Method Development For Preconcentration And Quantification Of Critical And Valuable Elements In Permian Basin Produced Waters

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METHOD DEVELOPMENT FOR PRECONCENTRATION AND QUANTIFICATION OF CRITICAL AND VALUABLE ELEMENTS IN PERMIAN BASIN PRODUCED WATERS

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METHOD DEVELOPMENT FOR PRECONCENTRATION AND QUANTIFICATION

OF CRITICAL AND VALUABLE ELEMENTS IN

PERMIAN BASIN PRODUCED WATERS

by

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Chapter 1: Introduction

Produced waters are the most voluminous oil and gas extraction waste product. In 2017, the United States generated ~24 billion barrels of produced waters with ~10 billion barrels alone from Texas oil and gas wells. Subsurface injection has dominated the produced water management strategy in the past and continues to do so today (Veil, 2020). However, over the last 15 years hydrocarbon production has primarily shifted to low permeability reservoirs in which wastewater cannot be re-injected. Consequently, produced water injection is increasingly focused into shallow salt water disposal zones (Scanlon et al., 2017). In some cases, these saltwater disposal zones have become over pressured leading to concerns about induced seismicity (Skoumal and Trugman, 2021) or have become drilling hazards (Lemons et al., 2019). Moreover, disposal of vast quantities of water in arid and semi-arid areas have led to calls to treat or utilize produced waters to offset local freshwater withdrawals (https://www.env.nm.gov/new-mexico-produced-water/wp-content/uploads/sites/16/2019/11). Thus, new produced waters management solutions which minimize injection volumes and increase produced water treatment and reuse are necessary. New treatment technologies and reuse options are being developed, but at costs much greater than current produced water disposal. Alternative means to defray higher produced water management costs could fundamentally rebalance water disposal and reuse paradigms in the Permian Basin and other oil and gas producing provinces.

Considering their high salinity, owing to extended residence time in the subsurface, produced waters from oil and gas reservoirs possibly embody a source of valuable mineral resources. For example, produced waters from the Permian Basin can be > 300 g/L total dissolved solids (TDS) compared to 35 g/L for bulk seawater (Figure 1). High salinity in large volumes of subsurface natural waters can create the opportunity for leaching of elements in the surrounding country rock and concentrating them in solution. Presently, bromine, calcium chloride, iodine, lithium, magnesium, and sodium chloride are commercially extracted from domestic subsurface brines (USGS National Minerals Information Center, 2020). This suggests that other minerals may
be present in economic concentrations in these high TDS waters, minerals herein referred to as Critical and Valuable Elements (CVEs). We define CVEs as including:

1) The Lanthanide Series (lanthanum, cerium, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium);
2) High Field Strength Elements (titanium, zirconium, hafnium, germanium, thorium, niobium, tantalum, arsenic, antimony, molybdenum, tungsten, uranium, selenium, tellurium);
3) Industrial Elements (iron, cobalt, nickel, copper, cadmium, lead, boron, gallium, thallium, vanadium, chromium, manganese);
4) Alkaline Elements (rubidium, cesium, beryllium, strontium, barium); and
5) Precious Metals (gold, silver, and the platinum group elements).

Still, methods to quantify these CVEs in basinal brines are poorly developed. These brines present a possible source of valuable mineral resources, which can be utilized to strengthen the domestic CVE supply chain. Currently the United States is import reliant for >80% of its CVEs (USGS, 2020).

Trace elements, lanthanides and other valuable mineral data concentrations are lacking for produced waters. The high TDS values for produced waters present a challenge for quantification via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). High TDS produced waters must be heavily diluted to compensate for the masking effect high salinity may cause. However, dilution alone can diminish the level of CVEs in solution and provide unreliable data when quantifying. This challenge can also be overcome by CVE preconcentration (McLing et al., 2014). To effectively quantify CVEs, techniques that address high salinity in natural waters and analytical interferences are required.

A national assessment of CVE mineral potential in Permian Basin produced waters was conducted by Ray (2016). She documented that magnesium and potassium tended to be the most valuable minerals, with samples exceeding > $2.00/barrel (BBL) in raw mineral value. Ray also noted a lack of trace metal concentration data availability, inferring that the value of CVEs in
produced waters is virtually unknown. A separate study conducted by Quillinan et al. (2019) analyzed REE concentrations in produced and geothermal waters across many U.S. basins including the Permian Basin. Economic analysis of the dataset, showed no samples appeared to be worth more than $0.01/BBL in terms of lanthanide value, compared to disposal costs of ~ $1/BBL or more. However, the number of produced waters samples analyzed was small (<125) with the majority coming from outside of the Permian Basin. Studies conducted by Daitch (2018), using the same data source as Ray (2016), showed that lithium is found to be valued at greater than $0.20/BBL in the Permian Basin. Currently, lithium is an element of great interest owing to the electric vehicle revolution, the emergence of new battery technologies and the overall need for the development of power storage technologies. These studies show that the economic potential of mineral commodities in produced waters exist but the lack of trace element data hinders an understanding of their CVE endowment.

![Figure 1](image.png)

**Figure 1.** Map of the Permian Basin showing major structural elements and total dissolved solids concentrations of produced waters. For reference, bulk seawater is approximately 35 g/L. Data from the USGS Produced Waters Data, version 2.3 (Blondes et al., 2018)
The ability to thermodynamically predict likely concentrations of CVEs in Permian Basin produced waters is hampered by their high salinity which requires Pitze type activity coefficients to accurately measure mineral saturation. However, Pitzer activity coefficients do not exist for the vast majority of minor and trace elements (Harvie et al., 1984). Similarly, a lack of reliable trace element data in pre-existing data sources necessitates the need for further data collection and direct measurement.

In this research I present a produced water specific method to quantify CVEs in samples from a range of reservoirs across the Permian Basin (supplied by Pioneer Natural Resources) using preconcentration followed by quantification via ICP-MS. Chelex-100 ion exchange resin, which is composed of paired iminodiacetic functional groups, was used for preconcentration and purification of CVEs. This resin has been well studied (Pai 1988a, 1988b, Strachen, 1989, Zhu, 2005) and is known for its capability to preferentially sorb multivalent ions as a function of pH (Figure 2). The carboxylic acid groups in the resin give it the ability to be a cation exchange resin. In neutral to low pH environments, Chelex-100 contains a positively charged amine group centered between the carboxyl groups. This positively charged amine may be capable of chelating small anions but is enclosed in the resin structure making this task difficult. From roughly 6 to 8 pH the paired carboxyl groups are negatively charged allowing the capture of metallic cations in solution. At pH 4 one of the carboxyl groups become protonated and below pH 3 both carboxyl functional groups have become protonated Figure 2.
Figure 2. Chelex-100 functional group structure as a function of pH (Source: Bio-Rad Laboratories).
Chapter 2: Summary of previous investigations on CVE preconcentration

Preconcentration methods for CVE specific to high salinity produced waters are not well developed or studied. However, many methods have been tested to preconcentrate CVEs in seawater utilizing ion exchange resins with ICP-MS quantification (Zhu et al., 2005; Rahmi et al., 2007; Sondergarard et al., 2015; Minami et al., 2015). While being less saline than brines, the two fluids are compositionally similar in terms of their relative ionic composition and exhibit related high-salt with organic matter matrix challenges. Most studies on CVE extraction from seawater have concentrated on the use of Chelex-100 resin, which is known for its preference to sorb multivalent cations from saline solutions (Pai, 1988a; 1988b; Rahmi et al., 2007). Other ion exchange resins, such as Dowex1-x8, have been investigated to sorb anions from seawater, such as the work of Fischer et al. (2018), who attempted to preconcentrate platinum and silver. These approaches are a reasonable starting place to develop brine specific methods, but largely have not been tested or adapted for saline solutions greatly exceeding bulk seawater TDS (~35g/L).

Quantifying trace amounts of CVEs in brines can be difficult because of high salinity. The presence of salt elements can cause salt precipitation and isobaric interferences with the analyte of interests Rapp et al. (2017) and TDS concentrations higher than 1 g/L can damage ICP-MS instruments. Dilution of brine samples to acceptable concentrations for direct ICP-MS analysis reduces sensitivity such that CVEs largely cannot be quantified (Simmons et al., 2019; Jubb et al., 2020). Consequently, preconcentration and matrix element removal are necessary prior to analysis. Idaho National Laboratory developed preconcentration procedures for lanthanides in brines (McLing et al., 2014 and Quillinan et al., 2018; both modified from the work of Strachan et al., 1989), where large volumes (~1-2 L) of produced water are preconcentrated using Chelex-100 ion exchange resin (16.25g) to reduce matrix effects and improve measurement sensitivity. They found that preconcentration of multivalent cations in saline solution was an effective method for
removing greater than 99% monovalent and divalent cations present as matrix elements. Pre-chromatographic preparation for these procedures consisted of converting the resin into its ammoniated form and treating the brines with ammonium acetate for pH amendment and maintenance. The removal of matrix elements increases the detection of CVEs while decreasing the formation of interfering oxides and lowering overall background interference. McLing et al. (2014) found that using sodium-form Chelex-100 resin in the 200-400 mesh size proved quite effective for accomplishing this task. Their method concentrated lanthanides by ~50-100 times while removing matrix ions, leading to less than 1 ng/L detection limits for nearly every lanthanide series element. McLing et al. (2014) and Quillinan et al. (2019) experiment resulted in a lanthanide capture efficiency exceeding 95% across the entire TDS range analyzed.

Despite this previous work, significant knowledge gaps exist regarding the ability of Chelex-100 resin to recover high (>90%) yield for a range of CVEs from brines. Further research is required to determine how CVE recovery varies as a function of pH, salinity, and major ion composition as well as interferences brought forth from occurring organic material and redox sensitive ions. With growing need for CVEs, this study can be a large step forward in assisting the United States in strengthening its domestic CVE supply chain while providing funding to subsidize more expensive produced water treatment and disposal practices.
Chapter 3: Thesis Objective

This thesis completes three primary tasks: 1) Documenting CVE yield from brines as a function of salinity, pH, water composition, and resin type using synthetic solution experiments; 2) quantify CVE concentrations and matrix spike yield in Permian Basin produced water samples; 3) utilize geochemical modeling software to interpret results and determine possibilities for poor yield.

1.) Testing CVE recovery from synthetic solutions: In contrast to seawater, which generally has a homogeneous bulk composition for most elements, Permian Basin produced waters exhibit a wide compositional range, particularly in terms of their Na/Ca ratio and salinity. CVE recovery from amended high purity Na-Ca-Cl solutions of differing Na/Ca ratios (5 to 50) and salinity (50-300 g/L TDS), were investigated. These ranged in Na/Ca composition and salinity are comparable to that of Permian Basin produced waters (Chaudhary et al., 2019). Preconcentration was conducted utilizing the Chelex-100 ion adsorption chelating resins using a modified method by Zhu et al. (2005). The solutions were adjusted to pH 4 and 6 to examine how these parameters affect element recovery, beyond variations in salinity and Na/Ca ratios of the solutions. Na and Ca mass recovery from Chelex-100 preconcentrated solutions were determined from ICP-OES. ICP-MS analyses of CVE spiked synthetic solution volumes were also investigated. The performance of this method was be used to determine parameters which proved most ideal for CVE quantification and yield. This allowed for us to properly determine initial conditions for analysis of produced water samples.

2.) CVE determination and yield of produced water samples: Utilizing information obtained from synthetic solution analyses, CVE concentrations and yield (using matrix spikes) were quantified for ~5 produced water samples from across the Permian Basin. Parameters which achieved maximum yields for the synthetic solutions were applied to
these samples. Prior to analysis, samples were exposed to ultraviolet light for 4 hours, in order to breakdown organic compounds that may interfere with ion exchange reactions and liberate organic-bound CVEs. A portion of the samples were adjusted with known concentrations of CVEs and their final yield after ICP-MS quantification was determined, as a means to evaluate method performance.

3.) **Revision of analytical methods:** Yields of CVEs displaying poor recovery in produced water samples were combined with pre-existing geochemical and water quality data so we may investigate causes of poor performance utilizing multivariate data analysis methods. Geochemical modeling of trace element speciation (using the MINTEQ thermodynamic database within the Visual MINTEQ graphical interface) was utilized to investigate possible mechanisms behind the poor yields. At this point additional pretreatment and/or modifications to the preconcentration and analysis procedures have been investigated.
Chapter 4: Method

The method utilized in this study is modified from a procedure for seawater preconcentration developed by Zhu et al. (2005). This method has been chosen because it requires relatively small volumes of resin (<1 ml) and sample (~50 ml) when compared to other methods, which can require sample volumes greater than 1 liter and resin volumes of 3 mL or more. This procedure focuses on testing CVE recovery from synthetic solutions created form high purity Na-Ca-Cl solutions containing minimal trace elements ranging from 50-300 g/L TDS amended with known CVE concentrations (10 μg/L). In this case, a miniature column is created by injecting ~250 μL of Chelex-100 resin into the tubing connecting two 0.45 μm syringe filters (Figure 3). This sealed column design minimizes contamination from other vessels and airborne particles because all fluids are pushed through the syringe filters by a syringe pump, preventing exposure of the sample and elution compounds to air. Zhu et al. (2005) examined transition metal recovery at pH values ranging from 2 to 9 and determined that a pH of 6 was optimal for recovery of the largest number of elements in seawater. Variables such as Ca/Na ratio variability, temperature, and salinity greater than 35 g/L were not explored by Zhu et al. (2005) and are investigated in these experiments. The method has not yet been tested on waters of extreme salinity (>35g/L), presenting an opportunity for investigation in this study.

The method depends heavily on the behavior of Chelex-100 resin, whose efficacy for chelation in saline waters is highly pH dependent. Because Chelex-100 contains weakly acidic functional groups, the pH of a column is often affected by the resin itself and may be changed during the sorption processes if an external buffer system is not used (Pai, 1988). When using this resin in its sodium, potassium, or ammonium forms it is advisable to incorporate an outside buffer to the system, most effectively acetates, to compensate for pH changes. In this method 1 molar ammonium acetate adjusted to pH 6 is employed to prevent pH change in the resin. We converted the Chelex-100 sodium form to ammonium form initially adjusted to pH 4 and 6 using 1 molar
ammonium acetate amended with hydrochloric acid. The change of the resin from sodium or hydrogen form to ammonium form, increases the resin volume and over all chelating capabilities.

Investigations completed in this research focus on two general types of experiments:
1) matrix recovery experiments to determine to what degree sodium and calcium (dominant cations in the sample matrix) appreciably sorb to the Chelex-100 resin and are eluted in the final sample; and 2) CVE matrix spike experiments documenting the recovery of CVEs from amended Na-Ca-Cl solutions and Permian Basin produced water samples, under a range of conditions. These experiments are discussed in great detail in the Results portion of this thesis.

The synthetic Na-Ca-Cl solutions, either Na-rich or Ca-rich, were created by amending high purity solutions (created by High Purity Standards, North Charleston, South Carolina) with known concentrations of CVEs (10 µg/L). The Na-rich (Na/Ca molar ratio of 50) solutions ranged over a salinity of 50 to 300 g/L TDS and the Ca-rich solution (Na/Ca ratio of 5) ranged from 50 to 150 g/L.

Both synthetic and spiked produced water samples were loaded on pre-cleaned Chelex-100 resin, washed, and eluted, as described below. The eluent was either analyzed directly or dried to completeness and brought up in 2% ultrapure nitric acid. Concentrations of the eluent were determined by Q-ICP-MS analysis and converted to units of µg/L in the initial sample volume. Comparison of starting mass versus measured mass was used to determine percent recovery of the matrix spike for the synthetic solutions. For produced water samples, the samples were run both spiked and unspiked and the mass difference between the two was used to determine element recovery. Recovery experiments are completed in triplicate to assess variability.
A generalized preconcentration procedure of Zhu et al., (2005) is as follows:

- 50 mL sample solutions were adjusted to a pH of 6 using ultrapure ammonium hydroxide and/or hydrochloric acid. pH was monitored using Sper Scientific Benchtop pH-mV meter.
- 0.25 mL of pre-treated Chelex-100 resin slurry stored in 1 molar ammonium acetate solution (pH adjusted to 6) was packed into mini columns (tubing connecting two 0.45 μm syringe filters) with pipettor. (Figure 3).
- 50 ml solutions were loaded onto resin in 60 ml BD syringes at a flowrate of 3 mL/ min using a Braintree Scientific BS-9000-8 Multi syringe pump.
- Sample matrix elements are washed from the resin by passing 8 ml of 1 molar ultrapure ammonium acetate and 5 ml of 18.2 MΩ/cm water, consecutively, through the column at a flow rate of 1 mL/min.
- Elements of interest are eluted from the Chelex-100 resin using 4 ml of 2 molar ultrapure nitric acid pumped at a flow rate of 0.5 mL/min and captured in a 7 mL Teflon vial, within a class 100 laminar flow hood.
• The eluted sample was then dried down at 80°C in a class 100 laminar flow hood and brought up in 5 mL of 2% ultrapure nitric acid, concentrating the sample by a factor of 10.

• Element concentrations were determined using a Thermo Scientific iCAP-Q-ICP-MS at the University of Texas at El Paso using the KED (collision cell) mode. The system was run in collision cell mode to minimize the effects of polyatomic species. $^{115}$Indium was used as an internal standard to improve the stability and performance of the instrument.
Chapter 5: Results

The results of this study have been portioned into separate sections, for organization and ease of reading. The first results displayed are focused on the matrix ion removal test which was conducted to ensure that matrix ions could be successfully removed from the solutions and the TDS of the aliquots decreased to a level safe for ICP-MS analysis. After the completion of matrix ion removal tests 2 synthetic solution tests are conducted to test percent recovery of CVEs. The first synthetic solution tests are conducted in a so-called Na-rich solution which is composed of Na/Ca molar ratio of 50, the second solution is a Ca-rich matrix with a Na/Ca ration of 5. These two synthetic solutions have been created to test the variability of matrix environments in Permian Basin produced waters. Following the synthetic solution tests an eluent volume efficiency test has been conducted to ensure that 4mL of eluent is sufficient for full CVE recovery. Results for produced water samples and considerations taken for organic compounds have been are discussed after the initial tests.

5.1.0. Matrix Ion Removal Test
To test the ability of this method to capture and remove matrix ions and diminish TDS values of samples prior to analyses, a matrix ion removal test was conducted. In this test the matrix wash portion of our method was tested for matrix cation removal efficiency. Synthetic solutions of varying Ca/Na ratios were created by dissolving solid calcium chloride, sodium chloride and ammonium acetate in 250 mL of de-ionized (DI) water. A so-called Na-rich 300 TDS solution was created by combining solid 2.74 g calcium chloride, 72.26 g sodium chloride, and 19.27 g ammonium acetate into 250 mL of deionized water. A so-called Ca-rich solution was created combining 20.62 g calcium chloride, 54.36 g sodium chloride, and 19.27 g ammonium acetate into 250 mL of deionized water. Both solutions were diluted to 50 mL samples of TDS values ranging of 50, 100, 200, and 300 g/L respectively. These samples were processed through chromatography and analyzed via ICP-OES.
Results showed the method was greatly effective removing sodium in both solutions (Na-rich and Ca-rich) even at concentrations of 300 g/L. Sodium recoveries were <0.1 mg/L in both solutions (Fig. 4). In the Na-rich solution, Ca was also effectively removed with the highest recovery being just over 0.2 mg/L, while in the Ca-rich solution, the recovery was well below 0.1 mg/L. This matrix ion removal demonstrated that Ca and Na were not retained on the chelating resin in appreciable quantities. Matrix ion removal decreased overall TDS to values <1g/L, an acceptable value for analyses via ICP-MS. Data displaying the ability of this method to remove matrix elements is displayed in Figure. 4.

![Figure 4](image-url)  
**Figure 4.** Results for matrix element removal using matrix washing method during column chemistry. Matrix wash for Na-rich and Ca-rich solutions are greatly effective. Matrix wash has removed mono and divalent cations to <1% Recovery, even in 300g/L TDS solutions.
5.2.0. Synthetic Na-rich Solution tests at pH 4 and pH 6

Na-rich (Na/Ca molar ratio of 50) solutions ranging 50-300 g/L TDS carrying very low quantities of trace elements (created by High Purity Standards, North Charleston, South Carolina) were spiked with 10 μg/L concentrations of a range of lanthanides, high field strength elements, industrial elements, Alkali and alkaline Earth elements, and precious metals, to quantify CVE recovery. The samples were loaded on pre-cleaned Chelex-100 resin, washed, and eluted, as described in the Methods portion of this thesis. The eluent was either analyzed directly or dried to completeness and brought up in 2% ultrapure HNO3. Concentrations of the eluent were determined by Q-ICP-MS analysis and converted to masses. Comparison of starting mass versus measured mass was used to determine percent recovery. Samples were created in triplicate to assess variability. Analytical blanks composed of 2% nitric acid were also put through the chromatography method and analyzed via ICP-MS to quantify potential contamination from materials and reagents.

5.2.1. Lanthanide Series % Recovery

The lanthanide series elements otherwise known as Rare Earth Elements (REEs), encompass elements of atomic numbers 57-71. Promethium atomic #61, is not considered in this study because it does not occur naturally in nature. The lanthanides displayed promising recoveries in both the pH 4 and pH 6 solutions. Salinity proved to be an effective constraint on the capturing capability of the Chelex-100 resin. Recoveries for lanthanides in 300g/L TDS samples were not as favorable as the 50 g/L samples. The large TDS values containing higher amounts of monovalent and divalent matrix ions creates competition for ligand sites on the resin which did not allow the full chelation of elements of interest and consequentially lead to poor recoveries. In 50 g/L environments at both pH 4 and 6 the light lanthanides recovered at ~80%, only erbium,
thulium, ytterbium and lutetium were recovered below 80%. In 300 g/L solutions recovery was clearly reduced. At pH 4 lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium were the only elements displaying a meaningful recovery (>50%). The heavy lanthanides exhibited recoveries <50%. At pH 6, lanthanum, cerium and praseodymium recover above 60% with the rest of the lanthanides steadily decreasing with atomic mass. According to this data, lanthanide recoveries are most favorable in a pH 4 environment using this approach. The results for lanthanide analyses are displayed below in Figure 5. The end members (50g/L and 300g/L) of the TDS values analyzed are displayed to illustrate variability in recovery due to salinity. Blank data displayed in Table 1 shows that outside contamination for these samples was relatively insignificant.
Figure 5. Results for Lanthanide Series % Recovery. Red boxes indicate region of recovery <50%. Lanthanide Elements have an affinity for high recovery in pH 4 solution. All Lanthanides recover favorably at 50 g/L TDS. Salinity is proven to be an inhibiting factor when analyzing Lanthanides with recoveries dropping below 50 % in both pH 4 and 6.

Table 1. Ratio of sample spike concentrations to mean blank concentrations. For samples highlighted in red ~25% (i.e., 0.25) of the recovery can be attributed to contamination.
5.2.2. High Field Strength Elements% Recovery

High Field Strength (HFS) elements are tetravalent and pentavalent transition metals which behave similar in geochemical processes owing to their high valence, similar ionic radii and intermediate electronegativity values (Chakhmourdian, 2006). In this study, HFS elements are defined as the +4 valence elements (Ti, Zr, Hf, Ge, Th), +5 valence elements (Nb, Ta, As, Sb) and +6 valence elements (Mo, W, U, Se, Te). HFS elements have been arranged by valence for data representation Figure 6.

Analyses concluded HFS elements have difficulty producing favorable recoveries in the environments tested. Salinity does not appear to be an inhibiting factor when analyzing HFS elements but pH may be a parameter which can affect recovery. At pH 4, titanium, molybdenum, thorium and uranium display ideal recoveries ranging from 80-100%. However, the remaining HFS elements showed steep drop offs with recoveries below 50 %. At pH 6 all HFS elements displayed mean recovery values below 50%. Standard deviation data displays the capability of tungsten to perform well at pH 6 with recoveries reaching ~80%. Recovery data for HFS elements are displayed below in Figure 6. According to Table 2, contamination is not a contributing factor to HFS recoveries in the matrix spikes.
Figure 6. Results for High Field Strength Elements % Recovery. Ti, Th, Mo and U are the only elements capable of favorable recoveries at pH 4 conditions. TDS does not seem to be an inhibiting factor, variation between 50g/L and 300g/L samples is minimal. At pH 6 conditions all HFS elements recover poorly at mean value.

Table 2. Ratio of sample spike concentrations to mean blank concentrations for HFS. Samples highlighted red may have up to 25% of their recovery attributed to contamination.
5.2.3. Industrial Elements % Recovery

Industrial Elements (IE) in this study are defined as (Fe, Co, Ni, Cu, Cd, Pb, B, Ga, Tl, V, Cr, Mn). Samples were analyzed at 50, 100, 200 and 300g/L TDS. The end members of the samples 50g/L and 300g/L are displayed to show the effects of salinity on recoveries of IEs at pH 4 and 6. At both pH 4 and 6, recoveries in the lower salinity solutions of 50g/L performed more favorably than in the 300g/L samples.

At pH 4 nickel showed the most promising results with ~100% recovery at 50g/L and ~75% recovery at 300g/L. Copper recovered at ~98% at 50g/L and ~63% at 300g/L. Gallium recovered at ~43% in 50g/L and ~32% in 300g/L. Cobalt recovered favorably in low TDS samples at 77% and with 66% recovered in high TDS samples. Iron recovered higher than 50% in 50g/L samples and just 32% in 300g/L samples. Vanadium recovered well in both TDS environments, ~82% in 50 g/L samples and 70% in 300 g/L samples. Cadmium, boron, thallium and manganese performed poorly with <10% recovered in all samples. Lead recoveries were ~10 % in all samples analyzed. Variable recoveries in the pH 4 environment clearly display that IE recoveries can be inhibited by the presence of matrix elements in high TDS samples. However, anomalous recoveries do occur. Chromium recovers better in high TDS environments ~18% in 300g/L, ~7% in 50g/L).

At pH 6, matrix spike recovery data remains consistent for chromium, this element performs better in high salinity conditions. At pH 6, chromium recovers more favorably than pH 4. Chromium recovers at ~60% in high TDS samples while recovering only at 40% in 50g/L conditions. Nickel was most favorably recovered at pH 6 (100%) in 50 g/L TDS samples and 70% in 300 g/L TDS samples. In both high and low TDS samples copper was fully recovered (100%). Gallium was recovered ~88% in 50 g/L and 62% in 300g/L synthetic brines. Vanadium recovered at~75% in 50g/L and ~73% in 300g/L showing that salinity is not an inhibiting factor controlling spike recoveries for these elements. In contrast, cobalt was favorable recovery at 50g/L with (~95%), while a significant drop off (36%) was observed at 300 g/L. Manganese recovered better in 50g/L samples than in 300g/L (~60% in 50g/L, 32% in 300g/L). Cadmium, lead, boron, and
thallium favored poorly with recoveries <10% in both 50 and 300 g/L samples with the exception of lead and cadmium whose recoveries in 50g/L brines were ~82% and ~77% respectively. Iron recovered between 50% and 70% in both TDS solutions. Results for the pH 6 recoveries show that salinity played a role as a stronger inhibiting factor for IE recoveries at pH 4.

Results for IE recoveries display that most IEs perform better in near neutral environments (pH6) than in more acidic environments (pH4). Most notably cadmium and manganese which displayed near 0% recoveries at pH 4, and displayed more favorable recoveries (>50%) at pH 6. In the pH 4 experiment iron, thallium, and chromium were the most susceptible to salinity interferences during recovery while in the pH6 solutions cobalt, cadmium, and lead were the most affected. pH 6 and TDS ~50g/L conditions appear to be the most conducive environments to maximize recovery of IEs. All recovery data for industrial elements analyzed at pH 4 and 6 are displayed in Figure 7.
Figure 7. Results for industrial elements, similar trends can be noted in both the pH 4 and 6 experiments. Low TDS environments perform better than high TDS.

Table 3. Ratio of sample spike concentrations to mean blank concentration for industry elements. pH 4 trials contamination impacts from blanks were negligible. In pH 6 trials most elements may have suffered contamination according to data provided. Samples highlighted red may have as much as 25% of their recovery attributed to contamination.
5.2.4. Alkali and Alkaline Earth Elements % Recovery

Alkali and Alkaline Earth Elements (AE) are the constituents of the 1st and 2nd groups (columns) of the periodic table of the elements. These groups are composed of monovalent and divalent elements some of which contribute to the matrix composition of basinal brines, notably Na, Mg and Ca. During analyses of CVEs, 5 AEs were investigated (Rb, Cs, Be, Sr, Ba) for matrix spike recovery at pH 4 and 6 in 50g/L and 300g/L TDS solutions.

In both pH 4 and 6 experiments Rubidium recoveries were ~1% with samples at 50g/L performing slightly better than there 300g/L counterparts. Cesium recoveries were < 1% in both pH and TDS samples. Beryllium showed significantly better recoveries in the pH 6 experiments (~25%) in both low and high TDS solutions. Beryllium recoveries were <1% in pH 4 experiments. Strontium recoveries were ~ 5% in all parameters tested. Barium recoveries were significantly higher than 100% in all environments. In pH 4 solutions, barium recoveries are 170% at 50g/L and ~300% at 300g/L. In pH 6 experiments barium recoveries are >300%.

Alkali and Alkaline Earth Elements are monovalent and divalent ions. The matrix wash portion of our method is geared toward removing ions of this valence. Barium being the exception, all AEs analyzed display recoveries <30% (Figure 8).
Figure 8. Results for alkali and alkaline earth elements. Monovalent Rb and Cs have no recovery capabilities while the divalent Be, Sr, Ba display recovery capabilities.

Table 4. Ratio of sample spike concentration to mean blank concentration for alkalis and alkaline earth elements. Contamination may be responsible for the majority of results in the pH 6 trial.

<table>
<thead>
<tr>
<th>pH 4</th>
<th>Sample</th>
<th>Rb</th>
<th>Cs</th>
<th>Be</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50g/L</td>
<td>0.0115</td>
<td>0.995</td>
<td>0.0578</td>
<td>1.0292</td>
<td>0.000000</td>
</tr>
<tr>
<td></td>
<td>300g/L</td>
<td>0.0245</td>
<td>1.0073</td>
<td>0.0357</td>
<td>0.6564</td>
<td>0.000000</td>
</tr>
<tr>
<td>pH 6</td>
<td>Sample</td>
<td>Rb</td>
<td>Cs</td>
<td>Be</td>
<td>Sr</td>
<td>Ba</td>
</tr>
<tr>
<td></td>
<td>50g/L</td>
<td>1.1086</td>
<td>0.6</td>
<td>2.0647</td>
<td>0.8802</td>
<td>0.74405</td>
</tr>
<tr>
<td></td>
<td>300g/L</td>
<td>5.5246</td>
<td>1.8605</td>
<td>0.6881</td>
<td>0.59258</td>
<td></td>
</tr>
</tbody>
</table>
5.2.5. Precious Metals % Recovery

Precious Metals (PM) in this study are defined as gold, silver and the platinum group elements (PGEs) ruthenium, rhodium, palladium, osmium, iridium, and platinum. Across TDS and pH analyzed precious metals displayed poor recoveries. Gold and iridium showed the best recoveries at pH 4 with gold displaying ~10% recovery and iridium recovering <10%. All other PMs displayed near zero matrix spike recoveries. At pH 6 ruthenium and rhodium recovered highest with ruthenium displaying nearly 30 % recovery and rhodium ~5%. All other PMs recovered <5%. Salinity does not appear to be a contributing factor for poor recoveries as there is little to no variability between 300g/L and 50g/L TDS recoveries. According to blank data, the data obtained for the pH 6 trials may be composed of considerable contamination. Ruthenium is the only PM which displayed a mentionable recovery in that set.
Figure 9. Precious metal recoveries are consistently below 30% in both pH 4 and 6 environments.

Table 5. Ratio of sample spike concentration to mean blank concentration for precious metal blanks. pH 6 data are suspect as the entirety of the samples analyzed have been subject to considerable contamination.

<table>
<thead>
<tr>
<th>pH 4</th>
<th>Sample</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50g/L</td>
<td>0.0002</td>
<td>0.0018</td>
<td>0.0022</td>
<td>0.0534</td>
<td>0.0041</td>
<td>0.0213</td>
<td>0.0019</td>
<td>0.9714</td>
</tr>
<tr>
<td></td>
<td>300g/L</td>
<td>0.0002</td>
<td>0.0024</td>
<td>0.0137</td>
<td>0.0279</td>
<td>0.0033</td>
<td>0.0424</td>
<td>0.0031</td>
<td>2.3142</td>
</tr>
<tr>
<td>pH 6</td>
<td>Sample</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Ag</td>
</tr>
<tr>
<td></td>
<td>50g/l</td>
<td>1.3621</td>
<td>6.1337</td>
<td>2.2371</td>
<td>0.9754</td>
<td>1.7918</td>
<td>20.178</td>
<td>0.9114</td>
<td>18.039</td>
</tr>
<tr>
<td></td>
<td>300g/l</td>
<td>1.4341</td>
<td>15.941</td>
<td>2.3587</td>
<td>0.99</td>
<td>6.1115</td>
<td>106.86</td>
<td>0.6176</td>
<td>21.045</td>
</tr>
</tbody>
</table>
5.3.0. Synthetic Ca-rich Solution tests at pH 6

Often times when analyzing subsurface brines, the chemistry of the matrix elements can vary from sodium dominant to calcium dominant. Depending on the matrix composition of the waters, the ability to recover CVEs may be compromised, as a result of this change. Chelex-100 ion exchange resin has been utilized in this study has a high preference for multi valent ions. As a consequence, if matrix ions in solution are divalent as opposed to monovalent, this can lead to competition for ligand sites in the resin. If ligand sites are occupied by matrix ions, CVEs of interests may wash through the system resulting in poor recoveries. To determine whether this may be an issue of concern when analyzing a calcium dominant matrix in basinal brines, an experiment was conducted using a synthetic calcium rich solution. Ca-rich (Na/Ca molar ratio of 5) solutions ranging 50-150 g/L TDS carrying very low quantities of trace elements (created by High Purity Standards, North Charleston, South Carolina) were spiked with 10 μg/L concentrations of a range of lanthanides, high field strength elements, industrial elements, alkali and alkaline earth elements and precious metals to quantify CVE recovery. The effects of a calcium dominant matrix in brines are explained further in this chapter. Sodium rich matrix are compared to calcium rich matrix to display differences in recovery capabilities when analyzing these waters. Samples are analyzed in triplicate and analytical blanks have been incorporated for quality control.

5.3.1. Lanthanides % Recovery

When analyzing the lanthanides, it is immediately apparent that a calcium dominant matrix in brines inhibits the ability of Chelex-100 to recovery these elements. For both Na-rich and Ca-rich solutions, 50g/L samples recover more favorably than do the 300g/L and 150g/L samples. This displays that salinity does have an effect on recovery likely due to competition for ligand sites on the resin. The difference between recovery for 50g/L samples and 150g/L samples in Ca-rich solutions is far less than the recovery difference for 50g/L and 300g/L samples in the Na-rich solutions. However, overall recoveries in the Ca-rich solution are much less favorable than those
of the Na-rich solutions. These findings suggest a clear inhibiting factor the calcium in the solution has on lanthanide recoveries.

In the Ca-rich solutions lanthanum recovered favorably at >80% in both the 50g/L and 150g/L samples. Cerium displays an abnormally high recovery (>100%) possibly due to polyatomic and oxide interferences. Praseodymium is the heaviest lanthanide that was recovered above 50% in the 50g/L sample. Praseodymium recovered ~20% in its 150g/L sample. The remaining lanthanides from neodymium to lutetium steadily declined from ~40% to ~1% in the 50 g/L samples and from ~20% to ~1% in the 150g/L samples. When compared to the Na-rich solutions, all lanthanides which recovered poorly (<50%) in the Ca-rich solution, recovered >50% in the Na-rich solution at 50 g/L. At 300g/L, elements La-Nd recovered favorably (>50%) in the Na-rich solutions while only lanthanum and cerium recovered favorably at 150g/L in the Ca-rich solution. This data shows that even extreme salinity (300g/L) in Na-rich waters can produce a greater lanthanide recovery than intermediate salinity (150g/L) in Ca-rich waters. It can be concluded that the divalent nature of calcium inhibits lanthanide recovery. Analytical blank data displayed in Table 6, suggests that outside contamination does not play a major role in the recoveries of lanthanides in the Ca-rich series.
Figure 10. Results for lanthanide series percent recovery in Ca-rich environment. A divalent matrix environment displays clear recovery inhibiting qualities for lanthanides. TDS doesn’t appear to effect recovery as significantly as shown in the Na-rich environment.

Table 6. Ratio of sample spike concentrations to mean blank concentrations for the lanthanides show no significant outside contribution to lanthanide recoveries

<table>
<thead>
<tr>
<th>Sample</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>50g/L</td>
<td>0.0268</td>
<td>0.0051</td>
<td>0.0013</td>
<td>0.0056</td>
<td>0.0013</td>
<td>0.0007</td>
<td>0.0014</td>
<td>0.0014</td>
<td>0.001</td>
<td>0.0014</td>
<td>0.0006</td>
<td>0.0021</td>
<td>0.0015</td>
</tr>
<tr>
<td>100g/L</td>
<td>0.0389</td>
<td>0.0051</td>
<td>0.0024</td>
<td>0.0103</td>
<td>0.0019</td>
<td>0.001</td>
<td>0.0011</td>
<td>0.0005</td>
<td>0.0005</td>
<td>0.0001</td>
<td>0.0003</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td>150g/L</td>
<td>0.0296</td>
<td>0.0043</td>
<td>0.0029</td>
<td>0.0131</td>
<td>0.0027</td>
<td>0.0015</td>
<td>0.0029</td>
<td>0.0017</td>
<td>0.0008</td>
<td>0.0002</td>
<td>0.0005</td>
<td>0.0002</td>
<td></td>
</tr>
</tbody>
</table>
5.3.2. High Field Strength Elements % Recovery

Experiments conducted in calcium rich solutions showed considerable differences for HFS recoveries when compared to the results for the Na-rich solutions. During the Na-rich experiments at pH 6, high salinity was not a contributing factor to poor recoveries. In some of the elements analyzed the mean recoveries are more favorable in high TDS samples. This proved to be the same case when considering recoveries in the Ca-rich solutions tested. Analyses of HFS elements in the Ca-rich solutions were conducted at TDS values of 50g/L and 150g/L and pH 6. Salinity is not a parameter inhibiting to many HFS elements but in samples that displayed variability due to salinity, HFS elements preferred a high TDS environment (150g/L).

Titanium recoveries dropped from 50% in Na-rich solutions relative to <10% in Ca-rich solutions. Titanium recovered at 7% in 50g/L samples and 3% in 150g/L samples. Zirconium recoveries improved in Ca-rich solutions. Zirconium recovered ~16%, regardless of pH, in Ca-rich solutions but were recovered from the Na-rich solutions at <1%. Hafnium, germanium, and thorium showed no difference in recovery capability when comparing results from Na-vs-Ca-rich solutions. Niobium recoveries increased 5x with 30% in the Ca-rich experiment. Tantalum recoveries did not change from the Na-rich experiments. Arsenic recoveries dropped by 4x going from 20% in the Na-rich solutions to 5% in the Ca-rich solutions. Antimony and molybdenum improved significantly in the Ca-rich experiments with ~39% and 57% recovered respectively. Tungsten has been completely lost in the Ca-rich experiments. Uranium recoveries are slightly better and selenium recoveries drop by 5x from the Na-rich experiments. Tellurium recoveries increased 3x, going from 15% in the Na-rich solutions to 45% in the Ca-rich solutions.

Experiments conducted in the Ca-rich solutions showed that the matrix composition of the samples can have an inhibiting effect on some of the HFS elements while others recovery capability increases. Many of the elements analyzed such as zirconium, niobium, antimony, molybdenum, uranium and tellurium displayed an increase in recovery capability. Elements such as titanium, arsenic, tungsten and selenium display sharp decreases in their ability to be recovered in the Ca-rich environment. Hafnium, germanium and thorium did not show any difference in
recovery when compared to the Na-rich experiments. Blank data concludes there is no significant contribution to recoveries through outside sources Table 7.

**Figure 11.** Results for high field strength elements displaying similar trends among recoveries in both environments. Results show for some elements high salinity and Ca-rich environments are more favorable for HFS elements.
Table 7. Ratio of samples spike concentration to mean blank concentration for HFS results.
No contributions from outside sources in documented in blank data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tl</th>
<th>Zr</th>
<th>Hf</th>
<th>Ge</th>
<th>Sn</th>
<th>Th</th>
<th>Nb</th>
<th>Ta</th>
<th>As</th>
<th>Sb</th>
<th>Mo</th>
<th>W</th>
<th>U</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>50g/L</td>
<td>-0.002</td>
<td>0.089</td>
<td>0.0513</td>
<td>0.0027</td>
<td>0.0053</td>
<td>0.002</td>
<td>0.0198</td>
<td>0.0219</td>
<td>0.0063</td>
<td>0.0068</td>
<td>-0.0009</td>
<td>0.0014</td>
<td>0.0006</td>
<td>0.0018</td>
<td>-6.5101E-05</td>
</tr>
<tr>
<td>100g/L</td>
<td>-0.001</td>
<td>0.0812</td>
<td>0.0521</td>
<td>0.0038</td>
<td>0.0058</td>
<td>0.0022</td>
<td>0.0155</td>
<td>0.017</td>
<td>0.0064</td>
<td>0.0098</td>
<td>-0.0011</td>
<td>0.0017</td>
<td>0.0005</td>
<td>0.0024</td>
<td>-7.2381E-05</td>
</tr>
<tr>
<td>150g/L</td>
<td>-0.001</td>
<td>0.1251</td>
<td>0.1002</td>
<td>0.0049</td>
<td>0.0066</td>
<td>0.0026</td>
<td>0.017</td>
<td>0.0199</td>
<td>0.0112</td>
<td>0.0147</td>
<td>-0.0014</td>
<td>0.0017</td>
<td>0.0005</td>
<td>0.0034</td>
<td>-0.00010636</td>
</tr>
</tbody>
</table>

5.3.3. Industrial Elements % Recovery

Many Industrial Elements (IE) recoveries were shown to be greatly affected by a Ca-rich matrix. The divalent nature of calcium may inhibit the ability for many of these elements to attach to the Chelex-100 chelating resin due to competition for ligand sites. Although exceptions exist for the Industrial Elements, in the conditions analyzed low TDS environments perform best for positive recoveries.

Iron recoveries in high and low TDS samples are 20%, showing iron recovery capability is not restricted by salinity. Cobalt, copper and nickel display steep drop offs in recovery from the Ca-rich solutions, when compared to the Na-rich recovery data. Each of these metals display at least a 50% drop in recovery ability. Results for cadmium recovery do not change when analyzed at 50g/L but 150g/L samples recovered at 25%, much better than in the 300g/L samples in Na-rich solutions. Boron and tellurium recoveries do not show appreciable changes in recovery capability in the two environments. Lead recoveries increase for samples in the Ca-rich experiments. In high TDS solutions (300 g/L) lead recovery lead increased 6 times. Gallium recoveries in the Ca-rich experiments dropped substantially to only 13% for both 50g/L and 150g/L samples. Vanadium, chromium and manganese results did not record any large variation in recovery ability between the two matrix environments.

The Ca-rich matrix environment has proven to be an inhibiting factor for percent recovery of many of the elements. Many elements in this experiment however do not display noticeable changes brought forth by the change in matrix composition. The trend in recovery data stays more
or less consistent when observing the results for the sodium and calcium rich matrix environments. Blank data suggests outside contamination may have affected data for copper and boron Table 8.

Figure 12. Results for industrial elements. Similar trends are displayed when comparing the two matrix environments.

Table 8. Ratio of sample spike concentration to mean blank concentration for IEs. Copper and boron are the only elements which may have been affected by outside interference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
<th>B</th>
<th>Al</th>
<th>Ga</th>
<th>Tl</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>50g/L</td>
<td>0.32035</td>
<td>0.0142</td>
<td>0.1765</td>
<td>2.8327</td>
<td>0.0005</td>
<td>0.02168</td>
<td>2.579</td>
<td>0.0709</td>
<td>0.0085</td>
<td>0.1341</td>
<td>0.0255</td>
<td>0.0124</td>
<td>0.0532</td>
</tr>
<tr>
<td>100g/L</td>
<td>0.06684</td>
<td>0.0277</td>
<td>0.1953</td>
<td>2.0127</td>
<td>0.0008</td>
<td>0.02065</td>
<td>1.6705</td>
<td>0.0605</td>
<td>0.0093</td>
<td>0.154</td>
<td>0.0295</td>
<td>0.0089</td>
<td>0.068</td>
</tr>
<tr>
<td>150g/L</td>
<td>0.31506</td>
<td>0.0318</td>
<td>0.2194</td>
<td>1.2147</td>
<td>0.0015</td>
<td>0.01276</td>
<td>1.0426</td>
<td>0.0505</td>
<td>0.0082</td>
<td>0.0926</td>
<td>0.0365</td>
<td>0.0095</td>
<td>0.0735</td>
</tr>
</tbody>
</table>
5.3.4. Alkali and Alkaline Earth Elements % Recovery

Alkali and Alkaline Earth Elements display a similar trend when comparing Na-and Ca-rich endmember solutions. Both of the monovalent AEs recovered at 1% or less in both end-member solutions, while all three of the divalent AEs show the ability to be recovered at 10% or greater.

In Ca-rich solutions, Rb and Cs were recovered at rates <1% in both low (50g/L) and high (300g/L) TDS extremes. Beryllium was recovered at ~10% in both TDS extremes while strontium was recovered at ~5%. Barium displayed the greatest recoveries with recoveries of 292% and 439% in 50g/l and 150g/L samples respectively, suggesting analytical problems or contributions of barium from the high purity salt solutions.

Owing to the monovalent nature of rubidium and cesium their results are reasonable and expected. Poor recoveries for beryllium and strontium can also be expected because of their divalent nature. Recall that Chelex-100 has a high preference for multivalent ions and that during our method we purposefully incorporate a step to remove monovalent ions so to decrease the overall TDS values of our samples. Blank data displayed in Table 9 suggests strontium and barium may have outside contributions to their recoveries, which are likely due to small masses present in the high purity Na-Ca-Cl solutions used in these experiments.
Figure 13. Results for alkaline elements displaying similar trends in recovery for both matrix environments.

Table 9. Ratio of sample spike concentrations to mean blank concentration for AEs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb</th>
<th>Cs</th>
<th>Be</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>50g/l</td>
<td>0.1462018</td>
<td>0.092957</td>
<td>-0.00199</td>
<td>0.734088</td>
<td>0.697074</td>
</tr>
<tr>
<td>100g/l</td>
<td>0.0603223</td>
<td>0.1041</td>
<td>-0.0016</td>
<td>0.79237</td>
<td>0.785283</td>
</tr>
<tr>
<td>150g/L</td>
<td>0.0845933</td>
<td>0.066666</td>
<td>-0.00133</td>
<td>0.491676</td>
<td>0.463895</td>
</tr>
</tbody>
</table>
5.3.5. Precious Metals % Recovery

During the analyses of precious metals in Ca-rich matrix samples some noticeable variations were recorded when comparing the results for recovery in the Na-rich matrix samples. In general, higher recoveries were exhibited for 50 g/L samples than 150g/L samples, in the Ca-rich matrix. Gold recoveries dropped in the Ca-rich experiments by roughly half, going from ~12% in the Na-rich experiment to ~6% in the Ca-rich. Silver recoveries which were <1% in the Na-rich solutions increased to ~3% in the Ca-rich solutions. Ruthenium recoveries increased generously in the Ca-rich solutions with recoveries of ~23% and >30% in the high and low TDS samples respectively. Rhodium recoveries were <5% and palladium, osmium, iridium and platinum recoveries were below 1%. It is clear that though the differences in recovery are not overwhelmingly variable, the change in matrix environment affects recovery capability for precious metals. Blank data for the precious metal trial in a Ca-rich environment show no outside contributions to the percent recovery of the samples.
Figure 14. Results for precious metals show an increase in recovery for Ag, Ru, and Rh in the Ca-rich environment. Au and Ir prefer Na-rich environment for better recoveries.

Table 10. Ratio of sample spike concentrations to mean blank concentration for precious metal data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>50g/L</td>
<td>0.000146</td>
<td>0.000501</td>
<td>0.06415</td>
<td>0.039086277</td>
<td>0.0014189</td>
<td>0.009943</td>
<td>0.003027</td>
<td>-0.02147</td>
</tr>
<tr>
<td>100g/L</td>
<td>0.000157</td>
<td>0.000457</td>
<td>0.082125</td>
<td>0.072252828</td>
<td>0.0008985</td>
<td>0.031309</td>
<td>0.003128</td>
<td>-0.0238</td>
</tr>
<tr>
<td>150g/L</td>
<td>0.000227</td>
<td>0.000888</td>
<td>0.125306</td>
<td>0.15202597</td>
<td>0.0014658</td>
<td>0.053005</td>
<td>0.003535</td>
<td>-0.03289</td>
</tr>
</tbody>
</table>
5.4.0. Elution Volume Verification Test

A test to ensure that poor recovery in certain elements in the above tests was not a result of too little solution volume during the elution stage of chromatography, an elution volume test was performed prior to the analysis of produced water samples. Throughout the range of CVEs tested for percent recovery in this study, variable recoveries have been documented. In experiments where poor recoveries were observed it is necessary that an insufficient volume of eluent be ruled out as a parameter effecting recovery. In this elution volume verification test samples are prepared utilizing the same method as for Na- and Ca-rich matrix solution tests. The only part of the method which was manipulated is the elution step. Instead of eluting the samples with 4ml of 2 molar nitric acid, the samples were eluted with 10, 1 mL elution steps totaling 10 mL of 2 molar nitric acid being sent through the column. Each 1mL elution was collected and analyzed independently. Cumulative percent recovery for each element was calculated for each 1mL eluted sample.

Molybdenum, titanium, and tellurium were selected to display the results of this experiment Figure 15. Molybdenum and titanium have been selected for their favorable recoveries of ~110% and ~90%, while tellurium has been selected for its intermediate recovery of ~80%. Molybdenum was fully recovered in the first 1mL of elution. In the 1st mL, titanium has recovered ~55%, ~10% in the 2nd mL, ~18% in the 3rd mL and ~5% in the 4th mL. Tellurium is recovered at ~45% in the 1st mL, ~10% in the 2nd mL, ~20% in the 3rd mL, and ~5% in the 4th mL.

The conclusion of this experiment suggests that 4 mL of 2 molar nitric acid is sufficient for CVE removal during elution. While recoveries are documented through the first 6 mL of elution’s in this experiment, CVE recoveries are not happening in a meaningful manner after mL 4 of this test. The results of this test have confirmed that eluent volume is not a contributing factor to poor recovery during chromatography.
Figure 15. Elution volume efficiency tests. 4 mL of 2M HNO3 has proven to be a sufficient amount of eluent for full recovery of CVEs during chromatography. Eluent volume is sufficient for removing CVEs from ~250µL of Chelex-100 resin.
5.5.0. Considerations Prior to Produce Water Analyses

Produced waters can differ significantly from synthetic brines in composition and metal concentrations. Variables for synthetic brines tested in this study, their chemical makeup and salinity are under strict control during production. Produce waters can contain organic carbon dissolved in solution, which is a parameter not considered during synthetic solution tests. Natural brines can also have extreme levels of iron and manganese leached from the wells during travel time to the surface. Both of these variables need to be considered when preconcentrating and analyzing produced waters. An initial organic compound digestion test has been conducted using ultraviolet (UV) light exposure and Total Organic Carbon (TOC) analysis for organic matter breakdown assessment.

5.5.1 Ultra Violet Digestion

An ultraviolet light exposure test was administered for produced water samples which likely contain organic carbon compounds in solution. An enclosed chamber with two UV lights model (Sankyo Denki G15T8 15W black ray and sterilizing UV bench lamp by Analytik Jena US) on either side has been constructed for sample exposure at 254nm Figure 16. The enclosure was created with 12in x 1.6in wood blocks and the dimensions of the chamber built is roughly 1.6ft x 2 ft. the depth of the chamber is ~ 12 in. UV light intensity was measured to be 2.61 mW/cm² using a General UV512C UV meter. Four produced water samples were chosen to test organic matter breakdown using this UV system, based on variability in visible oil and hydrocarbons in the samples (Figure 17). Sample 21.Bro.01-050d (Shade 4) was chosen because it is nearly completely opaque signifying a high concentration of organic carbon compounds. Sample 21.Bro.01-087d (Shade 3) was less opaque than Shade 4 and contained visible free oil in solution. Sample 21.Bro.01-034d (Shade 2) was roughly the same level of opacity as Shade 3 and contained slightly less visible free oil. Sample 21.Bro.01-062d (Shade 1) was translucent and contained no visible free oil. These four samples were chosen for their likely range of organic
carbon constituents based on visible free oil and their level of opacity. The sample were placed in the enclosed UV chamber and monitored for changes in visible compound levels hourly. By the fourth hour of exposure free oil in all samples was completely liberated Figure 18. All samples had changed to the same golden-brown color after UV exposure. From these observations, four hours of UV exposure time was chosen for samples to undergo UV treatment prior to preconcentration and analyses.

Total Organic Carbon (TOC), Total Carbon (TC) and Inorganic Carbon (IC) analyses was conducted to test the efficiency of UV exposure to digest organic complexes. Ten samples of five produced waters were tested, five being exposed to UV light and five not undergoing exposure. Data obtained from the trials on the Shimadzu TOC-VCSH have displayed that there is no significant reduction in TOC, TC or IC after UV exposure. Data obtained for carbon concentrations is displayed in Table 11.

Figure 16. Samples inside UV exposure chamber. Samples are exposed to 254nm of UV light for 4 hours to digest organic compounds which can inhibit % recovery.
Figure 17. Samples for UV digestion tests are chosen based on opacity and visible free oil in solution.

Figure 18. After 4 hours of UV exposure all samples have been changed to the same hue and all visible free oil has been digested from the solutions.
Table 11. Results for organic carbon concentration analyses. No sufficient decrease in TOC is displayed after exposure to UV light. (Data displayed in mg/L)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>TOC</th>
<th>TC</th>
<th>IC</th>
</tr>
</thead>
<tbody>
<tr>
<td>069d no UV</td>
<td>271.7</td>
<td>287.4</td>
<td>15.7</td>
</tr>
<tr>
<td>069d UV</td>
<td>286</td>
<td>301</td>
<td>15</td>
</tr>
<tr>
<td>163d no UV</td>
<td>191</td>
<td>206.1</td>
<td>15.1</td>
</tr>
<tr>
<td>163d UV</td>
<td>196</td>
<td>216.1</td>
<td>14.8</td>
</tr>
<tr>
<td>149a no UV</td>
<td>201.6</td>
<td>217.2</td>
<td>15.5</td>
</tr>
<tr>
<td>149 UV</td>
<td>196</td>
<td>215.3</td>
<td>15.3</td>
</tr>
<tr>
<td>179a no UV</td>
<td>79.8</td>
<td>94.8</td>
<td>15</td>
</tr>
<tr>
<td>179 UV</td>
<td>86.8</td>
<td>101.9</td>
<td>15</td>
</tr>
<tr>
<td>178a no UV</td>
<td>68.6</td>
<td>83.5</td>
<td>14.8</td>
</tr>
<tr>
<td>178a UV</td>
<td>74.8</td>
<td>89.6</td>
<td>14.7</td>
</tr>
</tbody>
</table>

5.5.2 Iron Complex Precipitation in Columns

During chromatography of produced water samples, high concentrations of iron precipitates in mini columns becomes visible (Figure 19). High concentrations of iron are not a variable considered during the synthetic solution trials. During the ascent of basinal brines to the surface during oil and gas production, it is likely large quantities of iron are leached from the surrounding well Dresel and Rose (2010). This is a variable that may impact percent recovery and method revision may be necessary to combat this issue.
**Figure 19.** Iron precipitation in mini columns during chromatography.

**Figure 20.** Iron precipitation in two mini columns directly after elution of CVEs. Observations conclude that not all Fe has been removed from the mini columns and as a consequence full recovery of other CVEs may have also been inhibited.
5.6.0. Produced Water Samples % Recovery

When analyzing produced waters in this study, all samples were diluted to a TDS of ~50g/L. This dilution was performed to lessen the ability of salinity to inhibit percent recovery. Before being spiked with 10 µg/L of CVEs the samples were exposed to ultraviolet light (254nm) and their pH adjusted to 6. Results from the synthetic solution experiments and Chelex-100 resin structure at pH 6 suggests this is the pH level most favorable for recovery of CVEs. Sample 21.Bro.10-130a was the only sample which was analyzed in triplicate. All samples were put through column chemistry as described in the methods section of this paper and analyzed via ICP-MS. Analytical blanks have been incorporated with the produced water samples for quality assurance and control.

5.6.1. Lanthanide Series

The lanthanides are all dominantly trivalent in the environments tested. Due to the trivalent nature of the lanthanides and the favorable results displayed for recovery in the preliminary experiments, it can be expected to see the lanthanides perform well when analyzing produced water samples. However, the experiments conducted here suggested otherwise.

The PW sample that displayed the most favorable results is 21.Bro.01-079a. This sample recovered ~18% of all lanthanides originally amended to the sample. Sample 21.Bro.01-069d recovered all lanthanides with between ~16 and 17% efficiency. Lanthanum recovered highest at >17%. Sample 21.Bro.01-130a recovered all lanthanides at ~16%. In the sample lanthanum showed the highest recovery at ~16.5% and europium showed the lowest recovery of the sample with ~15% recovery. In contrast to the other samples, lanthanum has the lowest recovery in sample 21.Bro.01-040a. Lanthanum percent recovery was just below 14% with the highest recovery being that of cerium with nearly 16% recovered. All other lanthanides recover at ~15% in this sample. For sample 21.Bro.01-163d all of the lanthanides recover at ~14% with lanthanum being recovered just below 16%. Data for lanthanide % recovery is displayed in Figure 19.
According to the data for percent recovery of the lanthanides, sample21.Bro.01-179a displays the most recovery while sample 21.Bro.01-163d the least. All of the samples show a similar trend in lanthanide recovery for most elements. It is apparent that the effectiveness of the Chelex-100 ion exchange resin to recover lanthanides has been compromised when analyzing produced waters. Blank data suggests there was no significant contribution from outside sources for the recoveries displayed.

Figure 21. Results for lanthanide percent recovery in produced water samples. All lanthanides are recovered between 13 and 19% in the samples analyzed.
5.6.2. High Field Strength Elements

During this experiment on Permian Basin produced water samples, no sample completely outperforms another for HFS percent recoveries. The trend in recovery for these elements is rather well grouped and consistent for all HFS elements. Titanium, zirconium, hafnium and germanium recovered between 13 and 17% for sample 21.Bro.01-079a. These are some of the most favorable recoveries for these elements in this experiment. Thorium, niobium and tantalum recoveries were between 15 and 18% for this sample. Arsenic recovery was ~15% while antimony, molybdenum, tungsten, and selenium recoveries were <10%. Uranium has the best recovery for this sample with a 31% recovery. Tellurium recovered at just 17%. Titanium had the best recovery in sample 21.Bro.01-163d with 30% recovered. Zirconium, hafnium, germanium, niobium, tantalum, arsenic, molybdenum, tungsten, selenium and tellurium displayed recoveries <15 % in all samples analyzed. Uranium had the highest recoveries (~30%) in all samples. According to Table 13, blank contributions to HFS recoveries are measurements were not significant.

Table 12. Ratio of sample spike concentrations to mean blank concentrations for lanthanides in produced water samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.Bro.01-079a.</td>
<td>0.0631</td>
<td>0.0123</td>
<td>0.0015</td>
<td>0.0009</td>
<td>0.0075</td>
<td>0.0007</td>
<td>0.0005</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>21.Bro.01-163d.</td>
<td>0.0739</td>
<td>0.0158</td>
<td>0.0019</td>
<td>0.0081</td>
<td>0.0012</td>
<td>0.0006</td>
<td>0.0009</td>
<td>0.0006</td>
<td>0.0003</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0002</td>
</tr>
<tr>
<td>21.Bro.01-040a.</td>
<td>0.0739</td>
<td>0.0138</td>
<td>0.0018</td>
<td>0.0078</td>
<td>0.0011</td>
<td>0.0006</td>
<td>0.0008</td>
<td>0.0005</td>
<td>0.0003</td>
<td>0.0004</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.0002</td>
</tr>
<tr>
<td>21.Bro.01-069d.</td>
<td>0.0666</td>
<td>0.0135</td>
<td>0.0017</td>
<td>0.0070</td>
<td>0.0010</td>
<td>0.0005</td>
<td>0.0008</td>
<td>0.0005</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.0002</td>
</tr>
<tr>
<td>21.Bro.01-130a.</td>
<td>0.0696</td>
<td>0.0141</td>
<td>0.0018</td>
<td>0.0073</td>
<td>0.0011</td>
<td>0.0006</td>
<td>0.0008</td>
<td>0.0005</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.0002</td>
</tr>
<tr>
<td>21.Bro.01-130a.</td>
<td>0.0663</td>
<td>0.0134</td>
<td>0.0017</td>
<td>0.0070</td>
<td>0.0010</td>
<td>0.0005</td>
<td>0.0008</td>
<td>0.0005</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.0002</td>
</tr>
<tr>
<td>21.Bro.01-130a.</td>
<td>0.0704</td>
<td>0.0152</td>
<td>0.0019</td>
<td>0.0080</td>
<td>0.0012</td>
<td>0.0006</td>
<td>0.0009</td>
<td>0.0006</td>
<td>0.0003</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0002</td>
</tr>
</tbody>
</table>
Figure 22. The majority of HFS elements recover between 50 and 0 %. Phosphorous displays negative recoveries.

Table 13. Ratio of sample spike concentrations to mean blank concentrations for HFS elements.

<table>
<thead>
<tr>
<th>samples</th>
<th>Ti</th>
<th>Zr</th>
<th>Hf</th>
<th>Ge</th>
<th>Th</th>
<th>Nb</th>
<th>Ta</th>
<th>As</th>
<th>Sb</th>
<th>Mo</th>
<th>W</th>
<th>U</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.Bro.01-079a.</td>
<td>0.0863</td>
<td>0.0173</td>
<td>0.0101</td>
<td>0.0012</td>
<td>0.0016</td>
<td>0.0045</td>
<td>0.0017</td>
<td>0.0019</td>
<td>0.0022</td>
<td>0.0129</td>
<td>0.1394</td>
<td>0.0008</td>
<td>0.0015</td>
<td>0.0045</td>
</tr>
<tr>
<td>21.Bro.01-163d.</td>
<td>0.042</td>
<td>0.036</td>
<td>0.0197</td>
<td>0.0024</td>
<td>0.0021</td>
<td>0.0099</td>
<td>0.00526</td>
<td>0.0018</td>
<td>0.0003</td>
<td>0.0074</td>
<td>0.1873</td>
<td>0.0009</td>
<td>0.001</td>
<td>0.0067</td>
</tr>
<tr>
<td>21.Bro.01-040a.</td>
<td>0.0857</td>
<td>0.0282</td>
<td>0.0163</td>
<td>0.0093</td>
<td>0.0019</td>
<td>0.005</td>
<td>0.0018</td>
<td>0.0029</td>
<td>0.0007</td>
<td>0.0139</td>
<td>0.3829</td>
<td>0.001</td>
<td>0.0027</td>
<td>0.0052</td>
</tr>
<tr>
<td>21.Bro.01-069d.</td>
<td>0.0874</td>
<td>0.217</td>
<td>0.1228</td>
<td>0.001</td>
<td>0.0018</td>
<td>0.0099</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0002</td>
<td>0.0074</td>
<td>0.157</td>
<td>0.0009</td>
<td>0.001</td>
<td>0.006</td>
</tr>
<tr>
<td>21.Bro.01-130a.1</td>
<td>0.0561</td>
<td>0.0359</td>
<td>0.0193</td>
<td>0.0016</td>
<td>0.0018</td>
<td>0.011</td>
<td>0.0285</td>
<td>0.002</td>
<td>0.0004</td>
<td>0.007</td>
<td>0.1654</td>
<td>0.0009</td>
<td>0.001</td>
<td>0.0061</td>
</tr>
<tr>
<td>21.Bro.01-130a.2</td>
<td>0.0882</td>
<td>0.0494</td>
<td>0.0254</td>
<td>0.0021</td>
<td>0.0018</td>
<td>0.0103</td>
<td>0.1487</td>
<td>0.0021</td>
<td>0.0005</td>
<td>0.0077</td>
<td>0.1748</td>
<td>0.0008</td>
<td>0.001</td>
<td>0.006</td>
</tr>
<tr>
<td>21.Bro.01-130a.3</td>
<td>0.1104</td>
<td>0.0471</td>
<td>0.0236</td>
<td>0.0032</td>
<td>0.0023</td>
<td>0.0144</td>
<td>0.0962</td>
<td>0.0026</td>
<td>0.0004</td>
<td>0.0099</td>
<td>0.216</td>
<td>0.0009</td>
<td>0.0012</td>
<td>0.0085</td>
</tr>
</tbody>
</table>
5.6.3. Industrial Elements

When analyzing percent recovery of IEs from produced water samples, noticeable differences in capture capability were recorded, when compared to synthetic solution tests. Most of the industrial elements display steep drop offs in recovery ability in produced waters. All produced water samples analyzed display a similar and consistent trend when plotted on a graph Figure 23.

In every sample analyzed recoveries for iron are the poorest. Iron percent recoveries dropped off completely staying near 0% for all samples, suggesting a serious inability for iron capture and recovery when analyzing produced water samples. Cobalt recoveries were consistently low in all samples (14% to 15%) exception being sample 21.Bro.01-040a whose recovery was the lowest at ~8%. Nickel recoveries were relatively consistent between all samples (15% to 18%). The percent recoveries for copper ranged tremendously dependent on sample. Samples 21.Bro.01-079a, 21.Bro.01-163d, and 21.Bro.01-130a exhibited negative copper recoveries of near 0%. Samples 21.Bro.01-040a and 21.Bro.01-069d produced recoveries of ~16% each for copper. Cadmium recoveries range from 16% to 19%. Lead recoveries range from 12% to 17% with the highest recoveries in sample 21.Bro.01-079a, and the lowest in 21.Bro.01-163d. Results for boron ranged from ~5% to ~0%. Recoveries for gallium ranged from 13% to 18% with the highest recovery being in 21.Bro.01-079a and the lowest in 21.Bro.01-130a. All samples record a percent recovery of less than 3% for thallium. vanadium and chromium recoveries range from 13% to 17%. Manganese recoveries are the highest for this experiment with values of up to ~450% and 740% in samples 21.Bro.01-163d and 21.Bro.01-040a respectively. The lowest recovery for manganese is in sample 21.Bro.01-069d at ~0%.

Results for industrial elements percent recoveries display similar trends throughout the samples analyzed. All samples display considerable trouble when attempting to recover iron while the ability to recovery manganese is incredibly high, suggesting polyatomic and oxide interference. Results for industrial elements percent recoveries are displayed below in Figure 23. Blank data suggests copper is the only element which may have been affected by outside reagent
or material contamination to a significant degree. Manganese have been removed from the plot in Figure 23 to better display data exhibiting reasonable results.

![Industrial Elements % Recovery](image)

**Figure 23.** Industrial elements displaying majority of recoveries between 10 and 50%. Iron has been completely lost while manganese recoveries reach ppm levels.

**Table 14.** Ratio of sample spike concentrations to mean blank concentrations for industrial elements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
<th>B</th>
<th>Ga</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.Bro.01-079a</td>
<td>0.0061</td>
<td>0.0021</td>
<td>0.1267</td>
<td>0.5367</td>
<td>0.0004</td>
<td>0.007</td>
<td>-0.042</td>
<td>0.0019</td>
<td>0.0007</td>
<td>0.0344</td>
<td>0.0336</td>
<td>0.0005</td>
</tr>
<tr>
<td>21.Bro.01-163d</td>
<td>0.0015</td>
<td>0.0021</td>
<td>0.1312</td>
<td>1.2385</td>
<td>0.0005</td>
<td>0.0131</td>
<td>-0.005</td>
<td>0.0025</td>
<td>0.0001</td>
<td>0.0431</td>
<td>0.0582</td>
<td>0.0004</td>
</tr>
<tr>
<td>21.Bro.01-040a</td>
<td>0.0302</td>
<td>0.0038</td>
<td>0.1826</td>
<td>1.3858</td>
<td>0.0005</td>
<td>0.0096</td>
<td>-0.052</td>
<td>0.0021</td>
<td>0.0012</td>
<td>0.0412</td>
<td>0.0522</td>
<td>0.0004</td>
</tr>
<tr>
<td>21.Bro.01-069d</td>
<td>0.0021</td>
<td>0.0021</td>
<td>0.1575</td>
<td>0.9451</td>
<td>0.0005</td>
<td>0.0102</td>
<td>-0.013</td>
<td>0.0022</td>
<td>6E-05</td>
<td>0.0371</td>
<td>0.0498</td>
<td>0.0006</td>
</tr>
<tr>
<td>21.Bro.01-130a1</td>
<td>0.0019</td>
<td>0.0021</td>
<td>0.1678</td>
<td>0.9807</td>
<td>0.0004</td>
<td>0.0106</td>
<td>-0.004</td>
<td>0.0023</td>
<td>0.0005</td>
<td>0.0379</td>
<td>0.0545</td>
<td>0.0005</td>
</tr>
<tr>
<td>21.Bro.01-130a2</td>
<td>0.0019</td>
<td>0.0021</td>
<td>0.1598</td>
<td>0.6246</td>
<td>0.0005</td>
<td>0.0113</td>
<td>-0.004</td>
<td>0.0023</td>
<td>0.0002</td>
<td>0.0418</td>
<td>0.0562</td>
<td>0.0006</td>
</tr>
<tr>
<td>21.Bro.01-130a3</td>
<td>0.0056</td>
<td>0.0023</td>
<td>0.1774</td>
<td>0.5833</td>
<td>0.0004</td>
<td>0.0129</td>
<td>-0.027</td>
<td>0.0029</td>
<td>8E-05</td>
<td>0.0506</td>
<td>0.0707</td>
<td>0.001</td>
</tr>
</tbody>
</table>
5.6.4. Alkali and Alkaline Earth Elements

Alkali and alkaline earth elements displayed similar trends in produced water samples as they did for synthetic solution tests. Considering their monovalent and divalent nature the difference in recovery abilities from synthetic solutions to produced water samples may not be as variable when considering the other sets of CVEs in this study.

The monovalent alkalis (Rb and Cs) in this experiment all have recoveries <1%, which can be expected after column chemistry in the matrix wash step. The divalent alkalis clearly show the resins preference for multi valent ions as recoveries in many of the samples increase significantly. However, some samples do display considerable inability to recovery some of the divalent alkalis. Beryllium recoveries range from 5% to 13% with the highest recovery in sample 21.Bro.01-079a and the lowest in sample 21.Bro.01-130a. The majority of strontium recoveries in this experiment are considerably low with values near 0%. The only positive recovery for strontium is in sample 21.Bro.01-163d at 727%, suggesting polyatomic oxide interference. Barium recoveries have recorded a wide variability between samples with percent recoveries ranging from ~0% to 127%. When analyzing the synthetic solutions in the preliminary experiments of this study, barium had the most favorable recoveries of the AE. However, when considering produced water samples barium displays poor recovery capability in most samples. Table 15 suggests blank contributions to the AE percent recoveries were negligible.
Figure 24. Alkaline elements display no recoveries for monovalent elements while divalent elements display better recovery capabilities.

Table 15. Ratio of sample spike concentrations to mean blank concentrations for AEs in produced waters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cs</th>
<th>Rb</th>
<th>Be</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.Bro.01-079a</td>
<td>0.0065</td>
<td>0.008</td>
<td>0.0005</td>
<td>0.0114</td>
<td>0.3985</td>
</tr>
<tr>
<td>21.Bro.01-163d</td>
<td>0.0032</td>
<td>0.0072</td>
<td>0.0007</td>
<td>0.0007</td>
<td>0.3089</td>
</tr>
<tr>
<td>21.Bro.01-040a</td>
<td>0.0054</td>
<td>0.0097</td>
<td>0.0007</td>
<td>0.003</td>
<td>0.2428</td>
</tr>
<tr>
<td>21.Bro.01-069d</td>
<td>0.0061</td>
<td>0.0097</td>
<td>0.0007</td>
<td>0.0027</td>
<td>0.2477</td>
</tr>
<tr>
<td>21.Bro.01-130a.1</td>
<td>0.0065</td>
<td>0.0098</td>
<td>0.001</td>
<td>0.0009</td>
<td>0.1191</td>
</tr>
<tr>
<td>21.Bro.01-130a.2</td>
<td>0.0227</td>
<td>0.0145</td>
<td>0.0012</td>
<td>0.0026</td>
<td>0.3229</td>
</tr>
<tr>
<td>21.Bro.01-130a.3</td>
<td>0.0452</td>
<td>0.0187</td>
<td>0.0013</td>
<td>0.0032</td>
<td>0.3108</td>
</tr>
</tbody>
</table>
5.6.5. Precious Metals

Precious metal recoveries in produced waters samples displayed vastly different results when compared to the synthetic solutions tests conducted in the first phase of this study. Ruthenium had the highest recoveries of the precious metals with values ranging from 12% to 16% the highest recovery in sample 21.Bro.01-069d and the lowest in 21.Bro.01-163d. Rhodium recoveries ranged from 9% to 14%, the highest recoveries were recorded in sample 21.Bro.01-069d and the lowest in 21.Bro.01-163d. Palladium, osmium, platinum and silver had recoveries <1% in all samples. Iridium recoveries range from 1.5% to 3.5% while gold recoveries range from ~1% to ~6%. The highest recovery for gold was recorded in sample 21.Bro.01-079a. Precious metal recoveries show similar trends throughout the samples analyzed in this experiment.
Figure 25. Ruthenium and Rhodium show the highest recoveries for precious metals. All recoveries are less than 20%.

Table 16. Ratio of sample spike concentrations to mean blank concentrations for precious metals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.Bro.01-079a</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0095</td>
<td>0.0254</td>
<td>0.0014</td>
<td>0.0105</td>
<td>0.0014</td>
<td>0.0237</td>
</tr>
<tr>
<td>21.Bro.01-163d.</td>
<td>0.0005</td>
<td>0.0004</td>
<td>0.0021</td>
<td>0.026</td>
<td>0.0006</td>
<td>0.0082</td>
<td>0.0051</td>
<td>0.4316</td>
</tr>
<tr>
<td>21.Bro.01-040a.</td>
<td>0.0005</td>
<td>0.0003</td>
<td>0.0115</td>
<td>0.0921</td>
<td>0.0004</td>
<td>0.0135</td>
<td>0.0015</td>
<td>0.0545</td>
</tr>
<tr>
<td>21.Bro.01-069d.</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0016</td>
<td>0.057</td>
<td>0.0005</td>
<td>0.0084</td>
<td>0.0039</td>
<td>0.0518</td>
</tr>
<tr>
<td>21.Bro.01-130a.1</td>
<td>0.0005</td>
<td>0.0004</td>
<td>0.0048</td>
<td>0.1062</td>
<td>0.0007</td>
<td>0.013</td>
<td>0.0127</td>
<td>0.1964</td>
</tr>
<tr>
<td>21.Bro.01-130a.2</td>
<td>0.0005</td>
<td>0.0004</td>
<td>0.0046</td>
<td>0.0932</td>
<td>0.0007</td>
<td>0.0152</td>
<td>0.0201</td>
<td>0.2689</td>
</tr>
<tr>
<td>21.Bro.01-130a.3</td>
<td>0.0006</td>
<td>0.0004</td>
<td>0.0054</td>
<td>0.024</td>
<td>0.0004</td>
<td>0.0043</td>
<td>0.0075</td>
<td>0.0399</td>
</tr>
</tbody>
</table>
6.1.0. Interpretation

The interpretations in this chapter discusses the results for the synthetic solution experiments and the results for the produced water sample trials. Geochemical modelling was employed to assists in determining the dominant speciation for certain CVEs as a function of pH. Speciation was determined using the Visual MINTEQ thermodynamic database with the Specific Ion Theory (SIT) activity model (Ciavatta, 1980) assuming the composition of the Na-rich 50 g/L solutions. The SIT model works accurately to ionic strengths of up to 2 or so, making it ideal for this work, as it does not require the complexity of viral coefficients. Speciation in these conditions provide insight into the observed CVE recoveries.

6.1.1. Lanthanides

Synthetic solution tests indicated that the lanthanides are capable of being fully recovered. Chelex-100 has a high preference for multi valent cations and lanthanides are available as 3+ valence cations in the conditions tested Table 17. The most successful recoveries are recorded in the Na-rich environment at pH 6 in samples of 50g/L TDS. Nearly the entire sodium mass in the matrix environment is either removed from the resin by the matrix wash step in the method during chromatography or is never captured by the ion exchange resin to begin with. If no sodium is occupying ligand space on the resin no competition exists for said space. Hence, lanthanides can be captured and successfully removed during elution.

When observing the results for percent recovery in the Ca-rich experiments, it is immediately noticeable that an inhibiting affect has reduced the ability for the Chelex-100 resin to capture the lanthanides. Owing to the divalent nature of calcium it is likely that competition for ligand sites exists where it did not in the Na-rich matrix. The presence of calcium has decreased the ability of the Chelex-100 resin to capture lanthanides by a factor of 4.
Produce waters displayed the most unfavorable of percent recoveries for lanthanides in all experiments. In both the Na-rich and Ca-rich experiments the lightest lanthanides recovered well at 80% or higher clearly displaying the method is capable of producing positive outcomes. However, in produced water samples the ability for favorable percent recovery has been drastically decreased. All samples have percent recoveries < 20%. This is a decrease in recovery efficacy by a factor of ~4 for all lanthanides. Produce waters contain constituents not present in the synthetic solutions such as organic matter and high metal concentrations such as iron, and manganese. Each of these variables may present complications when attempting to capture CVEs on chelating resin.

**Table 17.** Lanthanide speciation in a 50g/L Na-rich solution, as predicted from the Visual MINTEQ thermodynamic database with the SIT activity model.

<table>
<thead>
<tr>
<th>CVE</th>
<th>Predominant speciation at pH 4 and 6 in saline environment</th>
<th>Species %</th>
</tr>
</thead>
<tbody>
<tr>
<td>La³⁺</td>
<td>La³⁺</td>
<td>70%</td>
</tr>
<tr>
<td></td>
<td>LaCl₂⁺</td>
<td>~20%</td>
</tr>
<tr>
<td>Pr³⁺</td>
<td>Pr³⁺</td>
<td>65%</td>
</tr>
<tr>
<td></td>
<td>PrCl₂⁺</td>
<td>24%</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>Nd³⁺</td>
<td>85%</td>
</tr>
<tr>
<td></td>
<td>NdSO₄⁺</td>
<td>11%</td>
</tr>
<tr>
<td>Sm³⁺</td>
<td>Sm³⁺</td>
<td>85%</td>
</tr>
<tr>
<td>Ho</td>
<td>Ho³⁺</td>
<td>85%</td>
</tr>
<tr>
<td>Tm³⁺</td>
<td>Tm³⁺</td>
<td>66%</td>
</tr>
<tr>
<td></td>
<td>TmCl₂⁺</td>
<td>21%</td>
</tr>
<tr>
<td>Lu³⁺</td>
<td>Lu³⁺</td>
<td>73%</td>
</tr>
<tr>
<td></td>
<td>LuCl₂⁺</td>
<td>13%</td>
</tr>
</tbody>
</table>
6.1.2. High Field Strength Elements

Many HFS elements display difficulty for capture and recovery in both the Na and Ca-rich matrix environments tested. At pH 4 and 6 in the Na-rich matrix solutions the highest recoveries are recorded in the 300g/L TDS samples. When analyzing the Ca-rich matrix solutions the highest recoveries are recorded in the 150g/L samples. This trend suggests that these CVEs perform better when they are in a high TDS environment, contrasting significantly to the preference of the lanthanides for a low TDS environment.

According to Table 18, these elements are prone to form oxide and hydroxide complexes in the environments tested. Concluding, in a high TDS environment for both Na-rich and Ca-rich matrixes, sodium and calcium cations are readily available to combine with oxide and hydroxide anions leaving the monoatomic elements available for capture during chromatography. Sodium and calcium ions are not readily available for complexation in the lower TDS samples. Consequently, elements combine with those anions producing large anion complexes which are not capable of capture via Chelex-100 resulting in poor recoveries. This process coupled with large amounts of iron, and manganese competing for ligand sites on the resin may be responsible for poor recoveries across the board in produced water samples.
Table 18. HFS speciation in a 50g/L Na-rich solution, as predicted from the Visual MINTEQ thermodynamic database with the SIT activity model

<table>
<thead>
<tr>
<th>CVE</th>
<th>Predominant Speciation at pH 4 and 6 in saline environment</th>
<th>% Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>MoO$_4^{2-}$</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>HMoO$_4^-$</td>
<td>20%</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti(OH)$_4$</td>
<td>99%</td>
</tr>
<tr>
<td>W</td>
<td>WO$_4^{2-}$</td>
<td>47%</td>
</tr>
<tr>
<td></td>
<td>WO$_3$(H$_2$O)$_3$</td>
<td>37%</td>
</tr>
<tr>
<td>Sb</td>
<td>Sb(OH)$_6^{-1}$</td>
<td>95%</td>
</tr>
<tr>
<td></td>
<td>Sb(OH)$_5$</td>
<td>5%</td>
</tr>
<tr>
<td>Hf</td>
<td>HfOH$^{3+}$</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>Hf$^{4+}$</td>
<td>1%</td>
</tr>
<tr>
<td>Zr</td>
<td>Zr(OH)$_4$</td>
<td>100%</td>
</tr>
</tbody>
</table>

6.1.3. Industrial Elements

The majority of industrial elements analyzed in this study are available in the 2+ and 3+ valence state, making them readily available for capture using Chelex-100. All analytes displayed recoveries greater than 50% during pH 6 trials in Na-rich matrixes at 50 g/L with exception of boron and thallium. In these conditions thallium is available in the 1+ valence state and inability for Chelex-100 to capture can be expected. Boron is available as neutral boric acid in these conditions and cannot be collected with Chelex-100 (Table 19).

Iron displayed acceptable recovery potential during pH 6 experiments in Na-rich environments with ~70%. In the Ca-rich environment the recovery was just 19% showing that the calcium matrix likely created competition for ligand sites on the resin and did not catch iron in sufficient amounts. This competition for ligand sites negatively affected the other elements during
the Ca-rich trials as well. During produced water experiments iron recoveries dropped drastically with no iron being captured by the resin. Figure 18 shows that large amounts of iron have precipitated in the mini column and iron is not being eluted during chromatography. In fact, all industrial elements seem to be having trouble being eluted due to iron precipitation in the mini columns. Cobalt, nickel, copper, cadmium, lead, gallium, and vanadium displayed percent recoveries between 60 and 100% in pH 6 experiments. These elements displayed recoveries between 13 and 23% during produced water trials showing a clear recovery diminishing effect possibly due to iron precipitation in the column. In the synthetic solution experiments, manganese recoveries averaged 50%. During produced water trials manganese recoveries were as high as ~800% and as low as ~122%. These high concentrations can likely be attributed to polyatomic interferences during analyses. In the conditions tested many of the industrial elements are available in their monoatomic form and would be ready for capture via Chelex-100. Some of the these however are mostly present as hydroxyl or chloride complexes Table 19.
Table 19. Industry element speciation in a 50g/L Na-rich solution, as predicted from the Visual MINTEQ thermodynamic database with the SIT activity model

<table>
<thead>
<tr>
<th>CVE</th>
<th>Predominant speciation at pH 4 and 6 in saline environment</th>
<th>Species %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>H₃BO₃</td>
<td>100%</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(OH)₂⁺</td>
<td>98%</td>
</tr>
<tr>
<td>Co</td>
<td>CoOH²⁺</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>Co²⁺</td>
<td>1%</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu²⁺</td>
<td>72%</td>
</tr>
<tr>
<td></td>
<td>CuCl⁺</td>
<td>19%</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni²⁺</td>
<td>88%</td>
</tr>
<tr>
<td></td>
<td>NiCl⁺</td>
<td>7%</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb²⁺</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>PbCl⁺</td>
<td>32%</td>
</tr>
</tbody>
</table>
6.1.4. Alkali and Alkaline Earth Elements

All alkali and alkaline earth elements are either monovalent or divalent ions in solution. The +1 valence is not available for capture using Chelex-100. In this study the +1 alkalis rubidium, and cesium have been tested for, and in all experiments, recoveries were <2%. The 2+ valence alkalis beryllium, strontium, and barium were tested and have shown recovery potential. At pH 4 the worst recoveries were observed at 0.36%, 3%, and 171% for beryllium, strontium and barium respectively. In pH 6 Na-rich environments recoveries were 23%, 6% and 307%. The Ca-rich environment dropped recovery capabilities for Beryllium and Strontium while barium recoveries stayed near 300%. The high recoveries for barium may likely be the result of isobaric interferences during ICP-MS analysis or contributions from the salts in the high purity Na-Ca-Cl solutions.

When observing produced water results rubidium and cesium recoveries were as expected <1%. Beryllium recoveries ranged from 5% to 13%, strontium recoveries were as high as 727% and barium recoveries ranged from -13% to 127%. Some samples recovered barium at 14% and 22% showing a possible inhibiting factor due to iron precipitation in the mini columns. In the conditions tested barium and beryllium are readily available in their monoatomic state Beryllium is also available as a hydroxyl complex (Table 20).

<table>
<thead>
<tr>
<th>CVE</th>
<th>Predominant speciation at pH 4 and 6 in saline environment</th>
<th>Species %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>Ba$^{2+}$</td>
<td>85%</td>
</tr>
<tr>
<td></td>
<td>BaCl$^+$</td>
<td>14%</td>
</tr>
<tr>
<td>Be</td>
<td>Be$^{2+}$</td>
<td>42%</td>
</tr>
<tr>
<td></td>
<td>Be(OH)$_2$</td>
<td>48%</td>
</tr>
</tbody>
</table>
6.1.5. Precious Metals

Precious metals displayed the poorest recoveries of all CVEs analyzed in this study. In the initial tests conducted in a Na-rich matrix environment, all recoveries are <30%. Ruthenium displaying the highest recovery at ~30% in pH 6 solutions and gold recovering at ~10% in pH 4 solutions. In the pH 4 solutions gold recoveries are slightly more favorable in high TDS samples than in low TDS samples.

According to Table 21, gold is dominantly present as a large anionic hydroxide complex in the environments tested. As a large anionic complex, gold is not readily captured by Chelex-100. Gold likely performs better in an acidic environment due to the digestion of these complexes liberating ionic gold. In the pH 4 environment gold recoveries are recovered slightly more favorably in high TDS samples. An interpretation of this observation is that more matrix ions are available to mingle with hydroxide anions leaving ionic gold available for capture via Chelex-100.

Palladium is present as a large anionic chloride complex in all environments tested Table 21. It is likely that the other PGEs behave similar to Palladium in these experiments. Palladium, osmium and platinum all recovered <1% in every experiment while iridium recovered ~5% in Na-rich experiments. Poor recoveries for PGEs are likely due to large anionic chloride complexation.

<table>
<thead>
<tr>
<th>CVE</th>
<th>Predominant speciation at pH 4 and 6 in saline environment</th>
<th>%</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$^{3+}$</td>
<td>Au(OH)$_4^-$</td>
<td>92%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AuOH$^{2+}$</td>
<td>7%</td>
<td></td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>AgCl$_2^-$</td>
<td>66%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AgCl$_3^{2-}$</td>
<td>32%</td>
<td></td>
</tr>
<tr>
<td>Pd$^{2+}$</td>
<td>PdCl$_4^{2-}$</td>
<td>99%</td>
<td></td>
</tr>
</tbody>
</table>

Table 21. Precious metals speciation in a 50g/L Na-rich solution, as predicted from the Visual MINTEQ thermodynamic database with the SIT activity model.
7.0 Conclusion

This study is instrumental in developing methods for strengthening the US domestic CVE supply chain, offsetting the rising costs of produce water disposal and treatment, while also minimizing risks associated with current produced water management practices. Results have shown that recovery of most CVEs in Na-rich solutions can be accomplished favorably at both pH 4 and 6. Ca-rich matrixes inhibit the recovery of many CVEs, but not all are ill affected. When attempting to recover CVEs from produced waters an inhibiting affect takes place which was not present during synthetic solution trials. Further experimentation will be necessary to combat this issue.

This study has tested a method for preconcentrating and quantifying CVEs in produced waters, identifying some of the methods strengths and limitations. By adjusting parameters such as TDS dilution, pH amendments, and resin/sample ratios, CVEs of interest can be quantified. Once CVEs have been quantified, their economic value can be determined and a potential valuable resource thus discovered.
References


source of strategic mineral commodities, Report to U.S. Department of Energy (Award DE-EE0007603), 189 p


Vita

Joshua Matthew Lewis is a B.Sc. Geological Sciences from the University of Texas at El Paso. Joshua started his academic career at El Paso Community College in 2015 and began his geological studies at UTEP in 2017. He began his M.Sc. studies in Spring 2020 with ambitions of studying economic geology and mineral exploration prior to the COVID-19 pandemic. During the pandemic his focus in study shifted to analytical brine geochemistry. This opportunity allowed him to develop laboratory operation skills and deeper knowledge of geochemistry. Before his academic career at UTEP Joshua was an infantryman in the U.S. Army. He joined the army in 2009 at the age of 18 and deployed to Iraq 2009-2010 and to Afghanistan 2011-2012 where he was awarded the Purple Heart for wounds received in action and was recognized with an Army Commendation Medal ‘V’ for Valor in combat. Joshua was born in Northeast El Paso Texas and briefly attended Capt. John L. Chapin High School.

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