CHAPTER 10.14

Solvent Extraction

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Solvent extraction (SX), often referred to as *liquid–liquid extraction*, is a separation process in which a chosen metal is transferred from one immiscible liquid phase to another. Metals dissolved in the aqueous phase are extracted into an organic phase containing a suitable extractant.

In the late 1800s, Berthelot and Jungfleisch (1872) first identified the principle by which a metal ion can be extracted from the aqueous phase to the organic phase, eventually forming an equilibrium constant of the metal distributed between two immiscible liquids, which has led to the concept of the distribution ratio. During 1940–1950, the U.S. Manhattan Project spurred in-depth studies on SX and ion exchange for recovery and upgrading of uranium and other metals, mainly actinide group metals. In recent years, this technology has become a major force in the separation and/or production of various metals from leach liquors, including Cu, Ni, Co, U, Th, Zn, Au, Pt group metals; rare earth metals; and many more.

In SX, a chosen extractant is dissolved in an organic carrier, usually a hydrocarbon-based solvent diluent. The extractant and carrier solvent are contacted with an immiscible aqueous phase, in which metal ions are dissolved. Because of the affinity between the extractant and metal ion in the aqueous phase, the metal ion transfers from the aqueous to the organic phase.

In this chapter, definitions and nomenclatures, various kinds of extractants and diluents, and reaction mechanisms involved in SX will be presented and discussed. The chapter will also include SX thermodynamics to help expand the knowledge in development of better reagents and processes in recovering and purifying various industrial metals.

DEFINITIONS AND NOMENCLATURE

As shown in Equations 1 and 2, a metal ion M^{n+} or a metal salt MS in the aqueous phase reacts with an extractant HR or R in the organic phase to form an organic soluble metal complex. Here n stands for the valence of the metal M and is an integer.

$$M^{n+}(a) + n\mathrm{HR}(o) = \mathrm{MR}_n(o) + n\mathrm{H}^+(a) \qquad \textbf{(EQ 1)}$$

$$\mathrm{MS}(a) + n\mathrm{R}(o) = (\mathrm{MS})\mathrm{R}_n(o) \qquad \textbf{(EQ 2)}$$

The symbols (a) and (o) represent the aqueous phase and the organic phase, respectively. It should be noted that extractants are placed in the organic phase and, therefore, the chemical interaction between a metal ion and an extractant can take place when these two chemical moieties are in direct contact either in the aqueous phase, in the organic phase, or at the interface. There are various ways in which the chemical reaction can take place, dependent on the extractant utilized. Examples given in the preceding equations represent two different mechanisms. The reaction shown in Equation 1 takes place when the metal ion replaces the hydrogen ion associated with the extractant, while the reaction shown in Equation 2 represents a neutralized metal salt interacting with the extractant.

Figure 1 shows a simple flowchart depicting an industrial SX process. As seen in the figure, leach liquor containing various metals is mixed with the organic phase containing the extractant. In extraction, the metal of interest transfers into the organic phase, leaving a metal-depleted aqueous phase often referred to as *raffinate*. This raffinate may be subjected to further purification and/or metal recovery processes, or returned to leach. The organic phase loaded with metals may then be subjected to a scrubbing step to eliminate impurities from the organic followed by a stripping step to transfer the metal of interest from the organic phase to the aqueous. The organic phase depleted of metal may be recycled back to the extraction step.

Efficiency of metal removal is often described in terms of percent recovery as shown in Equation 3. An additional frequently used term is the distribution ratio, D, shown in Equation 4. These are defined as follows:

$$\%\ \text{recovery} = (c_f - c_r)/c_f \times 100 \qquad \textbf{(EQ 3)}$$

where c_f and c_r are the concentration of metal in the feed and raffinate streams.

$$D = \frac{C_o}{C_a} = \frac{M_o/V_o}{M_a/V_a} = \frac{V_a}{V_o} \times \frac{M_t - M_a}{M_a} \qquad \textbf{(EQ 4)}$$

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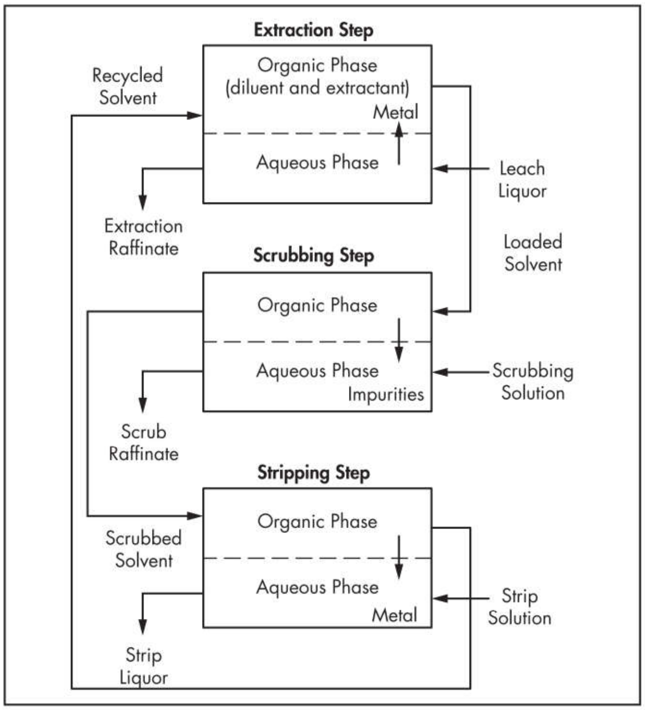


Figure 1 Flowchart of a simple solvent extraction operation

where C_o and C_a are the concentrations of the metal in the organic phase and the aqueous phase, respectively; M_o and M_a are the mass of metal in the organic phase and aqueous phase, respectively; V_o and V_a are the volumes of the organic phase and the aqueous phase, respectively; and M_t is the mass of the total metal ($M_a + M_o$). The distribution ratio is often referred to as *distribution coefficient* and *partition coefficient*.

Another commonly used term is the *separation factor* β as defined here:

$$\beta = \frac{D_A}{D_B} \qquad \textbf{(EQ 5)}$$

where D_A and D_B are distribution ratios of the species A and B, respectively.

The use of these equations and mass balance concepts significantly aid in the evaluation of the various SX extractants and in the design of circuits to treat the various feed streams. For example, D values may be used to estimate the number of stages required to achieve a given recovery. Multiple authors have covered these mathematical relationships and their interpretation (see Han 2002; Han and Fuerstenau 2003).

VARIOUS TYPES OF SOLVENT EXTRACTANTS

There are four common types of SX mechanisms: cationic, solvation, anionic, and chelation. These and one other less common method are discussed next.

Cationic

The cationic type, which can also include chelating extractants that release protons in exchange for cations, involves cations interacting with solvents as shown in the following equation (Mason et al. 1978; Zheng et al. 1991).

$$M^{n+}(a) + n\text{HA}(o) = \text{MA}_n(o) + n\text{H}^+(a) \qquad \textbf{(EQ 6)}$$

In the preceding equation, M represents an n valence metal ion, and HA represents a protonated extractant. The following equation shows the equilibrium constant between the reactants and products:

$$\text{K} = \frac{[\text{MA}_n](o)\ [\text{H}^+]^n(a)}{[\text{M}^{n+}](a)[\text{HA}]^n(o)} \qquad \textbf{(EQ 7)}$$

Using the D value and rearranging the terms, one can show

$$D = \frac{C_\text{M}(o)}{C_{\text{M}^{n+}}(a)} = \text{K}\frac{[\text{HA}]^n(o)}{[\text{H}^+]^n(a)} = \frac{\gamma_{\text{M}(o)}}{\gamma_{\text{M}^{n+}(a)}} \qquad \textbf{(EQ 8)}$$

$$\log D = \log \text{K} + n \log[\text{HA}](o) + n\ \text{pH} \qquad \textbf{(EQ 9)}$$

Here, K refers to the equilibrium constant; [ ] refers to the thermodynamic activity of each component; D is the distribution ratio; $C_M(o)$ and $C_{M^{n+}}(a)$ represent the molar concentration of the metal complexes in the organic phase and aqueous phase, respectively; and γ is the activity coefficient. Equation 9 assumes that the activity coefficients of the metal compounds in the organic phase and the aqueous phase cancel each other out, which may not be true in practice. This aspect will be discussed further in a later section.

$\text{pH}_{1/2}$ values are also commonly used to assist in the design or evaluation of SX flow sheets. $\text{pH}_{1/2}$ is defined as the pH when $D = 1$ or the pH when the metal extraction to the organic phase is 50%. It can easily be shown that $\log \text{K} = -n\ \text{pH}_{1/2} - n \log [\text{HA}](o)$. Because $\log D = \log \text{K} + n \log[\text{HA}](o) + n\ \text{pH}$,

$$\log D = n(\text{pH} - \text{pH}_{1/2}) \qquad \textbf{(EQ 10)}$$

As indicated by Equation 10, the lower the $\text{pH}_{1/2}$, the larger D will be and, as a result, the greater the metal extraction. The following are examples in this group:

- Carboxylic acids (e.g., Versatic 10, Versatic 911, and naphthenic acids)
- Phosphorous acids
  - Phosphoric acids, such as bis(2-ethylhexyl)phosphoric acid (DEHPA)
  - Phosphonic acids (e.g., EHEHPA, P507, PC-88A, and Ionquest 801)
  - Phosphinic acids (e.g., P229; Cyanex 272, 301, 302; and PIA-8)
- Aryl sulfonic acids (e.g., Synex 1051)
- Some oximes, such as ACORGA and LIX reagents

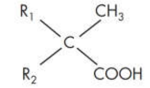
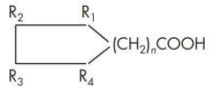
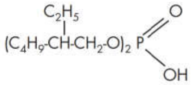
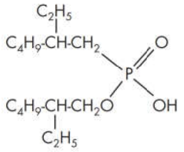
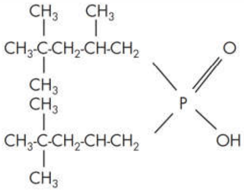
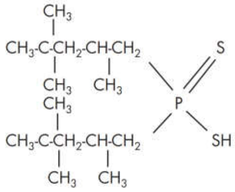
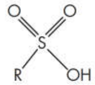
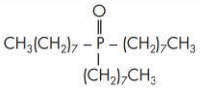
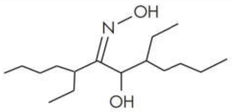
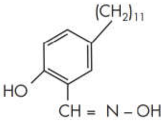
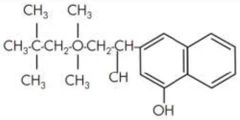
Ionquest 801 represents 2-ethylhexyl phosphonic acid; P229, di(2-ethylhexyl)phosphinic acid; Cyanex 272, bis(2,4,4-trimethyl pentyl)phosphinic acid; Cyanex 302, bis(2,4,4-trimethyl pentyl)thiophosphinic acid; PIA-8, bis(2-ethylhexyl) phosphinic acid; ACORGA, reagents based on C_9 aldoxime and C_9 ketoxime; and LIX, reagents based on alphatic and aromatic oximes. See Table 1 for others.

Solvation

The solvation exchange mechanism occurs in SX when the neutral metal salt complexes with the organic solvent (Peppard et al. 1957; Reddy et al. 1999; El-Nadi 2012). Some examples using tri-n-butyl phosphate (TBP) are shown in the following equations:

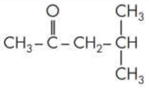
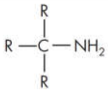
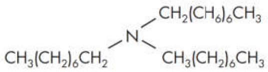
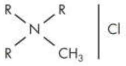
$$\text{M}^{3+} + 3\text{NO}_3^- + 3\text{TBP}(o) = \text{M(NO}_3)_3(\text{TBP})_3(o) \qquad \textbf{(EQ 11)}$$

Table 1 Some extractants used in solvent extraction

Extractant Type	Name	Structural Formula	Trade Name	Applications	References
Acidic Carboxylate	Versatic acids $R_1 + R_2$ = C7: 10 $R_1 + R_2$ = C6–C8: 911		Versatic 10 Versatic 911	Cu, Zn, Cd, Ni/Co, REE	Habashi 1993, Flett 2005
	Naphthenic acids R_1–R_4: Varying alkyl groups			Cu, Zn, Co, Ni, REE	Habashi 1993, Flett 2005
Phosphorus	Phosphoric acids: Di(2-ethylhexyl) phosphoric acid		D2EHPA P 204	U, REE, Co/Ni, Zn	Habashi 1993, Flett 2005
	Phosphonic acids: 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester		HEH/EHP PC-88A P 507	Co/Ni, Zn, Th, U, REE	Habashi 1993, Flett 2005
	Phosphinic acids: Organophosphinic acid		Cyanex 272 PIA-8	Co/Ni, Zn, Mn, Ca REE	Cytec Industries 2010
	Organodithiophosphinic acid		Cyanex 301	Ni, Co, Mn	Cytec Industries 2010, Cox 2010
	Aryl sulfonic acids R: Aryl		Syanex 1051	Mg	Cox 2010
Solvation Phosphorous ester	Tributyl phosphate	$(C_4H_9O)_3$-P = O	TBP	Th, Ce^{4+}, U, REE	Cox 2010
	Dibutyl phosphate	$C_{12}H_{27}O_3P$	DBBP	U, Fe, Zr/Hf, Au, REE	Cox 2010
Phosphinic oxides	Trioctylphosphinic oxide	 $CH_3(CH_2)_7-\overset{\overset{O}{\parallel}}{\underset{\underset{(CH_2)_7CH_3}{\mid}}{P}}-(CH_2)_7CH_3$	TOPO Cyanex 921	U, Zr/Hf, REE, Au	Cytec Industries 2010, Cox 2010
Hydroxyoxime derivatives	α-Alkarylhydroximes		LIX 63	Cu, Ni	Cox 2010
	β-Alkylarylhydroxyoximes		LIX 860	Cu, Ni	Cox 2010
Hydroxyoxine derivatives	8-Hydroxy-7-(4-ethyl-1-methyloctyl)-8-hydroxyquinonline		Kelex 100	Cu, Zn	Habashi 1993, Flett 2005

(continues)

Table 1 Some extractants used in solvent extraction (continued)

Extractant Type	Name	Structural Formula	Trade Name	Applications	References
Various alcohols	Methyl isobutyl ketone	 $CH_3-C(=O)-CH_2-CH(CH_3)-CH_3$	MIBK	Nb/Ta, Hf/Zr, Au, Li	Habashi 1993, Flett 2005
Anion	Primary amines	 R_3C-NH_2	Primene JMT	Fe(III), REE, Mo, Th	Habashi 1993, Cox 2010
	Secondary amines: Di-tridecyamine	$R_1, R_2 = CH_3(CH_2)_{12}NH$	Adegen 283	Th, U, Cr, Cu, Cd	Habashi 1993, Cox 2010
	Tertiary amines: Tri-octylamine Tri-isooctylamine		TOA/Alamine TiOA/Adogen 381	U, V, W, Mo, Cu, Co, REE	Habashi 1993, Cox 2010
	Quarternary amines: Tri-octyl methyl ammonium chloride		Aliquat 336	U, Mo, V, W, REE	Habashi 1993, Cox 2010

$$M^{4+} + SO_4^{2-} + 2HSO_4^- + 2B(o) = M(SO_4)(HSO_4)_2 2B(o) \qquad \textbf{(EQ 12)}$$

Other examples may include the interaction of Ce(IV) and Th(IV) with Cyanex 923 (Liao et al. 2001). Examples belonging to this group are

- Phosphorous ester, such as TBP and dibutyl-butyl phosphonate (DBBP);
- Phosphinic oxides, such as Cyanex 921 (TOPO) and Cyanex 923;
- Esters and thio analogs, such as Cyanex 471X; and
- Various ketones, such as methyl isobutyl ketone (MIBK) and di-isobutyl ketone (DIBK).

Cyanex 923 represents a mixture of four tryalkyl phosphine oxides; Cyanex 921, tri-n-octyl phosphine oxide; and Cyanex 471X, tri-isobutylphosphine sulfide.

Anionic

Anion-type exchangers (Rice and Stone 1962; El-Yamani and Shabana 1985; Cerna et al. 1992; Xie et al. 2014) extract metal ions as anionic complexes and therefore are only effective in the presence of strong anionic ligands. An example for an amine extractant is shown in the following equations:

$$2RNH_2(o) + H_2SO_4 = (RNH_3)_2SO_4(o) \qquad \textbf{(EQ 13)}$$

$$2La(SO_4)_3^{3-} + 3(RNH_3)_2SO_4(o) = 2(RNH_3)_3La(SO_4)_3^{3-}(o) + 3SO_4^{2-} \qquad \textbf{(EQ 14)}$$

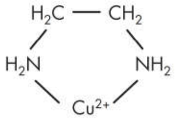
Examples in this group are

- Primary amines, such as Primene JMT and N1923;
- Tertiary amines, such as Alamine 336; and
- Quaternary amines, such as Aliquat 336 and Adogen 464.

N1923 represents primary amine; Alamine 336, trialkyl amine; Aliquat 336, trialkylmethylammonium; Adogen 464, a high molecular weight quaternary ammonium salt. See Table 1 for others.

Chelation

A metal ion forms a chelation compound with an organic anion, which is the chelation agent, for example, Cu^{2+} and ethylenediamine:



Ionic Liquid

Ionic liquids are a special kind of extractant, which is in the early stages of investigation. Ionic liquids are organic salts that consist entirely of ions typically having a melting point below 100°C (Seddon 1997; Earle et al. 2006). These types of special compounds have recently gained interest in SX applications because of their unique properties, such as low flammability (Smiglak et al. 2006), low vapor pressure (Earle et al. 2006), high thermal stability (Fox et al. 2003), and potential electrochemical applicability. Many investigators have attempted to use such liquids as viable extractants in SX applications for metal ions (Bartsch et al. 2002; Cieszyńska et al. 2007; Campos et al. 2008; Egorov et al. 2010; Okuno et al. 2006; Regel-Rosocka 2009; Srncik et al. 2009; Sun et al. 2010).

The most frequently applied in SX applications include 1-alkyl-3-methylimidazolium hexafluorophosphate $[C_n mim][PF_6]$, tetrafluoroborate $[C_n mim][BF_4]$, and bis(trifluoromethylsulphonyl) imide $[C_n mim][N(SO_2CF_3)_2]$ (an anion also abbreviated as $[Tf_2N]$) (Regel-Rosocka and Wisniewski 2011). A series of bifunctional ionic liquid extractants composed of A336 cation and phosphonic acid or carboxylic acid anions have also been tried for rare earth element extraction (Sun et al. 2010; Lachwa et al. 2006; Fukaya et al. 2007).

In addition to being used as potential extractants, significant interest has been shown by the industry in the use of ionic liquids as alternative carrier solvents.

Table 1 lists some extractants frequently used in SX practices and/or laboratory tests.

STRIPPING

In its simplest form, stripping is often (but not always) the reverse of the extraction reaction in SX. Using Equation 1 as an example,

$$M^{n+}(a) + nHR(o) \rightarrow MR_n(o) + nH^+(a) \qquad \textbf{(EQ 1)}$$

The reverse of Equation 1, as shown in Equation 15, represents stripping.

Table 2 Various stripping efficiencies for ferric iron under different stripping conditions

Reagent	Concentration, M	Ferric Iron Stripping, %
Nitric acid	6	1.8
Sulfuric acid	6	32.5
Hydrochloric acid	6	48.2
Oxalic acid	0.95	72.4
Sodium oxalate	0.4	12.2
Ammonium oxalate	0.8	65
Sodium + oxalate	0.4	50
Oxalic acid + ammonium oxalate	0.95	75

Adapted from Akhlaghi et al. 2010

$$nH^+(a) + MR_n(o) \rightarrow M^{n+}(a) + nHR(o) \qquad \textbf{(EQ 15)}$$

Stripping can be significantly more complicated and in some cases require an entirely different reaction.

Example

Stripping can also be very complicated depending on the type of metal complexes formed. As an illustration of this point, consider the stripping of ferric iron, Fe(III) DEHPA (Akhlaghi et al. 2010). In this extraction, Fe(III) may form a complex with DEHPA, such as $Fe(OH)R_2(HR)_2$ and/or $Fe(HR_2)_3$, resulting in a stable metal/extractant complex that is difficult to strip. Table 2 shows the different stripping efficiencies with different media.

Regardless of the stripping methodology used, it is critical that the SX reagent is sufficiently regenerated to allow it to be returned to the extraction section of the plant for further metal extraction.

SOLVENT EXTRACTION THERMODYNAMICS

There are many factors to consider when developing or designing an SX process flow sheet. This section discusses some of the relevant considerations and reviews some of the calculations that may be used to better understand the chemistry and assess a conceptual flow sheet.

In the case of uranyl ion (UO_2^{2+}) extraction with TBP, TBP is first dissolved in an organic phase with metallurgical-grade kerosene as the diluent. The reaction between UO_2^{2+} and TBP is supposed to take place as shown in the following equation:

$$\begin{aligned} &UO_2^{2+} + 2NO_3^- + 2TBP(o) \\ &\quad = UO_2(NO_3)_2(TBP)_2(o) \end{aligned} \qquad \textbf{(EQ 16)}$$

A possible schematic presentation of this reaction is given in Figure 2. Case 1 assumes TBP is partially soluble in water. In fact, the solubility of TBP in water is about 6 mL/L of water, and therefore the reaction mechanism suggested in Figure 2 is quite possible. However, if the solubility of the extractant in water is zero, then the following mechanism could be proposed as shown in Figure 3.

Cations in water, such as UO_2^{2+}, are surrounded by water molecules to form a hydrated species, such as hexahydrate uranyl ion ($UO_2(H_2O)_6^{2+}$), and therefore, they are very hydrophilic. As a result, the case shown in Figure 2 may be more likely than the case shown in Figure 3.

Because of the chemical affinity between UO_2^{2+} and TBP, TBP in the aqueous phase would react with UO_2^{2+} in water. Once they are combined, UO_2^{2+} would become hydrophobic due to the attachment of TBP, which makes the passage to the organic phase natural. Another important aspect on the interaction between TBP and UO_2^{2+} is that UO_2^{2+} should combine with NO_3^- before interaction with TBP. Therefore, this type of interaction is referred to as *solvation*. In solvation-type exchange mechanisms, the speciation of metal ions in the presence of various anions in the solution plays an important role in the interaction reaction. This aspect will be detailed further in the following section.

Like the TBP example, it is important to know in each system where or how the reaction is taking place. This can have a direct impact on how the system should be designed or provide important information for improving the extraction or stripping reactions.

The equilibrium constant K for the reaction given by the following equation would be

$$\begin{aligned} K &= \frac{[UO_2(NO_3)_2(TBP)_2](o)}{[UO_2^{2+}](a)[NO_3^-]^2(a)[TBP]^2(o)} \\ &= D\,\frac{1}{[NO_3^-]^2(a)[TBP]^2(o)} \end{aligned} \qquad \textbf{(EQ 17)}$$

It should be noted that the preceding treatment assumes that activity coefficients of the various species involved are assumed to be 1 (which can be misleading).

On this basis, $D = K\,[NO_3^-]^2[TBP]^2(o)$ and

$$\log D = \log K + 2\log[NO_3^-] + 2\log[TBP] \qquad \textbf{(EQ 18)}$$

From the preceding equation, one can see that the factors affecting the value D (the partition coefficient) are the concentration of NO_3^- and also the concentration of TBP.

Note, as shown in Equation 18, that the assumed stoichiometric coefficient of 2 for TBP needs justification. In fact, this value is often determined experimentally. In reality, this value can be any value—1, 2, 3—or some fraction, such as 1.5, and so on. The variation of n is primarily caused by the valence of the metal ion concerned and also by polymerization of the extractant during the course of SX.

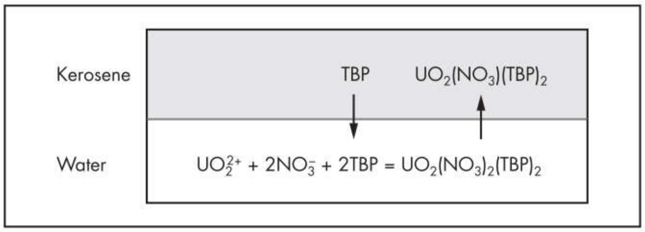


Figure 2 Case 1: Schematic presentation of a reaction between UO_2^{2+} and TBP

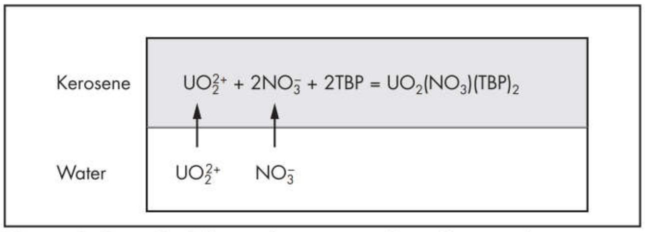


Figure 3 Case 2: Schematic presentation of a reaction between UO_2^{2+} and TBP

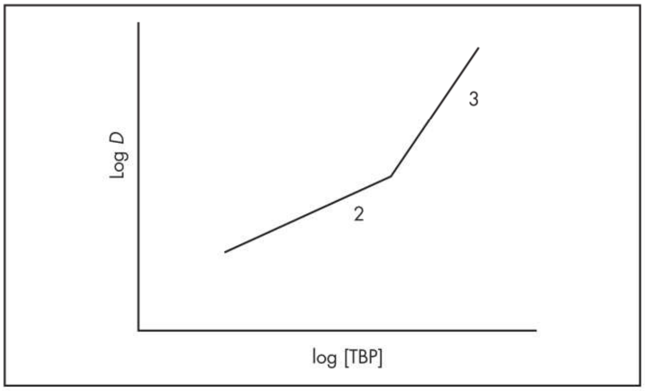


Figure 4 Log *D* versus log [TBP]

The stoichiometric value may be estimated by running a series of experiments, in which the value *D* is calculated as a function of the concentration of TBP in the organic phase. In such tests, the concentration of NO_3^- is held constant. The plot of log *D* versus log [TBP] as seen in Equation 17 produces a curve with a slope corresponding to the moles of extractant involved in the reaction. One often finds that the slope changes with the concentration of extractant. For example, the slope can be 2 up to a certain concentration, and it becomes 3 as the concentration increases beyond a certain point (see Figure 4).

Similar methodology as used for TBP (a solvation-type extractant) can also be used for a cation-type extractant such as di-(2-ethylhexyl) phosphoric acid (DEHPA). Abbreviating DEHPA as HA, the acid type of extractants will react with the metal ions in solution releasing H^+ as shown in Equation 19:

$$M^{3+}(a) + n\mathrm{HA}(o) = \mathrm{MA}_n(o) + n\mathrm{H}^+(a) \qquad \textbf{(EQ 19)}$$

$$\mathrm{K} = \frac{[\mathrm{MA}_n](o)\cdot[\mathrm{H}^+]^n(a)}{[\mathrm{M}^{n+}](a)\cdot[\mathrm{HA}]^n(o)} \qquad \textbf{(EQ 20)}$$

$$D = \frac{C_M(o)}{C_{M^{n+}}(a)} = \mathrm{K}\frac{[\mathrm{HA}]^n(o)}{[\mathrm{H}^+]^n(a)}\,\frac{\gamma_{M(o)}}{\gamma_{M^{n+}(a)}} \qquad \textbf{(EQ 21)}$$

Because DEHPA is a cation type extractant that exchanges protons, the numerical values of *K* and *D* will be very much affected by the pH of the solution as shown in Equations 20 and 21. The value *n* can be found experimentally by making a log-log plot as shown in Figure 4. However, in such experiments, the pH of the solution should be kept constant, which is not easy because the reaction will generate H^+. As a result, some researchers carry out experiments in a pH buffer solution.

It can be seen clearly that the *D* value for the TBP system is a function of NO_3^- and TBP, while that for DEHPA is a function of pH and DEHPA concentration.

In addition to using *D* values to better understand the stoichiometry of the reaction(s), the Gibbs standard free energy at room temperature $\Delta G^\circ_{R,25}$ for the reaction can be calculated by the K value through a set of experiments.

$$\Delta G^\circ_{R,25} = -\mathrm{RT}\ln \mathrm{K}_{25} \qquad \textbf{(EQ 22)}$$

However, there are some careful considerations required in conducting such experiments and interpreting the results. The equilibrium constant K can be easily calculated, provided the activities of the species involved in Equation 19 are known. The activity of H^+ can be measured relatively easily with the help of pH electrodes when the pH of the solution is relatively high, such as 2 or above. However, the accuracy of the activity of H^+ suffers when the pH of the solution is low (below 1) because the pH meter cannot serve to provide this information in a strong acidity. In such cases, the concentration H^+ should be obtained by titration, and then the corresponding activity should be found after obtaining the activity coefficient.

There are numerous equations for determining activity coefficients, which is outside the scope of this work.

Temperature Effects

When the SX reaction is studied at different temperatures, one can obtain the equilibrium constant K as a function of temperature. Such information is valuable because the establishment of K as a function of temperature (*T*) will allow one to predict the extraction reaction at any temperature using the Van't Hoff equation:

$$\ln\frac{\mathrm{K}_2}{\mathrm{K}_1} = -\frac{H^\circ_\mathrm{R}}{\mathrm{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \textbf{(EQ 23)}$$

When $\Delta H^\circ_\mathrm{R}$ and $\Delta G^\circ_\mathrm{R}$ are known, $\Delta S^\circ_\mathrm{R}$ can be determined by the following equation:

$$\Delta G^\circ_\mathrm{R} = \Delta H^\circ_\mathrm{R} - T\,\Delta S^\circ_\mathrm{R} \qquad \textbf{(EQ 24)}$$

As a result, any K at any temperature can be calculated.

Synergistic Effect

Many SX formulations have been blended and found to have better performance in combination than would have been expected based on the individual components. For example, when TBP and DEHPA are mixed (for rare earth applications), the resulting SX is much better than TBP or DEHPA alone. Such a synergistic effect (SE) is defined by the following equation:

$$\mathrm{SE} = \frac{D_\mathrm{overall}}{\sum D_i} \qquad \textbf{(EQ 25a)}$$

For two extractant systems, D_1 and D_2,

$$\mathrm{SE} = \frac{D_\mathrm{overall}}{D_1 + D_2} \qquad \textbf{(EQ 25b)}$$

where

SE > 1, synergism is present
SE = 1, no synergism
SE < 1, antagonistic effect is present

CHOICE OF DILUENTS

There are many diluents that can be used in SX test work. Some of the major properties considered in choosing the diluent may include water immiscibility, density, boiling and melting points, flash points, and also the dielectric constant. In addition, viscosity and price should be included in this decision-making process. Table 3 lists some of the important and frequently used diluents used in laboratory assessments.

In commercial and/or industrial applications, the most frequently used diluents are metallurgical-grade kerosene-based solvents. These tend to be a mixture of many organic compounds with branched- and straight-chain alkanes and naphthenes and aromatic hydrocarbons. The diluents listed in Table 3 are generally used in laboratory experiments,

Table 3 Physical properties of some diluents

Common Diluents	Boiling Point, °C	Melting Point, °C	Density, g/mL	Solubility, g/100 g water	Dielectric Constant	Flash Point, °C
Benzene	80.1	5.5	0.8765	0.18	2.28	–11
1-Butanol	117.7	–88.6	0.8095	6.3	17.8	37
Carbon tetrachloride	76.8	–22.6	1.594	0.08	2.24	N/A*
Chlorobenzene	131.7	–45.3	1.1058	0.05	5.69	28
Chloroform	80.7	–63.4	1.4788	0.795	4.81	N/A
Cyclohexane	80.7	6.6	0.7739	0.1	2.02	–20
1,2-Dichloroethane	83.5	–35.7	1.245	0.861	10.42	13
Dodecane	214	–10	0.78	—	2.0	N/A
Diethylene glycol	246	–10	1.1197	10	31.8	124
Diethyl ether	34.5	–116.2	0.713	7.5	4.267	–45
Di-butyl ether	142.4	–97.9	0.769	0.03	—	25
Ethyl acetate	77	–83.6	0.895	8.7	6	–4
Heptane	98	–90.6	0.684	0.01	1.92	–4
Hexane	69	–95	0.659	0.014	1.89	–22
Methylene chloride	39.8	–96.7	1.326	1.32	9.08	1.6
Nitro methane	101.2	–29	1.382	9.50	35.9	35
Pentane	36.1	–129.7	0.626	0.04	1.84	-49
Propyl alcohol	97	–126	0.803	Miscible	21.8	22
Tetrachloroethane	121.1	–19	1.622	0.15	2.5	Not flammable
Toluene	110.6	–93	0.867	0.05	2.38	4
Tri-ethyl amine	88.9	–114.7	0.728	0.02	2.4	–11
o-Xylene	144	–25.2	0.897	Insoluble	2.57	32
p-Xylene	138.4	13.3	0.861	Insoluble	2.27	27
m-Xylene	139.1	–47.8	0.868	Insoluble	2.37	27

Adapted from Reichardt 2003
*N/A = not applicable.

Table 4 Pertinent characteristics of ShellSol 2046 AR

Property	Unit	Range
Distillation, final boiling point	°C	230–275
Aromatics	% Volume	8
Flash point, Pensky-Martens closed cup	°C	80
Viscosity at 40°C	mm²/s	1.60–2.00

Source: Shell Chemicals 2016

especially when the SX chemistry is studied. However, kerosene and its derivatives are currently used in industry. Some of the industrial diluents that have been well defined are ShellSol, Orform SX, and Escaid-based solvents.

ShellSol 2046 AR is a special kerosene with a mixture of paraffins, naphthenes, and aromatics, which can be characterized as exhibiting a high flash point, low evaporation rate, and low vapor pressure. Some typical characteristics of this diluent are given in Table 4.

Orform SX, an industrially used SX diluent, is a petroleum distillate and applied in extraction of metals such as copper, cobalt, nickel, platinum, palladium, uranium, cadmium, beryllium, and lanthanide series metals. There are typically three different branches: Orform SX-11, Orform SX-12, and Orform SX-80. Some salient chemical properties are given in Table 5.

Table 5 Pertinent characteristics of Orform SX series

Property	SX-11	SX-12	SX-80
Gravity at 15.6°C, g/mL	0.795	0.82	0.82
Flash point, °C	114	76.7	76.7
Composition, wt %			
Alkyl aromatics	0.2	4–23	4–23
Cycloparaffins	0.01	42	42
Paraffins	97	34–53	34–53
Viscosity, mm²/s			
25°C	6.5	2.4	2.4
10°C	15.2	3.4	3.4
0°C	—	4.3	4.3

Source: Chevron Phillips Chemical Company 2013

LABORATORY TESTING METHODS AND ANALYSIS

In this section, various laboratory testing methods on SX will be briefly introduced and discussed. Laboratory tests are essential for the design or optimization of a successful SX operation. Such tests allow evaluation of both the physical and metallurgical properties of the system and their dependence on process variables such as the ratio of organic-to-aqueous phases, contact time, number of stages, and throughput as well as SX chemistry. Benchtop laboratory tests are typically completed to better understand the equilibrium conditions (extractant loading, stripping characteristics, and stoichiometry), selectivity, kinetics, solubility, and phase separation properties of the system before further testing of the system under dynamic conditions.

Once the chemistry (stoichiometric requirements, conditions under which the reaction will proceed, and desired metal separation) has been defined, laboratory test work is completed to validate the reagent capability to achieve the desired recovery or separation.

S Curves or Loading Curves

Loading curves are often generated to determine what metals within the feed solution are likely to load and under which conditions. The metal loading is often evaluated as a function of pH (for chelating or cation exchange–type reactants) or as a function of some other anion in the case of solvating reagents. The curves can be generated with the actual leach liquor (containing all the metals of interest) or can be generated with single metal solutions. These loading curves are used to determine the relative affinity the extractant may have for the various ions in solution. Dependent on what is present and what separation is desired, the aqueous feed may require a pretreatment to remove undesired impurities prior to the SX step or may require adjustment during the extraction or stripping process.

For example, consider the separation of Co from acidic leach liquors using phosphinic acid–based extractants. In this case, the reaction proceeds following Equations 26 and 27 as shown here:

$$M^{n+}(a) + n\mathrm{HA}(o) = \mathrm{MA}_n(o) + n\mathrm{H}^+(a) \qquad \textbf{(EQ 26)}$$

$$\mathrm{Co}^{2+} + 2\mathrm{HA} \leftrightarrow \mathrm{CoA}_2 + 2\mathrm{H}^+ \qquad \textbf{(EQ 27)}$$

The extractant chelates Co at a relatively high pH (pH >4) and exchanges the metal cation for protons. In addition to loading Co, the extractant would be expected to load many elements within the pH range under which Co loads (in this case Ca, Mg, Zn, Cu would also be expected to load based on the S curves). Some of these elements would not be stable at the pH at which cobalt extraction takes place. For these reasons, the leach liquor is often treated prior to the Co SX step to precipitate out Fe, Al, and Mn. Following impurity removal, the reaction can proceed; however, the metal loading would be limited by the generation of acid during extraction. For the extractant to continue loading metals, the acid that is generated because of the proton exchange would require neutralization as shown in the following equation:

$$\mathrm{Co}^{+2} + 2\mathrm{HA} + 2\mathrm{NaOH} + \mathrm{SO}_4^{=} \rightarrow \mathrm{CoA}_2 + 2\mathrm{H}_2\mathrm{O} + \mathrm{Na}_2\mathrm{SO}_4 \qquad \textbf{(EQ 28)}$$

Isotherm Generation

Simple and quick shake tests are often completed using beakers with overhead stirrers, jars with magnetic stirrers, separating funnels, or other agitation devices to contact the organic and aqueous phases together at various organic-to-aqueous ratios to determine the metal distribution between the phases as a function of the organic-to-aqueous volumetric ratio. SX is usually mass transfer controlled, and therefore, it normally takes less than 30 minutes to reach equilibrium.

Dependent on the type of extractant being used, these distribution curves may be generated directly by mixing the two phases (the aqueous feed and the extractant diluted to the correct stoichiometric reagent concentration) at the various volumetric ratios. In other cases, the distribution curves may need to be generated under more controlled conditions (e.g., if the pH needs to be held constant via the addition of base).

Once generated, the equilibrium curves can then be used to help design the circuit using McCabe–Thiele techniques (discussed later).

Kinetics Tests

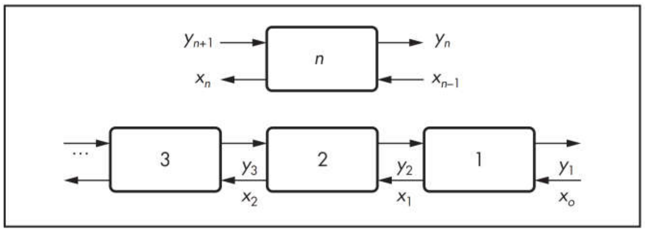
Typical SX test work also includes an evaluation of the reaction kinetics: The organic and aqueous phases are mixed together at a set organic-to-aqueous ratio, the dispersion is sampled, and phases are separated and analyzed to assess metal transfer as a function of time. For example, organic and aqueous are mixed together at a 1:1 ratio using a baffled beaker with an overhead stirrer at 1,000 rpm. Samples are taken at 30, 60, 120, 180, 300, and 900 seconds. The phases are allowed to separate, and the aqueous and/or organic are then subjected to chemical analysis using such devices as atomic absorption spectrometers, induction-coupled plasma devices, and visible and/or ultraviolet photometers. The test gives an indication of the mixing time required for the solutions to reach equilibrium and can be used to help design the mixers and understand the mixer retention time requirements.

Phase Separation Tests

Another typical test involves mixing the aqueous and organic together at a set mixing condition and for a set period of time (e.g., 3 minutes), then stopping the agitation and allowing the phases to separate, while recording the separation time. This test provides information on the settling time (at meters per second) and can be used to size the dynamic equipment. Phase separation tests are usually evaluated under both aqueous and organic continuity (because continuity frequently impacts phase separation characteristics). The longer it takes for the phases to separate, the larger the settler requirement (assuming mixer-settler equipment will be used). In addition to determining the time for the phases to separate, the phase separation tests can give an indication of the quality of the separation. For SX to work well, the phases should separate completely, leaving a clean interface. Presence of a third phase, a stable emulsion, or a crud layer (solid stabilized emulsion) would raise questions on the operability of the process and would require further study. Phase separation tests can also be used to obtain a first indication of the likelihood of entrainment of one phase or the other being an issue. Signs of a secondary haze or small droplets of organic in the aqueous phase may suggest the system would have high organic losses, or samples of the organic phase may be analyzed for entrained aqueous.

Each SX process is different, but there are common challenges that should be considered when developing a flow sheet for a potential SX process. These challenges can and should be identified through the initial benchtop testing. The common issues to investigate include the following:

- **Solubility.** Ensure that the phases are sufficiently immiscible so one phase does not leave with the other as a dissolved loss. Ensure that the ligand and/or metal ligand complex solubility is not exceeded, leading to preferential loss of the reagent. If soluble losses are likely to occur, then understanding the conditions to recover the dissolved species should be considered.



Source: Han 2002; Han and Fuerstenau 2003

Figure 5 Schematic showing countercurrent extraction process

- **Selectivity.** Ensure that the metal of interest is extracted preferentially or can be separated from other impurities through proper adjustment of the process conditions.
- **Stripping.** Ensure that the metals that load can be removed efficiently from the organic and/or ensure that separate stripping regimes are implemented to remove impurities that have a high affinity for the extractant. Making sure there is no *poisoning* of the ligand caused by minor metal loading is an important component of testing, and organics should be taken through multiple extract and strip cycles to fully understand the impact of any circulating load.
- **Stability.** Ensure that there are no elements that load and cannot be removed or there are no conditions that result in the ligand permanently losing its extraction capabilities.
- **Speed/kinetics.** Ensure that the targeted metal separation can be achieved with reasonable and practical mixer retention time.
- **Separation.** Similar to solubility, insufficient phase separation can lead to significant issues in the design and operation of the plant. To achieve the metal separation targets, the phases need to separate. Poor separation can also lead to excessive crud formation, which can also significantly impact the operability of the process. SX designs should include process equipment to allow easy removal of crud from the circuit as well as methodology or equipment to limit the influx of solids into the plant.

Of the issues highlighted, many can be overcome or sufficiently addressed using engineering controls if they are recognized and understood early within the process.

More extensive tests may include the use of mixer-settlers, columns, and centrifugal contactors to better assess the solution properties under dynamic conditions. Piloting tests are ideally used to confirm the metallurgical and physical behavior expected from the shake tests. There are a variety of sizes and shapes in each of these devices. The amounts of liquid samples used in these tests are also multiple because of the type of the equipment and purpose in carrying out such tests.

When the SX chemistry process is studied in a laboratory testing situation, cleaning the extractants and/or diluents (organic liquid) prior to the testing is often critical. The impurities in these chemicals can greatly affect SX chemistry. In some cases, a pretreatment of the extractant or diluent is advised.

SOLVENT EXTRACTION HARDWARE

Mixer-Settlers

The mixer-settler device is the most commonly used piece of SX equipment and consists of a mixing chamber followed by a settling compartment where the phases separate because of the gravity differences. This device can be used as a single unit as well as multiple units in series. Commercially available devices are available in the market or can be easily built in-house.

Columns

Generally, there are two types of columns used in SX: packed columns and pulse types with plates or trays for mixing. These devices are easy to use, but because columns do not have discrete stages, it is not convenient to study pertinent variables acting in the SX process. These devices are commercially available in the market or can be individually manufactured.

Centrifugal Contactors

Centrifugal contactors are discrete-stage units much like mixer-settlers, but the primary difference is the separation of the two-liquid phase mixture. Centrifugal contactors utilize a centrifugal force via a spinning rotor to enable fast and effective separation. Such devices are available commercially.

CONTINUOUS PROCESS

SX operations are often run continuously in a countercurrent mode as shown in Figure 5 (Han 2002; Han and Fuerstenau 2003).

Typically, the goal is to purify and concentrate a certain metal ion. In its simplest form, the process consists of two reaction sections:

1. **Extraction cascade.** The metal is selectively transferred from the aqueous phase to the organic phase in anywhere from one to multiple extraction stages.
2. **Stripping cascade.** The metal is transferred from the loaded solvent phase back to an aqueous phase (usually while concentrating the metal of interest), utilizing anywhere from one to multiple strip stages.

SX plants generally consist of mixer-settler units arranged in series with countercurrent flow. Both the aqueous and organic phases enter the mixer, where one phase is dispersed in the other to allow mass transfer. The dispersion then overflows the mixer into a settler where the phases are allowed to separate. The dispersion is discharged into the settler where it flows through a distribution fence and then separates by gravity as it passes down the length of the settler. The organic phase flows over the upper weir and into a collection launder while the aqueous phase passes over a lower weir, into a similar launder. Although mixer-settlers are the most common, other types of equipment—for example, pulsed columns, sieve-plate columns, centrifugal contactors, and in-line mixers—are also used or have been contemplated. Plants are typically designed and the operating conditions are optimized through the utilization of experimentally generated isotherms and McCabe–Thiele techniques.

Equilibrium and Distribution Isotherms

Isotherms define the extractant's metal loading capacity in both the extraction and stripping sections of the plant.

The *extract isotherm* defines the maximum amount of metal that may be removed from the feed liquor for each organic-to-aqueous (O/A) volumetric ratio. Organic (extractant plus diluent) is mixed with the feed liquor at various O/A ratios until equilibrium is obtained. The organic and aqueous are separated, and the metal concentration in each phase is analyzed. The data are graphed, with organic metal concentration on the y-axis and aqueous metal concentration on the x-axis.

The *strip isotherm* defines the maximum amount of metal that may be removed from the organic for each O/A ratio. Organic (loaded with metal) is mixed with the strip liquor at various O/A ratios until equilibrium is reached. The organic and aqueous are separated and the metal concentration in each phase is analyzed. The data are graphed, with aqueous metal on the y-axis and organic metal on the x-axis.

Once the extract and strip isotherms have been generated, it is possible to use McCabe–Thiele techniques to determine the number of stages required to achieve a given recovery or to produce a specific rich liquor. It is an iterative graphical procedure used to ensure that mass balance conditions are met between extraction and stripping cascades. Full explanation of McCabe–Thiele techniques can be found elsewhere (McCabe and Thiele 1925; Perry and Green 1984).

Equation 29 represents the mass balance for a metal ion being extracted from the aqueous phase to the organic phase through this process:

$$Ax_o + Oy_{n+1} = Ax_n + Oy_1 \ldots \qquad \textbf{(EQ 29)}$$

where A and O represent flow rates of aqueous phase and organic phase, respectively; x_o indicates the fractional composition of ion in aqueous phase entering and x_n represents the fractional composition of the ion in the aqueous phase exiting the countercurrent extraction operation; and y_{n+1} indicates the fractional composition of the ion in organic phase entering with y_1 representing the fractional composition of the ion in the organic phase exiting the countercurrent extraction process.

The y-axis of Figure 6 represents the concentration of the ion in the organic phase, and the x-axis represents the concentration of the same ion in the aqueous phase. The entering aqueous solution contains the ion to be extracted at x_0 denoted by port a in the graph. As this solution enters the first tank—stage 1—the ion will be subjected to transfer into the oil phase, and the final concentration of this ion in the stage will approach x_1 given a sufficient time, which is denoted by port b in the diagram. This represents the concentration of the ion in the new feed solution entering stage 2. This process will continue until a satisfactory composition of this metal has been reached in the *n*th stage. Such a plot is often referred to as a McCabe–Thiele diagram.

The loaded organic exiting the extraction cascade (y_1) is then fed to a stripping cascade to recover the metal of interest from the organic phase and to regenerate the organic solvent for further extraction.

Equation 29 can be rearranged to yield the following:

$$y_1 = \frac{A}{O}(x_o - x_n) + y_{n+1} \ldots \qquad \textbf{(EQ 30)}$$

Figure 7 shows the distribution isotherm line for an ion between the aqueous phase and organic phase together with the operating line given by Equation 30. It also shows the stripping isotherm for an ion between the aqueous phase and organic phase together with the operating line.

The y-axis of Figure 7 represents the concentration of the ion in the aqueous phase, and the x-axis represents the concentration of the same ion in the organic phase. The entering organic solution contains the ion to be stripped at y^*_1 denoted by port a in the graph. As this solution enters the first stage—stage 1—the ion will be subjected to transfer into the aqueous phase, and the final concentration of this ion in the tank will approach y^*_2 given a sufficient time, which is denoted by port b in the diagram. This represents the concentration of the ion in the organic solution entering stage 2. This process will continue until a satisfactory composition of this metal has been reached in the *n*th stage.

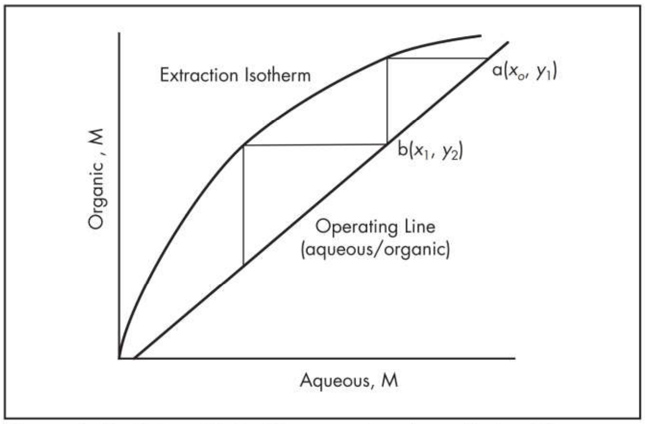


Figure 6 McCabe–Thiele diagram showing relationship between distribution isotherm and operating line

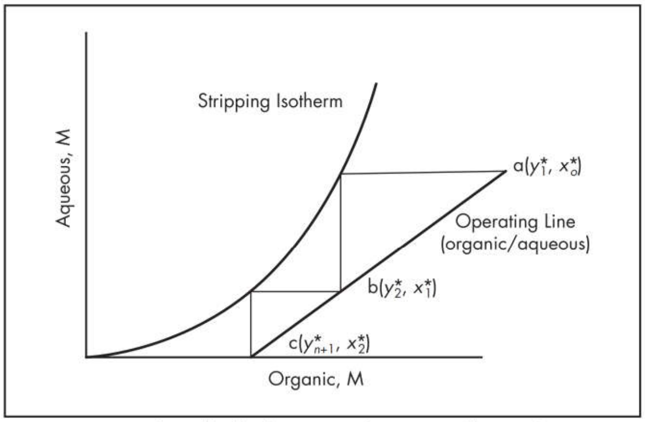


Figure 7 McCabe–Thiele diagram showing relationship between distribution isotherm and operating line for a two-stage stripping cascade

Equation 31 represents the mass balance for a metal ion being transferred from the organic phase to the aqueous phase in the process.

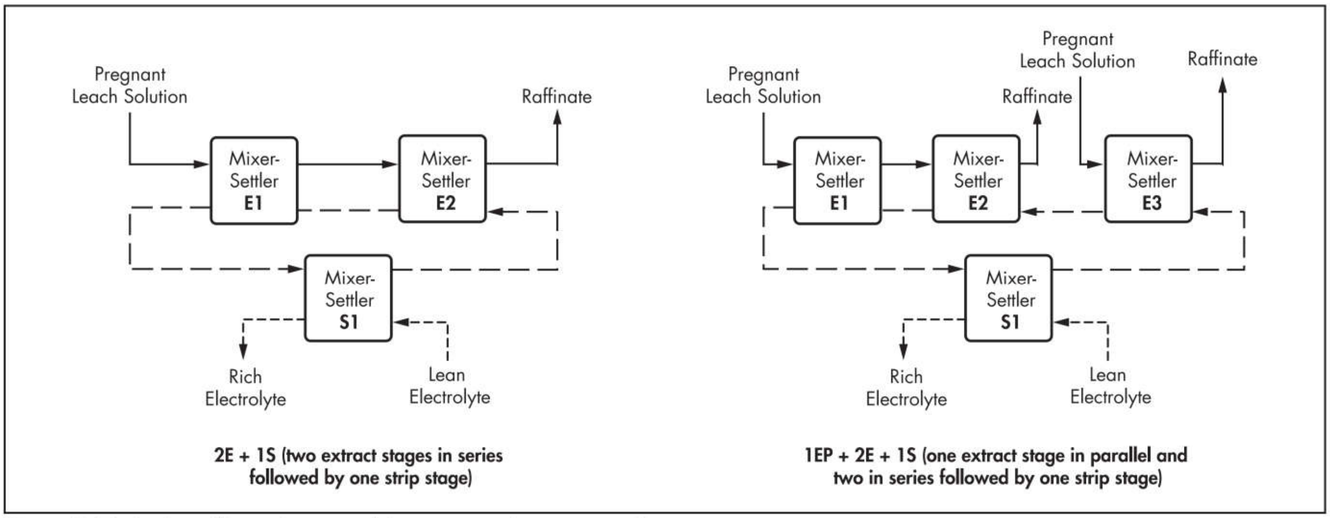
$$Ax^*_{n+1} + Oy^*_n = Ax^*_n + Oy^*_{n+1} \cdots \qquad \textbf{(EQ 31)}$$

Equation 31 can be rearranged to yield Equation 32:

$$x_1 = \frac{A}{O}(y_n - y_{n=1}) + x_{n \neq 1} \ldots \qquad \textbf{(EQ 32)}$$

The McCabe–Thiele technique will have achieved a satisfactory result when the composition in y^*_1 is equivalent to y_1 and y^*_{n+1} is equivalent to y_{n+1}.

In industrial practice, many different SX configurations are used, depending on the needs of the operation. Although countercurrent flow is the standard operation, it is not uncommon for the organic, feed liquor, and strip liquor streams to be operated in series or parallel flow. Operators also often



2E + 1S (two extract stages in series followed by one strip stage)

1EP + 2E + 1S (one extract stage in parallel and two in series followed by one strip stage)

Figure 8 Typical configurations used in copper solvent extraction

Table 6 Typical design parameters for a mixer-settler unit

Mix box organic-to-aqueous ratio	1:1
Mix box retention time	2–3 minutes
Mixer continuity	Variable*
Specific settler flow	3-8 $\text{m}^3/(\text{m}^2/\text{h})$
Organic phase velocity	3 cm/s

*Choose continuity to minimize entrainment.

consider options such as splitting the streams to redistribute flow or adding streams to enhance recovery or production. Depending on the extractant properties, additional stages may also be required for pre-neutralization or regeneration of the extractant.

One or more wash or scrub stages may be used if the feed solution contains high concentrations of impurities, which may be entrained into the strip liquor or if the extractant is not sufficiently selective for the ion of interest and the impurities need to be chemically removed.

SX configurations vary depending on the separation required and the extractant properties. In base metal separations, it is common to use one to five extract stages, one to three scrub and wash stages, and one to three strip stages. In rare earth separations, an SX plant can have hundreds of stages between extract scrub and strip with significant metal recycle from the rich liquor back to the scrub and extract cascades.

Typical flowcharts for copper SX with some flow information are shown in Figure 8. Extractants, extractant concentrations, and O/A ratios are chosen to achieve the desired metal separations and to concentrate and purify the metal of interest. Physical considerations are also extremely important in a commercial operation. The two immiscible fluids need to be mixed together to achieve the mass transfer, but the phases must also sufficiently separate to minimize entrainment of one phase into the other and to prevent the formation of solid stabilized emulsions. Typical design parameters for a mixer-settler unit are given in Table 6.

REFERENCES

Akhlaghi, M., Rashchi, R., and Vahidi, E. 2010. Stripping of Fe(III) from D2EHPA using different reagents. In *XXV International Mineral Processing Congress (IMPC) 2010: Smarter Processing for the Future.* Melbourne, Victoria: Australasian Institute of Mining and Metallurgy. pp. 255–262.

Bartsch, R.A., Chun, S., and Dzyuba, S.V. 2002. Ionic liquids as novel diluents for solvent extraction of metal salts by crown ethers. In *Ionic Liquids: Industrial Applications for Green Chemistry.* Edited by R.D. Rogers and K.R. Seddon. Washington, DC: American Chemical Society. pp. 58–68.

Berthelot, M., and Jungfleisch, J. 1872. Sur les lois qui preside nt ou partage d'un corps entre deue dissolvants. *Ann. Chim. Phys. [París].* 26:396.

Campos, K., Vincent, T., Bunio, P., Trochimczuk, A., and Guibal, E. 2008. Gold recovery from HCl solutions using Cyphos IL101 (a quaternary phosphonium ionic liquid) immobilized in biopolymer capsules. *Solvent Extr. Ion Exch.* 26(5):570–601.

Cerna, M., Volaufova, E., and Rod, V. 1992. Extraction of light rare earth elements by amines at high inorganic nitrate concentration. *Hydrometallurgy* 28(3):339–352.

Chevron Phillips Chemical Company. 2013. *Orform SX Solvent Extraction Diluents*. The Woodlands, TX: Chevron Phillips Chemical Company.

Cieszyńska, A., Regel-Rosocka, M., and Wiśniewski, M. 2007. Extraction of palladium(II) ions from chloride solutions with phosphonium ionic liquid Cyphos IL101. *Pol. J. Chem. Technol.* 9(2):99–101.

Cox, M. 2010. Liquid-liquid extraction and liquid membranes in the perspective of the twenty-first century. In *Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials.* Edited by M. Aguilar and J.L. Cortina. Boca Raton, FL: CRC Press.

Cytec Industries. 2010. *Mining Chemicals Handbook*, version 2. Woodland Park, NJ: Cytec Industries.

Earle, M.J., Esperanca, J.M.S.S., Gilea, M.A., Canongia Lopes, J.N., Rebelo, L.P.N., Magee, J.W., Seddon, K.R., and Widegren, J.A. 2006. The distillation and volatility of ionic liquids. *Nature* 439:831–834.

Egorov, V.M., Djigailo, D.I., Momotenko, D.S., Chernyshov, D.V., Torocheshnikova, I.I., Smirnova, S.V., and Pletnev, I.V. 2010. Task-specific ionic liquid trioctylmethylammonium salicylate as extraction solvent for transition metal ions. *Talanta* 80(3):1177–1182.

El-Nadi, Y.A. 2012. Lanthanum and neodymium from Egyptian monazite: Synergistic extractive separation using organophosphorous reagents. *Hydrometallurgy* 119-120:23–29.

El-Yamani, I.S., and Shabana, D.L. 1985. Solvent extraction of lanthanum(III) from sulfuric acid solutions by Primene JMT. *J. Less-Common Met*. 105(2):255–261.

Flett, D.S. 2005. Solvent extraction in hydrometallurgy: The role of organophosphorus extractants. *J. Organomet. Chem*. 690(10):2426–2438.

Fox, D.M., Awad, W.H., Gilman, J.W., Maupin, P.H., de Long, H.C., and Trulove, P.C. 2003. Flammability, thermal stability, and phase change characteristics of several trialkylimidazolium salts. *Green Chem*. 5:724–727.

Fukaya, Y., Sekikawa, K., Murata, K., Nakamura, N., and Ohno, H. 2007. Miscibility and phase behavior of water–dicarboxylic acid type ionic liquid mixed systems. *Chem. Commun.* 29:3089–3091.

Habashi, F. 1993. *A Textbook of Hydrometallurgy*. Sainte-Foy, QC: Metallurgie Extractive Quebec.

Han, K.N. 2002. *Fundamentals of Aqueous Metallurgy*. Littleton, CO: SME.

Han, K.N., and Fuerstenau, M.C. 2003. Hydrometallurgy and solution kinetics. In *Principles of Mineral Processing*. Edited by M.C. Fuerstenau and K.N. Han. Littleton, CO: SME.

Lachwa, J., Szydlowski, J., Makowska, A., Seddon, K.R., Esperanca, J.M.S.S., Guedes, H.J.R., and Rebelo, L.P.N. 2006. Changing from an unusual high-temperature demixing to a UCST-type in mixtures of 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide and arenes. *Green Chem.* 8(3):262–267.

Liao, W., Yu, G., and Li, D. 2001. Solvent extraction of Ce(IV) and F from sulphuric acid leaching of bastnasite by Cyanex 923. *Solvent Extr. Ion Exch.* 19(2):243–259.

Mason, G.W., Bilobron, I., and Peppard, D.F. 1978. Extraction of U(VI), Th(IV), Am(III) and Eu(III) by bis para-octyl phosphoric acid in benzene diluents. *J. Inorg. Nucl. Chem*. 40(10):1807–1810.

McCabe, W.L., and Thiele, E.W. 1925. Graphical design of fractionating columns. *Ind. Eng. Chem.* 17(6):605–611.

Okuno, M., Hamaguchi, H., and Hayashi, S. 2006. Magnetic manipulation of materials in a magnetic ionic liquid. *Appl. Phys. Lett.* 89:132506.

Peppard, D.F., Driscoll, W.J., Siromen, S.J., and Mason, G.W. 1957. Fractional extraction of the lanthanides as their dialkyl orthophosphates. *J. Inorg. Nucl. Chem*. 4:334–343.

Perry, R.H., and Green, D.W. 1984. *Perry's Chemical Engineers' Handbook*, 6th ed. New York: McGraw-Hill.

Reddy, M.L.P., Bosco Bharathi, J.R., Peter, S., and Ramamohan, T.R. 1999. Synergistic extraction of rare earths with bis(2,4,4-trimethyl pentyl) dithiophosphinic acid and trialkyl phosphine oxide. *Talanta* 50(1):79–85.

Regel-Rosocka, M. 2009. Extractive removal of zinc(II) from chloride liquors with phosphonium ionic liquids/toluene mixtures as novel extractants. *Sep. Purif. Technol.* 66(1):19–24.

Regel-Rosocka, M., and Wisniewski, M. 2011. Ionic liquids in separation of metal ions from aqueous solutions. In *Applications of Ionic Liquids in Science and Technology.* Edited by S. Handy. Rijeka, Croatia: InTech.

Reichardt, C. 2003. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed. Weinheim, Germany: Wiley-VCH Verlag.

Rice, C., and Stone, C.A. 1962. *Amines in Liquid-Liquid Extraction of Rare Earth Elements*. Report of Investigations 5923. Washington, DC: U.S. Bureau of Mines.

Seddon, K.R. 1997. Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* 68:351–356.

Shell Chemicals. 2016. ShellSol 2046 AR. Technical Datasheet 448, March. p. 3.

Smiglak, M., Reichert, W.M., Holbrey, J.D., Wilkes, J.S., Sun, L., Thrasher, J.S., Kirichenko, K., Singh, S., Katritzky, A.R., and Rogers, R.D. 2006. Combustible ionic liquids by design: Is laboratory safety another ionic liquid myth? *Chem. Commun.* 24:2554–2556.

Srncik, M., Kogelnig, D., Stojanovic, A., Körner, W., Krachler, R., and Wallner, G. 2009. Uranium extraction from aqueous solutions by ionic liquids. *Appl. Radiat. Isot.* 67(12):2146–2149.

Sun, X., Ji, Y., Zhang, L., Chen, J., and Li, D. 2010. Separation of cobalt and nickel using inner synergistic extraction from bifunctional ionic liquid extractant (Bif-ILE). *J. Hazard. Mater.* 182(1–3):447–452.

Xie, P., Zhang, T.A., Dreisinger, D., and Doyle, F. 2014. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* 56:10–28.

Zheng, D., Gray, N.B., and Stevens, D.W. 1991. Comparison of naphthenic acid, versatic acid, and D2EHPA for the separation of rare earths. *Solvent Extr. Ion Exch.* 9(1):85–102.