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Application of solvent extraction method for lithium recovery from shale gas-produced water

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서울대학교 공과대학원
에너지시스템공학부
장 은 영

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지도 교수 정 은 혜

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에너지시스템공학부
장 은 영

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위 원 장		(인)
부위원장		(인)
위 원		(인)

Abstract

Application of solvent extraction method for lithium recovery from shale gas-produced water

Eunyoung Jang

Energy Systems Engineering

The Graduate School

Seoul National University

Shale gas-produced water is a high saline wastewater generated during the development of shale gas. The shale gas development technique is hydraulic fracturing, and this process involves a massive water injection into the shale layer. After the hydraulic fracturing, the mixture of injected water and shale formation water flows back to the ground. This is shale gas-produced water, and it contains a relatively high concentration of lithium originating from the clay mineral of shale rock. Due to the increasing demand for lithium, recently, several studies have focused on seawater, whose lithium content is 0.17 mg/L, as a new source of lithium. The produced water in the Marcellus shale area contains about 95 mg/L of lithium; thus, if selective lithium recovery from produced water is possible, it will be much more efficient than recovery from seawater. Therefore, this study was conducted to examine the applicability of the solvent extraction method for lithium recovery from diluted shale gas-produced water.

The total dissolved solids (TDS) level of shale gas-produced water is very high, up to 200,000 mg/L, and the concentration of competitive cations with lithium in extraction is also high. Therefore, multi-stage solvent extraction has been suggested to reduce the effect of competitive cations and to improve the selectivity of lithium. In the first-stage, the divalent cations were removed

using di(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene. In the second-stage, tri-butyl phosphate (TBP) was applied as a synergistic additive with D2EHPA for selective lithium recovery.

After the first-stage solvent extraction with 50X diluted shale gas-produced water, about 97.9% of magnesium ions were removed, and all other divalent cations, including calcium, strontium, and barium were removed. In the second-stage extraction for lithium recovery, the aqueous solution obtained after an appropriate number of first-stage extractions was applied. Finally, the highest extraction efficiency of lithium ion after the two-stage extraction was 26.46%. Almost all of the divalent cations were removed from the first-stage extraction, and D2EHPA has a higher affinity with lithium ion compared with sodium ion, so the selectivity of lithium was very high. In conclusion, the multi-stage solvent extraction method can be applied for highly selective lithium recovery.

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Chapter 1. Introduction

There has been an increase in shale gas development due to the wide use of hydraulic fracturing and horizontal drilling. During the process of hydraulic fracturing, between 4 million and 19 million liters of highly pressurized fracturing fluid are injected into the shale layer to make fractures. After that, 20% to 50% of injected water flows back to the ground (International Energy Agency, 2012). In the case of the Marcellus shale area, more than 3000 m^3 of produced water are generated a day (Gregory et al., 2011). This large volume of flowback water is also called produced water.

Shale gas-produced water is a hypersaline wastewater, which is a combination of fracturing fluid and shale formation water; hence, this water contains a large amount of inorganic components derived from shale layer formation water and organic compounds that originate from both shale gas and the additives of fracturing fluid. Among these components, lithium is a useful resource, and it can be recovered from shale gas-produced water.

Lithium is a rare metal element, and it can be widely used as a raw material in rechargeable batteries and in aluminum-lithium alloys for aerospace applications and as a future nuclear fusion fuel (Nishihama et al., 2011). In particular, the use of lithium ion batteries has increased with the development of electric cars and portable devices; thus, the demand for lithium is dramatically increasing, as shown in Figure 1.
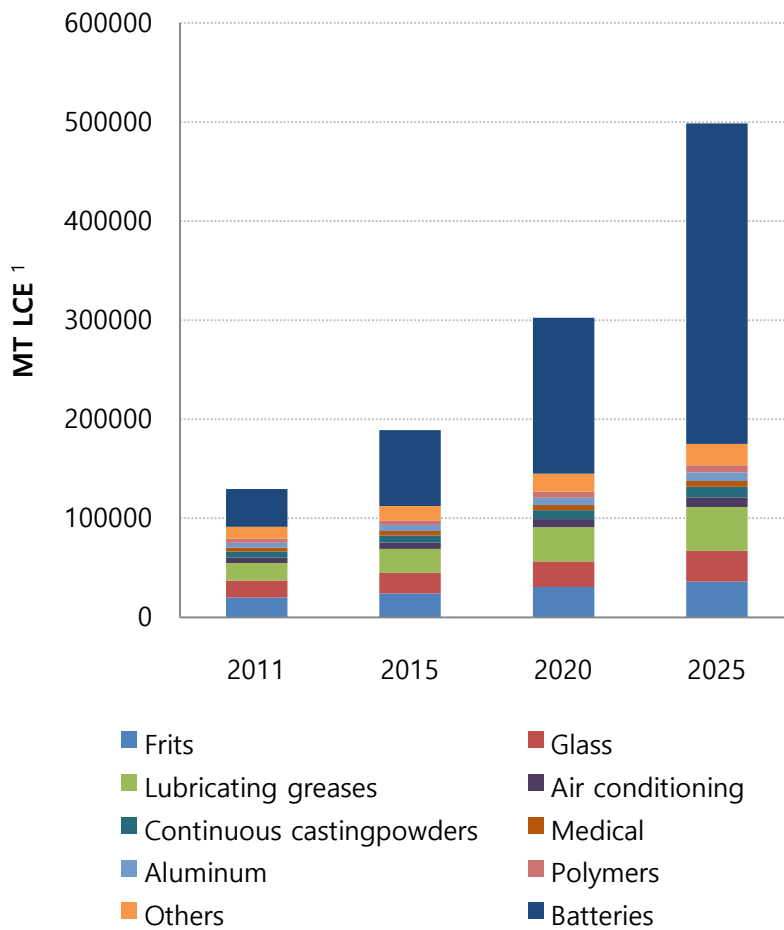
Figure 1. Lithium consumption by application (Estimated) (Cabeza et al., 2015)
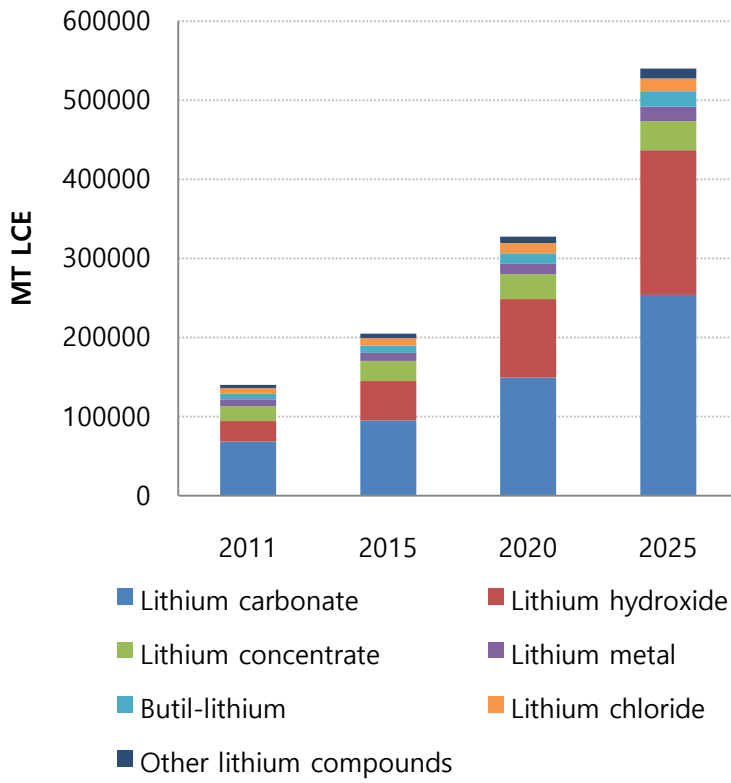
Figure 2. World lithium demand in merchant market by compound (estimated)
(Cabeza et al., 2015)

Additionally, Figure 2 shows the future demand for lithium by compound. Both Figures 1 and 2 were created based on the data of Cabeza et al. (2015) to show a forecast of the increase in lithium demand.

Historical statistics for lithium mine production are shown in Table 1. In 2015, the total demand for lithium was 205 k MT LCE (Figure 2), and the world mine production was 173 k MT LCE (Table 1). When comparing these amounts, it can be determined that the demand is greater than the amount produced. Thus, it can be estimated that the supply of lithium will be insufficient in the future.

At present, the main sources of lithium are mines and brine lakes, such as the Dead Sea and the Great Salt Lake. The supply of lithium from mines will soon be deficient, and these brine lakes are only located in certain countries, including Bolivia, Chile, the U.S.A., Argentina, and China; hence, other resources must be found. There are currently many studies on lithium recovery from seawater because of the vast volume of seawater. The concentration of lithium in seawater, however, is only 0.17 mg/L (Chitraker et al., 2001). This lithium concentration in seawater is very low compared with that of shale gas-produced water. The lithium concentration in produced water varies according to wells, but the median value is almost 100 mg/L (Haluszczak et al., 2012). Therefore, shale gas-produced water is considered another source of lithium. Additionally, if the selective recovery of lithium is possible, it will be more cost-effective than lithium recovery from seawater.

The methods for lithium recovery from aqueous solution include electrodialysis, the adsorption and desorption process, the electrochemical process with the principle of the rechargeable battery, and solvent extraction. Electrodialysis uses an electric field and organic membrane that absorbs ionic liquid, and the lithium ion moves to the cathode, through the membrane, faster

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than other cations because of the conductivity difference of the applied ionic liquid (Hoshino, 2013). In the process of adsorption and desorption, the lithium ion adheres to the surface of the adsorbent, which has a high affinity toward lithium ions, such as manganese oxide (Chitraker et al., 2001), and is then released from the surface of the adsorbent during the desorption process. The lithium ion can also be recovered by the electrochemical method using the anode, which reacts with lithium ions selectively. The principle of this process is the same as that with the rechargeable battery. While discharging, the lithium ion in the solution enters the lattice structures inside the anode, and while charging, the lithium ion is released from the anode (Kim et al., 2015). Liquid–liquid solvent extraction is a widely used method using an immiscible extractant, which has high solubility of lithium (Kislik, 2012).

In this paper, solvent extraction was adopted to recover lithium from the produced water, because it is a simple process and the operation time is short (Yang et al., 2003). Additionally, solvent can be reused after stripping (Goodenough et al., 1967), so solvent extraction is an economical process. In the case of lithium recovery by the solvent extraction method, other cations in the produced water can be co-extracted. The multivalent cations, especially Ca and Mg ions, have higher extractability than lithium; hence, multi-stage solvent extraction was conducted to improve the selectivity of lithium and to reduce the effect of divalent cations. The purpose of this research is to examine the applicability of the solvent extraction method for lithium recovery from shale gas-produced water.

Table 1. World lithium mine production(USGS 2012, 2014, 2016)

	Mine production [MT]	As MT LCE[2]
2010	28100	149576
2011	34000	180982
2012	35000	186305
2013	3500	186305
2014	31700	168739
2015	32500	172998

[2] LCE = lithium carbonate (Li_2CO_3) equivalent: determined by multiplying Li value by 5.323

Chapter 2. Theoretical background

2.1 Solvent extraction

Solvent extraction is a selective separation method for a target element using an extractant, which has high solubility for the target metal. Solvent extraction has several advantages. First, the operation time is short and the procedure is simple (Yang et al., 2003), so continuous operation is possible. Second, it is a cost-effective process, because the solvent can be reused after stripping (Goodenough et al., 1967). The extraction efficiency, however, can be affected greatly by the type of extractant and extraction method. Therefore, using an appropriate extractant and finding optimal conditions are important for effective extraction.

2.2 Previous studies on lithium recovery by solvent extraction

There are many studies that involve separating lithium from various solutions by the solvent extraction method. From those studies, it is found that the active solvents for the extraction of alkali-metal ions are crown ethers, alcohols, and esters that have a coordinating oxygen atom (Umetani et al., 1987). Metal cation extraction by ethers involves an ion-pair extraction system. Macrocyclic polyethers, such as dibenzo-18-crown-6, have been widely investigated for the solvent extraction of alkali-metals. The 18-crown-6 forms crystalline complexes where the extracted cation is located in the center of the ether ring. However, the extractability decreases in the order of K > Rb > Cs > Na > Li (Sadakane et al., 1975). Therefore, it

is difficult to achieve the selective extraction of lithium compared with other alkali-metals. In the case of alcohol including n-butanol, it contains strongly polar and electronegative atoms. Therefore, the electropositive metal ions are attracted by the electronegative extractant. N-butanol has high lithium selectivity compared with calcium (selectivity factor, $S_{Ca}^{Li} = 15$), but for a monovalent, such as sodium or potassium, it has relatively low lithium selectivity ($S_{Na}^{Li} = 0.26$ and $S_{K}^{Li} = 0.32$) (Gabra, 1978). This means that its extraction efficiency for other monovalent cations is higher than that for lithium. An ester such as di-(2-ethylhexyl) phosphoric acid (D2EHPA) deprotonates to form a hydrophobic anion, and this anion can make a chelate with cations in the aqueous phase. D2EHPA shows higher extractability of divalent cations than monovalent cations. However, among the monovalent cations, such as potassium, sodium, and lithium, lithium has higher selectivity compared with the others (Hano et al., 1992).

Among the three types of solvents, ether, alcohol, and ester, the ester, specifically D2EHPA, was selected as an extractant for the multi-stage solvent extraction study. There are two reasons for using D2EHPA. The first is the difference of the concentrations of the monovalent and divalent cations. In shale gas-produced water, the concentration of sodium (the median value is 36,400 mg/L) is much higher than that of divalent cations (the median values of Ca, Mg, Sr, and Ba are 11,200 mg/L, 875 mg/L, 2,330 mg/L, and 1,990 mg/L, respectively) (Haluszczak et al., 2012). When n-butanol and dibenzo-18-crown-6 were used as extractants, the extraction efficiency of lithium was lower than that of sodium. Therefore, if crown ether or alcohol is applied for lithium recovery from shale gas-produced water, much more sodium will be extracted than lithium, because the concentration of sodium is around 383 times that of lithium. In the case of D2EHPA, although the

extractability of lithium is lower than that of divalent cations, D2EHPA has higher selectivity for lithium than sodium. The concentrations of divalent cations in shale gas-produced water are also higher than that of lithium; however, the highest concentration among the divalent cations (calcium) is about 118 times that of lithium. When we compare these values, the concentrations of divalent cations are more than three times lower than that of sodium. Therefore, if these divalent cations are removed before lithium recovery, the selective recovery of lithium will be possible with D2EHPA.

The second reason for using D2EHPA is the applicability of D2EHPA to both divalent cation removal and lithium recovery by adjusting the concentration of D2EHPA. Lithium in the aqueous solution can be extracted if the concentration of D2EHPA is over 0.5 M. Thus, when D2EHPA is applied with less than a 0.5 M concentration, the separation of divalent cations from lithium is possible (Bukowsky et al., 1992). In addition, lithium extraction occurs with more than 0.5 M of D2EHPA, and the extractability can be increased by using a synergistic additive. When an organophosphorus compound is used as an extractant, the well-known synergistic reagents are tri-butyl phosphate (TBP) and tri-n-octylphosphine oxide (TOPO). In the research of Hano et al. (1992), TOPO did not show a synergistic effect, but the addition of TBP certainly increased the extraction efficiency of lithium. Consequently, D2EHPA was selected as an extractant for both divalent cations and lithium recovery, and for the lithium recovery, TBP was selected as an auxiliary reagent.

2.3 Metal extraction by D2EHPA

In solvent extraction, D2EHPA has been used for metal ion extraction.

D2EHPA is the most versatile extractant due to its advantages in the solvent extraction process. The advantages of D2EHPA are its chemical stability, good loading and stripping characteristics, and low solubility in the aqueous phase (Chagnes et al., 2015).

D2EHPA forms an anion by deprotonation (DEHPA, n.d.).

$$(C_8H_{17}O)_2\overset{\overset{\textstyle O}{\|}}{P}\text{-}OH \leftrightarrow (C_8H_{17}O)_2\overset{\overset{\textstyle O}{\|}}{P}\text{-}O^- + H^+ \tag{1}$$
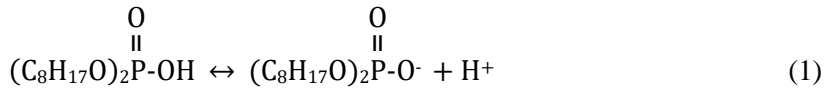
This hydrophobic anion creates a chelate with a cation from the aqueous phase, and the chelate complex dissolves in the organic phase.

D2EHPA exists predominantly as a dimer in nonpolar solvent. Thus, the general extraction reaction formula is as follows:

$$M^{n+} + \frac{n+x}{2}\overline{(HR)_2} \leftrightarrow \overline{MR_n(HR)_x} + nH^+ \tag{2}$$
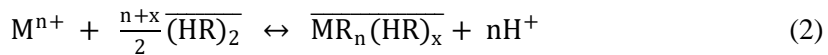
where M is the metal cation, n is the charge of the metal cation, HR is D2EHPA as a dimer, and x is the solvation number of the complex.

As shown in equation (2), the equilibrium shifts to the right side as the concentration of hydrogen ions decreased. It means that the formation of the D2EHPA-Li complex is favored as the pH value increased. Therefore, the extraction efficiency of cations rises as the pH increases. However, the acidic organophosphorus compound showed a high extraction ability in the weakly acidic region (Hano et al., 1992), so the optimal pH value is pH 4–6. The pH of shale gas-produced water is between 5.8 and 6.6, and in the case of diluted synthetic produced water, the pH is about 4.7. Therefore, D2EPA was selected

as an extractant.

2.4 Synergistic effect of TBP on lithium extraction

TBP was added to the extractant to improve the efficiency of lithium extraction. TBP is a synergistic additive when organophosphorus acidic reagent is used as an extractant. The addition of an appropriate concentration of TBP significantly improves the lithium extraction efficiency. In the research of Hano et al. (1992), the mechanism of the synergistic effect on lithium extraction was explained by the formation of mixed complexes. The lithium distribution ratio, D_{Li}, increases gradually with the increasing TBP concentration and then becomes constant. The effect of TBP concentration on the lithium distribution ratio can be explained by the following equations.

$$\text{LiR} \, x\text{HR} \; + \; \text{TBP} \; \leftrightarrow \; \text{LiR} \, (x - 1)\text{HRTBP} + \text{HR} \qquad\qquad (3)$$

$$\text{HR} \; + \; \text{TBP} \; \leftrightarrow \; \text{HRTBP} \qquad\qquad\qquad\qquad (4)$$

In equations (3) and (4), R is $(RO)_2POO$ and HR is $HOOP(RO)_2$ from equation (1). Equation (3) shows how the extraction increases with increasing TBP concentrations. With the addition of TBP during the extraction reaction, TBP substitutes one molecule of D2EHPA, and this D2EHPA molecule can react with the other lithium ion. Accordingly, the synergistic effect of TBP occurs and increases lithium extractability with increasing TBP concentrations. In the case of the excess addition of TBP, efficiency is rather decreased. This phenomenon can be explained by equation (4). The excess TBP molecule makes a complex with D2EHPA, so

this D2EHPA does not react with the lithium ion. Therefore, the addition of TBP in appropriate concentrations is important for the synergistic effect on lithium extraction.

Chapter 3. Materials and methods

3.1 Sample preparation

Synthetic produced water was prepared for the research based on a previous study on the components in the produced water in the Marcellus shale area (Haluszczak et al., 2012). Since produced water is a mixture of fracturing fluid and shale formation water, firstly, fracturing fluid was synthesized, and then various chemicals were added to meet the concentrations of elements in real produced water. The ratio of fracturing fluid to shale formation water was assumed to be 1:1. Produced water was synthesized for eight target ions, including Cl, Br, Ca, Li, Mg, Na, Sr, and Ba, and basic properties, such as pH and conductivity, were adjusted to meet the values of real produced water. In addition, as cations compete with lithium ion in the lithium recovery process, the concentrations of cations were matched to the median value of real produced water.

Synthetic fracturing fluid was prepared with the composition shown in Figure 3. The commonly used proppant in the Marcellus shale area is 40/70 mesh sands (Beckwith, 2011). Therefore, 40/70 mesh (212- 420 μm) silica sand was added to the synthetic fracturing fluid. After that, chemicals, such as lithium bromide solution and metal chlorides, were added to the fracturing fluid to meet the concentrations of each component in real produced water. The initial pH value of synthesized produced water was about 3, so the pH value was adjusted to the real produced water pH range of 5.8–6.6 using 1 N sodium hydroxide. Finally, synthetic produced water was settled for around 24 hr, and the supernatant liquid was used for the experiments.
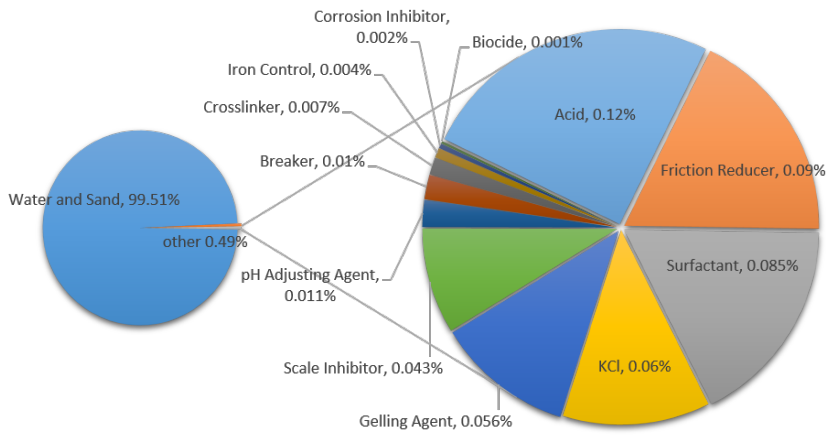
Figure 3. Volumetric composition of fracturing fluid (U.S. Department of
Energy, 2009)

3.2 Experimental methods

In all stages of the extraction experiments, D2EHPA with 97% purity (Sigma-Aldrich, USA) was used as an extractant. The chemical and physical properties of D2EHPA are represented in Table 2. D2EHPA was diluted in kerosene (Sigma-Aldrich, USA) to match the target concentrations. Equal volumes of organic and aqueous phase solutions were agitated at a constant speed, 150 rpm, for 30 min by a shaking incubator (SH-BSI16R, Samheung Instrument, Korea) at 25℃. After extraction, the mixed solution was settled for more than 20 min in separating funnel, and then the aqueous solutions were withdrawn. The pH and conductivity of the aqueous phase were analyzed by a multi-meter (Orion STAR A329, Thermo Fisher Scientific, USA). The aqueous solution was filtered with a 0.45μm polytetrafluoroethylene (PTFE) filter (Millipore, Germany), and then the metal concentrations of the aqueous solution were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8300, Perkin Elmer, USA) for cations and ion chromatography (IC, Dionex ICS-1100, Thermo Scientific, USA) for anions.

3.2.1 First-stage solvent extraction

In the first-stage extraction for the removal of divalent cations, including Ca, Mg, Sr, and Ba, extractants were prepared by diluting D2EHPA in kerosene. Extraction experiments were conducted with various extractant concentrations: 0.3, 0.5, 1, and 1.5 M. A preliminary test indicated that the extraction efficiency of divalent cations was unsatisfactory, as the high total dissolved solids (TDS) was present in the shale gas-produced water. Therefore,

extraction experiments with different dilution rates (1, 10, 25, and 50X) of shale gas-produced water were conducted to examine the effect of TDS on the cation extraction efficiency.

3.2.2 Second-stage solvent extraction

In the second-stage extraction for lithium recovery, organic phase solutions were prepared by dissolving D2EHPA in kerosene with synergistic additive, TBP (Dae Jung, Korea). The chemical and physical characteristics of TBP are shown in Table 3. The second-stage extraction experiments were performed with the aqueous solutions generated after the first-stage, at two different concentrations (1 M and 1.5 M) of D2EHPA. To see the effect of TBP concentration on lithium extraction, additional extraction experiments were conducted with different TBP concentrations, 0.5 M, 1 M, and 1.5 M.

Table 2. Chemical and physical properties of D2EHPA (Sigma-Aldrich, 2014)

Molecular formula	$C_{16}H_{35}O_4P$
Molecular weight	322.42 g/mol
Appearance[*]	Clear colorless to pale yellow liquid
Melting point	-60℃
Flash point	130℃
Density	0.965 g/cm^3 at 25℃
Solubility in water[*]	< 0.01%

* DEHPA, n.d.

Table 3. Chemical and physical properties of TBP (Sigma-Aldrich, 2015)

Molecular formula	$C_{12}H_{27}O_4P$
Molecular weight	266.31 g/mol
Appearance	Odorless colorless to pale yellow liquid
Melting point	-79℃
Boiling point[*]	289℃
Flash point	145℃ - closed cup
Density	0.979 g/cm^3 at 25℃
Solubility in water[*]	0.6%

* Tri-butyl phosphate, 2016

Chapter 4. Results and discussion

4.1 Composition of synthetic produced water

The synthetic produced water that was applied for the solvent extraction experiments was analyzed, and its compositions and concentrations are shown in Table 4. The second column represents the concentration ranges of synthetic shale gas-produced water, and the third column shows the values of real shale gas-produced water obtained from the literature (Haluszczak et al.,2012). It can be seen that, most of the numbers are within the range of flowback except alkalinity. The alkalinity of synthetic produced water was adjusted with sodium carbonate, but the alkalinity level was not as expected because of the addition of hydrochloric acid to the fracturing fluid. As shown in Figure 3, acid comprises 0.12% of the total fracturing fluid. The acid in fracturing fluid is added to dissolve minerals, and it initiates cracks in the shale rock during the hydraulic fracturing process. The representative reagent is hydrochloric acid in 15% concentration (Spellman, 2012). Therefore, the addition of diluted hydrochloric acid decreased the pH of synthetic shale gas-produced water to pH 3, and consequently, the high concentration of hydrogen ions reduced the alkalinity of synthetic produced water.

Table 4. Composition of synthetic and real shale gas-produced water (Haluszczak et al., 2012)

|	Synthetic produced water [mg/L]	Flowback water [mg/L]
Total dissolved solids	9,400–103,180	3,010–228,000
pH	5.86–6.8	5.8–6.6
Alkalinity [mg CaCO$_3$/L]	7–8	26–95
Ca	10,310–12,710	204–14,800
Li	97.7–106	4–202
Mg	856–947	22–1,800
Na	24,320–29,780	1,100–44,100
Sr	2,301–2,601	46–5,350
Ba	1,780–1,924	76–13,600
Cl	66,778–73,891	1,070–151,000
Br	998–1,172	16–1,190

4.2 Extraction of various metal ions by D2EHPA

The equilibrium concentration of metal ions in the organic phase was calculated from the concentration of metal ions in the aqueous phase by mass balance, and the extraction efficiency was calculated using the equation below.

Extraction efficiency % =

$$\frac{\text{Equilibrium concentation of metal ion in the organic phase}}{\text{Initial concentration of metal ion in the aqueous phase}} \times 100 \qquad (5)$$

The metal cations extraction experiment in 50X diluted shale gas-produced water was conducted to see the extraction tendency of cations. The preliminary test was performed with 1 M of D2EHPA and the other test conditions were same with other extraction tests. This preliminary extraction experiment has shown that the extractability decreases according to the following order, and the result is represented in Table 5.

$$Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+} > Li^{+} > Na^{+} \qquad (6)$$
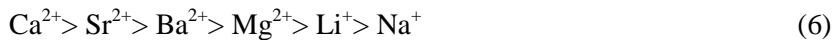
This trend is supported by the research of Hano et al. (1992), Shevchenko et al. (1974), and Cheng (2000). Hano et al. (1992) reported that the order of extraction was Ca > Mg > Li > Na ≒ K. Shevchenko et al. (1974) reported that the order of extraction was Am > Zn > Ca > Mn > Cr > Sr > Ba > Co > Ag > Na > Cs > Rb, and Cheng (2000) reported that it was Zn > Ca > Mn > Cu > Co > Ni > Mg. Therefore, the extraction tendency in formula (6) is reliable.

During metal extraction, D2EHPA replaces the water ligands that were combined with cations, and the affinity increases with the increasing charge density of the bare cation (Koopman et al., 1999). This means that a smaller ion has a higher extraction efficiency in the same charge state. Table 6 presents the effective diameters of six ions in unhydrated form. The order of extraction efficiency in equation (6) is related with the size of all the ions except magnesium. Calcium is the next smallest divalent cations after magnesium, thus, it has the highest charge density. As a result, Ca^{2+} showed the highest extractability, and the extraction efficiency decreased with the increasing diameter of the divalent cations. For the monovalent cations, a larger monovalent cation, sodium, has less charge density than a smaller monovalent cation, lithium, since both have one unit of charge. Consequently, lithium showed a higher extraction efficiency than sodium. The only exception to this charge density and extractability relationship is magnesium. Among the divalent cations, magnesium is the smallest ion. Therefore, it should have the highest extractability; however, it showed the lowest extraction efficiency among the divalent cations. This situation can be explained by the cation exchange reaction. Jakubec et al. (1986) studied the calcium separation from the concentrated magnesium solution by D2EHPA. They found that the equilibrium concentration of magnesium in the organic phase decreased with increasing concentrations of calcium and hydrogen ions in the aqueous phase. From the kinetic data, they testified that the extraction is rather slow, and the exchange reaction between Ca^{2+} and Mg^{2+} occurred as in the following consecutive reactions.

$$MgX_2 + 2H^+ \leftrightarrow 2\,HX + Mg^{2+} \tag{7}$$

$$Ca^{2+} + 2\,HX \leftrightarrow CaX_2 + 2\,H^+ \tag{8}$$

By combining equations (7) and (8), the Ca^{2+}–Mg^{2+} exchange reaction can be represented by:

$$Ca^{2+} + MgX_2 \leftrightarrow Mg^{2+} + CaX_2 \tag{9}$$

where HX denotes D2EHPA. In equation (7), the equilibrium shifts to the right side as the acidity increases. After one cycle of extraction, the pH decreased to about pH 1, so the H^+–Mg^{2+} exchange reaction increased. Consequentially, the magnesium ion reacts with D2EHPA at first, but the extraction is rather slow and the concentration of hydrogen ions continues to increase, so the exchange reaction between the magnesium ion and other divalent cations occurs. Consequently, the extraction efficiency decreased in the following order: $Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+} > Li^+ > Na^+$.

As shown in equation (6), it was found that the extractant, D2EHPA, shows a selectivity for lithium over the other monovalent cation, sodium, but that divalent cations have a much stronger affinity compared to monovalent cations. Therefore, the removal of divalent cations before lithium recovery is very important for selective lithium recovery. In this study, the multi-stage solvent extraction method is suggested for selective lithium recovery. The first stage involves the removal of divalent cations in the synthetic shale gas-produced water, and the second stage involves the selective lithium recovery.

Table 5. Extraction efficiency of metal cations by 1 M D2EHPA in 50X diluted shale gas-produced water

	Extraction efficiency [%]
Ca^{2+}	99.2
Sr^{2+}	54.5
Ba^{2+}	45.4
Mg^{2+}	41.8
Li^+	18.5
Na^+	3.3

Table 6. Effective diameter of unhydrated ions in Å (Kielland, 1937)

Ion	Diameter
Mg^{2+}	0.9
Ca^{2+}	1.4
Sr^{2+}	1.7
Ba^{2+}	2.1
Li^+	0.8
Na^+	1.0

4.3 First-stage solvent extraction for removal of divalent cations

4.3.1 Solvent extraction experiments with different dilution rates of shale gas-produced water

The solvent extraction experiment with 0.5 M extractant was conducted at different time (1 min, 5 min, 15 min, 30 min, 45 min, 1 hr, 2 hr, and 4 hr) to determine the efficient reaction time. From the extraction result, only the calcium ion showed a significant extraction efficiency because of the high TDS level of shale gas-produced water. Therefore, the result of calcium ion extraction was used for the reaction time determination. The time between 15 and 45 min showed the highest extraction efficiency for Ca^{2+}, so extraction experiments with different concentrations of extractant (0.25, 0.5, and 1M) were conducted for three different times (15, 30, and 45 min). As shown in Figure 4, the Ca^{2+} removal efficiency increased with reaction time. The extraction efficiencies of Ca^{2+} at 15, 30, and 45 min were 5%, 5%, and 6% with 0.25 M extractant, 14%, 17%, and 19% with 0.5 M extractant, and 15%, 18%, and 18% with 1 M extractant, respectively. The rate of increase, however, was small (1–2%) compared to the time interval. Especially, in the case of the 1 M extractant, the efficiency did not increase between 30 min and 45 min. Therefore, 30 min was chosen as the efficient reaction time.
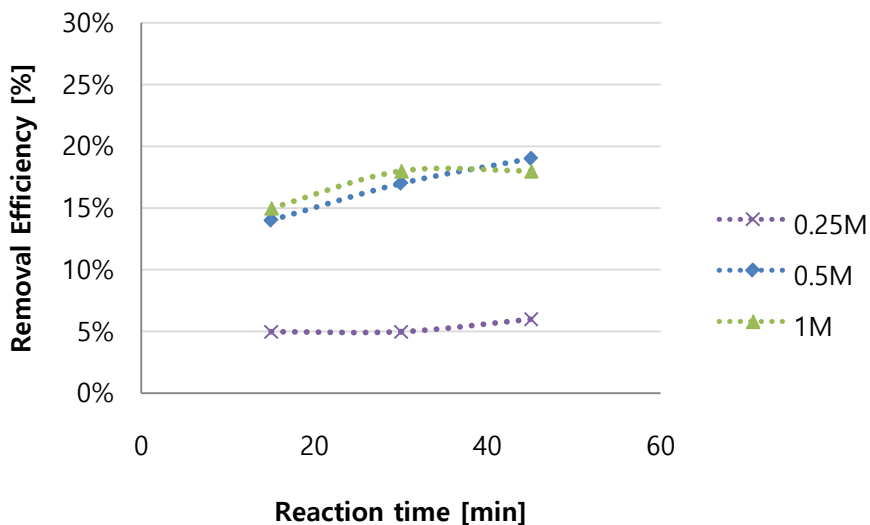
Figure 4. Extraction efficiency of Ca^{2+} by timein different D2EHPA concentrations
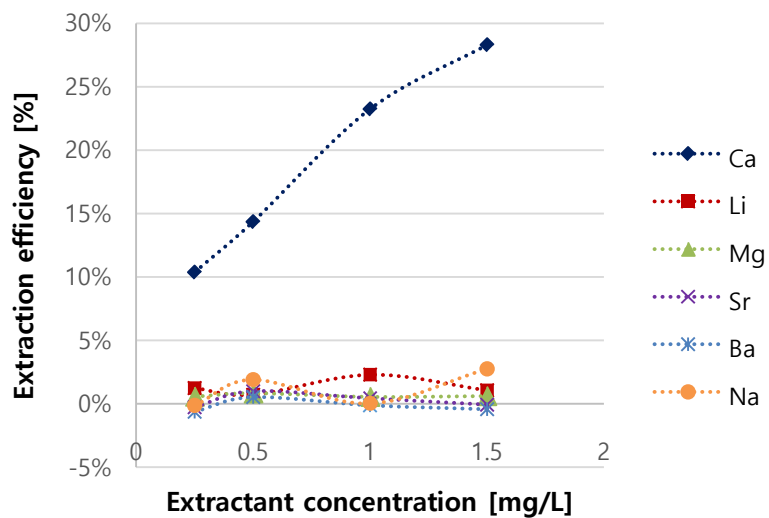

Figure 5. Extraction efficiency of various ions with different D2EHPA concentrations

Figure 5 shows the result of the extraction test with four different D2EHPA concentrations (0.25, 0.5, 1, and 1.5 M). The extraction rate of Ca^{2+} significantly increased with the increase of the concentration of D2EHPA, on the other hand, other components were not extracted. Given the trend in Figure 5, it can be assumed that the higher concentrations showed better efficiencies. The highest concentration of D2EHPA that can be prepared is 1.5 M because of the high molecular weight of D2EHPA (322.42 g/mol). Thus, the experiment was conducted with the highest concentration, 1.5 M, and the highest removal efficiency appeared at 1.5 M of D2EHPA.

The extraction test was repeated to improve the removal rate of divalent cations in shale gas-produced water. As mentioned earlier, the most efficient concentration, 1.5 M of D2EHPA was used for the repetition experiments. At first, solvent extraction was repeated eight times with synthetic shale gas-produced water (Figure 6). The extraction rate of Ca^{2+} increased with repetition up to 60.6%, and the final concentration in the aqueous phase was 4,059 mg/L (initial concentration was 10,310 mg/L). However, the other five components were not extracted. The TDS level of shale gas-produced water was considered the reason for the decline in the extraction efficiency. The TDS level of shale gas-produced water is very high, up to 200,000 mg/L. Therefore, the concentrations of cations that compete with lithium in the extraction are also high. The literature on lithium recovery by solvent extraction referred to setting the criterion of the dilution rate. One study used D2EHPA and TBP for lithium recovery from geothermal water (Hano et al., 1992). The TDS level of geothermal water was about 2,225 mg/L. The TDS level of synthetic shale gas-produced water was around 100,000 mg/L, and it is about 50 times higher than the TDS level of geothermal water. The higher concentration of lithium in the target shale gas-produced water is better for

lithium recovery, so the dilution rate of produced water was gradually increased up to 50 times. Extraction experiments with 10, 25, and 50X dilution were conducted to determine the effective dilution rate.
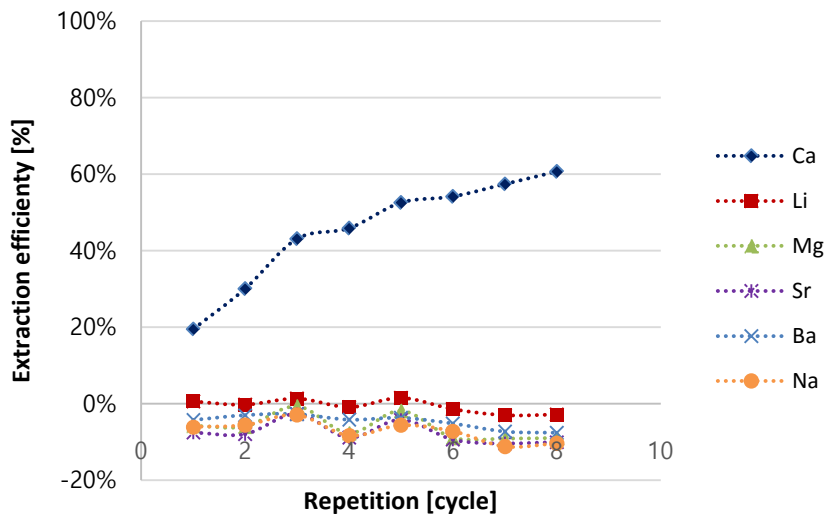
Figure 6. Repetitive extraction in shale gas-produced water using 1.5 M D2EHPA

The concentrations of metal cations in the organic phase were calculated by subtracting the final concentrations from the initial concentrations in the aqueous phase by mass balance, and the distribution ratio of the metal cation M was calculated by the equation below.

$$D_M = \frac{[MR_n(HR)_x]}{[M^{n+}]}$$

$$= \frac{\text{Concentration of all species metal ion in the organic phase}}{\text{Concentration of all species metal ion in aqueous phase}} \qquad (10)$$

The separation factor, S, of each cation M_1 from another cation M_2 in the extraction was calculated by equation (11) (Gabra, 1978).

$$S_{M_2}^{M_1} = \frac{Ratio\ of\ M_1\ ion\ in\ the\ organic\ phase\ /M_1\ ion\ in\ the\ aqueous\ phase}{Ratio\ of\ metal\ ion\ M_2\ in\ the\ ortanic\ phase\ /M_2\ ion\ in\ the\ aqueous\ phase}$$

$$= \frac{D_{M1}}{D_{M2}} \qquad (11)$$

The purpose of first-stage extraction is to remove divalent cations from the lithium-containing solution, so the separation factors were calculated with metal ion M compared to the lithium ion.

As shown in Figure 7, when 10X diluted produced water was applied, 99.9% of Ca^{2+} was removed after eight repetitions; however, other divalent cations showed relatively low extraction efficiency. The removal rates of Mg^{2+}, Sr^{2+}, and Ba^{2+} were only 34.5%, 47.2%, and 34.1%, respectively. The final concentrations of Mg^{2+}, Sr^{2+}, and Ba^{2+} were still much higher than that of Li^+ (Table7). Therefore, it was decided that the 10X dilution rate was too low for

the removal of divalent cations.

In the case of 25X dilution (Figure 8), after eight cycles, all Ca^{2+} was removed, and more than 80% of other divalent cations were removed. The extraction efficiencies of Mg^{2+}, Sr^{2+}, and Ba^{2+} were 83.7%, 95.2%, and 89.5%, respectively. Although the removal rates of divalent cations were high, more than 80%, the final concentrations of Mg^{2+}, Sr^{2+}, and Ba^{2+} in the aqueous phase after eight cycle repetitions were still higher than that of Li^+ (Table 8). Those divalent cations have higher separation factors compared to the lithium ion, so if this aqueous solution is applied for the second-stage extraction for lithium recovery, the remaining divalent cations will have more affinity with D2EHPA, resulting in the decrease of lithium selectivity. Therefore, the 25X dilution rate is not appropriate for the removal of divalent cations.

Figure 9 represents the repeated extraction result with 50X produced water diluent. In the first cycle of extraction, 99.4% of Ca^{2+} was removed, and more than 50% of other divalent cations, including Mg^{2+}, $Sr^{2+,}$ and Ba^{2+}, were removed. After the eight cycles, 97.9% of Mg^{2+} was removed, and all of the Ca^{2+}, Sr^{2+}, and Ba^{2+} were removed. It was shown that high removal efficiency for divalent cations, however, after eight cycles, 51.1% of Li^+ wasalso removed. The initial and final concentrations of each cation after eight cycles of repetition are shown in Table 9.

The eight repeated extraction experiments were conducted to determine the appropriate dilution rate of shale gas-produced water for divalent cation removal with 1.5 M of D2EHPA. All experimental results showed that the extractability decreased in order, $Ca^{2+}> Sr^{2+}> Ba^{2+}> Mg^{2+}> Li^+> Na^+$, as explained in Section 4.2. Therefore, the concentrations of divalent cations in the aqueous phase after a certain number of repetitions were important for the selectivity of lithium in the second-stage solvent extraction. The final

concentrations of divalent cations in the aqueous phase were lower than those of lithium ion only in the case of the 50X dilution rate. Therefore, to improve the selectivity of lithium in the second-stage extraction, 50X was chosen as the most efficient dilution rate.

Figure 7. Repetitive extraction in 10X diluted produced water using 1.5 M D2EHPA

Table 7. Distribution ratio and separation factor after eight cycle repetitions in 10X diluted shale gas-produced water

	Initial concentration [mg/L]	Final concentration in aqueous phase [mg/L]	D_M	S_{Li}^M
Ca^{2+}	1113	0.77	1443	9084
Sr^{2+}	234	124	0.895	5.635
Ba^{2+}	177	117	0.517	3.254
Mg^{2+}	85.9	56.3	0.527	3.318
Li^+	9.52	8.22	0.159	1
Na^+	2496	2533	-0.015	-0.092

Figure 8. Repetitive extraction in 25X diluted produced water using 1.5 M D2EHPA

Table 8. Distribution ratio and separation factor after eight cycle repetitions in 25X diluted shale gas-produced water

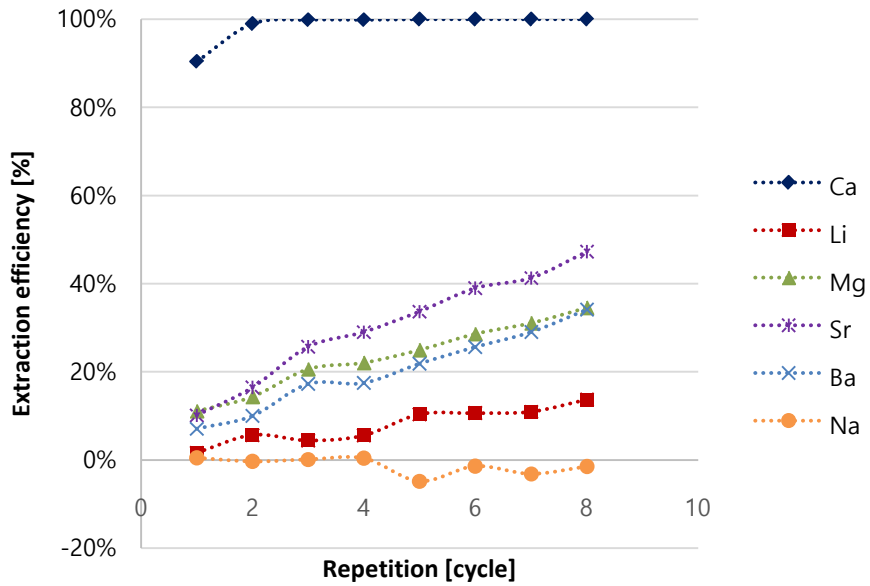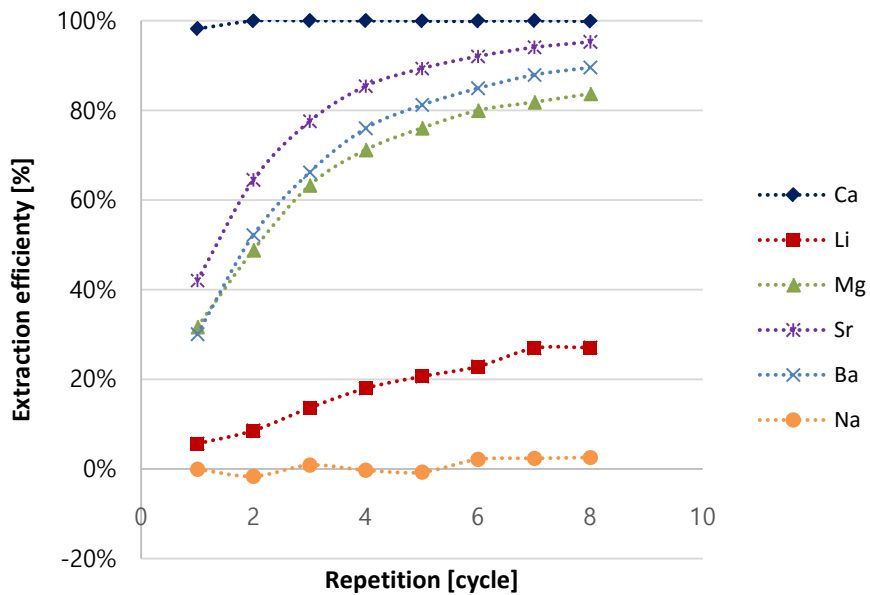|	Initial concentration [mg/L]	Final concentration in aqueous phase [mg/L]	D_M	S_{Li}^M
Ca^{2+}	452	< 0.69	650	1756
Sr^{2+}	83.9	4.19	20.1	54.14
Ba^{2+}	67.1	7.03	8.53	23.04
Mg^{2+}	32.2	5.25	5.14	13.88
Li^+	3.63	2.65	0.37	1
Na^+	971	946	0.026	0.071
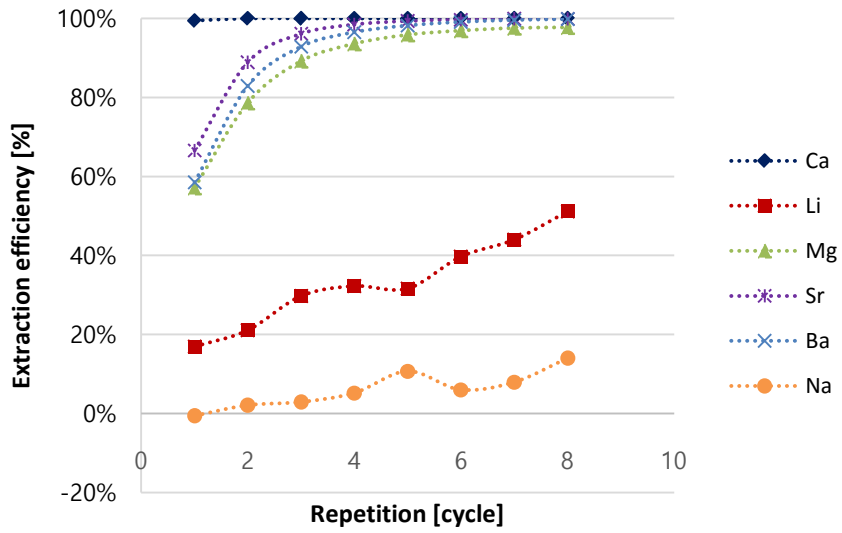
Figure 9. Repetitive extraction in 50X diluted produced water using 1.5 M D2EHPA

Table 9. Distribution ratio and separation factor after eight cycle repetitions in 50X diluted shale gas-produced water

	Initial concentration [mg/L]	Final concentration in aqueous phase [mg/L]	D_M	S_{Li}^M
Ca^{2+}	222	<0.16	1396	1335
Sr^{2+}	47.3	<0.04	1126	1076
Ba^{2+}	36.2	<0.08	469	448
Mg^{2+}	17.4	0.41	42	40
Li^+	1.98	0.97	1.046	1
Na^+	509	437	0.163	0.156

4.3.2 Extractability of divalent cations in different concentrations of D2EHPA

The 50X dilution rate was selected as an effective dilution rate for the first-stage solvent extraction. In the previous section, after the eight cycles of extraction with 1.5M of D2EHPA, 51.1% of lithium was lost. Therefore, to find out proper extractant concentration which removes almost all of divalent cations and shows relatively low lithium loss, the extraction experiments were conducted with different concentrations of D2EHPA in 50X diluted shale gas-produced water. Applied concentrations were 0.3, 0.5, 1, and 1.5 M of D2EHPA in kerosene. As shown in Figure 10, the extractability of divalent cations gradually increased up to 99.43%, 66.61%, 58.46%, and 57.11% for Ca, Sr, Ba, and Mg, respectively, with the increase of extractant concentrations. In the case of the lithium ion, extraction efficiency did not change at the lower concentration level (0.3 and 0.5 M), but it significantly increased at 1 M of extractant. The sodium ion showed the lowest extraction efficiency, and it was rarely extracted at any of the extractant concentrations.

The most favorable result of first-stage extraction is that almost all the divalent cations were extracted, while almost all the lithium ions remained. Figure 10 shows that the higher extractant concentration shows better removal efficiency of divalent cations. However, the extraction of lithium ions also increases with the extractant concentration. Thus, extraction repetition tests with four different D2EHPA concentrations were performed, and the results are presented in Figure 11.
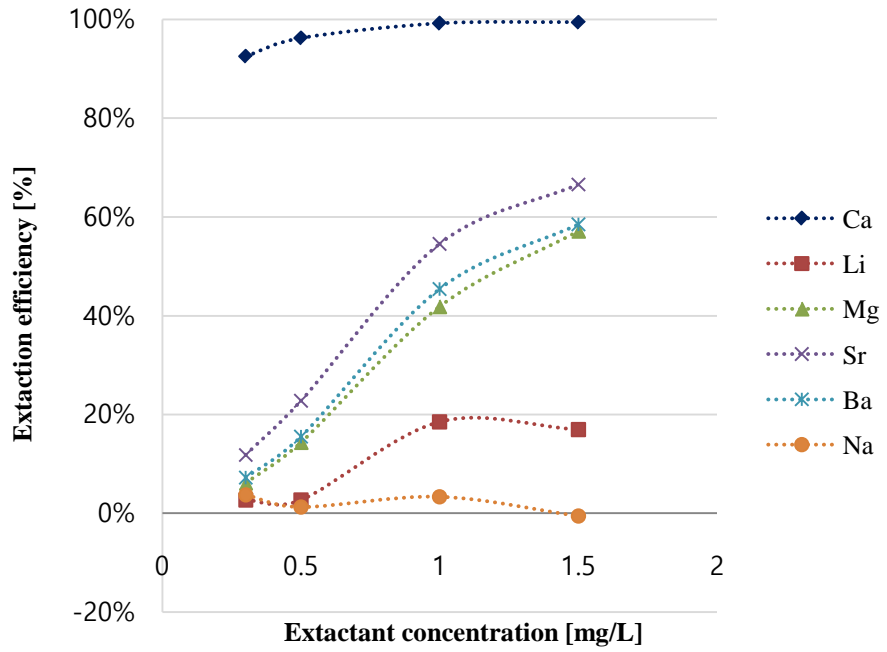
Figure 10. Extraction efficiency of metal cations in 50X diluted produced water in different concentrations of D2EHPA
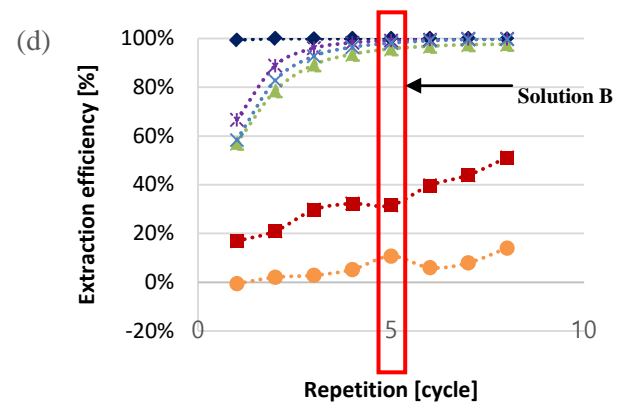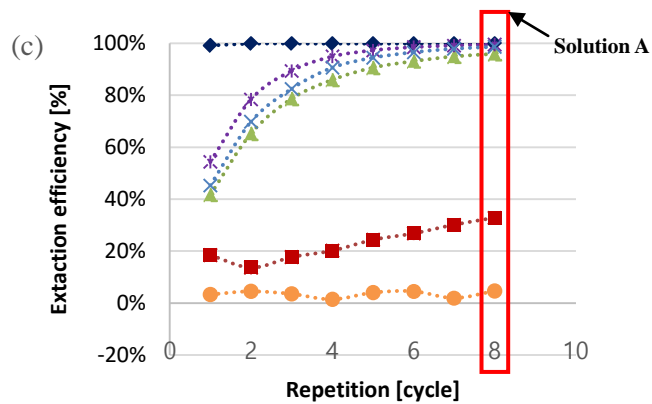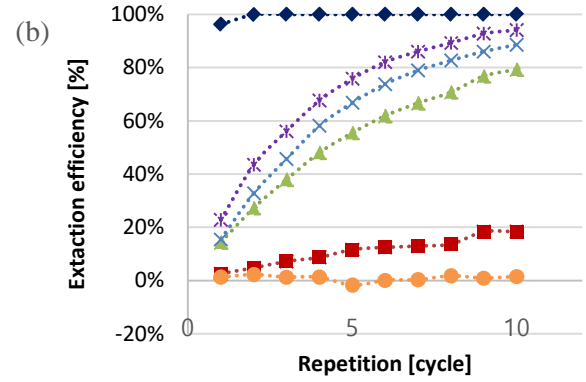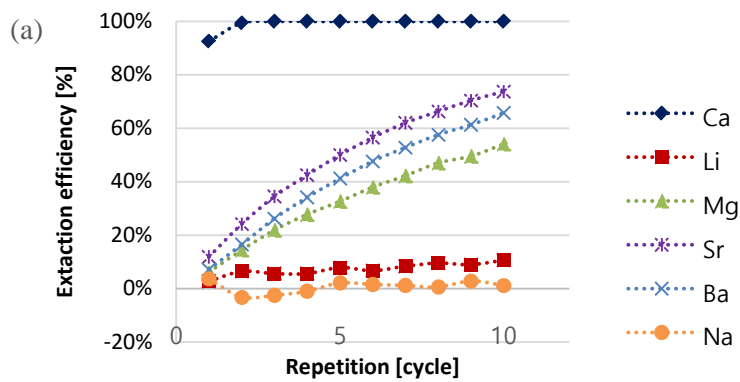
Figure 11. Repetitive extraction in 50X diluted produced water in different D2EHPA concentrations:

(a) 0.3 M, (b) 0.5 M, (c) 1.0 M, (d) 1.5 M

The repetition tests were conducted up to 10 cycles for 0.3 M and 0.5 M and up to 8 cycles for 1 M and 1.5 M. As shown in Figure 11, almost all of the calcium ion was removed at all concentrations, but the extraction efficiencies of Mg^{2+}, Sr^{2+}, and Ba^{2+} decreased at 0.3 M and 0.5 M despite proceeding with two more extractions. Table 10 presents the final concentrations of the metal cations in the aqueous phase after eight and ten repetitions. In the case of 1 M and 1.5 M, after eight cycles of extraction, the concentrations of all divalent cations were lower than that of lithium, while at the D2EHPA concentrations 0.3 M and 0.5 M, the concentrations of all divalent cations were still higher than that of lithium after ten cycles of extraction. Therefore, 1 M and 1.5 M were selected as the D2EHPA concentrations for the second-stage extraction experiments.

In Figure 11 (c) and (d), the extractability of lithium ions increases with repetition. After eight cycles, 33.0% and 51.1% of lithium ions at 1 M and 1.5 M were removed, respectively. This is an unfavorable result for second-stage extraction. Therefore, the appropriate number of repetitions, which shows lower concentrations of divalent cations than lithium in the aqueous phase, was determined by the repetition results.

For the repetition with 1 M D2EHPA, the number of cycles selected was eight because of the concentration of strontium ion. The extraction efficiencies of Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+} were 100%, 96.0%, 100%, and 98.6%, respectively. Expressed as concentrations, the concentrations of Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, and Li^+ were< 0.03, 0.70, < 0.21, 0.49, and 1.28 mg/L. At seven repetitions, the strontium ions remained, but after eight cycles, almost all of the Sr^{2+} was removed. The remaining Sr^{2+} has an impact on lithium recovery, so the number of cycles chosen was eight.

For the repetition with 1.5 M D2EHPA, the number of repetitions chosen was five. After five cycles of extraction, the extraction efficiencies of Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+} were 100%, 95.8%, 99.3%, and 98.2%, respectively, while that of Li^+ was 31.6%. Expressed as concentrations, the concentrations of Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, and Li^+ were< 0.04, 0.73, 0.34, 0.65, and 1.35 mg/L.

The aqueous phase solution generated after eight extraction repetitions with 1 M of D2EHPA was designated as "Solution A." In addition, the aqueous solution obtained after five extraction repetitions with 1.5 M of D2EHPA was denoted as "Solution B."

Table 10. Final concentrations of metal cations in aqueous phase treated with different extractant concentrations

|	D2EHPA concentration			
	0.3 M*	0.5 M*	1 M†	1.5 M†
Ca^{2+}	< 0.07	< 0.09	< 0.03	<0.16
Sr^{2+}	12.43	2.87	< 0.21	<0.04
Ba^{2+} [mg/L]	12.36	4.16	0.49	<0.08
Mg^{2+}	7.97	3.62	0.70	0.41
Li^+	1.71	1.60	1.28	0.97
Na^+	507	498	490	437

* After eight times repetitions

† After ten times repetitions

4.4 Second-stage solvent extraction for lithium recovery

In the first-stage of solvent extraction with D2EHPA, more than 90% of divalent cations were removed. The second-stage extraction experiments were conducted with the aqueous solution obtained from the first stage to recover lithium. To improve the extraction efficiency of lithium ion, TBP was used as a synergistic additive. From the research of Hano et al. (1992), the most effective concentration of TBP is 0.5 M. In addition, from the research of Bukowsky et al. (1992), when the concentration of D2EHPA is higher than 0.5 M, the extraction of lithium ion occurs. Therefore, the extraction tests were performed using 1 M or 1.5 M of D2EHPA with 0.5 M of TBP. The extractability of lithium ion improved in the 1.5 M D2EHPA + 0.5 M TBP system (efficiency of lithium was 7.1%) compared to the 1 M D2EHPA + 0.5 M TBP system (efficiency of lithium was 4.3%). This means that the higher extractant concentration showed a higher extraction efficiency of lithium ion. Therefore, the repetition tests were conducted using 1.5 M D2EHPA with Solution A or Solution B. Almost all of the divalent cations except magnesium ions were removed in the first stage, so only the extraction efficiencies of Li^+, Mg^{2+}, and Na^+ were considered.

4.4.1 Lithium recovery by D2EHPA

The general extraction formula shown in Section 2.3 is equation (2):

$$M^{n+} + \frac{n+x}{2}\overline{(HR)_2} \leftrightarrow \overline{MR_n(HR)_x} + nH^+ \qquad (2)$$
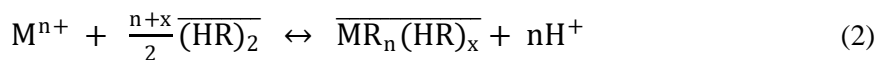
$$K_e = \frac{[MR_n(HR)_x][H^+]^n}{[M^{n+}][(HR)_2]^{\frac{n+x}{2}}} = \frac{D_M[H^+]^n}{[(HR)_2]^{\frac{n+x}{2}}} \tag{12}$$

where K_e is the extraction equilibrium constant, which can be calculated using equation (12) with the reaction of equation (2), and D_M is the distribution ratio, which can be presented as shown in Section 4.3.1 using equation (10).

$$D_M = \frac{[MR_n(HR)_x]}{[M^{n+}]} \tag{10}$$

By rearranging equation (10), the following formula can be obtained.

$$\log D_M = \frac{n+x}{2}\log[(HR)_2] + \log\frac{K_e}{[H^+]^n} \tag{13}$$

Figure 12 shows a graph based on equation (13) in the Li-D2EHPA system. The log value of the distribution ratio of lithium ion versus the log value of D2EHPA concentration was plotted to obtain the slope of the straight-line relationship. In this graph, the slope is denoted by $\frac{n+x}{2}$ in equation (13).

$$\text{slope} = \frac{n+x}{2} \tag{14}$$

In equation (14), n is 1 (the charge of the lithium ion), and from the straight trend line in Figure 12, the slope is 1.5425. Therefore, the solvation number, x, was calculated as approximately two (x = 2.085).

Consequentially, the extraction reaction of lithium ions with D2EHPA can be expressed in the following formula:

$$\text{Li}^+ + 3(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{-OH} \leftrightarrow [(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}O]\,\text{Li}[HO\overset{\overset{\displaystyle O}{\|}}{P}(RO)_2]_2 + \text{H}^+ \qquad (15)$$
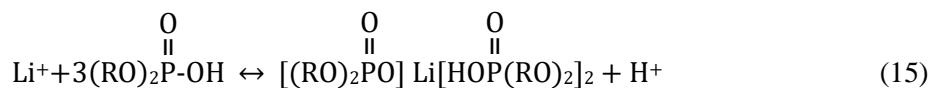
Therefore, equation (3) in Section 2.4 on the synergistic effect of TBP can be expressed with the following formula:

$$[(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}O]\,\text{Li}[HO\overset{\overset{\displaystyle O}{\|}}{P}(RO)_2]_2 + \text{TBP} \leftrightarrow$$

$$[(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}O]\,\text{Li}[HO\overset{\overset{\displaystyle O}{\|}}{P}(RO)_2]\text{TBP} + (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{-OH} \qquad (16)$$
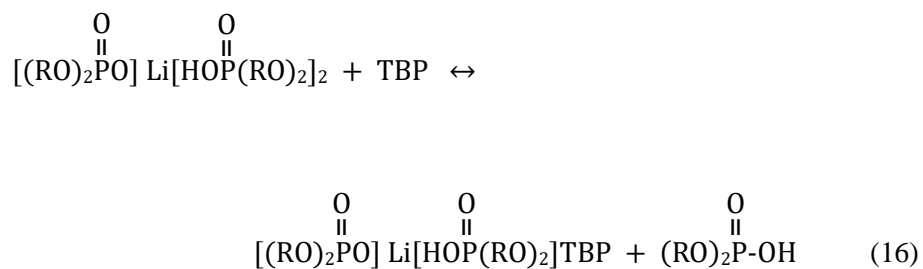
Figure 12. Determination of solvation number in Li-D2EHPA reaction

4.4.2 Lithium recovery in Solution A

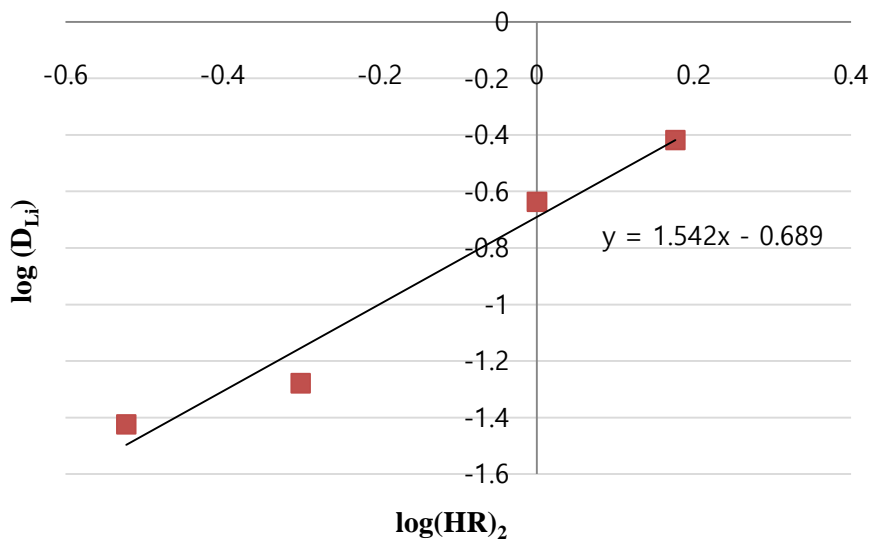Solution A was applied for lithium recovery. The concentration of D2EHPA for lithium extraction was 1.5 M, which was selected from the preliminary tests. In addition, to determine the effect of TBP concentration on lithium extraction, three different concentrations (0.5, 1, and 1.5 M) of TBP were applied.

Figure 13 shows the repeated extraction result with 0.5 M TBP. The extraction efficiency of lithium ion increased up to 34.19% with repetition, and the distribution ratio, D_{Li}, was 0.520. At the first stage of extraction, 22.6% of lithium ion was removed. Thus, the total extraction efficiency of lithium ion, after the two-stage solvent extraction, was 26.46%. For the other cations, sodium did not extract during the second-stage extraction, while the extraction efficiency of magnesium increased negatively. This means that the concentration in the aqueous phase was rather increased with extraction repetition, and this phenomenon will be explained in the next section.

Figure 14 represents the repetition of second-stage extraction with 1 M TBP. The extractability of lithium ion increased up to 32.6% after ten cycles of extraction, and the distribution ratio, D_{Li}, was 0.483. In addition, 22.6% of lithium ion was removed during first-stage solvent extraction, so the total extraction efficiency of lithium ion was 25.21%. The other cations, magnesium and sodium ions, showed the same trend. The extractability of both cations was gradually increased negatively, and the concentrations in the aqueous phase were gradually increased with repetition.
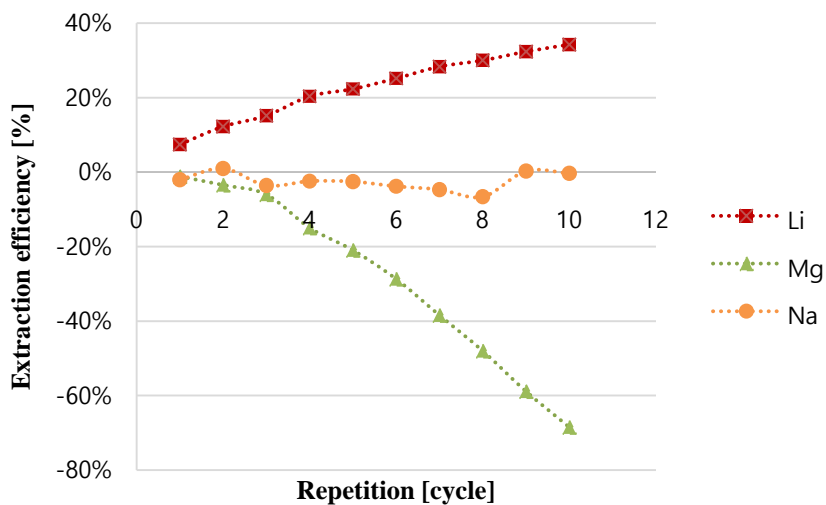
Figure 13. Repetitive extraction of lithium in Solution A with 1.5 M D2EHPA + 0.5 M TBP
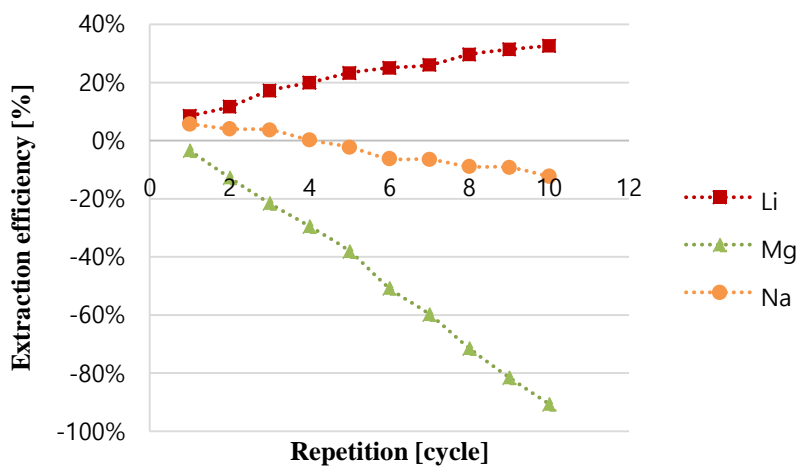

Figure 14. Repetitive extraction of lithium inSolution A with 1.5 M D2EHPA + 1 M TBP

The same phenomenon occurred in Figure 15, which shows the result of repeated extraction with 1.5 M TBP. The extractability of lithium ion increased up to 20.1%, and the distribution ratio, D_{Li}, was 0.251. The total extraction efficiency during two-stage solvent extraction was 15.55% because of the 22.6% removal in the first stage.

When comparing the total extraction efficiency of lithium ion from the results of three different concentrations of TBP, the highest efficiency was found in the 1.5 M D2EHPA and 0.5 M TBP system. This result is supported by the research of Hano et al. (1992) and explained by equation (4) in Section 2.4. When the concentration of TBP exceeds a certain range, the excess TBP reacts with the extractant, D2EHPA, resulting in the metal cation extraction efficiency being decreased. Consequently, 0.5 M was selected as the effective concentration of TBP.
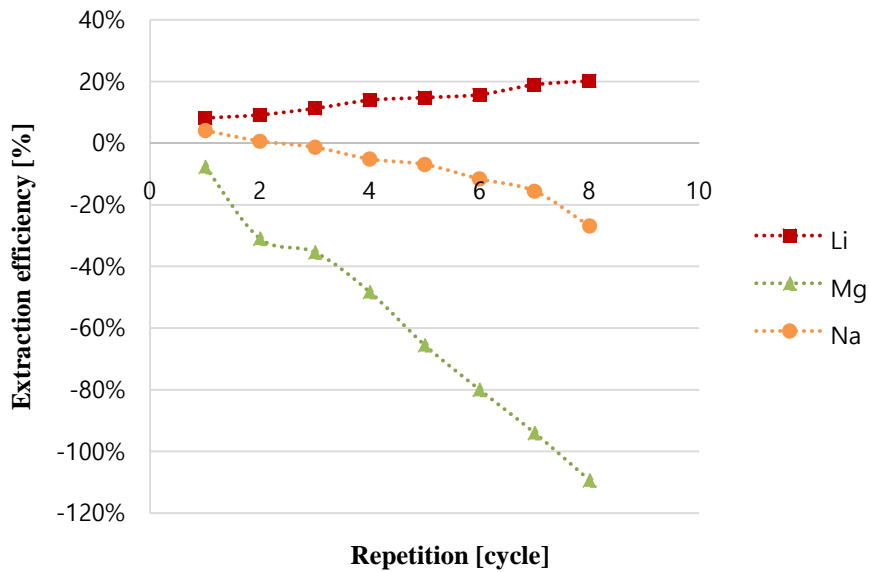
Figure 15. Repetitive extraction of lithium in Solution A with 1.5 M D2EHPA + 1.5 M TBP

4.4.3 Lithium recovery in Solution B

Solution B was applied for lithium recovery, and 1.5 M of D2EHPA was used for lithium extraction. From the previous section, the 0.5 M concentration of TBP showed the highest extraction efficiency, so 0.5 M TBP was added to the extraction experiments.

Figure 16 shows the extraction efficiency of three cations with repetition. The extractability of lithium ion gradually increased up to 39.41% with ten repetitions, and the distribution ratio, D_{Li}, was 0.650. This extraction system showed a relatively high distribution ratio for lithium ion. However, in the first-stage extraction, 35.9% of lithium ion was removed. Thus, the total extraction efficiency of lithium ion was 25.26%.

In all of the second-stage extraction experiments, the extraction efficiency of magnesium and sodium ions negatively increased with extraction repetition. This means that the concentrations of magnesium and sodium ions in the aqueous phase increased. Obviously, the extractant, D2EHPA, synergistic additive, TBP, and diluent, kerosene, do not contain magnesium or sodium. Therefore, this increased amount of both cations originated from the aqueous solution of the first-stage solvent extraction. Accordingly, this means that there was an unanalyzed magnesium and sodium compound in the aqueous solution of first-stage solvent extraction. This phenomenon can be explained by the hydration effect on the metal chelate extraction. The extraction with D2EHPA is a metal-chelate extraction system.

The formation of metal chelate is explained by the following equations (Choi, 2009).

$$M^{n+} + nR^- \leftrightarrow MR_n \tag{17}$$

$$H^+ + R^- \leftrightarrow HR \tag{18}$$

These two reactions occur competitively, and then the uncharged metal chelate, MR_n, is distributed in the aqueous and organic phases. During the reaction, if the coordination number of the metal ion is not satisfied by the extractant, the insufficient part can be stocked with water molecules, resulting in the creation of a hydrated complex, $HR_n \cdot xH_2O$. In this case, the distribution ratio of this metal cation is low. In this situation, if the base, B, is added, the reaction of the hydrated complex and base will occur as in the following formula:

$$MR_n(H_2O)_a + B(H_2O)_h \leftrightarrow MR_nB + (a+h)H_2O \qquad (19)$$
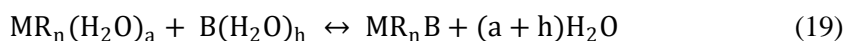
It can be assumed that, in the first extraction, the sodium and especially the magnesium ions formed the hydrated chelate complex with D2EHPA. This assumption can be supported by the extraction result of first-stage extraction, because the magnesium and sodium ions showed relatively low distribution ratios. Accordingly, this hydrated complex was located in the aqueous phase, and then it moved to the second-stage extraction system.

In the second-stage extraction, the TBP, which contains basic phosphorus, was added to the extraction reaction. These TBP molecules substituted for water molecules with equation (19). From the study of Choi (2009), the extractability of TBP decreases in the order of $Ca^{2+} > Li^+ > Sr^{2+} > Na^+$, and especially, magnesium and sodium ions cannot be extracted by TBP (distribution ratio is less than 10^{-2}). In addition, as explained in Section 2.4 equation (4), the TBP molecule can react with a D2EHPA molecule and form a HRTBP complex. Consequently, the substitution of water molecules by TBP molecules occurred, but the TBP molecule has a low affinity with

magnesium and sodium ions. Therefore, the metal chelate complex is resolved, and it forms a HRTBP complex. By this process, the concentrations of magnesium and sodium in the aqueous phase could be increased during second-stage extraction.
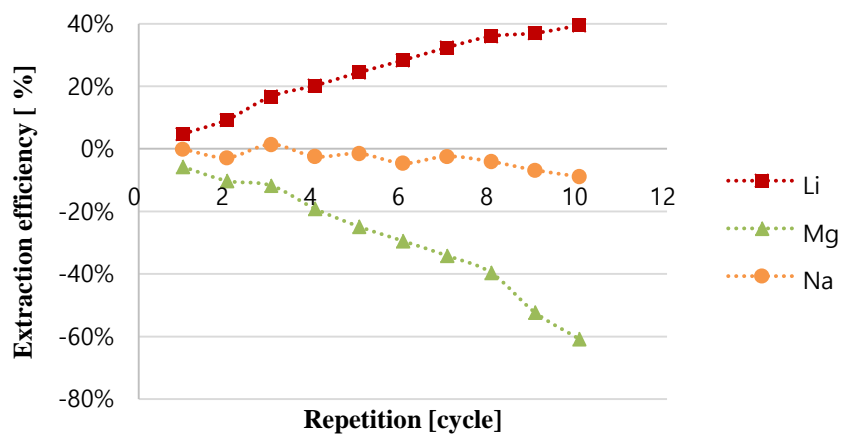
Figure 16. Repetitive extraction of lithium inSolution B with 1.5 M D2EHPA
+ 0.5 M TBP

Chapter 5. Conclusion

A study of lithium recovery from shale gas-produced water was conducted to determine the applicability of the solvent extraction method. The extraction efficiency of cations, except calcium ion, was low due to the high TDS level of produced water. Therefore, extraction experiments with different dilution rates were conducted, and then 50X was selected as an appropriate dilution rate. Then, metal cation extraction was tested using D2EHPA in kerosene to explore the separation trend of D2EHPA and find favorable conditions for selective lithium recovery.

(1) Metal cation extraction trend of D2EHPA

In all the extraction experiments, D2EHPA showed that the extraction efficiency decreased in the following order: $Ca^{2+}> Sr^{2+}> Ba^{2+}> Mg^{2+}> Li^+> Na^+$. Therefore, the multi-stage solvent extraction was proposed to reduce the effect of divalent cations on lithium extraction. The first-stage extraction was conducted to remove divalent cations in shale gas-produced water, and the second-stage extraction was performed to selectively recover lithium ion.

(2) Effect of TDS of shale gas-produced water on extraction

The extraction did not occur for cations, except calcium ion, because of the high TDS of shale gas-produced water. Therefore, extraction experiments with different dilution rates (1, 10, 25, and 50X) were conducted to determine the most efficient dilution rate. From the results, up to 25X diluted produced water showed relatively low extraction efficiency compared to the final concentration of lithium ion in the aqueous phase. Thus, 50X was selected as an appropriate dilution rate.

(3) First-stage extraction for divalent cation removal

The first-stage solvent extraction was tested by varying repetition numbers and D2EHPA concentrations with 50X diluted shale gas-produced water. The results showed that the extractability increased with increased extractant concentrations, and the effective repetition number varied with the applied D2EHPA concentrations. Eight cycles with 1 M of D2EHPA and five cycles with 1.5 M were selected as appropriate repetition numbers and extractant concentrations.

(4) Second-stage extraction for lithium recovery

The aqueous phase solution obtained after the appropriate number of first-stage extraction repetitions was applied for lithium recovery. In addition, to see the effect of TBP concentrations, three different concentrations (0.5, 1, and 1.5 M) were tested. From the results of repetition tests with eight repeated extractions aqueous solution using 1 M of D2EHPA, the lithium ion was extracted selectively, and the total extraction efficiencies of lithium ion were 26.46%, 25.21%, and 15.55% with the TBP concentrations of 0.5, 1, and 1.5 M, respectively. It showed that the TBP concentration of 0.5 M was the most efficient, so the experiment with five repetitions of first-stage extraction with 1.5 M D2EHPA was conducted with 1.5 M D2EHPA and 0.5 M TBP. The total extraction efficiency of lithium ion was 25.26%.

The highest extraction efficiency of lithium ion with D2EHPA and TBP was 26.46%. It may appear that the efficiency is not that high. However, almost all of the divalent cations were removed in the first-stage extraction, and the extractant, D2EHPA, has more affinity to lithium ion compared to other monovalent cations. Thus, in the second-stage extraction, only lithium ion was extracted, and the selectivity of lithium is very high. In conclusion, this multi-stage solvent extraction method can be applied for selective lithium recovery.

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초   록

셰일가스는 수압파쇄법을 통해 개발되는데, 이 과정에서 다량의
물이 셰일 지층으로 주입된다. 이후, 파쇄용수와 셰일 지층수가
결합된 환류수가 배출되며, 이를 셰일가스 생산수라고 한다.
셰일가스 생산수는 셰일가스 개발 중에 발생하는 고염도의
폐수이다. 셰일가스 생산수에는 셰일암의 점토광물로부터 기인하는
리튬이 상대적으로 많이 포함되어있다. 최근, 리튬의 수요가
증가함에 따라 해수에서 리튬을 회수하는 다양한연구가 진행
중인데, 해수 내 리튬의 농도는 0.17 mg/L로, 마셀러스 (Marcellus)
셰일 지역에서 발생하는 생산수가 약 95 mg/L의 리튬을 함유하고
있는 것과 비교하면 생산수 내 리튬 함량이 매우 높은 것을 알 수
있다. 그러므로 셰일가스 생산수에서 리튬을 선택적으로 회수할 수
있다면, 해수에서의 리튬 추출보다 효과적일 것으로 보인다. 본
연구는 희석된 셰일가스 생산수에 용매추출법을 적용하여 선택적인
리튬 회수가 가능한지 알아보기 위해 진행되었다. 셰일가스
생산수는200,000 mg/L에 이를 만큼 매우 높은 농도의 총 용존
고형물(Total Dissolved Solids: TDS)을 함유하고 있으며,
그에따라 용매추출 과정 시에 리튬 이온과 경쟁적으로 작용하는
양이온들의 농도도 매우 높다. 따라서 리튬 이온과 경쟁적으로
작용하는 다른 양이온들의 영향을 줄이고 리튬 이온 선택성을
향상시키기 위해 다단계 용매추출법을 적용하였다.

첫 번째 단계 추출에서는 추출제로di(2-ethylhexyl)
phosphoric acid (D2EHPA)를 사용하였으며, 두 번째 단계
추출에서는 추출제 D2EHPA에 보조첨가제 tri-butyl phosphate

(TBP)를 첨가하여 리튬 회수 효율을 향상시키고자 하였다. 50배 희석한 생산수를 이용하여 첫 단계 추출 실험을 진행한 결과, 약 97.9%의 마그네슘 이온과 거의 모든 칼슘, 스트론튬, 바륨 이온이 제거되었다. 두 번째 단계 추출 실험은 첫 단계를 일정 횟수 반복한 후 발생한 수용액 층을 사용하여 진행되었다. 다단계 용매추출 과정 이후, 가장 높은 리튬 이온 추출 효율은 26.46%였다. 첫 단계 용매추출 과정에서 거의 모든 다가 양이온이 제거되고, 두 번째 단계에서는 추출제 D2EHPA가 다른 일가 양이온에 비해 리튬 이온을 잘 추출해내므로 리튬 이온 선택성이 매우 향상되었다. 결론적으로 다단계 용매추출법은 높은 선택성이 필요한 리튬 회수에 적용 가능한 것으로 보인다.