



**NM WRRI Student Water Research Grant
Final Report**

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1. Student Researcher: Lin Chen (New Mexico State University)
Faculty Advisors: Dr. Frank Ramos (Department of Geological Sciences, NMSU)
Dr. Pei Xu (Department of Civil Engineering, NMSU)
2. Project title: Recovery of Rare Earth Elements and Potable Water from Produced Water
3. Description of research problem and research objectives.

Produced water (PW) is the largest waste stream generated during oil and gas production. PW is primarily composed of formation water and its composition is complex and varies considerably depending on geographic location of the field and the extraction method. In some PW, rare earth elements (REEs) such as lanthanum (La), neodymium (Nd), and europium (Eu), have been detected at concentrations that have potential economic profits. Energy-efficient treatment of PW for clean water generation and for recovery of critical materials, including REEs, provides an environmentally responsible and economically attractive solution to addressing the challenges of water scarcity, reducing the cost of PW disposal, and producing strategic mineral commodities.

The overarching goal of the study is to develop an energy-efficient and low-cost treatment system to produce clean water while optimizing the extraction of REEs from PW collected from the Permian Basin. Specific tasks include: **(1) production of clean water with high quality:** development of a bench-scale high-performance, solar driven distillation system (a single basin single slope solar still, SSSS) for generation of water meeting drinking water standards with total dissolved solids (TDS) no greater than 500 mg/L; **(2) recovery of REEs (La, Nd, Eu) in the PW brine concentrated in the SSSS:** a bench-scale, multi-stage separation and extraction system was built to treat the retentate stream (concentrated brine PW) from the SSSS to evaluate system performance. The clean water quality and purity of recovered REEs (La, Nd, Eu) were characterized.

4. Description of methodology employed.

Task 1. Clean water production. A single basin, single slope (SSSS), transparent solar still driven by solar radiation was used to treat the raw PW collected from the Permian Basin for generation of high-quality clean water. A stainless-steel metal basin was fabricated for solar light absorption and acting as anti-corrosion material for PW treatment. Vapor was generated due to heat from absorbance of solar light by the metal basin and condensed at the inside surface of the glass cover. Clean water of high quality was collected through a trough connected to a product water tank. To enhance the productivity of solar distillation, a Fresnel lens was used to improve energy input to the bulk water and for higher clean water output. The desalination process also concentrated the REEs in the PW, which further facilitated REE extraction and separation in Task 2.

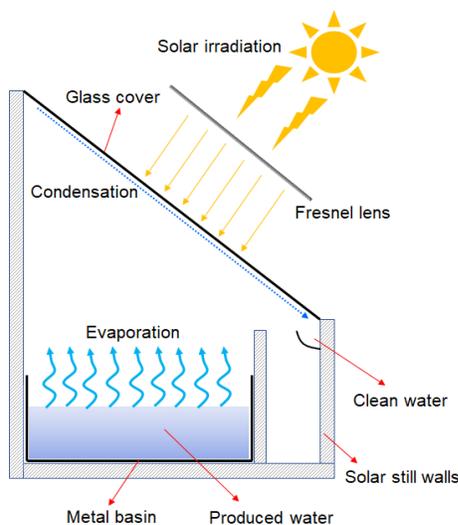


Figure 1. Schematic diagram of SSSS

Task 2. Multistage extraction and separation of REEs. A bench-scale system was built, and laboratory experiments were conducted under controlled conditions. First, a highly stable phosphorus based chelating extractant CYANEX[®]572 (Solvay, Belgian) was used for extracting REEs from the PW concentrate. CYANEX[®]572 was proven to be effective for extraction of REEs at higher pH conditions with less acid requirement as compared to other chelating agents. For example, a minimal extraction of 70% of La, Nd, and Eu requires an optimal pH of 2.35 (equilibrium pH of the raffinate after solvent extraction) with acid savings of 45.2%, 35.5%, and 29.3% for stripping of La, Nd, and Eu, respectively. A 6M hydrochloric acid (HCl) solution was

used for stripping REEs from the organic phase followed by cation exchange chromatography to remove unwanted cations such as Ca^{2+} , Mg^{2+} , and Fe^{3+} in the PW. Separation of individual REEs in the acid phase was conducted using highly selective di(2-ethylhexyl) orthophosphoric acid (HDEHP). Elemental contents were analyzed by inductively coupled optical emission spectrometry (ICP-OES).

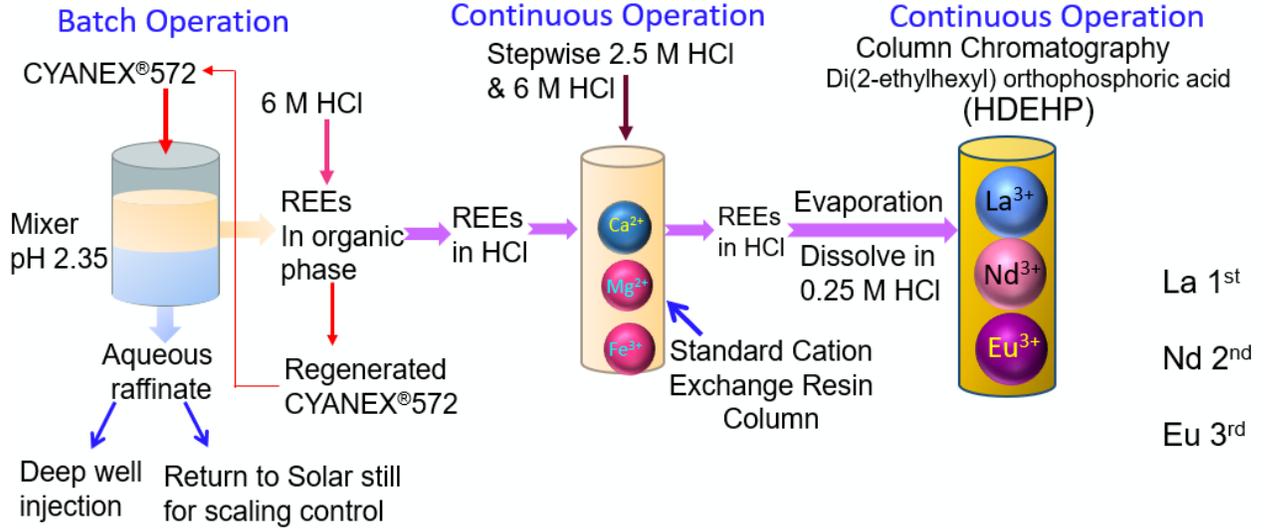


Figure 2. Schematic diagram of REE extraction and recovery process

CYANEX[®]572 is a mixture of extraction reagent consisting of phosphonic acid ester, organophosphorus compound, and 2,4,4-Trimethylpentene and manufactured by Solvay, Belgian. CYANEX[®]572 is a commercial phosphorus-based chelating extractant for solvent extraction, isolation, and selective recovery of individual REEs. Typically, CYANEX[®]572 is considered a mixture of equivalent amounts of phosphonic acid and phosphinic acid. The reaction between REEs and CYANEX[®]572 is described below (Eq. (1)) [1]:



where Ln^{3+} denotes any REEs, A denotes organic anions, and the overscoring symbol represents the species present in an organic phase.

Figure 3 shows the process for sample preparation and analysis of the REEs concentration in the precipitant. Figure 4 shows the process for extraction of REEs from feed wastewater containing REEs.

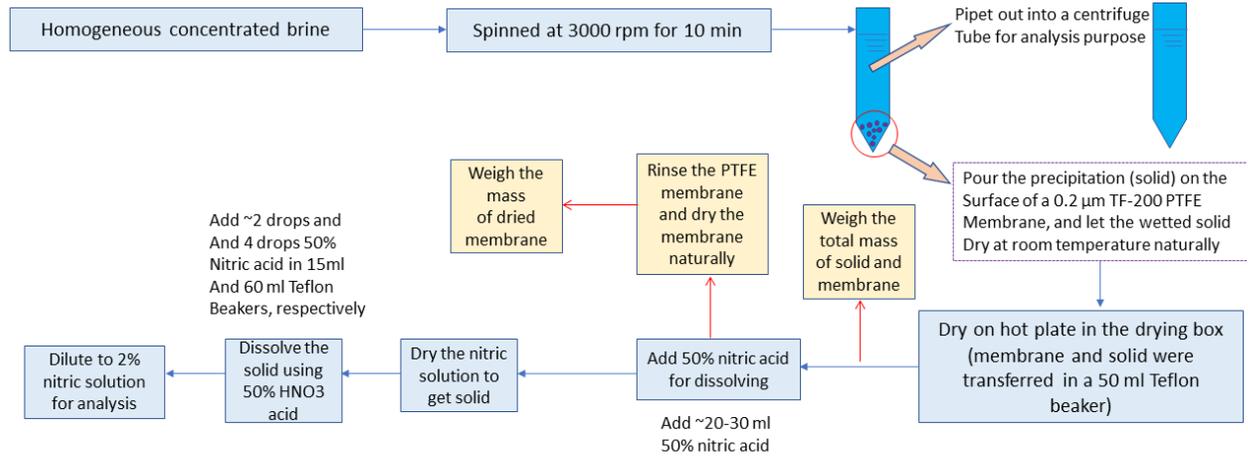


Figure 3. Flowchart showing preparation of solid samples from the concentrated brine after solar distillation

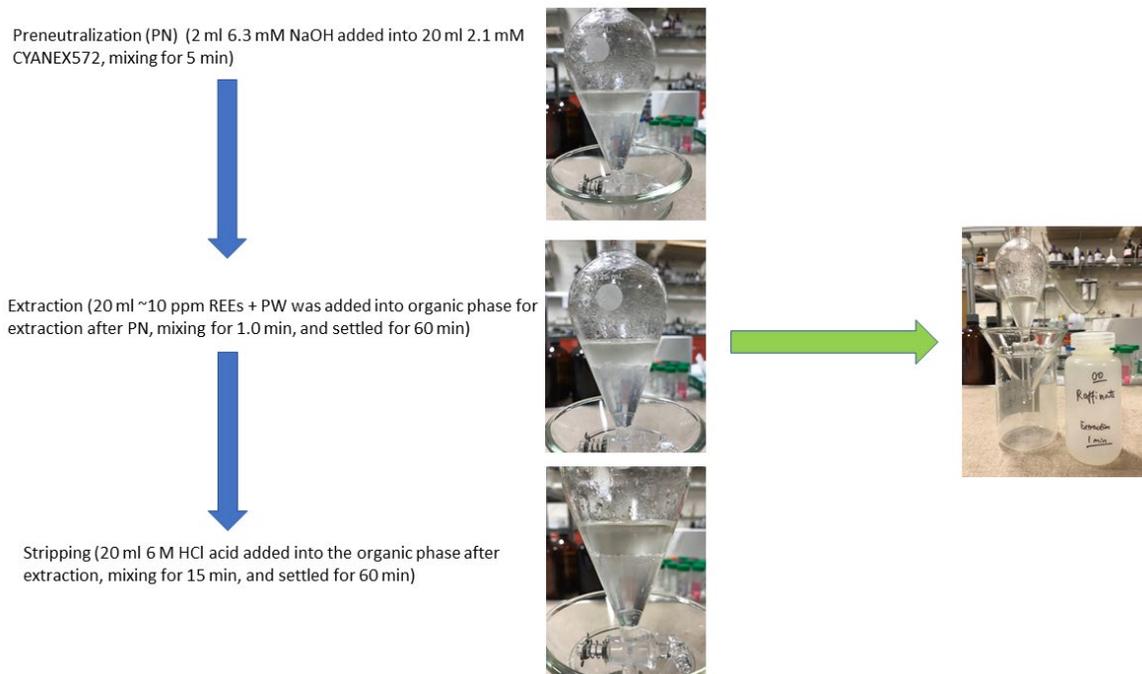


Figure 4. Flowchart and pictures showing process of extraction of REEs using CYANEX572 and stripping using HCl acid. The volume ratio of REE rich produced water to CYANEX®572 is 1:1.

Calculation methods.

Clean water recovery was calculated using Eq. (2).

$$\text{Clean water recovery, } r = \frac{V_p}{V_f} \quad (2)$$

where V_p and V_f are the volumes of product clean water collected in the SSSS and feed produced water volume, respectively.

REE recovery (%) was calculated using Eq. (3).

$$\text{REE recovery} = 100 \times \frac{C_{str}}{C_f} \% \quad (3)$$

where C_{str} and C_f represent concentrations of REEs in the aqueous phase after 6M HCl stripping from the organic phase and in the feed water samples, respectively.

5. Description of results; include findings, conclusions, and recommendations for further research.

(1) Findings

(i) Clean water recovery

Figure 5 shows the time course of clean product water recovery and clean water daily output during the outdoor experiments (in August 2020) using the SSSS. Volume of feed PW for solar distillation is 1,000 ml in each run. Experiments stopped when salt precipitation was observed. Clean water recoveries were between 12.8% - 14.9% under outdoor solar evaporation of feed PW. Due to high salinity and other constituents in the feed produced water, water vapor partial pressure was suppressed and daily distillation slowed down. In addition, the distillation almost stopped completely after the 4th day of each run.

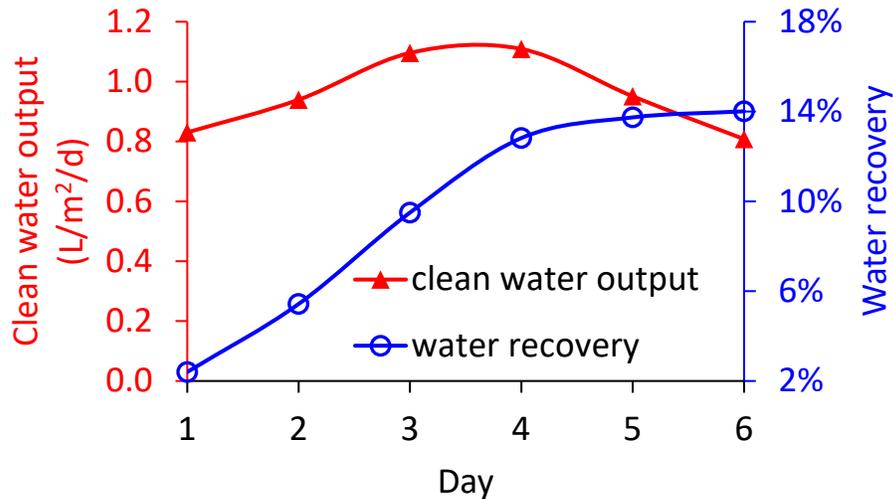


Figure 5. Time course of daily clean water output and water recovery during outdoor experiments using SSSS.

(ii) Clean water quality

We used the water quality analysis of actual produced water to evaluate the clean water production from solar still. The TDS of feed PW reduced from $144,703 \pm 2,314$ mg/L to 28.2 ± 2.7 mg/L in distillate water, which meets the USEPA requirement of 500 mg/L TDS concentration of secondary drinking water standards.

Table 1 *Elements Concentrations of Feed Produced Water and Clean Water Samples*

Analyte	Concentration		Removal Efficiency	US EPA drinking water standards		Meeting standards (Yes= \checkmark , No= \times)
	Clean Water	Produced Water		Primary	Secondary	
	$\mu\text{g/L}$	mg/L	%	mg/L	mg/L	
Li	743.4 \pm 22	18.8 \pm 0.3	96.05			
Be	0.03 \pm 0.02	0.02 \pm 0.0	99.85	0.004		\checkmark
B	511 \pm 4.2	122.3 \pm 19.1	99.58			
Na	1226.3 \pm 20.6	42720 \pm 2093	99.99			
Mg	39.5 \pm 1.6	727 \pm 54	99.99			
Al	1.47 \pm 0.06	4.7 \pm 0.1	99.97		0.05-0.2	\checkmark
Si	3805.7 \pm 7.5	179.3 \pm 29.3	97.88			
P	7.5 \pm 0.0	82.9 \pm 0.4	99.99			
K	401 \pm 5.2	901.6 \pm 4.5	99.95			
Ca	144.9 \pm 1.1	2674 \pm 11	99.99			
V	0.11 \pm 0.03	4.16 \pm 0.01	99.99			
Cr	1.11 \pm 0.05	0.25 \pm 0.08	99.56	0.1(total)		\checkmark
Mn	0.15 \pm 0.03	2.91 \pm 2.22	99.99		0.05	\checkmark
Fe	ND	11 \pm 9	>99.99		0.3	\checkmark
Co	0.03 \pm 0.01	0.11 \pm 0.00	99.97			
Ni	ND	0.85 \pm 0.07	>99.99			
Cu	0.86 \pm 0.02	0.54 \pm 0.14	99.84	action level 1.3	1	\checkmark
Zn	0.62 \pm 0.03	1.26 \pm 0.01	99.95		5	\checkmark
As	2.19 \pm 0.09	0.68 \pm 0.01	99.68	0.01		\checkmark
Se	1.25 \pm 0.25	28.1 \pm 1.1	99.99	0.05		\checkmark
Sr	6.14 \pm 0.14	418.2 \pm 0.3	99.99			
Mo	165.4 \pm 7.12	50 \pm 43.4	99.67			
Ag	0.01 \pm 0.01	0.01 \pm 0.01	99.9		0.1	\checkmark
Cd	ND	ND	/	0.005		\checkmark
Sn	400.8 \pm 4.3	177.5 \pm 26.2	99.77			
Ba	0.135 \pm 0.005	1.79 \pm 0.02	99.99	2		\checkmark
Tb	ND	ND	/			
Pb	0.015 \pm 0.005	0.07 \pm 0.00	99.98	action level 0.015		\checkmark

ND: Not Detected

To further investigate the removal of heavy metals and other constituents of concern in produced water, the collected purified water sample and the raw produced water sample were analyzed by ICP-OES (Table 1). The removal efficiency of each constituent was greater than 96%. Cd was not detectable in both samples, and Ni and Fe were not detectable in the purified water. The highest removal efficiency of 99.99% was achieved for Na, Mg, P, Ca, V, Mn, Fe, Ni, Se, and Sr.



Figure 6. Picture showing of salts precipitated in the metal basin during solar distillation

(iii) preliminary baseline testing of extraction of REEs from pure water using CYANEX®572

We first conducted optimization experiments for determining the pre-neutralization time (PN) and extraction time for REEs extraction and recovery (Fig. 7). Different pre-neutralization times of 1, 5, 10, and 20 minutes were applied for optimization of PN. Extraction time was kept the same as 10 min during PN optimization experiments. To investigate the composition of water matrix on extraction efficiencies of REEs, we first used pure water spiked with certain amounts of La, Nd, and Eu as the feed water for the baseline experiments. Measured Eu, La, and Nd in the pure water were 9.1, 10.1, and 8.8 mg/L.

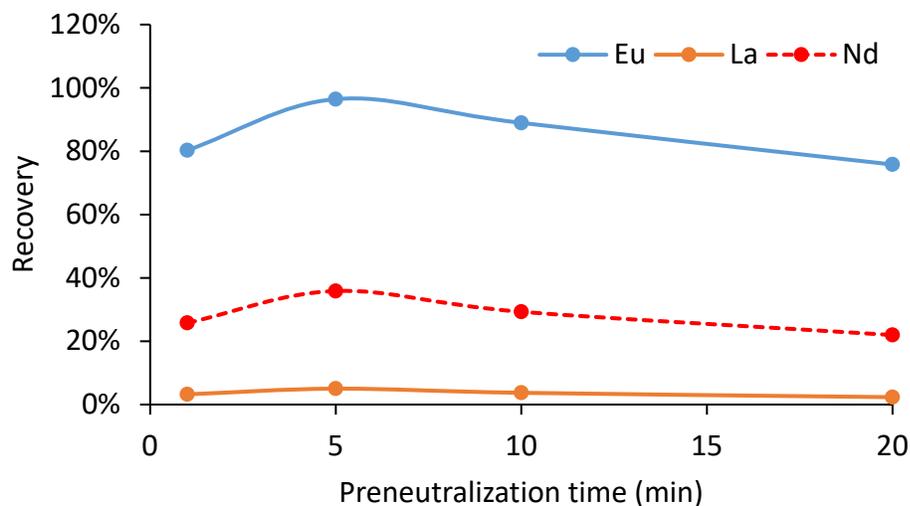


Figure 7. Optimization of pre-neutralization times using CYANEX[®]572

Recoveries of Eu, La, and Nd for PN times of 1, 5, 10, and 20 minutes were 80.3%, 3.2%, and 25.8% (1-min); 96.5%, 5%, and 35.9% (5-min); 89%, 3.7%, and 29.3% (10-min); and 75.8%, 2.3%, and 22% (20-min). The optimal preneutralization time for each REE was about 5-min, and was applied for all the subsequent experiments. Recoveries of each REE decreased slightly with increasing preneutralization time when it was above 5 min.

Before REE extraction, preneutralization was applied using 6.3 mM NaOH to CYANEX572 at an organic to aqueous volume ratio of 10:1 (O:A). Pure water spiked with REEs was then added into the separation funnel at an O:A ratio of 1:1 for various extraction times of 1, 5, 10, 20, and 30 minutes for optimization followed by stripping using 6 M HCl acid (organic phase : HCl acid volume ratio is equal to 1:1 as well). Concentrations of each REE in the aqueous phase (6M HCl solution) was analyzed using ICP-OES for calculating recovery efficiencies (Fig. 8).

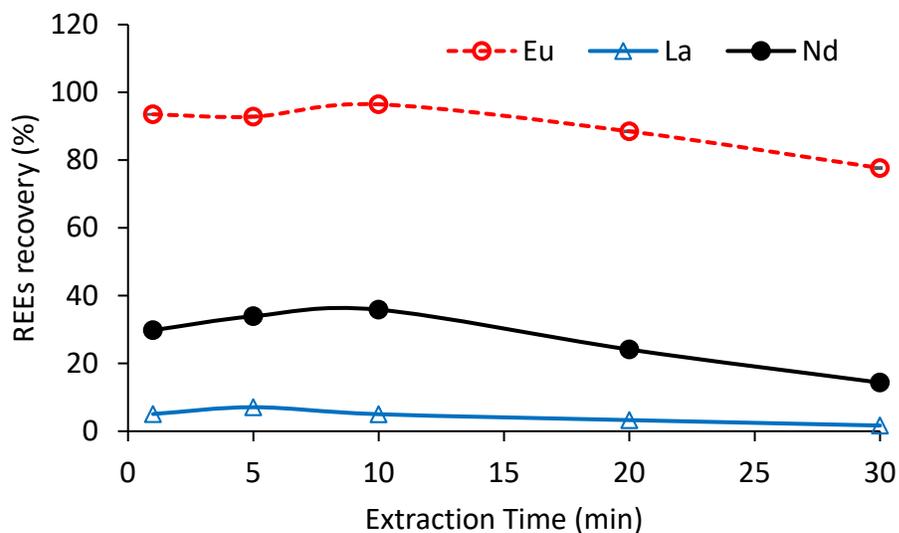


Figure 8. Optimization of extraction time using CYANEX[®]572

Recovery of each REE increased with increasing extraction reaction time. Maximum recovery of Eu, La, and Nd were 96.5%, 7.1%, and 35.9%, respectively. Extraction times greater than 10 minutes led to decreased recovery rates of each REE. Optimal extraction for Eu and Nd was 10 minutes, while 5-minutes was optimal for recovery of La. However, a recovery of 5.0% for La was achieved at extraction time of 10 minutes. To simplify the experiments, we selected 10-minutes as the extraction time for all REEs during the following experiments.

To confirm the lowest recovery of La, we prepared a solution spiked only La into pure water. Recoveries of La at extraction times of 1, 5, 10, 20, and 30 minutes were 3.74%, 21.49%, 21.53%, 22.40%, and 19.26%, respectively. Maximum recovery of 22.4% was achieved at an extraction time of 20 minutes. However, the peak value of La recovery was a little bit higher than the comparable recovery rates of 21.49% for 5 minutes and 21.53% for 10 minutes. It is worth noting that La recovery from the solution without Eu and Nd was higher than that in the cases of co-existing with Eu and Nd (Fig. 8). Therefore, the presence of Eu and Nd resulted in adverse effect on the recovery of La.

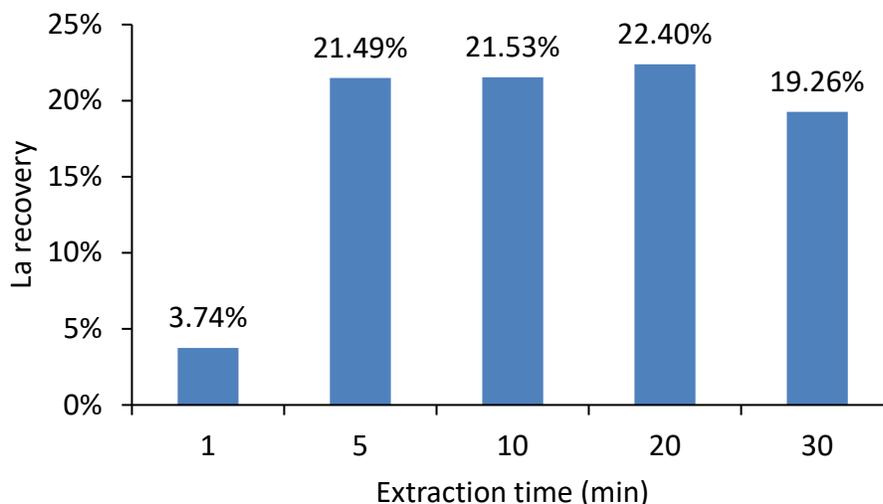


Figure 9. La recovery vs. extraction time without Eu and Nd using CYANEX®572

To investigate the stripping time effect for the REE recoveries, we conducted a series of experiments at various stripping times of 1, 5, 10, 15, and 30 minutes with the same concentration of 6M HCl for the experiments (Fig. 10). Recoveries of Eu for stripping times of 1, 5, 10, 15, and 30 minutes were 41.5%, 63.8%, 74.1%, 96.5%, and 89.5%, respectively. Recoveries of La for stripping times of 1, 5, 10, 15, and 30 minutes were 5.9%, 3.8%, 4.1%, 5.0%, and 3.5%, respectively. Recoveries of Nd for stripping times of 1, 5, 10, 15, and 30 minutes were 19.5%, 22.9%, 23.7%, 35.9%, and 28.4%, respectively. Clearly, recovery rates increase with increasing stripping times from 1 to 15 minutes and then decreased with a stripping time of 30 minutes for both Eu and Nd. However, recovery of La did not present the same trend. Maximum recovery of La was 5.9% at a stripping time of 1 minutes. To simplify our research, we chose a stripping time of 15 minutes for subsequent experiments.

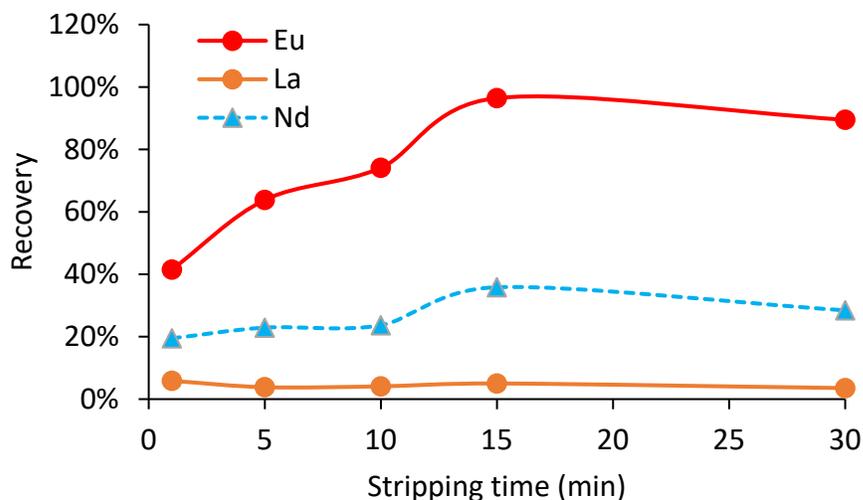


Figure 10. Optimization of stripping time using CYANEX®572

(iv) Extraction of REEs from actual produced water

Optimal reaction parameters obtained from the previous experiments were used for extraction of REEs from actual produced water, which was spiked with LaCl₃, NdCl₃ and EuCl₃. Preneutralization was also conducted for 5 minutes before extraction experiments. Results are shown in Figure 11. As expected, the highest recovery efficiency was achieved for Eu (~61.4%). However, recovery efficiency of Eu was much lower than that in the baseline experiments (using pure water spiked with REEs). Therefore, Eu had the maximum potential of extraction and recovery among the three rare earth elements evaluated.

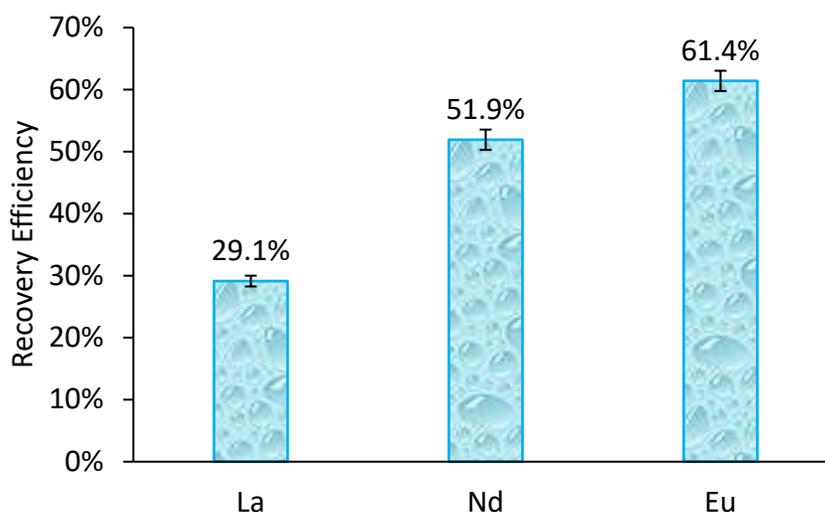


Figure 11. Extraction of La, Nd and Eu from actual produced water using CYANEX®572

(v) Separation of individual REEs from the REE extracted from PW

Individual REEs were separated from the combined REEs from the aqueous phase using standard cation exchange chromatography (Fig. 12) using stepwise 2.5M HCl followed by 6M HCl acid elution [2]. The REEs in the purified solution was then evaporated and re-dissolved using 7N nitric acid and dried followed by the addition of 0.25N HCl before being loaded to the HDEHP chromatography (Fig. 13) for separation and recovery of individual rare earth element.



Figure 12. Separation of REEs from PW concentrate using cation exchange chromatography (effective column length 7.75 inch and a cross-sectional area of 0.5 cm²).



Figure 13. Individual separation of La, Nd and Eu from the combined REE using HDEHP chromatography (white column).

To individually separate La, Nd and Eu with HDEHP chromatography, we collected four splits based on our previous separation and elution experiments: 1) early split (eluted using 0.25M HCl acid), 2) Nd split (eluted using 0.25M HCl), 3) late split (eluted using 0.4M HCl acid) and clean split (eluted using 6M HCl acid).

Table 2 shows the recovery ratio (amount of La, Nd and Eu divided by the corresponding amount of each from the loaded sample) of La, Nd and Eu in the REE split (separated using cation exchange chromatography). Eu has the highest recovery ratio of 77.5% followed by Nd of 76.6%. We demonstrate 77.5% of Eu and 76.6% of Nd can be separated and recovered without unwanted ions (such as Ca, Mg, etc) after cation exchange chromatography. Table 3 shows the individual separation results of each element after HDEHP chromatography. Eu was not detected in the early and Nd splits and mainly collected in the late (27.6%) and clean splits (43.6%). La and Nd were detected in all the four splits. The highest recovery ratio of 33% for La and 21.1% for Nd were achieved in the early split. Considering the late and clean sample, Eu can be recovered with an overall recovery ratio of 71.2% (from the late and clean splits) compared to the loaded sample.

Table 2 Recovery ratio of La, Nd and Eu after cation exchange chromatography

Elements	Recovery ratio
La	63.6%
Nd	76.6%
Eu	77.5%

Table 3 Recovery ratio of La, Nd and Eu after HDEHP chromatography

Samples	Elements	Recovery ratio	Samples	Elements	Recovery ratio
Early split	La	33%	Late split	La	2.6%
	Nd	21.1%		Nd	4.5%
	Eu	ND		Eu	27.6%
Nd split	La	1%	Clean split	La	1.3%
	Nd	20.6%		Nd	1.6%
	Eu	ND		Eu	43.6%

ND=Not Detected

(2) Conclusions

(i) Approximately 12.8~14.9% of clean water can be recovered from the produced water spiked with REEs during outdoor solar evaporation using SSSS in August 2020.

(ii) Removal efficiency of all metals in the distillate was higher than 96% while the highest removal efficiency of 99.99% was achieved for Na, Mg, P, Ca, V, Mn, Fe, Ni, Se, and Sr.

(iii) The bench-scale study demonstrated the highest recovery of Eu, La, and Nd were 96.5%, 5.0%, and 35.9% determined using spiked Eu, La, and Nd in pure water at optimal conditions (PN 5-min, extraction 10-min, and stripping 15-min), respectively.

(iv) REE recoveries increased with increasing extraction reaction time during baseline tests.

(v) Presence of Eu and Nd resulted in an adverse effect on the extraction and recovery of La.

(vi) The highest recovery efficiency of 61.4% was achieved for Eu in the actual produced water. Extraction efficiency of Eu in produced water was lower than that in baseline studies (pure water matrix).

(vii) The recovery ratios of Eu, Nd and La were 77.5%, 76.6% and 63.6% of the REEs separated using cation exchange chromatography.

(viii) A separation order of La > Nd > Eu is achieved using HDEHP chromatography. Eu can be separated and recovered at high purity in the late and clean splits and effectively separated from La and Nd. La and Nd, however, are not separated effectively from each other.

(3) Recommendation for further research

Future research should focus on improving the separation of individual REE using HDEHP chromatography to achieve higher purity. Individual separations of La, Nd and Eu using HDEHP chromatography needs to be refined to better separate La and Nd.

6. Provide a paragraph on who will benefit from your research results. Include any water agency that could use your results.

The research is at the forefront of produced water treatment, reuse, and resource recovery. The outcome of the research will benefit clean water challenged communities, desalination facilities, and other water-related industry to develop low-cost process for REEs recovery and clean water production.

7. Describe how you have spent your grant funds. Also provide your budget balance and how you will use any remaining funds. If you anticipate any funds remaining after May 15, 2021, please contact Carolina Mijares immediately. (575-646-7991; mijares@nmsu.edu)

The research fund was spent as planned and was used before May 15, 2021.

8. List presentations you have made related to the project.

I participated the 65th NM water conference (Oct. 2020) with e-poster presentation.

e-poster: Recovery of rare earth elements and potable water from produced water

9. List publications or reports, if any, that you are preparing. Remember to acknowledge the NM WRRRI funding in any presentation or report that you prepare.

None.

10. List any other students or faculty members who have assisted you with your project.

None.

11. Provide special recognition awards or notable achievements as a result of the research including any publicity such as newspaper articles, or similar.

- Lin Chen was the 2021 recipient of Colin Tyrie Scholarship awarded by the Produced Water Society for the research on produced water treatment and reuse.

12. Provide information on degree completion and future career plans. Funding for student grants comes from the New Mexico Legislature and legislators are interested in whether recipients of these grants go on to complete academic degrees and work in a water-related field in New Mexico or elsewhere.

Lin Chen is a PhD candidate in his 4th academic year. He will continue the work on desalination driven by solar thermal energy using membrane distillation after graduation in future.

References

- [1] Tunsu, C., Lapp, J.B., Ekberg, C. and Retegan, T., 2016. Selective separation of yttrium and europium using Cyanex 572 for applications in fluorescent lamp waste processing. *Hydrometallurgy*, 166, pp.98-106.
- [2] Diamond, R.M. and Whitney, D.C., 1966. Resin selectivity in dilute to concentrated aqueous solutions. *Ion exchange*, 1, pp.277-351.