During the batch extraction, the emulsion performed as expected, achieving nearly 98% Zn extraction. However, in the stripping step, when the extractant was separated and treated with deionized water, the extractant (oil) phase was not clear as shown in Figure 14. This suggests that the surfactant interacted unfavorably with the brine matrix, resulting in the formation of a precipitate or gel-like phase.

This behavior is likely due to the anionic nature of the surfactant, which can interact adversely with cationic species present in the brine. Consequently, a non-anionic surfactant was selected for subsequent experiments to improve emulsion stability.

Figure 14. Visual representation of batch extraction and stripping using sulfonate surfactant-based emulsion

Among the non-ionic surfactants, SF-3, SF-4, and SF-5 were selected for further evaluation. The extractant concentration in the emulsion was varied (2.5%, 5%, 10%, and 20%) to assess the stability of these non-ionic surfactant–stabilized emulsions at different concentrations. Figure 15 and Figure 16 show the visual phase-separation comparison at extractant concentrations of 20% and 10%, respectively. It appears that at 10% and 20% extractant concentrations, SF-5 performed better than the other surfactants.

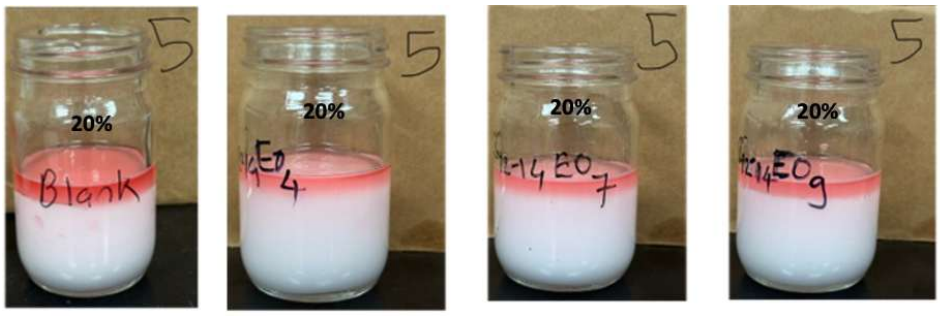


Figure 15. 5-Minute static emulsion stability screening test for 20% extractant concentration. Visual phase-separation comparison of non-ionic surfactants from left to right blank (water), SF-3, SF-4 and SF-5.

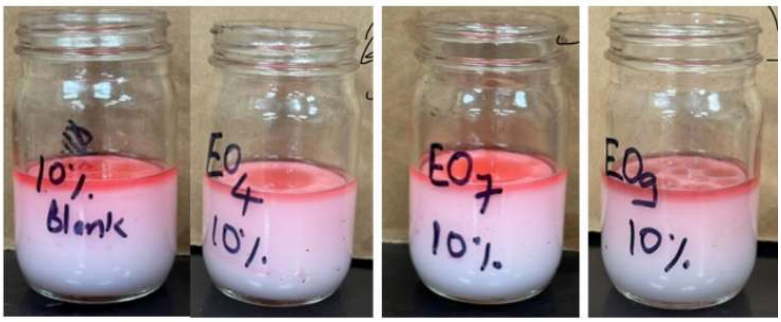


Figure 16. 5-Minute static emulsion stability screening test for 10% extractant concentration. Visual phase-separation comparison of non-ionic surfactant from left to right blank (water), SF-3, SF-4 and SF-5.

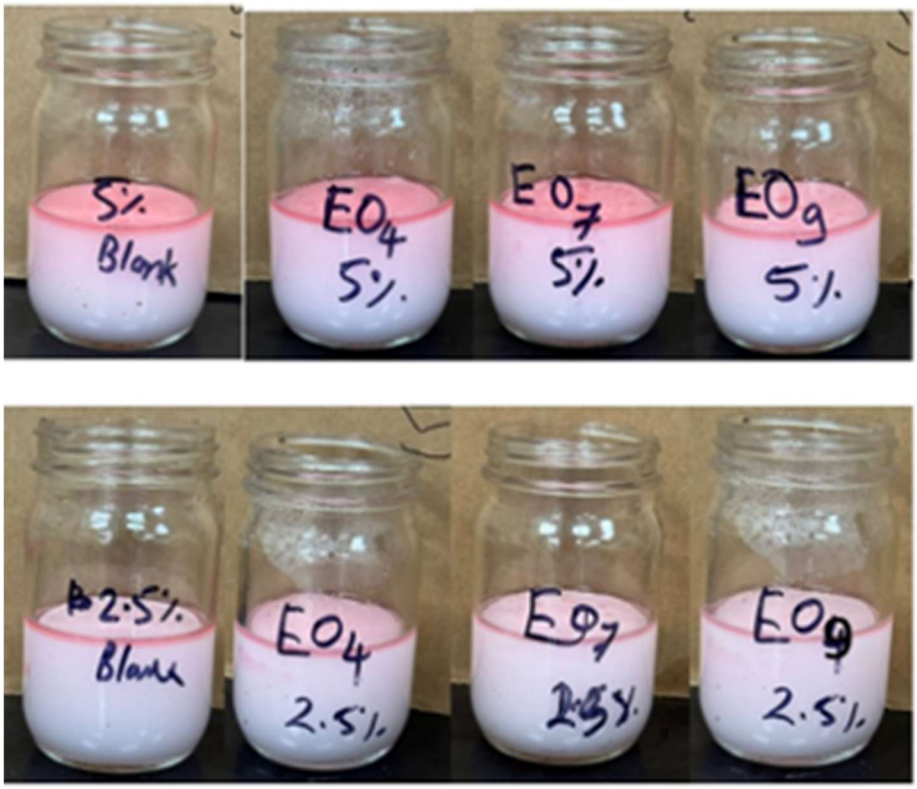


Figure 17. 5-Minute static emulsion stability screening test for 5% and 2.5% extractant concentration. Visual phase-separation comparison of non-ionic surfactants from left to right blank (water), SF-3, SF-4 and SF-5.

Visual inspection from Figure 17 indicates that at 2.5% and 5% extractant concentrations, all the surfactants behave similarly to the blank. This suggests that at these low concentrations, the surfactants do not significantly contribute to emulsion stabilization.

Based on the nonionic screening results, SF-3 showed the best performance across all extractant concentrations. This suggests that surfactants with lower EO numbers may provide better emulsion stability. Accordingly, SF-3 was selected as the surfactant for subsequent experiments.

Surfactant Recommendation: Based on these results, the selection of the optimal surfactant is conditionally dependent on the continuous column's designed organic holdup. SF-5 is recommended for low-holdup operation, while SF-3 is recommended for high-holdup operation. While these specific reagents do not provide absolute static stability (exhibiting partial phase separation over time), their interfacial activity may provide sufficient dynamic stabilization under

continuous mixing conditions, which may be highly effective under the continuous mixing conditions of the Task 3 apparatus.

6.4 Mechanical Dispersion Evaluation (Surfactant Free Alternative)

Purpose: To evaluate a parallel, purely mechanical methodology for overcoming bulk viscosity limitations without the use of any chemical emulsifiers.

While maintaining an open pathway for the SF-3/SF-5 emulsion strategy, the team simultaneously evaluated the use of 100% neat NE-1 with no surfactant whatsoever. To overcome the high bulk viscosity of the neat extractant, the team optimized the mechanical delivery system by fine-tuning gas sparging rates and frit porosities to generate a high-intensity bubble dispersion.

In dynamic column experiments, this purely mechanical dispersion of neat, surfactant-free NE-1 proved to be highly effective. Enhanced bubble dispersion and mixing mitigated the viscosity-related mass-transfer limitations, yielding excellent zinc extraction rates that equaled or exceeded those achieved with surfactant-stabilized emulsions under the conditions tested.

7. Verification Conclusions and Future Work

Purpose: To summarize the key findings of the Task 2 verification phase and clearly outline the strategic engineering pathways moving forward into the Task 3 continuous-column design phase.

7.1 Extractant Selection

Purpose: To formally state the verified extractant candidate and reaffirm the project's commitment to a sustainable, diluent-free chemical extraction process.

Following extensive speciation modeling, batch extraction screening, and field brine validation, the neutral extractant NE-1 is formally selected as the leading chemical candidate. It demonstrates high Zn extraction performance and feasible stripping under the extreme chloride concentrations of the Salton Sea geothermal matrix. Crucially, it is technically possible to deploy NE-1 in a 100% neat, diluent-free configuration to eliminate the use of toxic organic solvents, thereby fulfilling the CEC’s mandate for a sustainable, reduced-waste process.

7.2 Surfactant Selection as Brine Foaming Agent

Purpose: To document the initial evaluation of surfactants intended for bulk foam generation and explain why this conventional approach was deemed unsuitable for this specific brine matrix.

The project initially investigated standard foaming surfactants (e.g., SF-2, alkyl phosphate) to operate a conventional foam fractionation process. However, verification testing demonstrated that these traditional foaming agents are unsuitable for the highly saline Salton Sea proxy brines under the conditions tested. These candidates exhibited chemical incompatibility with NE-1, a lack of Zn/Mn selectivity, or severe adverse physical reactions-specifically, the anionics precipitated to form dense gels and filter cakes upon contact with the brine; for example, some anionic surfactants formed precipitates/gel-like residues in the high-ionic strength brine. Consequently, the strategy of utilizing surfactants as bulk "brine foaming agents" was de-emphasized in favor of alternative contacting strategies.

7.3 Surfactant Selection for Low-Viscosity Extractant Emulsions (Pathway A)

Purpose: To outline the first viable engineering pathway for Task 3, utilizing targeted nonionic surfactants as emulsifiers to mitigate the high bulk viscosity of the diluent-free extractant.

Shifting away from bulk foaming, the team repurposed surfactants to act strictly as emulsifiers aimed at lowering the effective viscosity of neat NE-1. Through comprehensive screening, specific moderate-to-low HLB nonionic alcohol ethoxylates were identified as leading candidates for this pathway. Testing indicated that the ideal surfactant is dynamically linked to the column's organic holdup volume: SF-5 is preferred for low organic holdup (0-20%), while SF-3 non-ionic surfactant (either linear or branched) is preferred for high organic holdup (~50%). While these surfactants exhibit transient static separation, their interfacial activity may provide sufficient dynamic stabilization for continuous column extraction.

7.4 Surfactant-Free Mechanical Dispersion (Pathway B)

Purpose: To present an alternative, purely physical engineering pathway for Task 3, relying entirely on mechanical shear to overcome viscosity without the use of any chemical additives.

In parallel with the emulsion pathway, the team evaluated a completely surfactant-free methodology. This pathway utilizes 100% neat NE-1 with zero chemical additives. It relies entirely on an optimized mechanical delivery system-specifically, specialized frit porosities and high-energy gas sparging-to overcome the bulk extractant viscosity. By generating a high-intensity bubble dispersion via intense cavitation, this purely mechanical approach successfully matched or exceeded the extraction kinetics of the surfactant-stabilized emulsions under the conditions tested.

7.5 Operational Dynamics and Task 3 Objectives

Purpose: To explicitly define the thermodynamic and operational dynamics of the selected diluent-free methods, establishing the primary engineering challenges that must be resolved during the Task 3 apparatus design.

The formal selection of a diluent-free extraction system-whether operated via pathway A (emulsion) or pathway B (surfactant-free)-requires optimizing three interconnected operational dynamics compared to traditional solvent-based extraction baselines:

1. Reduced Selectivity: Operating with 100% neat NE-1 can reduce Zn selectivity against competing trace ions (e.g., Mn).
2. Overall Extraction Kinetics: Eliminating the organic diluent drastically increases the bulk viscosity of the organic phase, which inherently limits mass transfer rates. While this is successfully mitigated by either transient emulsification or high-energy mechanical shear, the overall extraction kinetics must be carefully balanced against extractant injection and gas rate.
3. Increased Stripping Demand: The highly concentrated nature of the loaded neat extractant requires a significantly higher volume of aqueous stripping solution to completely reverse the complexation and recover the zinc.

Conclusion: The Task 2 verification phase is now complete. Moving into Task 3 (Design, Construct, and Lab Test), engineering efforts will focus on evaluating both pathway A and pathway B within a semi-continuous column prototype. The primary objective of the Task 3 design will be to physically and dynamically manage these operational dynamics-specifically, optimizing bubble size, reaction time, and injection rates to recover selectivity, while tuning phase holdup and evaluating the extractant mixture (comparing surfactant-assisted versus surfactant-free operation) to maximize overall extraction kinetics.